IUPAC-NIST Solubility Data Series. 74. Actinide Carbon Compounds

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(Received 15 August 2000; accepted 2 December 2000)

This volume presents solubility data of the carbonates, salts of carboxylic acids, and other carbon containing compounds of actinides. Covered are compounds of thorium, uranium, neptunium, plutonium, americium, and one system for curium. No solubility data on carbonates or other carbon containing compounds have been found for other actinide elements. The literature has been covered up to the end of 1999, and there was a great effort to have the literature survey as complete as possible. Only those published results that report meaningful data were considered for the volume. Papers that reported qualitative results with statements like ‘‘sparingly soluble’’ or ‘‘insoluble,’’ etc. were not considered. In addition to papers that published numerical data, some papers that presented data in graphical form only were considered as well. They were considered for the volume either if no other data were available for the system, if the data were published in difficult to obtain older literature, or if the data were considered to be of importance for other reasons. For many compounds it was not possible to provide the *Chemical Abstracts* Registry Numbers since these have not yet been assigned. For this reason, the Registry Number index is incomplete. © *2001 American Institute of Physics.*

Key words: actinides; actinide carbon compounds; aqueous solutions; nonaqueous solutions; solubility.

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1. Preface

This volume presents solubility data of the carbonates, salts of carboxylic acids, and other carbon containing compounds of actinides. Covered are compounds of thorium, uranium, neptunium, plutonium, americium, and one system for curium. No solubility data on carbonates or other carbon containing compounds have been found for other actinide elements. The literature has been covered up to the end of 1999, and there was a great effort to have the literature survey as complete as possible.

Only those published results that report meaningful data were considered for the volume. Papers that reported qualitative results with statements like ‘‘sparingly soluble’’ or ‘‘insoluble,’’ etc. were not considered. In addition to papers that published numerical data some papers that presented data in graphical form only were considered as well. They were considered for the volume either if no other data were available for the system, if the data were published in difficult to obtain older literature, or if the data were considered to be of importance for other reasons. The first two criteria led the compiler to include sometimes papers in which the authors failed to specify conditions such as temperature, equilibrium time, or methods of analysis. The last criterion has particularly been applied to many of the recent papers on the solubility of actinide carbonates where high precision pH titration technique was used to obtain the solubility data which were, however, reported in graphical form, or occasionally as solubility products, without reporting numerical solubility data. Another reason for including these data was their importance from the point of view of environmental science since carbonates of actinides are substances relevant to the chemical behavior of actinides in radioactive waste repositories. Phase diagrams were included for some of the multicomponent systems. Of the many systems covered by the volume relatively few were studied by more than one laboratory. Thus the opportunity to carry out evaluations has been limited, and only 17 systems have been evaluated. In some of these systems, however, there has been so much uncertainty that even tentative solubility values could not be recommended.

Of all published papers only two remained unavailable to the compiler, and could not be included. These are the following two reports from the Institute of Radiochemistry, Technical University, Munich, Germany: M. F. Bernkopf, J. I. Kim, Report RCM-02884, 1984, reporting the solubility of $Am(OH)CO_3$ in $0.1\,mol\,dm^{-3}$ $NaClO_4$, and W. Runde, J. I. Kim, Report RCM-01094, 1994, reporting the solubility of $NaAm(V)O_2CO_3$ in 3 and $5\,mol\,dm^{-3}$ NaCl. For many compounds it was not possible to show the *Chemical Abstracts* Registry Numbers since these have not been assigned. For this reason, the Registry Number index is incomplete.

2. Introduction to the Solubility Data Series: Solubility of Solids in Liquids

2.1. The Nature of the Project

The Solubility Data project (SDP) has as its aim a comprehensive review of published data for solubilities of gases, liquids, and solids in liquids or solids. Data of suitable precision are compiled for each publication on data sheets in a uniform format. The data for each system are evaluated and, where data from independent sources agree sufficiently, recommended values are proposed. The evaluation sheets, recommended values, and compiled data sheets are published on consecutive pages.

2.2. Compilations and Evaluations

The formats for the compilations and critical evaluations have been standardized for all volumes. A description of these formats follows.

2.2.1. Compilations

The format used for the compilations is, for the most part, self-explanatory. Normally, a compilation sheet is divided into boxes, with detailed contents described below.

Components Each component is listed according to IUPAC name, formula, and Chemical Abstracts (CA) Registry Number. The Chemical Abstracts name is also included if this differs from the IUPAC name, as are trivial names if appropriate. IUPAC and common names are cross-referenced to Chemical Abstracts names in the System Index.

The formula is given either in terms of the IUPAC or Hill [1] system and the choice of formula is governed by what is usual for most current users; i.e., IUPAC for inorganic compounds, and Hill system for organic compounds. Components are ordered on a given compilation sheet according to:

(a) saturating components,
(b) nonsaturating components, and
(c) solvents.

In each of (a), (b) or (c), the components are arranged in order according to the IUPAC 18-column periodic table with two additional rows:

Columns 1 and 2: H, alkali elements, ammonium, alkaline earth elements

Columns 3–12: transition elements

Columns 13–17: boron, carbon, nitrogen groups; chalcogenides, halogens

Column 18: noble gases

Row 1: Ce to Lu

Row 2: Th to the end of the known elements, in order of atomic number.

The same order is followed in arranging the compilation sheets within a given volume.

Original Measurements References are abbreviated in the forms given by Chemical Abstracts Service Source Index (CASSI). Names originally in other than Roman alphabets are given as transliterated by Chemical Abstracts. In the case of multiple entries (for example, translations) an asterisk indicates the publication used for compilation of the data.

Variables Ranges of temperature, pressure, etc., are indicated here.

Prepared by The names of all compilers are given here.

Experimental Data Components are described as (1), (2), etc., as defined in the ‘‘Components’’ box. Data are reported in the units used in the original publication, with the exception that modern names for units and quantities are used; e.g., mass percent for weight percent; mol dm^{-3} for molar; etc. Usually, only one type of value (e.g., mass percent) is found in the original paper, and the compiler has added the other type of value (e.g., mole percent) from computer calculations based on 1989 atomic weights.[2] Temperatures are expressed as $t/°C$, $t/°F$ or T/K as in the original; if necessary, conversions to T/K are made, sometimes in the compilations and always in the critical evaluation. However, the author’s units are expressed according to IUPAC recommendations[3] as far as possible.

Errors in calculations, fitting equations, etc., are noted, and where possible corrected. Material inserted by the compiler is identified by the word ‘‘compiler’’ or by the compiler’s name in parentheses or in a footnote. In addition, compiler-calculated values of mole or mass fractions are included if the original data do not use these units. If densities are reported in the original paper, conversions from concentrations to mole fractions are included, but otherwise this is done in the evaluation, with the values and sources of the densities being quoted and referenced.

Details of smoothing equations (with limits) are included if they are present in the original publication and if the temperature or pressure ranges are wide enough to justify this procedure and if the compiler finds that the equations are consistent with the data.

The precision of the original data is preserved when derived quantities are calculated, if necessary by the inclusion of one additional significant figure. In some cases, compilers note that numerical data have been obtained from published graphs using digitizing techniques. In these cases, the precision of the data can be determined by the quality of the original graph and the limitations of the digitizing technique. In some cases graphs have been included, either to illustrate data more clearly, or if this is the only information in the original. Full grids are not usually inserted all it is not intended that users should read data from the graphs.

Method The apparatus and procedure are mentioned briefly. Abbreviations used in Chemical Abstracts are often used here to save space, reference being made to sources of further detail if these are cited in the original paper.

Source and Purity of Materials For each component, referred to as (1), (2), etc., the following information (in this order and in abbreviated form) is provided if available in the original paper: source and specified method of preparation; properties; degree of purity.

Estimated Error If estimated errors were omitted by the original authors, and if relevant information is available, the compilers have attempted to estimate errors (identified by ‘‘compiler’’ or the compiler’s name in parentheses or in a footnote) from the internal consistency of data and type of apparatus used. Methods used by the compilers for estimating and reporting errors are based on Ku and Eisenhart.[4]

Comments and/or Additional Data Many compilations include this section which provides short comments relevant to the general nature of the work or additional experimental and thermodynamic data which are judged by the compiler to be of value to the reader.

References The format for these follows the format for the Original Measurements box, except that final page numbers are omitted. References (usually cited in the original paper) are given where relevant to interpretation of the compile data, or where cross reference can be made to other compilations.

2.2.2. Evaluations

The evaluator’s task is to assess the reliability and quality of the data, to estimate errors where necessary, and to recommend ‘‘best’’ values. The evaluation takes the form of a summary in which all the data supplied by the compiler have been critically reviewed. There are only three boxes on a typical evaluation sheet, and these are described below.

Components The format is the same as on the Compilation sheets.

Evaluator The name and affiliation of the evaluator(s) and date up to which the literature was checked.

Critical Evaluation (a) Critical text. The evaluator checks that the compiled data are correct, assesses their reliability and quality, estimates errors where necessary, and recommends numerical values based on all the published data (including theses, patents and reports) for each given system. Thus, the evaluator reviews the merits or shortcomings of the various data. Only published data are considered. Documented rejection of some published data may occur at this stage, and the corresponding compilations may be removed.

The solubility of comparatively few systems is known with sufficient accuracy to enable a set of recommended values to be presented. Although many systems have been studied by at least two workers, the range of temperatures is often sufficiently different to make meaningful comparison impossible.

Occasionally, it is not clear why two groups of workers obtained very different but internally consistent sets of results at the same temperature, although both sets of results were obtained by reliable methods. In such cases, a definitive assessment may not be possible. In some cases, two or more sets of data have been classified as tentative even though the sets are mutually inconsistent.

(b) Fitting equations. If the use of a smoothing equation is justifiable the evaluator may provide an equation representing the solubility as a function of the variables reported on all the compilation sheets, stating the limits within which it should be used.

(c) Graphical summary. In addition to (b) above, graphical summaries are often given.

(d) Recommended values. Data are recommended if the results of at least two independent groups are available and they are in good agreement, and if the evaluator has no doubt as to the adequacy and reliability of the applied experimental and computational procedures. Data are reported as tentative if only one set of measurements is available, or if the evaluator considers some aspect of the computational or experimental method as mildly undesirable but estimates that it should cause only minor error. Data are considered as doubtful if the evaluator considers some aspect of the computational or experimental method as undesirable but still considers the data to have some value where the order of magnitude of the solubility is needed. Data determined by an inadequate method or under ill-defined conditions are rejected. However, references to these data are included in the evaluation together with a comment by the evaluator as to the reason for their rejection.

(e) References. All pertinent references are given here, including all those publications appearing in the accompanying compilation sheets and those which, by virtue of their poor precision, have been rejected and not compiled.

(f) Units. While the original data may be reported in the units used by the investigators, the final recommended values are reported in SI units[3] when the data can be accurately converted.

2.3. Quantities and Units Used in Compilation and Evaluation of Solubility Data

2.3.1. Mixtures, Solutions, and Solubilities

A *mixture*[5] describes a gaseous, liquid or solid phase containing more than one substance, where the substances are all treated in the same way.

A *solution*[5] describes a liquid or solid phase containing more than one substance, when for convenience one of the substances, which is called the *solvent*, and may itself be a mixture, is treated differently than the other substances, which are called *solutes*. If the sum of the mole fractions of the solutes is small compared to unity, the solution is called a *dilute solution*.

The *solubility* of a solute 1 (solid, liquid, or gas) is the analytical composition of a saturated solution, expressed in terms of the proportion of the designated solute in a designated solvent.[6]

‘‘Saturated’’ implies equilibrium with respect to the processes of dissolution and precipitation; the equilibrium may be stable or metastable. The solubility of a substance in metastable equilibrium is usually greater than that of the same substance in stable equilibrium. (Strictly speaking, it is the activity of the substance in metastable equilibrium that is greater.) Care must be taken to distinguish true metastability from supersaturation, where equilibrium does not exist.

Either point of view, mixture or solution, may be taken in describing solubility. The two points of view find their expression in the reference states used for definition of activities, activity coefficients, and osmotic coefficients.

Note that the composition of a saturated mixture (or solution) can be described in terms of any suitable set of thermodynamic components. Thus, the solubility of a salt hydrate in water is usually given as the relative proportions of anhydrous salt in solution, rather then the relative proportions of hydrated salt and water.

2.3.2. Physicochemical Quantities and Units

Solubilities of solids have been the subject of research for a long time, and have been expressed in a great many ways, as described below. In each case, specification of the temperature and either partial or total pressure of the saturating gaseous component is necessary. The nomenclature and units follow, where possible, IUPAC Green Book.[3] A few quantities follow the ISO standards[7] or the German standard;[8] see a review by Cvitaš[9] for details.

A Note on Nomenclature The nomenclature of the IUPAC *Green Book*[3] calls the solute component B and the solvent component A. In compilations and evaluations, the first-named component (component 1) is the solute, and the second (component 2 for a two-component system) is the solvent. The reader should bear these distinctions in nomenclature in mind when comparing equations given here with those in the *Green Book*.

1. *Mole fraction* of substance 1, x_1 or $x(1)$ (condensed phases), y_1 (gases):

$$x_l = n_1 \Big/ \sum_{s=1}^{c} n_s\,, \tag{1}$$

where n_s is the amount of substance of *s*, and *c* is the number of distinct substances present (often the number of thermodynamic components in the system). *Mole percent* of substance 1 is $100\,x_1$.

2. *Ionic mole fractions* of salt *i*, x_{i+}, x_{i-}: For mixture of *s* binary salts *i*, each of which ionizes completely into n_{i+} cations and υ_{i-} anions, with $\upsilon_i = \upsilon_{i+} + \upsilon_{i-}$ and a mixture of *p* nonelectrolytes *k*, of which some may be considered as solvent components, a generalization of the definition in Robinson and Stokes gives:[10]

$$x_{+i} = \frac{\upsilon_{+i} x_{+i}}{1 + \Sigma_{j=1}^{s} (\upsilon_j - 1) x_j}, \quad x_{-i} = \frac{\upsilon_{-i} x_{+i}}{\upsilon_{+i}} \quad i = 1 \ldots s, \tag{2}$$

$$x_{0k} = \frac{x_j}{1 + \Sigma_{j=1}^{s} (\upsilon_j - 1) x_j}, \quad k = (s+1) \ldots c. \tag{3}$$

The sum of these mole fractions is unity, so that, with $c = s + p$

$$\sum_{i=1}^{s} (x_{+i} + x_{-i}) + \sum_{i=s+1}^{c} x_{oi} = 1. \tag{4}$$

General conversions to other units in multicomponent systems are complicated. For a three-component system containing nonelectrolyte 1, electrolyte 2, and solvent 3,

$$x_1 = \frac{\upsilon_{+2} x_{o1}}{\upsilon_{+2} - (\upsilon_2 - 1) x_{+2}} \quad x_2 = \frac{x_{+2}}{\upsilon_{+2} - (\upsilon_2 - 1) x_{+2}}. \tag{5}$$

These relations are used in solubility equations for salts, and for tabulation of salt effects of solubilities of gases.

3. *Mass fraction* of substance 1, w_1 or $w(1)$:

$$w_1 = g_1 \Big/ \sum_{s=1}^{c} g_s \tag{6}$$

where g_s is the mass of substance *s*. *Mass percent* of substance 1 is $100\,w_1$. The equivalent terms *weight fraction*, *weight percent*, and $g(1)/100\,\mathrm{g}$ *solution* are no longer used.

4. *Solute mole fraction* of substance 1, $x_{\upsilon,1}$:

$$x_{s,1} = m_1 \Big/ \sum_{s=1}^{c'} m_s = x_1 \Big/ \sum_{s=1}^{c'} x_s\,, \tag{7}$$

where c' is the number of solutes in the mixture. These quantities are sometimes called Jänecke mole (mass) fractions.[11,12] *Solute mass fraction* of substance 1, $w_{s,1}$, is defined analogously.

5. *Solvent mole fraction* of substance 1, $x_{\upsilon,1}$:

$$x_{\upsilon,1} = x_1 \Big/ \sum_{s=1}^{p} x_s\,. \tag{8}$$

Here, *p* is the number of solvent components in the mixture. *Solvent mass fraction* of substance 1, $w_{\upsilon,1}$, is defined analogously.

6. *Molality* of solute 1 in a solvent 2, m_1:

$$m_1 = n_1 / n_2 M_2 \tag{9}$$

SI base units: mol kg^{-1}. Here, M_2 is the molar mass of the solvent.

7. *Aquamolality, Solvomolality* of substance 1 in a mixed solvent with components 2, 3,[13] $m_1^{(3)}$:

$$m_1^{(3)} = m_1 \overline{M} / M_3 \tag{10}$$

SI base units: mol kg^{-1}. Here, the average molar mass of the solvent is

$$\overline{M} = x_{\upsilon,2} M_2 + (1 - \upsilon_{\upsilon,2}) M_3 \tag{11}$$

and x_υ, is the solvent mole fraction of component 2. This term is used most frequently in discussing comparative solubilities in water (component 2) and heavy water (component 3) and in their mixtures.

8. *Amount concentration* of solute 1 in a solution of volume V, c_1:

$$c_1 = [\text{formula of solute}] = n_1 / V \tag{12}$$

SI base units: $\mathrm{mol\,cm^{-3}}$. The symbol c_1 is preferred to [formula of solute], but both are used. The old terms *molarity*, *molar* and *moles per unit volume* are no longer used.

9. *Mass concentration* of solute 1 in a solution of volume V, ρ_1:

$$\rho_1 = g_1/V = c_1 M_1/V \tag{13}$$

SI base units: $\mathrm{kg\,m^{-3}}$.

10. *Mole ratio*, $r_{\mathrm{A,B}}$ (dimensionless):[9]

$$r_{n,12} = n_1/n_2 . \tag{14}$$

Mass ratio, symbol $\zeta_{\mathrm{A,B}}$, may be defined analogously.[9]

11. *Ionic strength*, I_m (molality basis), or I_c (concentration basis):

$$I_\mathrm{m} = \frac{1}{2}\sum_i m_i z_i^2, \quad I_c = \frac{1}{2}\sum_i c_i z_\mathrm{i}^\mathrm{z}, \tag{15}$$

where z_i is the charge number of ion i. While these quantities are not used generally to express solubilities, they are used to express the compositions of nonsaturating components. For a single salt i with ions of charge numbers z_+ and z_-,

$$I_m = |z_+ z_-| \upsilon m_i , \quad I_c = |z_+ z_-| \upsilon c_i . \tag{16}$$

Mole and mass fractions and mole ratios are appropriate to either the mixture of the solution point of view. The other quantities are appropriate to the solution point of view only. Conversions between pairs of these quantities can be carried out using the equation given in Table 1 at the end of this Introduction. Other useful quantities will be defined in the prefaces to individual volumes or on specific data sheets.

Salt hydrates are generally not considered to be saturating components since most solubilities are expressed in terms of the anhydrous salt. The existence of hydrates or solvates is noted carefully in the critical evaluation.

Mineralogical names are also quoted, along with their CA Registry Numbers, again usually in the text and CA Registry Numbers (where available) are given usually in the critical evaluation.

In addition to the quantities defined above, the following are useful in conversions between concentrations and other quantities.

12. *Density*, ρ:

$$\rho = g/V = \sum_{s\neq 1}^{c} \rho_s \tag{17}$$

SI base units: $\mathrm{kg\,m^{-3}}$. Here g is the total mass of the system.

13. *Relative density*, $d = \rho/\rho^0$: the ratio of the density of a mixture at temperature t, pressure p to the density of a reference substance at temperature t', pressure p'. For liquid solutions, the reference substance is often water at 4 °C, 1 bar. (In some cases 1 atm is used instead of 1 bar.) The term *specific gravity* is no longer used.

Thermodynamics of Solubility Thermodynamic analysis of solubility phenomena provides a rational basis for the construction of functions to represent solubility data, and thus aids in evaluation, and sometimes enables thermodynamic quantities to be extracted. Both these aims are often difficult to achieve because of a lack of experimental or theoretical activity coefficients. Where thermodynamic quantities can be found, they are not evaluated critically, since this task would involve examination of a large body of data that is not directly relevant to solubility. Where possible, procedures for evaluation are based on established thermodynamic methods. Specific procedures used in a particular volume will be described in the Preface to this volume.

2.4. References for the Introduction

[1] E. A. Hill, J. Am. Chem. Soc. **22**, 473 (1900).

[2] IUPAC Commission on Atomic Weights and Isotopic Abundances, Pure Appl. Chem. **63**, 975 (1989).

[3] L. Mills *et al.*, eds., *Quantities, Units and Symbols in Physical Chemistry* (The Green Book) (Blackwell Scientific Publications, Oxford, UK, 1993).

[4] H. H. Ku, p. 73; C. Eisenhart, p. 69; in H. H. Ku, ed., *Precision Measurement and Calibration* NBS Special Publication 300, Vol. 1 (NBS, Washington, 1969).

[5] V. Gold *et al.*, eds., *Compendium of Analytical Nomenclature* (The Gold Book) (Blackwell Scientific Publications, Oxford, UK, 1987).

[6] H. Freiser and G. H. Nancollas, eds., *Compendium of Analytical Nomenclature* (The Orange Book) (Blackwell Scientific Publications, Oxford, UK, 1987), Sect. 9.1.8.

[7] ISO Standards Handbook, *Quantities and Units* (International Standards Organization, Geneva, 1993).

[8] German Standard, DIN 1310, *Zusammensetzung von Mischphasen* (Beuth Verlag, Berlin, 1984).

[9] T. Cvitaŝ, Chem. Int **17**, 123 (1995).

[10] R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, 2nd ed. (Butterworths, London, 1959).

[11] E. Z. Jänecke, Anorg. Chem. **51**, 132 (1906).

[12] H. L. Priedman, J. Chem. Phys. **32**, 1351 (1960).

[13] J. W. Lorimer, R. Cohen-Adad, and J. W. Lorimer, *Alkali Metal and Ammonium Chlorides in Water and Heavy Water (Binary Systems)*, IUPAC Solubility Data Series, Vol. 47 (Pergamon, Oxford, UK, 1991), p. 495.

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December 1995

TABLE 1. Interconversions between quantities used as measures of solubilities c-component systems containing $c-1$ solutes i and single solvent c (ρ—density of solution: M_1—molar masses of i. For relations for two-component systems, set summations to 0).

	x_i	w_i	m_i	c_i
$x_i=$	x_i	$\frac{1}{1+\frac{M_i}{M_c}\left\{\frac{1}{w_i}-1+\sum_{j\neq 1}^{c-1}\left(\frac{M_c}{M_i}-1\right)\frac{w_j}{w_i}\right\}}$	$\frac{1}{1+\frac{1}{m_iM_c}+\sum_{j\neq i}^{c-1}}\frac{m_j}{m_i}$	$\frac{1}{1+\frac{1}{M_c}\left(\frac{\rho}{c_i}-M_i\right)+\sum_{j\neq 1}^{c-1}\frac{c_j}{c_i}\left(1-\frac{M_j}{M_c}\right)}$
$w_i=$	$\frac{1}{1+\frac{M_c}{M_i}\left\{\frac{1}{x_i}-1+\sum_{j\neq 1}^{c-1}\left(\frac{M_j}{M_c}-1\right)\frac{x_j}{x_i}\right\}}$	w_i	$\frac{1}{1+\frac{1}{m_iM_1}\left(1+\sum_{j\neq 1}^{c-1}m_jM_j\right)}$	$\frac{c_iM_i}{\rho}$
$m_i=$	$\frac{1}{M_c\left(\frac{1}{x_i}-1-\sum_{j\neq 1}^{c-1}\frac{x_j}{x_i}\right)}$	$\frac{1}{M_i\left(\frac{1}{w_i}-1-\sum_{j\neq 1}^{c-1}\frac{w_j}{w_i}\right)}$	m_i	$\frac{1}{\frac{1}{c_i}\left(\rho-\sum_{j\neq 1}^{c-1}c_jM_j\right)-M_i}$
$c_i=$	$\frac{\rho}{M_i+M_c\left\{\frac{1}{x_i}-1+\sum_{j\neq 1}^{c-1}\left(\frac{M_j}{M_c}-1\right)\frac{x_j}{x_i}\right\}}$	$\frac{\rho w_i}{M_i}$	$\frac{\rho}{\frac{1}{m_i}\left(1+\sum_{j\neq 1}^{c-1}m_jM_j\right)-M_j}$	c_i

3. The Solubility of Actinium Compounds

3.1. Actinium Oxalate

Components:

(1) Diactinium tris(oxalate); $Ac_2(C_2O_4)_3$; [7264-35-9]
(2) Water, H_2O; [7732-18-5]

Original Measurements:

D. M. Ziv and I. A. Shestakova, Radiokhimiya **7**, 166–75 (1965).

Variables:

T/K:294

Prepared by:

J. Hála and J. D. Navratil

Experimental Data

Solubility at 21 °C of $Ac_2(C_2O_4)_3$ in water[a]

Method	Ac^{3+a} (mg dm^{-3})	Ac^{3+b} 10^6 mol dm^{-3}	$Ac_2(C_2O_4)_3$ (10^6c_1 /mol dm^{-3})	$10^{27}K_{sp}^{0\ c}$ (mol^5 dm^{-15})	$10^{27}K_{sp}^{0\ d}$ (mol^5 dm^{-15})
Micro	0.86	3.86	1.90	2.70	2.67
Ultramicro	1.5	6.6	3.3	42.0	4.22
Ultramicro	1.7	7.5	3.7	80.0	7.69

[a] The composition of the equilibrium solid phases was not reported.

[b] The authors did not comment on the differences in results obtained by the two methods used.

[c] Calculated by the authors as $K_{sp}^0=[Ac^{3+}]^2[C_2O_4^{2-}]^3$. In solutions of $Ac_2(C_2O_4)_3$ in water the authors assumed the $C_2O_4^{2-}$ concentration to be equal to three times the experimentally found concentration of $Ac_2(C_2O_4)_3$, and $\gamma\pm=1.0$.

[d] Calculated by compiler according to the procedure outlined in footnote, c.

Auxiliary Information

Method/Apparatus/Procedure:

Two variations of the isothermal method were used. For ultramicroscale measurements, 30 μg (~2 mCi) of ^{227}Ac was dissolved in 0.01 ml 1.5 mol dm^{-3} HNO_3 and precipitated with 0.25 mol dm^{-3} $(NH_4)_2C_2O_4$ in a working cone (volume of 10–30 μl) under a microscope. After 1 h of standing the precipitate was centrifuged, mother liquor removed, repeatedly washed, covered with H_2O, and stirred for 10–15 h in a vessel filled with water or glycerine into which an ultrathermocouple was lowered to monitor the temperature. This stirring time was assumed to be sufficient to reach equilibrium, by analogy to a similar study of La(III) oxalate,[1] and also was suitable from the point of view of radiolysis effects (for equilibration times >24 h, the solution was ejected from the cone by gaseous radiolytic products). Samples from saturated solutions (~10^{-4} ml) were taken into calibrated capillaries and placed into a known volume of 1 mol dm^{-3} HNO_3. From this solution samples for counting of ^{227}Ac were taken. For microscale measurements, the work was done in 0.5–2 ml volumes. $Ac_2(C_2O_4)_3$ was precipitated from HNO_3 solution with a saturated solution of $(NH_4)_2C_2O_4$. The precipitate was centrifuged and repeatedly washed and covered with water. To prepare samples for counting, the samples were taken through a capillary filled with fine glass fiber by using a micropump, into 1 mL 1 mol dm^{-3} HNO_3 after which the pipette was washed several times with this solution.

Source and Purity of Materials:

Source and purity of ^{227}Ac preparation and of chemicals used not specified.

Estimated Error:

Temperature: precision ±1 K (authors)
Solubility: insufficient data given to allow for error estimate

References:

[1] R. V. Bryzgalova and N. V. Chernitskaya, Radiokhimiya **3**, 478 (1961).

Components:

(1) Diactinium tris(oxalate); $Ac_2(C_2O_4)_3$; [7264-35-9]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

D. M. Ziv and I. A. Shestakova, Radiokhimiya **7**, 166–75 (1965).

Variables:

T/K:294
c_2 /mol dm^{-3}:5×10^{-5}–0.5

Prepared by:

J. Hála and J. D. Navratil

Experimental Data

Composition of oxalic acid solutions saturated at 21 °C with $Ac_2(C_2O_4)_3$[a]

$C_2H_2O_4$ (c_2 /mol dm^{-3})	pH	Ac^{3+} (mg dm^{-3})	Ac^{3+} (10^6 mol dm^{-3})	$Ac_2(C_2O_4)_3$ (10^6c_1 /mol dm^{-3})	$C_2O_4^{2-\ b}$ (10^5 mol dm^{-3})
5×10^{-5}	3.4	2.5	11	5.5	0.69
5×10^{-4}	3.0	1.2	5.3	2.6	2.96
5×10^{-3}	2.3	0.96	4.2	2.1	5.85
5×10^{-1}	0.9	7.85[c]	34.6[c]	17.3[c]	8.0

[a] The composition of the equilibrium solid phases was not reported.

[b] Calculated by authors from total oxalic acid concentration, pH, and dissociation constants of oxalic acid, $K_{a1}=5.9\times10^{-2}$ mol dm^{-3}, $K_{a2}=6.4\times10^{-5}$ mol dm^{-3}.

[c] This increase in solubility of $Ac_2(C_2O_4)_3$ was explained by the authors by a sharper increase in the H^+ ion concentration in comparison with that of $C_2O_4^{2-}$ ion, and partly by complex formation.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method on microscale was used. $Ac_2(C_2O_4)_3$ was precipitated from HNO_3 solution with saturated solution of $(NH_4)_2C_2O_4$. The precipitate was centrifuged and repeatedly washed and covered with oxalic acid solution in which the solubility was to be determined, and stirred for 10–15 h. This stirring time was taken as sufficient to reach equilibrium, by analogy to a similar study of La(III) oxalate.[1] To prepare samples for ^{227}Ac counting (emanation method), centrifuging itself was not sufficient since a film of $Ac_2(C_2O_4)_3$ remained on the supernatant surface. The samples were taken through a capillary filled with fine glass fiber by using a micropump, into 1 ml 1 mol dm^{-3} HNO_3 after which the pipette was washed several times with this solution.

Source and Purity of Materials:

Source and purity of ^{227}Ac preparation and of chemicals used not specified.

Estimated Error:

Temperature: precision ±1 K (authors)
Solubility: Insufficient data given to allow for error estimate

References:

[1] R. V. Bryzgalova and N. V. Chernitskaya, Radiokhimiya **3**, 478 (1961).

Components:

(1) Diactinium tris(oxalate); $Ac_2(C_2O_4)_3$; [7264-35-9]
(2) Nitric acid; HNO_3 ; [7697-37-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

D. M. Ziv and I. A. Shestakova, Radiokhimiya **7**, 166–75 (1965).

Variables:

T/K:294

Prepared by:

J. Hála and J. D. Navratil

Experimental Data

Four measurements for the solubility of $Ac_2(C_2O_4)_3$ in 0.01 mol dm^{-3} HNO_3 at 21 °C[a]

Ac^{3+} (mg dm^{-3})	Ac^{3+} (10^4 mol dm^{-3})	$Ac_2(C_2O_4)_3$ ($10^5 c_1$ /mol dm^{-3})	K_{sp}[d] (10^{26} mol^5 dm^{-15})	$C_2O_4^{2-}$ (10^6 mol dm^{-3})	K_{sp}^{0}[e] (10^{27} mol^5 dm^{-15})
41.0[b]	1.8	9.0	14.8	1.66	7.5
40.0[c]	1.76	8.8	13.2	1.62	6.7
34.0[c]	1.50	7.5	4.2	1.23	2.1
30.0[c]	1.3	6.5	2.96	1.2	1.5

[a] The composition of the equilibrium solid phases was not reported.

[b] pH = 1.85.

[c] pH = 2.00.

[d] Calculated by authors as $K_{sp}=[Ac^{3+}]^2[C_2O_4^{2-}]^3$. Total oxalate concentration in the saturated solutions was assumed to be equal to three times the experimentally found concentration of $Ac_2(C_2O_4)_3$. The equilibrium concentration of $C_2O_4^{2-}$ was then calculated by using the dissociation constants of oxalic acid, $K_{a1}=5.9\times10^{-2}$ mol dm^{-3} and $K_{a2}=6.4\times10^{-5}$ mol dm^{-3} (source not reported), and the experimentally determined pH.

[e] Calculated by the authors by taking $\gamma_{\pm}=0.55$ as the mean ionic activity coefficient of $Ac_2(C_2O_4)_3$.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method on microscale was used. $Ac_2(C_2O_4)_3$ was precipitated from HNO_3 solution with saturated solution of $(NH_4)_2C_2O_4$. The precipitate was centrifuged and repeatedly washed and covered with oxalic acid solution in which the solubility was to be determined, and stirred for 10–15 h. This stirring time was taken as sufficient to reach equilibrium, by analogy to a similar study of La(III) oxalate.[1] To prepare samples for ^{227}Ac counting (emanation method), centrifuging itself was not sufficient since a film of $Ac_2(C_2O_4)_3$ remained on the supernatant surface. The samples were taken through a capillary filled with fine glass fiber by using a micropump, into 1 ml 1 mol dm^{-3}HNO_3 after which the pipette was washed several times with this solution.

Source and Purity of Materials:

Source and purity of ^{227}Ac preparation and of chemicals used not specified.

Estimated Error:

Temperature: precision ±1 K (authors)
Solubility: insufficient data given to allow for error estimate.

References:

[1] R. V. Bryzgalova and N. V. Chernitskaya, Radiokhimiya **3**, 478 (1961).

Components:

(1) Diactinium tris(oxalate); $Ac_2(C_2O_4)_3$; [7264-35-9]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Nitric acid; HNO_3; [7697-37-2]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

M. L. Salutsky and H. W. Kirby, Anal. Chem. **28**, 1780–2 (1956).

Variables:

c_2 /mol dm^{-3}:0.25
c_3 /mol dm^{-3}:0.1

Prepared by:

J. Hála and J. D. Navratil

Experimental Data

Two measurements were made at an unspecified room temperature. The two values of actinium concentration in solution of 0.25 mol dm^{-3} oxalic acid and approximately 0.1 mol dm^{-3} HNO_3 (pH=1.2) saturated with actinium oxalate were 0.0149 and 0.0158 mg Ac/ml. These were recalculated by the compilers to the solubility of $Ac_2(C_2O_4)_3$ as 0.0179 and 0.0190 mg $Ac_2(C_2O_4)_3$ /ml or 3.28×10^{-5} and 3.48×10^{-5} mol dm^{-3}. The average solubility is then $c_1=3.4\times10^{-5}$ mol dm^{-3}.

Auxiliary Information

Method/Apparatus/Procedure:

The solubility data were obtained from the mass balance during the preparative work on carrier free precipitation of macroconcentrations (7 mg or 0.5 mCi/mL) of ^{227}Ac. After two precipitations with dimethyloxalate, actinium oxalate was stirred at 60–70 °C for 30 min, then for an additional 90 min at an unspecified room temperature, and filtered. The filtrates were analyzed radiochemically for ^{227}Ac.[1] ^{227}Th was removed by double thorium iodate precipitation, then ^{223}Ra was removed by double precipitation of $Ba(NO_3)_2$ in 80% HNO_3. Aliquots of the solution containing the freshly purified actinium were mounted on stainless steel disks and α-counted for 1 day or more after purification. The counts were corrected for the growth of the actinium decay products.

Source and Purity of Materials:

Macroconcentrations of ^{227}Ac were prepared by neutron irradiation of radium. From the actinium fraction obtained by ion exchange on Dowex 50 resin, actinium oxalate was prepared by double homogeneous precipitation with dimethyloxalate at 60–70 °C. Dimethyloxalate was recrystallized from methanol.

Estimated Error:

Solubility: insufficient data given to allow for error estimate.

References:

[1] H. W. Kirby, U.S.A.E.C. Report MLM-773, 1952.

4. The Solubility of Thorium Compounds

4.1. Thorium Oxocarbonate

Components:

(1) Thorium oxocarbonate; $ThOCO_3$; [ ]
(2) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

O. I. Zakharov and G. G. Mikhailov, Izv. VUZ Khim. Khim. Tekhnol. **3**, No. 1, 45–8 (1960).

Variables:

T/K: 293
c_2 /mol dm^{-3}: 0 and 3

Prepared by:

J. Hála

Experimental Data

Solubility at 20 °C of $ThOCO_3$ in water and 3.0 mol dm^{-3} $NaClO_4$

$NaClO_4$ (c_2 /mol dm^{-3})	$ThOCO_3$ (mg L^{-1})	$ThOCO_3$ ($10^5 c_1$ /mol dm^{-3})	$NaClO_4$ (c_2 /mol dm^{-3})	$ThOCO_3$ (mg L^{-1})	$ThOCO_3$ ($10^5 c_1$ /mol dm^{-3})
0	22.1		3.000	25.9	
	23.0			23.6	
	21.2			25.3	
	22.1±1.1[a]	7.17[b]		24.9±1.2[a]	8.08

[a] Average value (authors).
[b] Calculated by compiler for the average value.

Additional information:
Solubility product of $ThOCO_3$ was calculated by the authors as $K^0_{sp} = [ThO^{2+}][CO_3^{2-}] = 9\times10^{-9}$ mol^2 dm^{-6} assuming unit activity coefficients. Solid phases were not investigated but based on measurements in the $ThOCO_3$–Na_2CO_3–$NaClO_4$–H_2O system in the same document, compiler assumes this to be $ThOCO_3\cdot8H_2O$, [ ].

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess solid was equilibrated for 3–10 h in a thermostat. Freshly prepared solid was used since the solubility of $ThOCO_3$ was found to be somewhat dependent on the age of the product. Saturated solutions were analyzed radiometrically for thorium.

Source and Purity of Materials:

$ThOCO_3\cdot8H_2O$ was prepared by precipitation of $Th(NO_3)_4$ solution labeled with UX_1 (^{234}Th), with an equivalent amount of Na_2CO_3 solution.[1] The precipitate was washed with water and air dried. Analysis (mass %): found 57.5 ThO_2, 10.4 CO_2, 32.4 H_2O, calculated for octahydrate (compiler) 58.39 ThO_2, 9.73 CO_2, 31.87 H_2O. UX_1 was prepared from aged uranium salts according to Sollmann and Brown,[2] and its radiochemical purity was checked by measuring its half-life and maximum beta energy. $Th(NO_3)_4$ was purified from beta active decay products of ThB by coprecipitation with lead sulfide. Source of materials used not specified. $NaClO_4$ was a chemically pure product, and was recrystallized from water.

Estimated Error:

Temperature: precision ±0.05 K (authors)
Solubility: precision of the radiometric method ±(2–3%) (authors).

References:

[1] G. T. Seaborg, Editor, *The Actinides* (Russian translation) (Inizdat, Moscow, 1995), p. 454.
[2] T. Sollmann and E. D. Brown, Am. J. Phys. **18**, 427 (1907).

Components:

(1) Thorium oxocarbonate; $ThOCO_3$; [ ]
(2) Sodium carbonate; Na_2CO_3; [497-19-8]
(3) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

O. I. Zakharov and G. G. Mikhailov, Izv. VUZ Khim. Khim. Tekhnol. **3**, No. 1, 45–8 (1960).

Variables:

T/K: 293
c_2 /mol dm^{-3}:0–0.97 at constant ionic strength of 3.00 mol dm^{-3}

Prepared by:

J. Hála

Experimental Data

Solubility at 20 °C of $ThOCO_3$ in Na_2CO_3–$NaClO_4$ solutions[a]

Na_2CO_3 (c_2 /mol dm^{-3})	Th (Mg L^{-1})	$ThOCO_3$ (10^2 mol dm^{-3})[b]	Solid phase[c]
0	25.3	0.0109	$ThOCO_3\cdot8H_2O$, [ ]
0.007	60.2	0.0259	-
0.014	242	0.1043	Th:CO_2=1.0:1.5
0.023	585	0.252	Th:CO_2=1.0:1.8
0.031	1000	0.431	Th:CO_2=1.0:1.99
0.044	1560	0.672	Th:CO_2=1.0:2.16
0.077	2560	1.10	-
0.091	2810	1.21	-
0.146	3800	1.64	[d]
0.161	4730	2.04	[d]
0.191	5150	2.22	[d]
0.209	5770	2.49	[d]
0.272	6660	2.87	[d]
0.375	8370	3.61	[d]
0.415	9120	3.93	[d]
0.54	10550	4.55	[d]
0.74	11200	4.83	[d]
0.97	13170	5.68	[d]

[a] Ionic strength kept constant at 3.00 mol dm^{-3} by using $NaClO_4$.
[b] Calculated by compiler.
[c] Results based on two or three analyses in each measurement.
[d] The solid phase showed the Na:Th:CO_3:H_2O ratio of 6:1:5:12. The authors suggested three possible formulas for it, i.e., $Na_6Th(CO_3)_5\cdot12H_2O$, $Na_4Th(CO_3)_4\cdot Na_2CO_3\cdot12H_2O$, and $Na_2Th(CO_3)_3\cdot2Na_2CO_3\cdot12H_2O$. Of these they preferred the last one with coordination number of 6 for thorium(IV). Since the $Th(CO_3)_5^{6-}$ ion is a well established species,[3] the compiler tentatively suggests the $Na_6Th(CO_3)_5\cdot12H_2O$ [12386-47-9] as a more probable solid phase.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess solid was equilibrated for 3–10 h in a thermostat. Freshly prepared solid was used since the solubility of $ThOCO_3$ was found to be somewhat dependent on the age of the product. The solid was equilibrated with $NaClO_4$ /Na_2CO_3 solutions at constant ionic strength of 3.0 mol dm^{-3}. Saturated solutions were analyzed for thorium either radiometrically or gravimetrically, depending on thorium concentration, and for carbonate titrimetrically using a standard HCl solution. Solid phases were analyzed for water and carbon dioxide gravimetrically during thermal decomposition, and in the residue Na_2CO_3 was determined titrimetrically and thorium gravimetrically.

Source and Purity of Materials:

$ThOCO_3 \cdot 8H_2O$ was prepared by precipitation of $Th(NO_3)_4$ solution labeled with UX_1 (^{234}Th), with an equivalent amount of Na_2CO_3 solution.[1] The precipitate was washed with water and air dried. Analysis (mass %): found 57.5 ThO_2, 10.4 CO_2, 32.4 H_2O, calculated for octahydrate (compiler) 58.39 ThO_2, 9.73 CO_2, 31.87 H_2O. UX_1 was prepared from aged uranium salts according to Sollmann and Brown,[2] and its radiochemical purity was checked by measuring half-life and maximum beta energy. $Th(NO_3)_4$ was purified from beta active decay products of ThB by coprecipitation with lead sulfide. Source of materials used not specified. Sodium salts used were chemically pure products, and were recrystallized from water.

Estimated Error:

Temperature: precision ±0.05 K (authors).

Radiometric method: precision ± (2–3)% (authors).

References:

[1] G. T. Seaborg, Editor, *The Actinides* (Russian translation) (Inizdat, Moscow, 1995), p. 454.

[2] T. Sollmann and E. D. Brown, Am. J. Phys. **18**, 427 (1907).

[3] J. Dervin and J. Faucherre, Bull. Soc. Chim. France, 2930 (1973).

4.2. Salts of Pentakis(carbonato) Thorate (6-) Evaluation of the $Na_6Th(CO_3)_5+Na_2CO_3+H_2O$ System

Components:	**Evaluator:**
(1) Hexasodium pentakis(carbonato)thorate; $Na_6Th(CO_3)_5$; [19610-62-9] (2) Sodium carbonate; Na_2CO_3; [497-19-8] (3) Water; H_2O; [7732-18-5]	J. Hála, Department of Inorganic Chemistry Masaryk University, 611 37 Brno, Czech Republic, February 2000

Critical Evaluation

The solubility in this system was reported in two documents.[1,2] Considerable discrepancies between the two sets of data, exceeding those which could be due to different conditions (i.e., ionic strength, range of Na_2CO_3 concentration) used, are obvious. Luzhnaya and Kovaleva[1] reported the solubility at 298.15 K of $Na_6Th(CO_3)_5$ as a function of sodium carbonate concentration above 0.78 mol dm^{-3} Na_2CO_3. In this concentration range, the solubility of the salt was reported to decrease with increasing Na_2CO_3 concentration (the authors were unable to measure the solubility at lower Na_2CO_3 concentrations because of hydrolysis of $Na_6Th(CO_3)_5$). On the contrary, Dervin and Faucherre[2] reported the solubility of $Na_6Th(CO_3)_5$ to increase with increasing Na_2CO_3 concentration above 0.4 mol dm^{-3} Na_2CO_3 and explained the data by the formation of the $Th(CO_3)_6^{8-}$ ion in solution. At Na_2CO_3 concentration below 0.4 mol dm^{-3} and at ionic strength of 2.0 mol dm^{-3}, the solubility of $Na_6Th(CO_3)_5$ was reported to be independent on Na_2CO_3 concentration. Since there does not seem to be any obvious reason for giving preference to one set of data over the other, reinvestigation of this system would be needed before a final conclusion about the solubility of $Na_6Th(CO_3)_5$ in aqueous Na_2CO_3 solutions could be made.

References:

[1] N. P. Luzhnaya and I. S. Kovaleva, Zh. Neorg. Khim. **6**, 1440 (1961).

[2] J. Dervin and J. Faucherre, Bull. Soc. Chim. France, 2930 (1973).

Components:

(1) Hexasodium pentakis(carbonato)thorate; $Na_6Th(CO_3)_5$; [19610-62-9]
(2) Sodium carbonate; Na_2CO_3; [497-19-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

N. P. Luzhnaya and I. S. Kovaleva, Zh. Neorg. Khim. **6**, 1440–2 (1961).

Variables:

T/K: 298
$10^2\ w_2$ /mass %:7.60–22.97

Prepared by:

J. Hála

Experimental Data

Solubility 25 °C of $Na_6Th(CO_3)_5$ in Na_2CO_3 solutions

Na_2CO_3 (mass %)	Na_2CO_3 (mol kg^{-1})[a]	Na_2CO_3 (mol dm^{-3})[a]	$Th(CO_3)_2$ (mass %)	$Th(CO_3)_2$ (mol kg^{-1})[a]	$Th(CO_3)_2$ (mol dm^{-3})[a]	Density (g cm^{-3})	Solid phase[b]
7.60	0.7802	0.7887	2.20	0.06928	0.07412	1.0960	A
8.59	0.8902	0.8984	2.05	0.06517	0.07047	1.1062	A
10.88	1.152	1.157	1.64	0.05325	0.05903	1.1293	A
14.57	1.604	1.595	1.34	0.04527	0.05199	1.1668	A
18.67	2.155	2.114	1.09	0.03859	0.04603	1.2090	A
20.02	2.347	2.310	1.01	0.03633	0.04425	1.2336	A
22.81	2.767	2.676	0.86	0.03200	0.03975	1.2562	A+B
22.97	2.796	2.698	0.96	0.03585	0.04447	1.2561	A+B
22.70	2.750	2.664	0.86	0.03196	0.03970	1.2562	A+B
22.60	2.723	2.631	0.53	0.01959	0.02433	1.2503	A
22.55	2.709	2.617	0.38	0.01401	0.01741	1.2488	B
22.77	2.730	2.621	—	—	—	1.2433	B

[a] Calculated by compiler.
[b] A:$Na_6Th(CO_3)_5\cdot 12H_2O$; [12386-47-9] B:$Na_2CO_3\cdot 10H_2O$ [6132-02-1].

Additional information:

The solubility branch corresponding to the crystallization of $Na_6Th(CO_3)_5\cdot 12H_2O$ was studied only up to 2.20 mass % $Th(CO_3)_2$ (i.e., at Na_2CO_3 concentrations >7.60 mass %) since the salt hydrolyzed at higher thorium concentrations. The phase diagram showed one triple point at 22.83 mass % Na_2CO_3+0.86 mass %$Th(CO_3)_2$ with A and B as the coexisting solid phases.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Mixtures were equilibrated in a thermostated bath for 2 days which was sufficient to reach equilibrium. Samples of the saturated solutions and the solid phases were analyzed gravimetrically for thorium, sodium and carbonate. Thorium was determined as ThO_2 and sodium as Na_2SO_4. To determine carbonate, the sample was reacted with dilute HCl and the carbon dioxide evolved was absorbed in a weighed U tube filled with ascarite. Solid phases were also characterized by the method of wet residues, x-ray diffraction and thermal analysis.

Source and Purity of Materials:

Source, purity, or method of preparation of $Na_6Th(CO_3)_5$ was not specified. Na_2CO_3 was prepared from reagent grade decahydrate (source not specified) by heating it in a silver dish.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data were given to allow for error estimate.

Components:

(1) Hexasodium pentakis(carbonato)thorate; $Na_6Th(CO_3)_5$; [19610-62-9]
(2) Sodium carbonate; Na_2CO_3; [497-19-8] or Sodium hydrogencarbonate; $NaHCO_3$; [144-55-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

J. Dervin and J. Faucherre, Bull. Soc. Chim. France pt. 1, 2930–3 (1973).

Variables:

T/K: 298
c_2 /mol dm^{-3}: 0.15–1.0 (Na_2CO_3 or $NaHCO_3$)

Prepared by:

J. Hála

Experimental Data

Solubilities at 25 °C of $Na_6Th(CO_3)_5$ in aqueous solutions of Na_2CO_3 or $NaHCO_3$

CO_3^{2-} or HCO_3^- (c_2 /mol dm^{-3})	$Na_6Th(CO_3)_5$ (mol dm^{-3})	K_{sp}[d] (mol^7 dm^{-21})	Solid phase
$[CO_3^{2-}]<0{,}4$[a,b,e]	0.0215	1.37	$Na_6Th(CO_3)_5\cdot 12H_2O$
$[HCO_3^-]=0.15-1.0$[a,c]	0.0208[f]	1.34	not reported

[a] Solutions contained constant concentration of Na^+ ions of 2.0 mol dm^{-3}.
[b] Solutions of Na_2CO_3.
[c] Solutions of $NaHCO_3$.
[d] $K_{sp}=[Th(CO_3)_5^{6-}][Na^+]^6$.
[e] At higher carbonate ion concentration the solubility of $Na_6Th(CO_3)_5$ increased (results were presented in graphical form only) which was interpreted by the authors as being due to the formation of the $Th(CO_3)_6^{8-}$ ion in the saturated solution.
[f] Obtained by authors as the average of eight measurements.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess solid was equilibrated for 48 h with Na_2CO_3 or $NaHCO_3$ solutions of constant Na^+ ion concentration in polyethylene bottles. The salt used to maintain Na^+ concentration at the constant value was not specified. After equilibration, thorium was determined in the saturated solutions titrimetrically with EDTA. The equilibrium solid phases were analyzed to ascertain that their composition did not change during equilibration.

Source and Purity of Materials:

$Na_6Th(CO_3)_5$ was prepared by crystallization from 1 mol dm−3 $Th(NO_3)_4$ on addition of Na_2CO_3 solution according to Dervin *et al.*[1] Compiler assumes that $Na_6Th(CO_3)_5\cdot 12H_2O$ was prepared. Source and purity of materials used were not specified.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

References:

[1] J. Dervin, J. Faucherre, P. Herpin, and S. Volitois, Bull. Soc. Chim. France 2634 (1973).

Components:

(1) Hexaguanidinium pentakis(carbonato)thorate; $(CH_6N_3)_6Th(CO_3)_5$; [51407-02-4]
(2) Guanidinium carbonate; $(CH_6N_3)_2CO_3$; [593-85-1]; or Guanidinium hydrogencarbonate; $(CH_6N_3)HCO_3$; [124-46-9]
(3) Guanidinium nitrate; $(CH_6N_3)NO_3$; [506-93-4]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

J. Dervin and J. Faucherre, Bull. Soc. Chim. France pt. 1, 2930–3 (1973).

Variables:

T/K: 298
c_2 /mol dm^{-3}: 0.25–1.0($(CH_6N_3)_2CO_3$); 0.20–0.60($(CH_6N_3)HCO_3$)

Prepared by:

J. Hála

Experimental Data

Solubilities at 25 °C of $(CH_6N_3)_6Th(CO_3)_5$ in aqueous solutions of guanidinium carbonate or guanidinium hydrogencarbonate

CO_3^{2-} or HCO_3^- (c_2 /mol dm^{-3})	$(CH_6N_3)_6Th(CO_3)_5$ (mol dm^{-3})	K_{sp}^{d} (mol^7 dm^{-21})	Solid phase
0.25–0.35(CO_3^{2-})[a,b]	0.0017[c]	0.109	$(CH_6N_3)_6Th(CO_3)_5\cdot 4H_2O$
0.2–0.60(HCO_3^-)[e]	0.00157[f]	0.10	not reported

[a] Guanidinium carbonate solutions; guanidinium ion concentration kept at 2.0 mol dm^{-3}, ionic strength varied from 2.25 to 3.0 mol dm^{-3}.

[b] At higher carbonate ion concentrations, the solubility of the salt increased with increasing carbonate ion concentration (results presented in graphical form only). The increasing solubility was explained By the authors as being due to the formation of the $Th(CO_3)_6^{8-}$ ion in the saturated solutions.

[c] Average value of four measurements (authors).

[d] $K_{sp}=[Th(CO_3)_5^{6-}][CH_6N_3^+]^6$.

[e] Guanidinium hydrogencarbonate solutions; guanidinium ion concentration and ionic strength kept at 2.0 mol dm^{-3}.

[f] Obtained by authors as the average of seven measurements.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess solid was equilibrated for 48 h with guanidinium carbonate or guanidinium hydrogencarbonate solutions in polyethylene bottles. Ionic strength was kept at the desired value by using guanidinium nitrate. After equilibration, thorium was determined in the saturated solutions titrimetrically with EDTA. The equilibrium solid phases were analyzed to ascertain that their composition did not change during equilibration.

Source and Purity of Materials:

$(CH_6N_3)_6Th(CO_3)_5\cdot 4H_2O$ was prepared by precipitation with guanidinium carbonate of a 1 mol dm^{-3} $Th(NO_3)_4$ solution according to Dervin *et al.*[1] Source and purity of materials used were not specified.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

References:

[1] J. Dervin, J. Faucherre, P. Herpin, and S. Volitois, Bull. Soc. Chim. France 2634 (1973).

4.3. Guanidinium Trisfluorotris(carbonato) Thorate (6-)

Components:

(1) Pentaguanidinium tris(fluoro)-tris(carbonato)thorate; $(CH_6N_3)_5ThF_3(CO_3)_3$; [55328-36-4]
(2) Guanidinium carbonate; $(CH_6N_3)_2CO_3$; [593-85-1]
(3) Guanidinium fluoride; CH_6N_3F; [38078-70-5]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

J. Dervin and F. Fromage, Bull. Soc. Chim. France pt. 1, 133–7 (1975).

Variables:

T/K: 293
c_2 /mol dm^{-3}: 0.05–0.30
c_3 /mol dm^{-3}: 0.03–0.30

Prepared by:

J. Hála

Experimental Data

Solubility at 20 °C of $(CH_6N_3)_5ThF_3(CO_3)_3$ in aqueous solutions of guanidinium carbonate and guanidinium fluoride[a]

CO_3^{2-} (mol dm^{-3})	F^- (mol dm^{-3})	$(CH_6N_3)_3ThF_3(CO_3)_3$ (mol dm^{-3})
0.30[b]	0.25–0.30[b]	0.0032[d]
0.05–0.30[c]	0.30[c]	0.032[d]

[a] Solid phase was $(CH_6N_3)_6Th(CO_3)_5$ [55328-36-4].

[b] Solutions containing varying fluoride ion concentration and constant guanidinium ion concentration of 1.0 mol dm^{-3} at constant ionic strength of 1.3 mol dm^{-3}.

[c] Solutions containing varying carbonate ion concentration and constant guanidinium ion concentration of 1.0 mol dm^{-3}. Ionic strength varied from 1.0 to 1.3 mol dm^{-3}.

[d] The equilibrium solid phase was not stated explicitly. The compiler assumes this to be $(CH_6N_3)_3ThF_3(CO_3)_3$. At the concentrations of CO_3^{2-} and F^- ions used, the solid phase was in equilibrium with the $ThF_3(CO_3)_3^{5-}$ ion. At fluoride ion concentrations < 0.20 mol dm^{-3}, the solubility of $(CH_6N_3)_3ThF_3(CO_3)_3$ decreased to that of $(CH_6N_3)_6Th(CO_3)_5$ (Dervin and Faucherre[1]) due to the transformation of the $ThF_3(CO_3)_3^{5-}$ ion to $Th(CO_3)_5^{6-}$.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess solid was equilibrated for 36 h with solutions containing desired concentrations of guanidinium carbonate and fluoride. The suspension was centrifuged and filtered, and the solid residue was analyzed to ascertain that its composition did not change during equilibration. In the saturated solutions thorium was determined gravimetrically as ThO_2 after evaporation of the solution and ignition the residue to 800 °C.

Source and Purity of Materials:

$(CH_6N_3)_5ThF_3(CO_3)_3$ was prepared by precipitation at 50 to 60 °C from solutions containing 1 mol dm^{-3} guanidinium ion with F^-/CO_3^{2-} ratio varying from 1 to 6, by adding a concentrated solution of $Th(NO_3)_4$. Analysis (mass %): found 30.4 Th, 7.45 F, 12.2 C, 27.5 N, 3.91 H, 17.3 CO_2; calculated 30.2 Th, 7.41 F, 12.5 C, 27.3 N, 3.90 H, 17.2 CO_2. Source and purity of materials used was not specified.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

References:

[1] J. Dervin and J. Faucherre, Bull. Soc. Chim. France 2930 (1973).

4.4. Hexamminecobalt(III) Pentakis(carbonato)Aqua Thorate (6-)

Components:

(1) Bis(hexamminecobalt(III)) pentacarbonato-aquathorate; $[Co(NH_3)_6]_2[Th(CO_3)_5H_2O]$; [ ]
(2) Water; H_2O; [7732-18-5] or Acetone; C_3H_6O; [67-64-1]

Original Measurements:

K. Ueno and M. Hoshi, J. Inorg. Nucl. Chem. **32**, 3817–22 (1970)

Variables:

T/K: 293

Prepared by:

J. Hála

Experimental Data

Solubility at 20 °C of $[Co(NH_3)_6]_2[Th(CO_3)_5H_2O]$ in water and acetone[a]

Solvent	Th (mg/100 g) solvent	$[Co(NH_3)_6]_2[Th(CO_3)_5H_2O]$ $(10^5 m_1$ /mol kg$^{-1})$[b]
Water	0.5	2.15
Acetone	0.1	0.431

[a] Equilibrium solid phases were not investigated.
[b] Calculated by compiler.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess of dry thorium compound was allowed to stand in the solvent for 24 h. The amount of $^{60}Co(NH_3)_6^{3+}$ in the saturated solution was determined radiometrically.

Source and Purity of Materials:

$[Co(NH_3)_6]_2[Th(CO_3)_5H_2O]$ was prepared by precipitation with $^{60}Co(NH_3)_6Cl_3$ of thorium(IV) from 2 mol dm^{-3} $(NH_4)_2CO_3$. The precipitate was washed with water, and vacuum dried. Analysis (mass %): found Th 25.03, $Co(NH_3)_6$ 34.89, CO_3 32.42; calculated for $[Co(NH_3)_6]_2[Th(CO_3)_5H_2O]\cdot 3H_2O$, Th 25.05, $Co(NH_3)_6$ 34.78, CO_3 32.39. Thorium solution used was purified by ion exchange and solvent extraction methods. Source and purity of thorium salt used not specified. $Co(NH_3)_6Cl_3$ was prepared according to Biltz.[1] Distilled water and reagent grade acetone (source not specified) were used.

Estimated Error:

Temperature: precision ± 0.5 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] W. Biltz, Z. Anorg. Allgem. Chem. **83**, 177 (1914)

4.5. Thorium Formate

Components:

(1) Thorium tetrakis(formate); $Th(HCO_2)_4$; [562-99-2]
(2) Formic acid; H_2CO_2; [64-18-6]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

B. Claudel and B. Mentzen, Bull. Soc. Chim. France 1547–50 (1966).

Variables:

T/K: 298

Prepared by:

J. Hála

Experimental Data

Phase diagram of the $Th(HCO_2)_4$–H_2CO_2–H_2O (composition in mass %) at 25 °C was reported in graphical form (see Fig. 1). The only numerical value reported was that of the solubility of $Th(HCO_2)_4$ in water, i.e., 80.7 g $Th(HCO_2)_4.3H_2O$ in 1 dm^{-3} water. This was recalculated by the compiler to $m_1 = 0.172$ mol kg^{-1}.

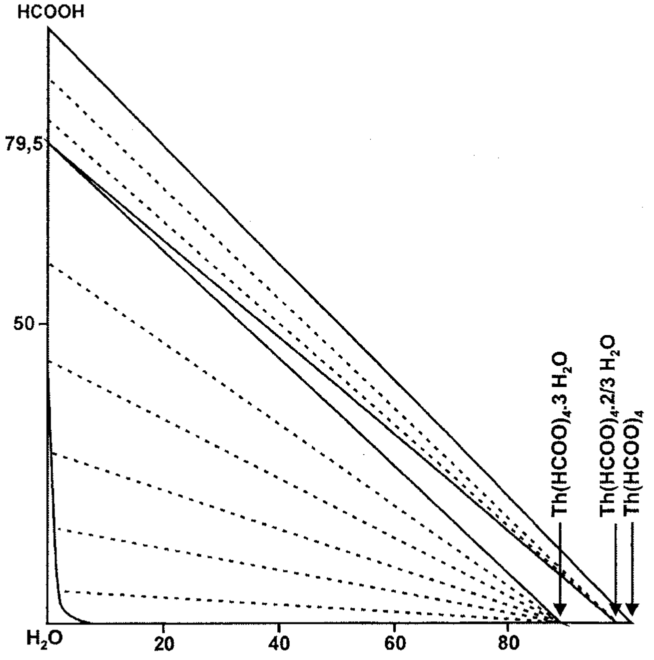

FIG. 1. Thorium tetrakis(formate)–formic acid–water system.

Auxiliary Information

Method/Apparatus/Procedure:

Nothing specified.

Source and Purity of Materials:

$Th(HCO_2)_4\cdot 3H_2O$ was prepared by action of hot 40% formic acid on freshly precipitated $Th(OH)_4$. The salt crystallized upon evaporation or cooling. Analysis, found/calculated, for $Th(HCO_2)_4\cdot 3H_2O$(mass %): Th 49.82/49.78, HCO_2^- 38.65/38.63, H_2O 12.45/11.59.

4.5.1. Thorium Formate Trihydrate

Components:

(1) Thorium tetrakis(formate) trihydrate; $Th(HCO_2)_4 \cdot 3H_2O$; [13266-86-9]
(2) Various solvents

Original Measurements:

B. Claudel and B. Mentzen, Bull. Soc. Chim. France 1547–50 (1966).

Variables:

T/K: 298

Prepared by:

J. Hála

Experimental Data

Solubility of $Th(HCO_2)_4 \cdot 3H_2O$ at 25 °C in various solvents[a]

Solvent	$Th(HCO_2)_4.3H_2O$ (mg L^{-1})	$Th(HCO_2)_4.3H_2O$ ($c_1/10^5$ mol dm^{-3})[b]
oxirane (ethylene oxide); C_2H_4O; [95-21-8]	10.7	2.30
acetone; C_3H_6O; [67-64-1]	17.2	3.69
trichloroethylene; C_2HCl_3; [79-01-6]	17.2	3.69
ethanol; C_2H_6O; [64-17-5]	23.6	5.06
benzene; C_6H_6; [71-43-2]	36.5	7.83
carbon tetrachloride; CCl_4; [56-23-5]	47.2	10.1
2-propanol; C_3H_8O; [67-63-0]	57.9	12.4
methanol; CH_4O; [67-56-1]	137.3	29.5

[a] Equilibrium solid phases were not investigated.
[b] Calculated by compiler.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method was used. The solvents were equilibrated with excess $Th(HCO_2)_4 \cdot 3H_2O$ labeled with ^{228}Th (10 μCi g^{-1}; 3.7×10^5 Bq g^{-1}) until equilibrium was reached. A sample of 1 cm^3 of the saturated solution was analyzed for Th content by measuring γ activity in the range of 0–4 MeV. Activities of the saturated solutions were compared against that of a standard solution containing 1 g $Th(HCO_2)_4 \cdot 3H_2O/dm^3$ with specific activity of 0.01 μCi cm^{-3} (370 Bq cm^{-3}).

Source and Purity of Materials:

^{228}Th-labeled $Th(HCO_2)_4 \cdot 3H_2O$ was prepared by action of hot 40% formic acid on freshly precipitated $^{228}Th(OH)_4$, prepared from $^{228}Th(NO_3)_4$. The salt crystallized upon evaporation or cooling. For analysis, see the data sheet for the $Th(HCO_2)_4$–HCO_2–H_2O system of the same original document.

Estimated Error:

Temperature: precision not reported.
Solubility: precision not specified specified; for the $Th(HCO_2)_4$–HCO_2–H_2O system reported in the same document the authors stated precision of ± 0.05 K for temperature and ± (2–3) % for the radiometric method used for thorium determination.

4.6. Thorium Acetate

Components:

(1) Thorium tetrakis(acetate); $Th(C_2H_3O_2)_4$; [13075-28-0]
(2) Water; H_2O; [7732-18-5]

Original Measurements:

K. N. Kovalenko, D. V. Kazachenko, and O. N. Samsonova, Zh. Neorg. Khim **8**, 2222–5 (1963).

Variables:

T/K: 298

Prepared by:

J. Hála

Experimental Data

The solubility of $Th(C_2H_3O_2)_4$ at 25 °C is reported to be 1.5 g $Th(C_2H_3O_2)_4$ in 100 g water (compiler calculated $m_1 = 0.0320$ mol kg^{-1}).

Additional information:

The pH of 0.000 25–0.008 mol dm^{-3} solutions of $Th(C_2H_3O_2)_4$ varied from 4.22 to 3.95. Under the assumption that the hydrolysis of the salt proceeded to $Th(OH)_4$ the authors calculated the salt to be hydrolyzed to 84.2%. In a more recent study,[1] the products of hydrolysis were identified to be a mixture of basic thorium acetates which formed colloid solutions, and the solubility of $Th(C_2H_3O_2)_4$ was reported to vary within the range of 1.5–1.9 g/100 g water.

Auxiliary Information

Method/Apparatus/Procedure:

Nothing specified.

Source and Purity of Materials:

Anhydrous thorium acetate was obtained by reacting $Th(NO_3)_4 \cdot 5H_2O$ with excess acetic anhydride. The product, insoluble in acetic anhydride, was filtered, washed with acetic anhydride and vacuum dried over NaOH. Analysis, found/calculated for $Th(C_2H_3O_2)_4$ (mass %): Th 49.24/49.56, C 20.25/20.50, H 2.52/2.56.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

References:

[1] A. K. Molodkin, O. M. Ivanova, and G. A. Skotnikova, Zh. Neorg. Khim. **12**, 116 (1967).

Components:

(1) Thorium tetrakis(acetate); $Th(C_2H_3O_2)_4$; [13075-28-0]
(2) Solvents

Original Measurements:

T. Muniyappan and B. Anjaneyalu, Proc. Indian Acad. Sci. **A45**, 412–7 (1957), Curr. Sci. **26**, 319–20 (1957).

Variables:

T/K: 303

Prepared by:

J. Hála

Experimental Data

Solubility at 30 °C of $Th(C_2H_3O_2)_4$ in three solvents[a]

Solvent	$Th(C_2H_3O_2)_4$ (g/100 cm^3 solution)	$Th(C_2H_3O_2)_4$ (mol dm^{-3})	$Th(C_2H_3O_2)_4$ (g/100 g solvent)	$Th(C_2H_3O_2)_4$ (m_1 /mol kg^{-1})[b]
1,2-ethanediamine; $C_2H_8N_2$; [107-15-3]	3.73	0.08	4.30	0.0884
2-aminoethanol; C_2H_7NO; [141-43-5]	[c]	[c]	70.81	1.456
1,2-ethanediol; $C_2H_6O_2$; [107-21-1]	[c]	[c]	0.41	0.00843

[a] Solid phases were not investigated.
[b] Calculated by compiler.
[c] Not reported.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method. Anhydrous materials were handled and solutions prepared in moisture- and CO_2-free air in a glove box. Solubility measurements were carried out in test tubes fitted with ground glass stoppers sealed with Dow-Corning silicone high-vacuum grease. The solvents were equilibrated with excess solid salt in a thermostated bath for 5 days with frequent agitation. The tubes were then centrifuged for 20 min and opened in the dry box. The thorium content was determined by precipitating hydrous oxide upon addition of water, and weighing the ignited oxide.

Source and Purity of Materials:

Anhydrous Th(IV) acetate was obtained by the reaction of Th nitrate with acetic anhydride.[1] The composition of the product was established by ignition to ThO_2. 1,2-ethanediamine monohydrate (B.D·H.) was dehydrated and purified before use. The purified product had a specific conductance of 1.35 $\times 10^{-6}$ Ω^{-1} cm^{-1} at 30 °C, and was stored in glass stoppered flasks which were kept in a desiccator over soda lime, Mg perchlorate and P_2O_5. Anhydrous 2-aminoethanol and 1,2-ethanediol were used.

Estimated Error:

Temperature: precision ±0.05 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] D. Patnaik and S. Panda, J. Indian. Chem. Soc. **12**, 877 (1956).

4.7. Thorium Carboxylates

Components:

(1) Thorium tetrakis (carboxylates); $Th(O_2C(CH_2)_nCH_3)_4$
(2) Potassium nitrate; KNO_3; [7757-79-1]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

L. D. Skrylev, O. V. Perlova, V. F. Sazonova, and C. V. Feldman, Izv. VUZ Tsvet. Metal No. 4, 23–8 (1990).

Variables:

T/K: 293
c_2 /mol dm^{-3}:0.018

Prepared by:

J. Hála

Experimental Data

Solubility in water of thorium carboxylates at 20 °C[a]

Salt	$Th(O_2C(CH_2)_nCH_3)_4$ ($c_1/10^6$ mol dm^{-3})
Thorium tetrakis(decanoate); $Th(O_2C(CH_2)_8CH_3)_4$;[ ]	1.25
Thorium tetrakis(undecanoate); $Th(O_2C(CH_2)_9CH_3)_4$;[134893-75-7]	0.91
Thorium tetrakis(dodecanoate); $Th(O_2C(CH_2)_{10}CH_3)_4$;[107305-72-6]	0.67
Thorium tetrakis(tridecanoate); $Th(O_2C(CH_2)_{11}CH_3)_4$;[134893-76-8]	0.51
Thorium tetrakis(tetradecanoate); $Th(O_2C(CH_2)_{12}CH3)_4$;[107176-04-5]	0.37
Thorium tetrakis(pentadecanoate); $Th(O_2C(CH_2)_{13}CH_3)_4$;[ ]	0.27
Thorium tetrakis(hexadecanoate); $Th(O_2C(CH_2)_{14}CH_3)_4$;[ ]	0.19

[a] All saturated solutions showed pH of 6.0, contained 0.0108 mol dm^{-3} KNO_3, and were of colloidal nature.

Auxiliary Information

Method/Apparatus/Procedure:

Potassium salts of the corresponding carboxylic acids, in the form of 0.01 mol dm^{-3} solutions, were added to a $Th(NO_3)_4$ solution in stoichiometric amounts required for the formation of the corresponding thorium salts. Saturated solutions were analyzed for the thorium content nephelometrically.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

4.8. Thorium O-Alkylcarbonodithioates

Components:
(1) Thorium tetrakis(O-alkylcarbonodithioates); (xanthogenates); $Th(OS_2C(CH_2)_nCH_3)_4$
(2) Potassium nitrate; KNO_3; [7757-79-1]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
L. D. Skrylev, O. V. Perlova, V. F. Sazonova, and C. V. Feldman, Izv. VUZ Tsvet. Metal No. 4, 23–8 (1990).

Variables:
T/K: 293
c_2 /mol dm^{-3}:0.018

Prepared by:
J. Hála

Experimental Data

Solubility in water of thorium xanthogenates at 20 °C[a]

Salt	$Th(OS_2C(CH_2)_nCH_3)_4$ ($c_1/10^6$ mol dm^{-3})
$Th(OS_2C(CH_2)CH_3)_4$; [134902-18-4]	36.60
$Th(OS_2C(CH_2)_3CH_3)_4$; [134902-19-5]	20.60
$Th(OS_2C(CH_2)_5CH_3)_4$; [134902-20-8]	12.00
$Th(O_2C(CH_2)_9CH_3)_4$; [134902-21-9]	4.33

[a] All saturated solutions showed pH of 6.0, contained 0.0108 mol dm^{-3} KNO_3, and were of colloidal nature.

Auxiliary Information

Method/Apparatus/Procedure:
Potassium salts of the corresponding xanthogenic acids, in the form of 0.01 mol dm^{-3} solutions, were added to a $Th(NO_3)_4$ solution in stoichiometric amounts required for the formation of the corresponding thorium salts. Saturated solutions were analyzed for the thorium content nephelometrically.

Source and Purity of Materials:
Nothing specified.

Estimated Error:
Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

4.9. Thorium Oxalate

4.9.1. Evaluation of the $Th(C_2O_4)_2+H_2O$ System

Components:
(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Water; H_2O; [7732-18-5]

Evaluator:
J. Hála, Department of Inorganic Chemistry, Masaryk University, 611 37 Brno, Czech Republic, February 2000

Critical Evaluation:

There are five values available for the solubility of thorium oxalate in water of which three have been extracted from documents dealing with ternary systems.[2,3,5] At 298.15 K, the solubility of $Th(C_2O_4)_2$ has been reported to be $(4.1-4.8)\times10^{-5}$ (Grinberg, Petrzhak, and Evteev[1]), 1.84×10^{-6} (Luzhnaya and Kovaleva[2]), and 4.74×10^{-5} (Kurnakova and Shubochkin[3]), all in mol kg^{-1}, and 2.7×10^{-7} mol dm^{-3}.[4] These values differ from one another by 2 orders of magnitude and were obtained under different equilibration conditions. It seems that the value of 2.7×10^{-7} mol dm^{-3} (Spitsyn[4]) could have resulted from rather short equilibration time applied (6 h only) since in other documents considerably longer equilibration took place. The reason for the discrepancy between the data in Refs. 2 and 3, where roughly the same equilibration time of 5–6 days was used, is not clear. The value of Colani,[5] although obtained at different temperatures, seems again to be pointing to the importance of equilibration conditions. In this document equilibration took place for 3 months, and the obtained solubility is in good agreement with the data of Grinberg and Petrzhak[1] and Kurnakova and Shubochkin.[3] Since Grinberg and Petrzhak[1] reported a range for the solubility rather than a single value the evaluator recommends the solubility value of Kurnakova and Shubochkin[3] be used as a tentative value at 298.15 K.

References:

[1] A. A. Grinberg, G. I. Petrzhak, and L. I. Evteev, Zh. Neorg. Khim **3**, 204 (1958).
[2] N. P. Luzhnaya and I. S. Kovaleva, Zh. Neorg. Khim. **6**, 1436 (1961).
[3] A. S. Kurnakova and L. K. Shubochkin, Zh. Neorg. Khim. **8**, 1249 (1963).
[4] V. I. Spitsyn, Zh. Russ. Fiz. Khim. Obsh. **49**, 357 (1917).
[5] M. Colani, Compt. Rend. **156**, 1075 (1913); **156**, 1907 (1913).

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Water; H_2O; [7732-18-5]

Original Measurements:

A. A. Grinberg, G. I. Petrzhak, and L. I. Evteev, Zh. Neorg. Khim. **3**, 204–11 (1958).

Variables:

T/K: 298

Prepared by:

J. Hála

Experimental Data

The solubility of $Th(C_2O_4)_2 \cdot 6H_2O$ at 25 °C in water was reported to be $(2.1-2.5)\times 10^{-2}$ g salt/kg water or $(4.1-4.8)\times 10^{-5}$ mol kg^{-1}.

Additional information:

pH and molar conductivity of the saturated solutions were 5.9 and approximately 200 S cm^2 mol^{-1} on average, respectively. From this the authors concluded that in the saturated solutions Th(IV) oxalate was dissociated mainly to $Th(C_2O_4)^{2+}$ and $C_2O_4^{2-}$ ions.

Auxiliary Information

Method/Apparatus/Procedure:

Nothing specified.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: not reported.
Solubility: insufficient data given to allow for error estimate.

4.9.2. Thorium Oxalate Dihydrate

Components:

(1) Thorium bis(oxalate) dihydrate; $Th(C_2O_4)_2 \cdot 2H_2O$; [14041-32-8]
(2) Ammonia; NH_3; [7664-41-7]

Original Measurements:

G. W. Watt, W. A. Jenkins, and J. M. McCuiston, J. Am. Chem. Soc. **72**, 2260–2 (1950).

Variables:

T/K: 298

Prepared by:

J. Hála

Experimental Data

The solubility of $Th(C_2O_4)_2 \cdot 2H_2O$ at 25 °C was reported to be 0.51 g $Th(C_2O_4)_2 \cdot 2H_2O$/100 g NH_3. Compiler calculated the solubility to be $m_1 = 0.0115$ mol kg^{-1}. The equilibrium solid phase was $Th(C_2O_4)_2 \cdot 2H_2O$; [14041-32-8].

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. 2 g of $Th(C_2O_4)_2.2H_2O$ were treated with liquid NH_3 for 3 h in a special reactor[1] at 25 °C. The method for Th determination in the saturated solution was not specified. The composition of the equilibrium solid phase was confirmed by chemical analysis. Excess NH_3 from the saturated solution was evaporated, the solid was washed and vacuum dried. There was no visual evidence of a reaction of the solid with NH_3, and $Th(C_2O_4)_2 \cdot 2H_2O$ was recovered unchanged except for a small retention of NH_3.

Source and Purity of Materials:

Dihydrate of the salt was obtained by dehydration of $Th(C_2O_4)_2 \cdot 6H_2O$ at 110 °C. The latter was prepared from $Th(NO_3)_4 \cdot 4H_2O$ (A.D. MacKay Co.) and reagent grade oxalic acid. The dihydrate was analyzed for Th content: found 52.3%, calculated for $Th(C_2O_4)_2 \cdot 2H_2O$,52.3%.

Estimated Error:

Temperature: not reported.
Solubility: insufficient data given to allow for error estimate.

References:

[1] G. W. Wat and T. E. Moore, J. Am. Chem. Soc. **70**, 1197 (1948).

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Hydrogen chloride; HCl; [7647-01-0]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

G. Hauser and F. Wirth, Z. Anorg. Chem. **78**, 75–94 (1912).

Variables:

T/K: 298
$100w_2$ /mass%: 24.8–37.6

Prepared by:

J. Hála

Experimental Data

Composition of HCl solutions saturated with $Th(C_2O_4)_2$ at 25 °C[a]

HCl ($100w_2$ /mass%)	ThO_2 (g kg^{-1} solution)	$Th(C_2O_4)_2$ (mol kg^{-1} solution)[b]
24.8	0.100	3.79×10^{-4}
37.0	3.450	0.0131
37.6	3.492	0.0133

[a] Equilibrium solid phase was reported to be $3Th(C_2O_4)_2\cdot ThCl_4\cdot 20H_2O$, [ ].
[b] Calculated by compiler.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method[1] used. Excess $Th(C_2O_4)_2\cdot 6H_2O$ was equilibrated in a thermostated bath with solutions of the desired composition for at least 24 h. The solid phase was allowed to settle in the bath, and some 60–100 g of the saturated solution was withdrawn through a filter layer. The aliquot was evaporated and ignited to ThO_2. A small correction was applied for the mass of silicates dissolved from glassware. The equilibrium solid phase was characterized by chemical analysis: calculated/found (mass %) for $3Th(C_2O_4)_2\cdot ThCl_4\cdot 20H_2O$:$ThO_2$ 47.37/47.11, Cl 7.24/7.00.

Source and Purity of Materials:

$Th(C_2O_4)_2\cdot 6H_2O$ was prepared by precipitating it with concentrated HCl from the solution of the salt in ammonium oxalate. The procedure was repeated several times to purify the thorium oxalate from lanthanides. After air drying the product contained, in mass %, 50.68 ThO_2, 27.47 C_2O_3, and 21.67 H_2O. Calculated for the hexahydrate (respective values): 51.21, 27.88, and 20.91. Oxalic acid used did not show any residue on ignition.

Estimated Error:

Temperature: precision ±0.1 K (Hauser and Wirth[1]).
Solubility: insufficient data given to allow for error estimate.

References:

[1] O. Hauser and F. Wirth, Z. Anal. Chem. **47**, 389 (1908).

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Hydrogen chloride; HCl; [7647-01-0]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

M. Colani, Compt. Rend. **156**, 1075–6 (1913); **156**, 1907–9 (1913).

Variables:

T/K: 285–323
$100w_2$ /mass%: 0–35

Prepared by:

J. Hála

Experimental Data

Solubility of $Th(C_2O_4)_2$ in aqueous HCl solutions

Temperature (°C)	HCl ($100w_2$ /mass %)	HCl (m_2 /mol kg^{-1})[a]	Th (mass %)	$Th(C_2O_4)_2$ (10^3m_1 /mol kg^{-1})[a]	Solid phase[b]
12	3.2	0.907	0.0027	0.1202	A
	23.0	8.200	0.072	4.03	B
	29.9	11.73	0.16	9.86	B
	33.1	13.63	0.31	20.1	B
15	26.3	9.80	0.10	5.86	B
	32.5	13.16	0.28	18.0	B
	35.0	14.91	0.60	40.2	B
17	0	0	0.001	0.0431	A
	1.2	0.333	0.002	0.0872	A
	3.6	1.024	0.0035	0.156	A
	4.6	1.322	0.0054	0.244	A
	8.4	2.515	0.010	0.471	A
	13.1	4.136	0.016	0.799	A
	16.2	5.303	0.022	1.13	A
	19.8	6.775	0.037	1.99	A
50	0	0	0.0010	0.0431	A
	4.1	1.137	0.0058	0.261	A
	8.4	2.515	0.016	0.753	A
	12.4	3.884	0.033	1.62	A
	16.1	5.286	0.059	3.03	A
	18.0	6.026	0.077	4.05	A
	19.9	6.822	0.097	5.26	A
	21.6	7.569	0.133	7.32	A
	21.2	7.588	0.17	9.56	B
	23.0	8.235	0.20	11.3	B
	26.8	10.08	0.27	16.0	B
	29.8	11.72	0.44	27.2	B
	32.3	13.26	0.88	56.8	B
	34.6	14.85	1.51	102	B

[a] Calculated by compiler.
[b] (A) $Th(C_2O_4)_2\cdot 6H_2O$, [16788-62-8]; (B) $Th_4(C_2O_4)_6Cl_4\cdot 20H_2O$, [ ].

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method was used. No details were given except that at 17 °C 3 months were necessary to bring the solution into equilibrium with solid $Th(C_2O_4)_2\cdot 6H_2O$. Experiments at >21 mass % were carried out using $Th_4(C_2O_4)_6Cl_4\cdot 20H_2O$ as the starting solid phase. The composition of the latter as the equilibrium solid phase was confirmed by chemical analysis.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

Components:	**Original Measurements:**
(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0] (2) Hydrogen chloride; HCl; [7647-01-0] (3) Water; H_2O; [7732-18-5]	V. I. Spitsyn, Zh. Russ. Fiz. Khim. Obsh. (J. Russ. Phys. Chem. Soc.) **49**, 357–70 (1917).
Variables:	**Prepared by:**
T/K: 298 c_2 /mol dm^{-3}: 0.04–1.0	J. Hála

Experimental Data

Solubility at 25 °C of $Th(C_2O_4)_2$ in HCl solutions[a]

HCl (c_2 /mol dm^{-3})	ThO_2 (mg dm^{-3})	$Th(C_2O_4)_2$[b] ($10^5 c_1$ /mol dm^{-3})
0.04	0.6	0.23
0.09	1.7	0.65
0.23	4.7	1.81
0.38	7	2.69
0.48	8.5	3.29
0.50	12	4.61
0.64	16	6.15
0.82	21	8.08
1.0	24	9.23

[a] Solid phases not investigated. Based on the data pertaining to the range of HCl concentration used (Colani[1]), compiler assumes this to be $Th(C_2O_4)_2 \cdot 6H_2O$, [16788-62-8].
[b] Calculated by compiler.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess $Th(C_2O_4)_2 \cdot 6H_2O$ labeled with ^{234}Th was equilibrated with the solution of the desired composition for 6 h which was found sufficient for saturation to be reached. After equilibration, 100–200 mL of the saturated solution was evaporated on a porcelaine dish and β activity of the residue was measured in an electroscope. The amount of thorium was obtained by comparing the measured activity with that of a known amount of labeled $Th(C_2O_4)_2 \cdot 6H_2O$.

Source and Purity of Materials:

Labeled $Th(C_2O_4)_2 \cdot 6H_2O$ was prepared by precipitation. An aliquot of UX_1 (^{234}Th) preparation was added to a solution of $Th(NO_3)_4$, and $Th(C_2O_4)_2 \cdot 6H_2O$ was precipitated by adding hot solution of oxalic acid. The precipitate was washed several times with hot water. After several decantations with cold water the precipitate turned into crystalline form.

Estimated Error:

Temperature: not reported.

Thorium concentration: precision ±(1–2)% (author).

References:

[1] M. Colani, Compt. Rend. **156**, 1075 (1913); **156**, 1907 (1913).

4.9.3. Evaluation of the $Th(C_2O_4)_2+HNO_3+H_2O$ System

Components:	**Evaluator:**
(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0] (2) Nitric acid; HNO_3; [7697-37-2] (3) Water; H_2O; [7732-18-5]	J. Hála, Department of Inorganic Chemistry, Masaryk University, 611 37 Brno, Czech Republic, February 2000

Critical Evaluation:

Four sets of data are available for the solubility of $Th(C_2O_4)_2$ in aqueous HNO_3 solutions[1–4] of which the data of Pazukhin *et al.*[4] have been extracted from the study of the quarternary system $Th(C_2O_4)_2$–oxalic acid–HNO_3–H_2O. While the data from documents[1,3,4] seem to agree with one another within experimental error, the data of Kurnakova and Shubochkin[2] are higher by a factor ranging from 1.5 to 3.5. To illustrate the situation, the data for $m_2 < 4$ mol HNO_3 /kg from Refs. 1–4 have been summarized in a graphical form (see Fig. 2). This difference in solubilities seems to coincide well with the different equilibration times used. While Kurnakova and Shubochkin[2] used equilibration time of 5–6 days, the authors of other studies equilibrated the systems for a few hours only. It seems thus likely that true equilibrium was not reached in Refs. 1, 3, 4. It is noteworthy that the same problem appears in the binary system $Th(C_2O_4)_2$–H_2O (see Critical Evaluation) in this section. Moreover, Kurnakova and Shubochkin[2] used a more sensitive radiometric method for the determination of thorium, and Bryzgalova *et al.*[3] reported rather low precision for their colorimetric method. The very good agreement of some of the data from Ref. 3 and 4 (e.g., for 0.5, 1.6, and 2.7 mol HNO_3 /kg) can thus be fortituous. The evaluator therefore recommends the data of Kurnakova and Shubochkin[2] be used as tentative ones.

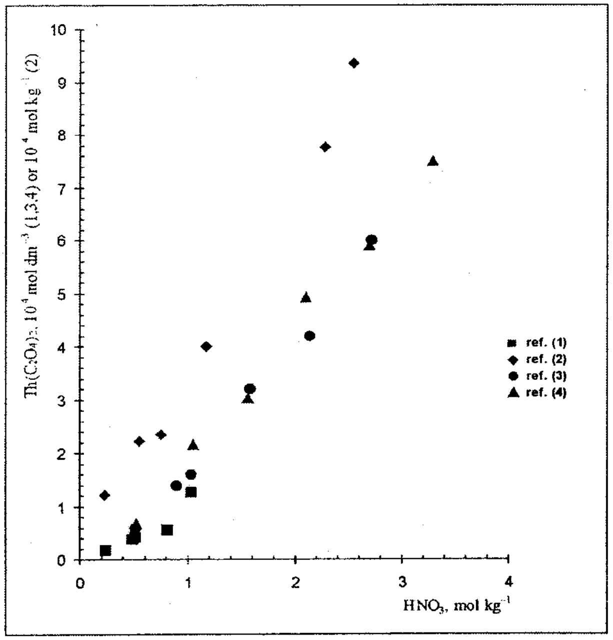

FIG. 2. Thorium bix(oxalate)–nitric acid–water system

References:

[1] V. I. Spitsyn, Zh. Russ. Fiz. Khim. Obsh. **49**, 357 (1917).
[2] A. G. Kurnakova and L. K. Shubochkin, Zh. Neorg. Khim. **8**, 1249 (1963).
[3] R. V. Bryzgalova, Yu. M. Rogozin, and I. V. Chernitskaya, Radiokhimiya **12**, 286 (1970).
[4] E. M. Pazukhin, E. A. Smirnova, A. S. Krivokhatskii, and Yu. L. Pazukhina, Radiokhimiya **27**, 606 (1985).

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Nitric acid; HNO_3; [7697-37-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

V. I. Spitsyn, Zh. Russ. Fiz. Khim. Obsh. (J. Russ. Phys. Chem. Soc.) **49**, 357–70 (1917).

Variables:

T/K: 298
c_2 /mol dm^{-3} = 0.016–1.0

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $Th(C_2O_4)_2$ in HNO_3 solutions[a]

HNO_3 (c_2 /mol dm^{-3})	HNO_3 (m_2 /mol kg^{-1})[b,c]	ThO_2 (mg dm^{-3})	$Th(C_2O_4)_2$[b] ($10^5 c_1$ /mol dm^{-3})
0.016	0.016	0.3	0.12
0.06	0.06	1.3	0.50
0.24	0.24	4.5	1.73
0.47	0.48	10.1	3.88
0.50	0.509	11	4.23
0.78	0.805	14.4	5.54
1.0	1.034	33	12.7

[a] Solid phases not investigated. With reference to another study of the solubility in the $Th(C_2O_4)_2$–HNO_3–H_2O system,[1] compiler assumes this to be $Th(C_2O_4)_2 \cdot 6H_2O$, [16788-62-8].

[b] Calculated by compiler.

[c] Calculated by using densities of HNO_3 solutions from Ref. 2.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess $Th(C_2O_4)_2 \cdot 6H_2O$ labeled with ^{234}Th was equilibrated with the solution of the desired composition for 6 h which was found sufficient for saturation to be reached. After equilibration, 100–200 mL of the saturated solution was evaporated on a porcelaine dish and β activity of the residue was measured in an electroscope. The amount of thorium was obtained by comparing the measured activity with that of a known amount of labeled $Th(C_2O_4)_2 \cdot 6H_2O$.

Source and Purity of Materials:

Labeled $Th(C_2O_4)_2 \cdot 6H_2O$ was prepared by precipitation. An aliquot of UX_1 (^{234}Th) preparation was added to a solution of $Th(NO_3)_4$, and $Th(C_2O_4)_2 \cdot 6H_2O$ was precipitated by adding hot solution of oxalic acid. The precipitate was washed several times with hot water. After several decantations with cold water the precipitate turned into crystalline form.

Estimated Error:

Temperature: precision not reported. Solubility: precision ±(1–2)% (author).

References:

[1] A. G. Kurnakova and L. K. Shubochkin, Zh. Neorg. Khim. **8**, 1249 (1963).
[2] *Physico-Chemical Tables*, Publ. House Tech. Lit., Prague, (1953), Vol. 1, p. 213.

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Nitric acid; HNO_3; [7697-37-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. G. Kurnakova and L. K. Shubochkin, Zh. Neorg. Khim. **8**, 1249–54 (1963); Russ. J. Inorg. Chem. **8**, 647–50 (1963).

Variables:

T/K: 298
m_2 /mol kg^{-1}: 0–23.74

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $Th(C_2O_4)_2$ in HNO_3 solutions[a]

HNO_3 (w_2 /mass %)	HNO_3 (mol kg^{-1})[b]	HNO_3 (m_2 /mol kg^{-1})[c]	Th (mass %)	Th (10^4 mol kg^{-1})[b]	Th (10^4 m_1 /mol kg^{-1})
0	0	0	0.0011	0.47	0.474
1.45	0.23	0.234	0.0029	1.25	1.27
3.45	0.55	0.567	0.0050	2.15	2.23
4.74	0.75	0.790	0.0052	2.24	2.35
7.40	1.17	1.27	0.0086	3.69	4.00
14.34	2.28	2.66	0.0154	6.63	7.75
16.07	2.55	3.04	0.0182	7.84	9.35
18.63	2.96	3.63	0.0221	9.52	11.71
20.85	3.31	4.18	0.0304	13.10	16.56
27.52	4.37	6.03	0.0481	20.72	28.62
31.34	4.97	7.25	0.0685	29.51	43.04
36.80	5.84	9.25	0.0981	42.26	67.00
46.92	7.45	14.09	0.238[d]	102.53	194.1
53.06	8.42	18.13	0.485[d]	208.9	450.0
59.28	9.41	23.74	1.093[d]	467.0	1188

[a] The equilibrium solid phase was $Th(C_2O_4)_2 \cdot 6H_2O$, [16788-62-8], in all solutions.

[b] Mol solute per kg solution.

[c] Calculated by compiler using densities of HNO_3 solutions from Ref. 1.

[d] The sharp increase of $Th(C_2O_4)_2$ solubility at high HNO_3 concentrations was ascribed by the authors to the formation of nitrato and/or nitrato–oxalato complexes of thorium in these solutions.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Solutions with excess solid were agitated for 5–6 days. The concentration of HNO_3 in the saturated solutions was determined by titration with 0.1 N NaOH. Thorium concentration was determined radiometrically. After centrifugation, five to eight drops of the saturated solution were weighed out onto an ashless filter for β-counting. From solutions of dilute HNO_3 where the solubility of $Th(C_2O_4)_2$ is low, 0.3–5 g of the solution were withdrawn in 15 separate portions with drying after each addition, and counted. The β activity of the saturated solutions was compared with that of the standards prepared from labeled $Th(C_2O_4)_2 \cdot 6H_2O$. At high $Th(C_2O_4)_2$ concentrations, thorium in the saturated solutions was determined gravimetrically (method not specified). The composition of the equilibrium solid phases was determined by optical microscopy, in solutions containing high HNO_3 concentrations by chemical analysis and the method of wet residues.

Source and Purity of Materials:

$Th(C_2O_4)_2 \cdot 6H_2O$ was prepared from thorium nitrate of unspecified source and purity. To increase β activity of thorium for its subsequent radiometric determination, aged $UO_2(NO_3)_2$ in radioactive equilibrium with the thorium isotope UX_1 (^{234}Th) was added to $Th(NO_3)_4$, and $Th(C_2O_4)_2 \cdot 6H_2O$ was precipitated from hot solution with a stoichiometric amount of oxalic acid. The labeled $Th(C_2O_4)_2 \cdot 6H_2O$ was filtered, washed ten times with boiling water, and air dried for 4–5 days. Freshly distilled 60.4% HNO_3 was used.

Estimated Error:

Temperature: precision ±0.1 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] *Physico-Chemical Tables*, (Publ. House Tech. Liter., Prague, 1953), Vol. 1,p. 213.

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Nitric acid; HNO_3; [7697-37-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

R. V. Bryzgalova, Yu. M. Rogozin, and I. V. Chernitskaya, Radiokhimiya **12**, 286–91 (1970).

Variables:

T/K: 298
c_2 /mol dm^{-3}=0.5–2.5

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $Th(C_2O_4)_2$ in HNO_3 solutions[a]

HNO_3 (c_2 /mol dm^{-3})[b]	HNO_3 (m_2 /mol kg^{-1})[c]	$Th(C_2O_4)_2$ ($10^4 c_1$ /mol dm^{-3})	K_{sp}[d] (10^{21} mol^3 dm^{-9})
0.5	0.509	0.6	1.2
0.865	0.890	1.4	1.9
1.0	1.034	1.6	2.0
1.5	1.576	3.2	1.2
2.0	2.140	4.2	1.4
2.5	2.715	6.0	1.1

[a] The nature of the equilibrium solid phases was not investigated. With reference to Ref. 1 compiler assumes this to be the hexahydrate, $Th(C_2O_4)_2 \cdot 6H_2O$, [16788-62-8].

[b] The method for the determination of HNO_3 concentration in the saturated solutions was not specified. Compiler assumed that the data reported refer to initial acid concentration.

[c] Calculated by compiler using densities of HNO_3 solutions from Ref. 2.

[d] The K_{sp} values were obtained in a two-step approximation. First, full dissociation of $Th(C_2O_4)_2$ was assumed. By using the K_{sp} so obtained (1.5×10^{-21} mol^3 dm^{-9}) the instability constants of $Th(C_2O_4)^{2+}$ and $Th(C_2O_4)_2$ complexes were calculated as $K_1 = 9.5\times10^{-9}$ mol dm^{-3} and $K_2 = 2.5\times10^{-5}$ mol^2 dm^{-6}, respectively, and, in turn, used to calculate the refined K_{sp} values. The average value recommended by authors is 1.2×10^{-21} mol^3 dm^{-9}. The effect of ionic strength and complexing of thorium(IV) with nitrate ion were not taken into account.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. 20–100 mg of $Th(C_2O_4)_2 \cdot 6H_2O$ were stirred with a rotary stirrer at 200–600 rpm with 10 mL solution until equilibrium was reached (a few hours). Excess solid was filtered off in a thermostated space at 25 °C. Thorium in the filtrate was determined colorimetrically with arsenazo III.[3] Data reported are average values of 3–4 determinations.

Source and Purity of Materials:

$Th(C_2O_4)_2 \cdot 6H_2O$ was prepared by precipitation from 0.1 mol dm^{-3} solutions of $Th(NO_3)_4$ and oxalic acid. The precipitate was allowed to stand for 1 day, the mother liquor decanted, and the precipitate stirred with 0.1 mol dm^{-3} HNO_3 for 5–6 h. The washing was repeated until the wash solution contained equivalent concentrations of thorium and oxalic acid. The precipitate was then filtered, washed with water, ethanol and ether, and air dried at room temperature. The composition of the product as found by analysis was Th:oxalate:H_2O=1:1.98:6.3.

Estimated Error:

Temperature:precision ±0.2 K (authors).
Thorium concentration:precision ±10% for $C_{Th} > 1.2\times10^{-6}$ mol dm^{-3} and ±(20–30)% for $C_{Th} < 1.2\times10^{-6}$ mol dm^{-3} (authors).

References:

[1] A. G. Kurnakova and L. K. Schubochkin, Zh. Neorg. Khim **8**, 1249 (1963).
[2] *Physico-chemical Tables* (Publ. House of Technical Literature, Prague, 1953), Vol. 1, p. 213.
[3] A. A. Nemodruk and N. E. Kochetkova, Zh. Analit. Khim. **17**, 330 (1962).

4.9.4. Evaluation of the $Th(C_2O_4)_2+H_2SO_4+H_2O$ System

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Sulfuric acid; H_2SO_4; [7664-93-9]
(4) Water; H_2O; [7732-18-5]

Evaluator:

J. Hála, Department of Inorganic Chemistry, Masaryk University, 61137 Brno, Czech Republic, June 2000

Critical Evaluation:

The solubility of $Th(C_2O_4)_2$ in aqueous H_2SO_4 solutions has been reported in three documents.[1–3] In all documents measurements have been performed at 298.1 K. A strict comparison is not possible due to different units used for thorium concentration, i.e., mg ThO_2 per kg saturated solution[1,2] or mg ThO_2 per dm^3 saturated solution.[3] If this difference is disregarded, approximate comparison can be made for two concentrations of H_2SO_4 only, i.e., 0.25 and 0.50 mol dm^{-3}. For these two H_2SO_4 concentrations the solubility of $Th(C_2O_4)_2$ reported by Wirth and Hauser[1,2] is higher than that of Spitsyn[2] by a factor of approximately 2.5. It may be of relevance that Wirth and Hauser[1,2] used 24 h equilibration time while Spitsyn[3] equilibrated the systems for 6 h only. Since details of actual equilibration techniques used are not available it is not certain to what extent whether the different equilibrium times used contributed to the differences in the solubilities. However, the data of Wirth and Hauser[1,2] seem more likely to represent the true equilibrium values and, as such, should be given preference.

References:

[1] F. Wirth, Z. Anorg. Chem. **76**, 174 (1912).
[2] O. Hauser and F. Wirth, Z. Anorg. Chem **78**, 75 (1912).
[3] V. I. Spitsyn, Zh. Russ. Fiz. Khim. Obsh. **49**, 357 (1917).

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Sulfuric acid; H_2SO_4; [7664-93-9]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

[1] F. Wirth, Z. Anorg. Chem. **76**, 174–200 (1912).
[2] O. Hauser and F. Wirth, Z. Anorg. Chem. **78**, 75–94 (1912).

Variables:

T/K: 298
c_2 /mol dm^{-3} = 0.125–4.225

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $Th(C_2O_4)_2$ in H_2SO_4 solutions[a]

H_2SO_4 (c_2 /mol dm^{-3})[b]	ThO_2 (g/kg solution)	$Th(C_2O_4)_2$ (10^3 mol/kg solution)
0.125[c]	0.07	0.264
0.25[c]	0.14	0.529
0.50[c]	0.26	0.983
0.50[d]	0.258	0.977[e]
1.00[d]	0.39	1.48[e]
1.05[c]	0.418	1.58
1.60[c]	0.71	2.68
2.16[d]	1.1	4.17[e]
2.45[c]	1.32	4.99
3.09[d]	1.513	5.73[e]
3.34[d]	1.794	6.79[e]
4.225[d]	2.473	9.37[e]

[a] Equilibrium solid phase $Th(C_2O_4)_2 \cdot 6H_2O$, [16788-62-8], in all saturated solutions.
[b] Concentration of H_2SO_4 reported in normality in the original documents. Recalculated to mol dm^{-3} by compiler. The data refer to the initial acid concentration.
[c] Data from original document.[2]
[d] Data from original document.[1]
[e] Calculated by compiler.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method according to Hauser and Wirth[1] was used. Excess $Th(C_2O_4)_2 \cdot 6H_2O$ was equilibrated in a thermostated bath with solutions of the desired composition for at least 24 h. The solid phase was allowed to settle in the bath, and some 60–100 g of the saturated solution was withdrawn through a filter layer. The aliquot was evaporated and ignited to ThO_2. A small correction was applied for the mass of silicates dissolved from glassware.

Source and Purity of Materials:

$Th(C_2O_4)_2 \cdot 6H_2O$ was prepared by precipitating it with concentrated HCl from the solution of the salt in the solution of NH_4^+ oxalate. The procedure was repeated several times to purify Th oxalate from lanthanides. After air drying the product contained (in mass %) 50.68 ThO_2, 27.47 C_2O_3, and 21.67 H_2O. The respective calculated for $Th(C_2O_4)_2 \cdot 6H_2O$ are 51.21, 27.88, and 20.91. Oxalic acid used did not yield any residue on ignition.

Estimated Error:

Temperature: precision ±0.1 K (Hauser and Wirth[1]).
Solubility: insufficient data given to allow for error estimate.

References:

[1] O. Hauser and F. Wirth, Z. Anal. Chem **47**, 389 (1908).

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Sulfuric acid; H_2SO_4; [7664-93-9]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

V. I. Spitsyn, Zh. Russ. Fiz. Khim. Obsh. (J. Russ. Phys. Chem. Soc.) **49**, 357–70 (1917).

Variables:

T/KK: 298
c_2 /mol dm^{-3} = 0.0035–0.59

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $Th(C_2O_4)_2$ in H_2SO_4 solutions[a]

H_2SO_4 (c_2 /mol dm^{-3})[b]	ThO_2 (mg dm^{-3})	$Th(C_2O_4)_2$[c] ($10^4 c_1$ /mol dm^{-3})	H_2SO_4 (c_2 /mol dm^{-3})[b]	ThO_2 (mg dm^{-3})	$Th(C_2O_4)_2$[c] ($10^4 c_1$ /mol dm^{-3})
0.0035	0.8	0.031	0.24	46	1.74
0.01	2	0.076	0.245	53	2.01
0.015	3	0.114	0.25	55	2.08
0.03	6.9	0.262	0.29	60	2.27
0.05	12	0.454	0.45	90	3.41
0.10	18	0.682	0.49	108	4.09
0.20	43	1.63	0.59	120	4.54

[a] Nature of the equilibrium solid phases was not investigated. With reference to Wirth[1] the compiler assumes this to be the hexahydrate, $Th(C_2O_4)_2 \cdot 6H_2O$, [16788-62-8].
[b] Concentration given in normality in the original document. Recalculated to mol dm^{-3} by compiler.
[c] Calculated by compiler.

Additional information:

Also reported was the solubility of $Th(C_2O_4)_2$ in sulfuric acid solutions saturated with $Ce_2(C_2O_4)_3$. The concentration of the latter was not reported.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method was used. Excess $Th(C_2O_4)_2 \cdot 6H_2O$ labeled with ^{234}Th was equilibrated with the solution of the desired composition for 6 h which was found sufficient for saturation to be reached. After equilibration, 100–200 mL of the saturated solution was evaporated on a porcelaine dish and β activity of the residue was measured in an electroscope. The amount of thorium was obtained by comparing the measured activity with that of a known amount of labeled $Th(C_2O_4)_2 \cdot 6H_2O$.

Source and Purity of Materials:

Labeled $Th(C_2O_4)_2 \cdot 6H_2O$ was prepared by precipitation. An aliquot of UX_1 (^{234}Th) preparation was added to a solution of $Th(NO_3)O_4$, and $Th(C_2O_4)_2 \cdot 6H_2O$ was precipitated by adding hot solution of oxalic acid. The precipitate was washed several times with hot water. After several decantations with cold water the precipitate turned into crystalline form.

Estimated Error:

Temperature: precision not reported.
Solubility: precision ±(1–2)% (author).

References:

[1] F. Wirth, Z. Anorg. Chem. **76**, 174 (1912).

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

M. Colani, Compt. Rend., **156**, 1075–6 (1913).

Variables:

T/K: 323
$100w_2$ /mass % = 1.7–23

Prepared by:

J. Hála

Experimental Data

Solubility at 50 °C of $Th(C_2O_4)_2$ in oxalic acid solutions[a]

$C_2H_2O_4$ ($100w_2$ /mass %)	$C_2H_2O_4$ (m_2 /mol kg^{-1})[a]	Th (mass %)	$Th(C_2O_4)_2$ (10^5m_1 /mol kg^{-1})[b]
1.7	0.192	0.0002	0.876
6.5	0.772	0.0007	3.23
9.3	1.14	0.001	4.75
23.0	3.32	0.003	16.8

[a] Equilibrium solid phase was $Th(C_2O_4)_2 \cdot 6H_2O$, [16788-62-8], in all solutions.
[b] Calculated by compiler.

Auxiliary Information

Method/Apparatus/Procedure:

Nothing specified.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: not reported.
Solubility: insufficient data given to allow for error estimate.

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. G. Kurnakova and L. K. Shubochkin, Zh. Neorg. Khim. **8**, 1249–54; Russ. J. Inorg. Chem. **8**, 647–50 (1963).

Variables:

T/K: 298
$m_2$mol kg^{-1} = 0–1.296

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $Th(C_2O_4)_2$ in $C_2H_2O_4$ solutions

$C_2H_2O_4$ ($100w_2$ /mass %)	$C_2H_2O_4$ (mol kg^{-1})[a]	$C_2H_2O_4$ (m_2 /mol kg^{-1})[b]	Th (mg kg^{-1})[c]	Th (10^4 mol kg^{-1})[a]	Th ($m_1/10^4$ mol kg^{-1})
0	0	0	11	0.474[e]	0.474[f]
0.35	0.039	0.039	12[d]	0.517	0.519[f]
2.39	0.265	0.272	15	0.646	0.662[f]
3.50	0.389	0.403	17	0.732	0.759[f]
4.85	0.539	0.566	18	0.775	0.815[f]
10.45	1.161	1.296	18	0.775	0.866[g]

[a] Mol per kg solution.
[b] Calculated by compiler.
[c] Miligrams per kg solution.
[d] The value of 22 mg kg^{-1} solution given in the original document is obviously a misprint, as follows from the authors' corresponding mol kg^{-1} solution value.
[e] Recalculated by compiler; the authors reported 0.454×10^{-4} mol kg^{-1} solution.
[f] Equilibrium solid phase was $Th(C_2O_4)_2 \cdot 6H_2O$, [16788-62-8].
[g] Equilibrium solid phases were $Th(C_2O_4)_2 \cdot 6H_2O$, [16788-62-8] and $C_2H_2O_4 \cdot 2H_2O$, [6153-56-6].

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Solutions with excess solid were agitated for 7 days. The concentration of $C_2H_2O_4$ in the saturated solutions was determined by titration with 0.05 N $KMnO_4$. Thorium concentration was determined radiometrically by β counting. After centrifugation, 4–5 g of the saturated solution were weighed out in several additions onto an ashless filter with drying after each addition. The β activity of the saturated solutions was compared with those of the standards prepared from labeled $Th(C_2O_4)_2 \cdot 6H_2O$. The composition of the equilibrium solid phases was determined by optical microscopy.

Source and Purity of Materials:

$Th(C_2O_4)_2 \cdot 6H_2O$ was prepared from thorium nitrate of unspecified source and purity. To increase β activity of thorium for its subsequent radiometric determination, aged $UO_2(NO_3)_2$ in radioactive equilibrium with the thorium isotope UX_1 (^{234}Th) was added to $Th(NO_3)_4$, and $Th(C_2O_4)_2 \cdot 6H_2O$ was precipitated from hot solution with a stoichiometric amount of oxalic acid. The labeled $Th(C_2O_4)_2 \cdot 6H_2O$ was filtered, washed ten times with boiling water and air dried for 4–5 days. Oxalic acid (c.p.) was recrystallized and air dried.

Estimated Error:

Temperature: precision ±0.1 K (authors).
Solubility: insufficient data given to allow for error estimate.

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Sodium oxalate; $Na_2C_2O_4$; [62-76-0]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

H. T. S. Britton and M. E. D. Jarrett, J. Chem. Soc., 1494–5 (1936).

Variables:

T/K: 298
c_2 /mol dm^{-3}: 0.01–0.27

Prepared by:

J. Hála

Experimental Data

Composition of $Na_2C_2O_4$ solutions saturated with $Th(C_2O_4)_2$ at 25 °C

$Na_2C_2O_4$ (c_2 /mol dm^{-3})	$Th(C_2O_4)_2$ (c_1 /mol dm^{-3})	Solid phase[a]	$Na_2C_2O_4$ (c_2 /mol dm^{-3})	$Th(C_2O_4)_2$ (c_1 /mol dm^{-3})	Solid phase[a]
0.01002	0.000901	A	0.2281	0.03920	B
0.02005	0.002762	A	0.2879	0.03852	B
0.03844	0.009055	A	0.3257	0.04543	B
0.04839	0.01338	A	0.3184	0.03900	B+C
0.05520	0.01550	A	0.3110	0.03490	C
0.07554	0.02398	A	0.3022	0.03036	C
0.09158	0.03051	A	0.2793	0.01166	C
0.1408	0.04634	A	0.2672	0.00361	C
0.1679	0.05128	A+B	0.2676	0	C
0.1945	0.04420	B			

[a](A) $Th(C_2O_4)_2\cdot6H_2O$, [16788-62-8]; (B) $Na_4Th(C_2O_4)_4\cdot6H_2O$, [ ]; (C) $Na_2C_2O_4$ [62-76-0].

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method was used. Suitable mixtures of solutions of each oxalate were allowed to come to equilibrium in a thermostated bath which took about 3 weeks. The content of oxalate in the saturated solutions was determined by titration with $KMnO_4$ solution, the content of thorium was determined gravimetrically as thorium oxalate precipitated from 1 to 2 mol dm^{-3} HCl solutions. The solid phases were analyzed after being filtered, freed from adhering liquid by pressure between filter papers, and air dried.

Source and Purity of Materials:

$Th(C_2O_4)_2\cdot6H_2O$ was obtained by precipitating thorium chloride solution with oxalic acid. Analysis (mass %): ThO_2 found 51.20, calculated 51.16. $Na_2C_2O_4$ was of antireflection (A. R.) quality.

Estimated Error:

Temperature: precision ±0.1 K (authors).
Solubility: insufficient data given to allow for error estimate.

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Potassium oxalate; $K_2C_2O_4$; [583-52-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

N. P. Luzhnaya and I. S. Kovaleva, Zh. Neorg, Khim. **6**, 1436–9 (1961); Russ. J. Inorg. Chem. **6**, 736–8 (1961).

Variables:

T/K: 298
m_2 /mol kg^{-1}: 0–2.69

Prepared by:

J. Hála

Experimental Data

Composition of $K_2C_2O_4$ solutions saturated with $Th(C_2O_4)_2$ at 25 °C

$K_2C_2O_4$ (w_2 /mass %)	$K_2C_2O_4$ (m_2 /mol kg^{-1})[a]	$Th(C_2O_4)_2$ (w_1 /mass %)	$Th(C_2O_4)_2$ (m_1 /mol kg^{-3})	Density (g cm^{-3})	Solid phase[b]
0	0	7.5×10^{-5}	1.84×10^{-6}	—	A
0.96	0.0586	0.56	0.0139	1.0088	A
0.98	0.600	0.72	0.0179	1.0107	A
1.85	0.155	1.53	0.0388	1.015	A
2.90	0.183	1.71	0.0439	1.037	A+B
3.19	0.202	1.70	0.0438	1.036	A+B
3.19	0.202	1.85	0.0477	1.037	A+B
6.58	0.431	1.65	0.0441	1.059	B
9.32	0.632	1.97	0.0544	1.085	B
14.22	1.028	2.58	0.0760	1.132	B
28.22	2.55	5.10	0.187	1.284	B
29.37	2.69	5.06	0.189	1.288	B+C
29.32	2.69	5.11	0.191	1.288	B+C
27.90	2.46	3.73	0.137	1.246	C
27.41	2.31	1.16	0.0398	1.232	C
27.23	2.25	—	—	1.214	C

[a]Calculated by compiler.

[b](A)$Th(C_2O_4)_2\cdot6H_2O$, [16788-62-8]; (B) $K_4Th(C_2O_4)_4\cdot4H_2O$, [ ]; (C) $K_2C_2O_4\cdot H_2O$, [6487-48-5].

Additional Information:

The solubility isotherm of the $K_2C_2O_4$–$Th(C_2O_4)_2$–H_2O system showed three branches corresponding to the crystallization of $Th(C_2O_4)_2\cdot6H_2O$, $K_4Th(C_2O_4)_4\cdot4H_2O$, and $K_2C_2O_4\cdot H_2O$. There were two ternary points on the isotherm: the eutonic point at 29.35 mass % $K_2C_2O_4$ and 5.08 mass % $Th(C_2O_4)_2$, and the transition point at 3.09 mass % $K_2C_2O_4$ and 1.75 mass % $Th(C_2O_4)_2$.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Solutions with excess solid were stirred in a thermostated vessel at 25 °C for 2 days which was found sufficient to reach equilibrium. Samples for analysis were taken after 3 days. In the saturated solutions and solid phases, potassium was determined gravimetrically as K_2SO_4 or $K_3Co(NO_2)_6$, thorium gravimetrically as ThO_2, and oxalate titrimetrically with standard $KMnO_4$ solution. The composition of the equilibrium solid phases was also determined by the method of wet residues, and the phases were also characterized by x-ray diffraction and thermal analysis.

Source and Purity of Materials:

Twice recrystallized potassium and thorium oxalates were used. No other details were reported.

Estimated Error:

Temperature: precision ±0.1 K (authors).
Solubility: insufficient data given to allow for error estimate.

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Potassium oxalate; $K_2C_2O_4$; [583-52-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

E. M. Pazukhin, E. A. Smirnova, A. S. Krivokhatskii, Yu. L. Pazukhina, and S. M. Kochergin, Radiokhimiya, **27**, 606–11 (1985).

Variables:

T/K: 293
Equilibrium oxalate ion concentration/mol dm^{-3}: 0.114–0.298

Prepared by:

J. Hála

Experimental Data

Solubility at 20 °C of $Th(C_2O_4)_2$ in $K_2C_2O_4$ solutions[a]

$K_2C_2O_4$[b] (c_2 /mol dm^{-3})	$C_2O_4^{2-}$[c] (mol dm^{-3})	pH	$[C_2O_4^{2-}]$[d] (mol dm^{-3})	$Th(C_2O_4)_2$ (mol dm^{-3})
0.20	0.213	6.12	0.212	0.0289
0.20	0.215	6.06	0.214	0.0323
0.394	0.298	6.25	0.298	0.0463
0.093	0.134	4.54	0.116	0.0212
0.093	0.129	4.61	0.114	0.0191
0.2	0.213	6.12	0.212	0.0289
0.2	0.215	6.06	0.214	0.0323
0.4	0.276	6.15	0.275	0.0327
0.4	0.298	6.25	0.298	0.0463
0.1	0.131	4.54	0.116	0.0212
0.1	0.129	5.61	0.114	0.0191
0.1	0.118	5.96	0.117	0.0280
0.1	0.122	5.68	0.121	0.0312
0.1	0.1225	5.84	0.122	0.0267
0.1	0.117	6.14	0.117	0.0262

[a] Solid phases were not investigated. It was mentioned, however, that $Th(C_2O_4)_2\cdot 6H_2O$ did not undergo any change during equilibration.
[b] Initial concentration.
[c] Equilibrium total oxalate ion concentration.
[d] Equilibrium concentration of the $C_2O_4^{2-}$ ion calculated by authors from total oxalate concentration and the measured pH by using dissociation constants of oxalic acid, $K_{a1}=1.05\times10^{-1}$ and $K_{a2}=1.88\times10^{-5}$.[1]

Additional Information:

In the range of equilibrium oxalate ion concentration covered in this study of the $Th(C_2O_4)_2$–$K_2C_2O_4$–H_2O system, the solubility of $Th(C_2O_4)_2$ was found to fit the equation:

$$\log C_{Th}=0.893 \log[C_2O_4^{2-}]-0.852.$$

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess $Th(C_2O_4)_2\cdot 6H_2O$ was equilibrated in thermostated vessels for 6 h which was found sufficient to reach equilibrium. The equilibrium concentration of oxalate ion in the solutions was varied by varying either acidity at constant oxalate concentration, or total oxalate concentration at a fixed acidity. After equilibration the saturated solutions were centrifuged and the concentration of thorium was determined colorimetrically with arsenazo III .[2] The methods of pH measurement and of the determination of total equilibrium oxalate concentration were not specified.

Source and Purity of Materials:

$Th(C_2O_4)_2\cdot 6H_2O$ was prepared by precipitation according to Rabchikov and Golbraikh.[3]

Estimated Error:

Temperature: precision ±0.2 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] A. V. Stepanov and E. M. Pazukhin, Zh. Neorg. Khim. **15**, 1483 (1970).
[2] S. B. Savvin, *Arsenazo III* (Atomizdat, Moscow, 1966) (in Russian), p. 107.
[3] D. I. Rabchikov and E. K. Golbraikh, *Analytical Chemistry of Thorium*, (Publ. House Acad. Sci. USSR, Moscow, 1960) (in Russian), p. 33.

4.9.5. Evaluation of the $Th(C_2O_4)_2+(NH_4)_2C_2O_4+H_2O$ System

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Ammonium oxalate; $(NH_4)_2C_2O_4$; [1113-38-8]
(3) Water; H_2O; [7732-18-5]

Evaluator:

J. Hála, Department of Inorganic Chemistry, Masaryk University, 611 37 Brno, Czech Republic, February 2000

Critical Evaluation:

Although this system has been studied in five documents there seems to be much uncertainty in both the solubility of $Th(C_2O_4)_2$ in ammonium oxalate solutions and in the nature of the equilibrium solid phases. In two studies[1,2] where the results were reported in mol dm^{-3} units, the $(NH_4)_2C_2O_4$ concentration range covered was 6×10^{-4}–5×10^{-2},[1] and 0.025–0.1 mol dm^{-3}.[2] If the difference in temperature, i.e., 298.1 K in Ref. 1 and 293.1 K in Ref. 2, is neglected then the solubility of $Th(C_2O_4)_2$ can be compared only at two $(NH_4)_2C_2O_4$ concentrations: for 0.05 mol dm^{-3} $(NH_4)_2C_2O_4$ the solubility of $Th(C_2O_4)_2$ was reported to be 0.012[2] and 0.0385 mol dm^{-3},[1] while for 0.025 mol dm^{-3} $(NH_4)_2C_2O_4$ the solubilities were 0.05–0.083[2] and 0.017[1] mol dm^3. Apart from the discrepancy in solubilities, the work of Pazukhin *et al.*[2] indicates that the solubility of $Th(C_2O_4)_2$ in $(NH_4)_2C_2O_4$ solutions is pH dependent since changes in pH affect the equilibrium oxalate ion concentration. In Refs. 1 and 2 equilibration time of 6 was used.

In Refs. 3 and 4 the results were reported in mass % or mol per kg saturated solution so that the data could be recalculated to molalities. These two studies agree in that equilibrium in the $Th(C_2O_4)_2$–$(NH_4)_2C_2O_4$–H_2O system is attained very slowly so that equilibrium times of several weeks were needed. James *et al.*[3] reported that, in order to avoid metastable systems, equilibration of several months was necessary in the vicinity of transition points. Meaningful comparison which would reveal serious discrepancies can be performed for $(NH_4)_2C_2O_4$ concentrations of the order of 10^{-2} mol kg^{-1}. For 0.039–0.064 mol kg^{-1} $(NH_4)_2C_2O_4$, James *et al.*[3] reported the solubility of $Th(C_2O_4)_2$ to range from 0.0049 to 0.0086 mol kg^{-1} which neglecting different concentration units, is considerably lower than are the respective data in Refs. 1 and 2. On the contrary, Hauser and Wirth[4] reported the solubility of $Th(C_2O_4)_2$ to be 0.0122 and 0.0214 mol kg^{-1} at 0.04 and 0.09 mol kg^{-1} $(NH_4)_2C_2O_4$ which is closer to the data in Refs. 1 and 2. Controversy seems to exist also as far as the nature of the solid phases is concerned. While Pazukhin *et al.*[2] reported the solid phase to be $Th(C_2O_4)_2\cdot 6H_2O$, Hauser and Wirth[4] reported $(NH_4)_2Th_2(C_2O_4)_5\cdot 7H_2O$ to exist in this system. There seems to be a relatively good agreement of solubility data at $(NH_4)_2C_2O_4$ concentrations above 0.4 mol kg^{-1}.[3,4] However, different solid phases were identified in this region. While Hauser and Wirth[4] reported $(NH_4)_2Th(C_2O_4)_3\cdot 3H_2O$, James *et al.*[3] reported thorium oxalate of unspecified composition and $(NH_4)_2Th_2(C_2O_4)_5\cdot 2H_2O$. Phase diagram of the $Th(C_2O_4)_2$–$(NH_4)_2C_2O_4$–H_2O system was studied by Claudel *et al.*[5] who, however, reported their data in graphical form only.

Thus, due to discrepancies in the requirements for equilibration time necessary to reach true equilibrium, to the importance of pH of equilibrium solutions, and to discrepancies in the nature of equilibrium solid phases, none of the reported sets of data can be given preference and it seems that the system would need a thorough reinvestigation.

References:

[1] V. I. Spitsyn, Zh. Russ. Fiz. Khim. Obsh. **49**, 357 (1917).
[2] E. M. Pazukhin, E. A. Smirnova, A. S. Krivokhatskii, Yu. L. Pazukhina, and S. M. Kochergin, Radiokhimiya **27**, 606 (1985).
[3] C. James, C. F. Whittemore, and H. C. Holden, J. Am. Chem. Soc. **36**, 1853 (1914).
[4] O. Hauser and F. Wirth, Z. Anorg. Chem. **78**, 75 (1912).
[5] B. Claudel, G. Lang, and A. Navarro, Bull. Soc. Chim. France 2094 (1966).

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Ammonium oxalate; $(NH_4)_2C_2O_4$; [1113-38-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

O. Hauser and F. Wirth, Z. Anorg. Chem. **78**, 75–94 (1912).

Variables:

T/K: 298
m_2 /mol kg^{-1}: 0.00033–2.52

Prepared by:

J. Hála

Experimental Data

Composition of $(NH_4)_2C_2O_4$ solutions saturated with $Th(C_2O_4)_2$ at 25 °C

$(NH_4)_2C_2O_4$ (mol kg^{-1})[a]	$(NH_4)_2C_2O_4$ (m_2 /mol kg^{-1})[b]	ThO_2 (g kg^{-1})[a]	$Th(C_2O_4)_2$ (mol kg^{-1})[a]	$Th(C_2O_4)_2$ (m_1 /mol kg^{-1})[b]	Solid phase[c]
0.000 33	0.000 33	[d]	0.000 050	0.000 050	A
0.000 44	0.000 44	[d]	0.000 081	0.000 081	A
0.000 72	0.000 72	0.032	0.000 120	0.000 120	A
0.001 09	0.001 09	0.053	0.000 200	0.000 200	A
0.001 20	0.001 20	0.055	0.000 208	0.000 208	A
0.001 30	0.001 30	0.057	0.000 220	0.000 220	A
0.001 48	0.001 48	0.066	0.000 250	0.000 250	A
0.001 53	0.001 53	[d]	0.000 260	0.000 260	A
0.0023	0.0023	0.1	0.000 38	0.000 38	B
0.041	0.0414	3.2	0.0121	0.0122	B
0.090	0.0918	5.554	0.0210	0.0214	B
0.145	0.150	10.104	0.0382	0.0395	B
0.225	0.237	15.844	0.0599	0.0632	B
0.25[f]	0.265	17.60	0.0665	0.0706	B
0.25[f]	0.265	17.75	0.0670	0.0712	B
0.3012	0.326	25.128	0.0950	0.103	C
0.3700	0.409	31.820	0.1203	0.133	C
0.6012[e]	0.711	51.577	0.1950	0.231	C
0.601[e]	0.711	51.57	0.195	0.231	C
0.880	1.142	78.17	0.295	0.383	C
1.181	1.739	112.9	0.427	0.629	C
1.420	2.35	142.8	0.540	0.895	C
1.471	2.50	148.1	0.560	0.951	C
1.480	2.52	148.9	0.563	0.960	C

[a] Mol per kg solution.
[b] Calculated by compiler.
[c] A: $Th(C_2O_4)_2\cdot 6H_2O$, [16788-62-8]; B: $(NH_4)_2Th_2(C_2O_4)_5\cdot 7H_2O$, [ ]; C: $(NH_4)_2Th(C_2O_4)_3\cdot 3H_2O$, [ ].
[d] Not reported.
[e] These two measurements were reported to show that both ways of approaching equilibrium yielded identical results.
[f] Data obtained by prolonged equilibration of $Th(C_2O_4)_2\cdot 6H_2O$ in such a way that the supernatant solution was repeatedly replaced by fresh portions in order to eliminate the influence of the decrease of $(NH_4)_2C_2O_4$ concentration in the solution due to the formation of the complex solid phase.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Since the dissolution of thorium oxalate in dilute solutions of ammonium oxalate is a very slow process, the systems in the first three series of measurements (see above) were prepared by diluting solutions of the NH_4–Th–oxalate complex with the required amount of water. Solutions with the precipitated solid phase were allowed to stand for 3 weeks with frequent shaking. In the fourth series, excess $Th(C_2O_4)_2\cdot 6H_2O$ was equilibrated for several days with ammonium oxalate solutions presaturated with $Th(C_2O_4)_2\cdot 6H_2O$, and in the presence of solid $(NH_4)_2C_2O_4$ introduced to the system in a silk bag immersed into the solution. As in Hauser and Wirth,[1] some 60–100 g of the saturated solution was withdrawn through a filter layer, weighed, evaporated and ignited. A small correction for silicates dissolved from glassware was applied. Solid phases were identified by chemical analysis and optical microscopy.

Source and Purity of Materials:

$Th(C_2O_4)_2\cdot 6H_2O$ was prepared by precipitation from a solution of thorium oxalate in concentrated $(NH_4)_2C_2O_4$ solution by action of concentrated HCl. The precipitation procedure was repeated several times to purify thorium oxalate from lanthanides. After air drying the product contained (in mass %) 50.86 ThO_2, 27.47 C_2O_3, and 21.67 H_2O. The respective calculated values for $Th(C_2O_4)_2\cdot 6H_2O$ are 51.21, 27.88 and 20.91.

Estimated Error:

Temperature: precision ± 0.1 K (authors in Ref. 1).
Solubility: insufficient data given to allow for error estimate.

References:

[1] O. Hauser and F. Wirth, Z. Anal. Chem. **47**, 389 (1908).

Components:	**Original Measurements:**
(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0] (2) Ammonium oxalate; $(NH_4)_2C_2O_4$; [1113-38-8] (3) Water; H_2O; [7732-18-5]	C. James, C. F. Whittemore, and H. C. Holden, J. Am. Chem. Soc. **36**, 1853–6 (1914).
Variables:	**Prepared by:**
T/K:298 $100w_2$ /mass% = 0.03–17.49	J. Hála

Experimental Data

Composition of $(NH_4)_2C_2O_4$ solutions saturated with $Th(C_2O_4)_2$ at 20 °C

$(NH_4)_2C_2O_4$ ($100w_2$ /mass%)	$(NH_4)_2C_2O_4$ (m_2 /mol kg^{-1})[a]	$Th(C_2O_4)_2$ ($100w_1$ /mass%)	$Th(C_2O_4)_2$ (m_1 /mol kg^{-1})[a]	Solid phase[b]
0.03	0.00242	0.03	0.000735	A
0.48	0.0389	0.20	0.00490	A
0.52	0.0426	0.36	0.00882	A
0.79	0.0644	0.35	0.00858	A
0.89	0.0728	0.57	0.0142	B
1.50	0.124	1.31	0.0331	B
1.65	0.137	1.38	0.0348	B
4.83	0.432	5.06	0.138	B
6.93	0.655	7.79	0.224	B
10.27	1.069	12.35	0.391	B
12.20	1.357	15.35	0.519	B
15.07	1.857	19.54	0.732	B
17.49[c]	2.375	23.19	0.958	B
5.62	0.487	1.43	0.0377	A
6.93	0.628	4.07	0.112	A
8.70	0.836	7.40	0.216	A
11.68	1.246	12.76	0.414	A
11.68	1.246	12.77	0.414	A
14.52	1.730	17.84	0.646	A
17.11[c]	2.270	22.18	0.895	A
17.13[c]	2.274	22.16	0.894	A

[a] Calculated by compiler.

[b] A: authors described this solid phase as thorium oxalate without reporting on the number of molecules of water of crystallization; B: $2Th(C_2O_4)_2 .(NH_4)_2C_2O_4 \cdot 2H_2O$, [ ].

[c] The authors report these points to be transition points, and assumed that within the range of these compositions the equilibrium solid phase was $2Th(C_2O_4)_2 \cdot (NH_4)_2C_2O_4 \cdot 7H_2O$ reported in Brauner.[1]

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Mixtures containing water and desired amounts of thorium and ammonium oxalates were rotated in bottles for several weeks in a thermostated bath and allowed to settle at the same temperature. In the vicinity of transition points it was necessary to equilibrate the mixtures for several months to avoid metastable systems. In the clear saturated solutions, thorium was determined gravimetrically by evaporating a weighed aliquot in a platinum dish and igniting the residue to ThO_2. Oxalate content was determined titrimetrically against standard $KMnO_4$ solution.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

References:

[1] J. Brauner, J. Chem. Soc. **73**, 951 (1898).

Components:	**Original Measurements:**
(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0] (2) Ammonium oxalate; $(NH_4)_2C_2O_4$; [1113-38-8] (3) Water; H_2O; [7732-18-5]	V. I. Spitsyn, Zh. Russ. Fiz. Khim. Obsh. (J. Russ. Phys. Chem. Soc.) **49**, 357–70 (1917).
Variables:	**Prepared by:**
T/K: 298 c_2 /mol dm^{-3}: 0.0006–0.05	J. Hála

Experimental Data

Solubility at 25 °C of $Th(C_2O_4)_2$ in $(NH_4)_2C_2O_4$ solutions[a]

$(NH_4)_2C_2O_4$ (c_2 /mol dm^{-3})	ThO_2 (mg dm^{-3})	Th[b] (10^4 mol dm^{-3})
0.0006	2.3	0.088
0.0010	4	0.154
0.0025	10	0.385
0.005	40	1.54
0.0075	70	2.69
0.010	100	3.85
0.015	180	6.92
0.020	340	13.1
0.025	450	17.3
0.030	600	23.1
0.050	1000	38.5

[a] Equilibrium solid phases were not investigated.

[b] Calculated by compiler.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method was used. Excess $Th(C_2O_4)_2 \cdot 6H_2O$ labeled with ^{234}Th was equilibrated with the solution of the desired composition for 6 h which was found sufficient for saturation to be reached. After equilibration, 100–200 mL of the saturated solution was evaporated on a porcelaine dish and β activity of the residue was measured in an electroscope. The amount of thorium was obtained by comparing the measured activity with that of a known amount of labeled $Th(C_2O_4)_2 \cdot 6H_2O$.

Source and Purity of Materials:

Labeled $Th(C_2O_4)_2 \cdot 6H_2O$ was prepared by precipitation. An aliquot of $UX_1(^{234}Th)$ preparation was added to a solution of $Th(NO_3)_4$, and $Th(C_2O_4)_2 \cdot 6H_2O$ was precipitated by adding hot solution of oxalic acid. The precipitate was washed several times with hot water. After several decantations with cold water the precipitate turned into crystalline form.

Estimated Error:

Temperature: precision not reported.
Thorium concentration: precision ±(1–2)% (author).

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Ammonium oxalate; $(NH_4)_2C_2O_4$; [1113-38-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

B. Claudel, G. Lang, and A. Navarro, Bull. Soc. Chim. France 2094–9 (1966).

Variables:

T/K: 298
composition

Prepared by:

J. Hála

Experimental Data

Phase diagram (Fig. 3) of the $Th(C_2O_4)_2$–$(NH_4)_2C_2O_4$–H_2O system at 25 °C.

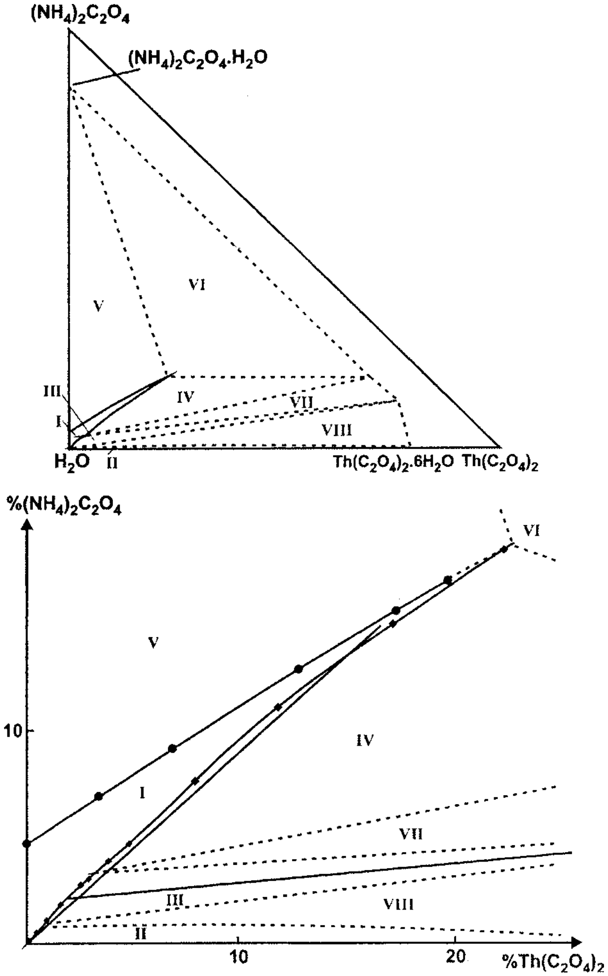

FIG. 3. Thorium bis(oxalate)–ammonium oxalate–water system. (I) homogeneous solutions; (II–VIII) heterogeneous regions, saturated solutions in equilibrium with: (II): $Th(C_2O_4)_2 \cdot 6H_2O$, [16788-62-8], (III) $2Th(C_2O_4)_2 \cdot (NH_4)_2C_2O_4 \cdot 7H_2O$, [ ], (IV) $Th(C_2O_4)_2 \cdot (NH_4)_2C_2O_4 \cdot 3H_2O$,[ ], (V) $(NH_4)_2C_2O_4 \cdot H_2O$, [6000-70-7], (VI) $Th(C_2O_4)_2 \cdot (NH_4)_2C_2O_4 \cdot 3H_2O + (NH_4)_2O_4 \cdot H_2O$, (VII) $Th(C_2O_4)_2 \cdot (NH_4)_2C_2O_4 \cdot 3H_2O + 2Th(C_2O_4)_2$, $(NH_4)_2C_2O_4 \cdot 7H_2O$, (VIII) $Th(C_2O_4)_2 \cdot 6H_2O + 2Th(C_2O_4)_2 \cdot (NH_4)_2C_2O_4 \cdot 7H_2O$

Auxiliary Information

Method/Apparatus/Procedure:

Nothing specified.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Nothing specified.

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Ammonium oxalate; $(NH_4)_2C_2O_4$; [1113-38-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

E. M. Pazukhin, E. A. Smirnova, A. S. Krivokhatskii, Yu. L. Pazukhina, and S. M. Kochergin, Radiokhimiya **27**, 606–11 (1985).

Variables:

T/K: 293
c_2 /mol dm^{-3}: 0.025–0.1

Prepared by:

J. Hála

Experimental Data

Solubility at 20 °C of $Th(C_2O_4)$ in $(NH_4)_2C_2O_4$ solutions[a]

$(NH_4)_2C_2O_4$[b] (c_2 /mol dm^{-3})	$C_2O_4^{2-}$ [c] (mol dm^{-3})	pH[d]	$[C_2O_4^{2-}]$[e] (10^2 mol dm^{-3})	$Th(C_2O_4)$ (10^4c_1 /mol dm^{-3})
0.1	0.0981	2.66	0.634	14.9
0.1	0.0981	2.64	0.613	14.9
0.1	0.096	2.42	0.364	7.20
0.1	0.096	2.39	0.344	7.20
0.1	0.0988	1.84	0.0890	0.754
0.1	0.100	1.59	0.0452	0.164
0.1	0.0970	1.15	0.0109	0.0680
0.1	0.0970	1.12	0.0109	0.0396
0.0995	0.0997	1.27	0.0178	0.101
0.0995	0.0994	1.64	0.0534	0.221
0.0995	0.0994	1.62	0.05237	0.221
0.1	0.1	1.96	0.124	0.668
0.1	0.1	2.17	0.209	3.55
0.0995	0.106	2.84	1.01	32.3
0.1	0.107	2.66	0.832	230
0.1	0.159	5.77	15.73	297
0.1	0.138	6.26	13.8	218
0.1	0.117	3.46	3.02	71.1
0.1	0.200	6.18	20.0	409
0.1	0.141	6.52	14.1	284
0.05	0.0830	4.74	7.59	120
0.05	0.074	4.80	6.76	120
0.1	0.131	4.62	11.6	236
0.1	0.141	4.68	12.7	224
0.1	0.136	6.13	13.6	231
0.1	0.134	6.21	13.4	228
0.1	0.131	4.62	11.6	236
0.1	0.141	4.68	12.7	224
0.1	0.136	6.13	13.66	231
0.1	0.134	6.21	13.4	228
0.05	0.0830	4.74	7.59	120
0.05	0.0740	4.80	6.76	120
0.025	0.0375	4.90	3.55	530
0.025	0.0355	4.98	3.39	500
0.1	0.117	3.41	2.82	71.1

[a] Equilibrium solid phases were not investigated. The compiler assumes this to be $Th(C_2O_4)_2\cdot 6H_2O$, [16788-62-8] since the authors reported that the initial solid phase did not undergo any change during equilibration.

[b] Initial concentration.

[c] Equilibrium total oxalate ion concentration.

[d] Solutions with pH$<$3 were brought to the desired acidity by adding HNO_3.

[e] Equilibrium concentration of the $C_2O_4^{2-}$ ion calculated by using dissociation constants of oxalic acid, $K_{a1}=1.05\times10^{-1}$ and $K_{a2}=1.88\times10^{-5}$ (Ref. 1) from total oxalate concentration and H^+ ion concentration. In solutions of $(NH_4)_2C_2O_4$ not acidified with HNO_3, the concentration of H^+ ion was obtained as $\log[H^+]=-pH-\log\gamma(H^+)$, where $-\log\gamma(H^+)=0.5063\sqrt{I}/(1+1.51\sqrt{I})-0.2395I$ (I is ionic strength). In acidified $(NH_4)_2C_2O_4$ solutions, the concentration of H^+ ion was obtained from the equation $[H^+]=C_{HNO_3}-[HC_2O_4^-]-2[H_2C_2O_4]$ and dissociation constants of oxalic acid.

Additional information:
The solubility of $Th(C_2O_4)_2$ in the $Th(C_2O_4)_2$–$(NH_4)_2C_2O_4$–H_2O system at equilibrium oxalate ion concentrations $\leqslant$0.01 mol dm^{-3} was shown by the authors to fit the same equation as in the $Th(C_2O_4)_2$–$C_2H_2O_4$–H_2O system, i.e.,

$$\log C_{Th}=0.2683(\log[C_2O_4^{2-}])^2+2.947\log[C_2O_4^{2-}]+2.330.$$

At higher oxalate concentrations the solubility could be expressed as

$$\log C_{Th}=0.893\log[C_2O_4^{2-}]-0.852.$$

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess $Th(C_2O_4)_2\cdot 6H_2O$ was equilibrated in thermostated vessels for 6 h which was found sufficient to reach equilibrium. The equilibrium concentration of oxalate ion in the solutions was varied by varying either acidity at constant oxalate concentration, or total oxalate concentration at a fixed acidity. After equilibration the saturated solutions were centrifuged and the concentration of thorium was determined colorimetrically with arsenazo III.[2] The methods of pH measurement and of the determination of total equilibrium oxalate concentration were not specified.

Source and Purity of Materials:

$Th(C_2O_4)_2\cdot 6H_2O$ was prepared by precipitation according to Ref. 3.

Estimated Error:

Temperature: precision ±0.2 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] A. V. Stepanov and E. M. Pazukhin, Zh. Neorg. Khim. **15**, 1483 (1970).
[2] S. B. Savvin, *Arsenazo III* (Atomizdat, Moscow, 1966) (in Russian), p. 107.
[3] D. I. Ryabchikov and E. K. Golbraikh, *Analytical Chemistry of Thorium* (Publ. House Acad. Sci. USSR, Moscow, 1960) (in Russian), p. 33.

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Salts
(3) Water; H_2O; [7732-18-5]

Original Measurements:

V. I. Spitsyn, Zh. Russ. Fiz. Khim. Obsh. (J. Russ. Phys. Chem. Soc.) **49**, 357–70 (1917).

Variables:

T/K: 298

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $Th(C_2O_4)_2$ in solutions of various salts[a]

Salt	Salt (c_2 /mol dm^{-3})	ThO_2 (mg dm^{-3})	$Th(C_2O_4)_2$ ($10^5 c_1$ /mol dm^{-3})[b]
None	—	0.07	0.027
Sodium chloride; NaCl; [7647-14-5]	0.1	0.2	0.077
Sodium sulfate; Na_2SO_4; [7757-82-6]	0.05	0.6	0.231
Potassium hydrogen sulfate; $KHSO_4$; [7646-93-7]	0.5	30	11.5
	1.0	77	29.6
Ammonium chloride; NH_4Cl; [12125-02-9]	0.1	0.3	0.115
Ammonium sulfate; $(NH_4)_2SO_4$; [7783-20-2]	0.05	1.0	0.385

[a] Equilibrium solid phases were not investigated.
[b] Calculated by compiler.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method was used. Excess $Th(C_2O_4)_2 \cdot 6H_2O$ labeled with ^{234}Th was equilibrated with the solution of the desired composition for 6 h which was found sufficient for saturation to be reached. After equilibration, 100–200 mL of the saturated solution was evaporated on a porcelaine dish and β activity of the residue was measured in an electroscope. The amount of thorium was obtained by comparing the measured activity with that of a known amount of labeled $Th(C_2O_4)_2 \cdot 6H_2O$.

Source and Purity of Materials:

Labeled $Th(C_2O_4)_2 \cdot 6H_2O$ was prepared by precipitation. An aliquot of $UX_1(^{234}Th)$ preparation was added to a solution of $Th(NO_3)_4$, and $Th(C_2O_4)_2 \cdot 6H_2O$ was precipitated by adding hot solution of oxalic acid. The precipitate was washed several times with hot water. After several decantations with cold water the precipitate turned into crystalline form.

Estimated Error:

Temperature: precision not reported.
Solubility: precision ±(1–2)% (author).

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Hydrogen chloride; HCl; [7647-01-0]
(3) Sodium chloride; NaCl; [7647-14-5]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

I. M. Korenman and V. V. Korolikhin, Trudy Khim. Khim. Tekhnol. **3**, 106–9 (1960).

Variables:

T/K: 293
c_2 /mol dm^{-3}: 0.01–2.0
ionic strength/mol dm^{-3}: 0.5, 1.0, and 2.0

Prepared by:

J. Hála

Experimental Data

Solubility at 20 ° of $CTh(C_2O_4)_2$ in HCl–NaCl solutions[a]

HCl (c_2 /mol dm^{-3})	Ionic strength (mol dm^{-3})	Total oxalate (10^4 mol dm^{-3})	K_{sp}[b] (10^{22} mol^3 dm^{-9})	K_{sp}[c] (10^{22} mol^3 dm^{-9})
0.01	0.5	0.2	440	0.853
0.025	0.5	0.3	830	1.215
0.1	0.5	0.5	49	1.435
0.25	0.5	0.9	10	1.435
0.5	0.5	1.3	2.4	0.797
0.01	1.0	0.1	200	0.404
0.025	1.0	0.3	690	1.215
0.1	1.0	0.6	54	1.843
0.25	1.0	1.0	13	1.731
0.5	1.0	1.4	2.3	0.940
0.75	1.0	2.0	1.5	0.772
1.0	1.0	2.5	1.0	0.588
0.5	2.0	1.7	4.6	1.436
0.75	2.0	2.75	4.0	1.629
1.0	2.0	3.1	3.0	1.008
1.5	2.0	4.4	1.0	0.723
2.0	2.0	6	0.9	0.648

[a] Equilibrium solid phases were not investigated.
[b] Calculated by authors as $K_{sp} = [Th^{4+}][C_2O_4^{2-}]^2$ as the first approximation under the assumption that no complex formation of Th^{4+} with oxalate ion takes place in the saturated solutions. The concentrations of $C_2O_4^{2-}$ and Th^{4+} were obtained as $[C_2O_4^{2-}] = [oxal]_{tot} Z^{-1}$ and $[Th^{4+}] = [oxal]_{tot}/2$, where $[oxal]_{tot}$ is the experimentally determined oxalate concentration in the saturated solution and $Z = (1 + [H^+]/K_{a2} + [H^+]^2/K_{a1}K_{a2})$. The authors used $K_{a1} = 5.9 \times 10^{-2}$ mol dm^{-3} and $K_{a2} = 6.4 \times 10^{-5}$ mol dm^{-3} for the dissociation constants of oxalic acid. The definite trend in the K_{sp} values so obtained led the authors to assume the formation of the $Th(C_2O_4)^{2+}$ complex in the saturated solutions for which they obtained from their solubility data the instability constant as $K = [Th^{4+}][C_2O_4^{2-}] \times [Th(C_2O_4)^{2+}]^{-1} = (1.5 \pm 0.5) \times 10^{-9}$ mol dm^{-3}. Then the concentration of the oxalate anion became $[C_2O_4^{2-}] = [oxal]_{tot}/(Z + [oxal]_{tot}/2\ K)$ and $K_{s0} = 2\ K^2 [oxal]_{tot}^3/(2KZ + [oxal]_{tot})^2$. The authors reported only one refined value obtained from this equation as $K_{s0} = (1 \pm 0.1) \times 10^{-22}$ mol^3 dm^{-9} with no specification of the meaning of the deviation and with no indication as to whether the refined K_{s0} value was the mean of all values obtained at various ionic strengths.
[c] Calculated by compiler by using the authors' refined formula for K_{sp} . No mean value was calculated because of the definite trend in K_{sp} values in each series of measurements for different ionic strengths.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess solid was shaken with (H/Na)Cl solutions at constant ionic strength for 4–6 h which was found sufficient to reach equilibrium. The oxalate concentration in 20 mL aliquots of the saturated solution was determined by titration with 0.05 N $KMnO_4$. Several parallel experiments were run for each HCl concentration, and two or three aliquots for oxalate determination were taken from each saturated solution.

Source and Purity of Materials:

$Th(C_2O_4)_2 \cdot 6H_2O$ was prepared by precipitation, washed with water and air dried at room temperature. Source and purity of chemicals used were not specified.

Estimated Error:

Temperature: precision not reported.
Oxalate concentration: the authors stated the error of titration as $\leq \pm 0.015$ mL 0.05 $N\ KMnO_4$. Considering the volumes of 0.05 N $KMnO_4$ solution needed for titrations (0.015–0.48 mL) the compiler estimates an error of ±(3–100)%.

Components:
(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Perchloric acid; $HClO_4$; [7601-90-3]
(3) Ammonium perchlorate; NH_4ClO_4 ; [7790-98-9]
(4) Water; H_2O; [7732-18-5]

Original Measurements:
A. I. Moskvin and L. N. Essen, Zh. Neorg. Khim., **12**, 688–93 (1967); Russ. J. Inorg. Chem. **12**, 359–62 (1967).

Variables:
T/K: 298
c_2 /mol dm^{-3}: 0.01–1.0
c_3 /mol dm^{-3}: 0.25–1.0

Prepared by:
J. Hála

Experimental Data

Solubility at 25 °C of $Th(C_2O_4)$ in $(H+NH_4)ClO_4$ solutions of constant ionic strength of 1.0 mol dm^{-3a}

$HClO_4$ (c_2 /mol dm^{-3})	NH_4ClO_4 (c_3 /mol dm^{-3})	$Th(C_2O_4)_2$ (10^5c_1 /mol dm^{-3})
—	1.0	1.20
0.01	1.0	1.25
0.1	0.9	2.46
0.25	0.75	4.07
0.50	0.50	7.17
0.75	0.25	8.14
1.0	—	9.01

[a] Equilibrium solid phases were not investigated.

Additional information:
In the saturated solutions, $Th(C_2O_4)_2$, $Th(C_2O_4)^{2+}$ and Th^{4+} species were considered to exist. From the solubility data the equilibrium constant for the reaction $Th(C_2O_4)_2+4H^+ \rightleftarrows Th^{4+}+2C_2H_2O_4$ was obtained as $K=(2.7\pm1.2)\times10^{-12}$ mol^{-2} dm^6, and from this the solubility product of $Th(C_2O_4)_2$ was obtained as $K_{sp}=(K_{a1}K_{a2})^2K=4.3\times10^{-22}$ mol^3 dm^{-9}. The dissociation constants of oxalic acid, $K_{a1}=0.118$ mol dm^{-3} and $K_{a2}=1.06\times10^{-4}$ mol dm^{-3}, for ionic strength of 1.0 mol dm^{-3}, were obtained from unspecified thermodynamic constants by using Davies' equation.[1] Also calculated were overall stability constants of the $Th(C_2O_4)^{2+}$ and $Th(C_2O_4)_2$ complexes as $\beta_1=1.7\times10^8$ mol^{-1} dm^3 and $\beta_2=2.8\times10^{16}$ mol^{-2} dm^6, respectively.

Auxiliary Information

Method/Apparatus/Procedure:
Isothermal method was used. Excess $Th(C_2O_4)_2\cdot6H_2O$ was stirred with $(H+NH_4)ClO_4$ solutions for 4 h in a thermostated apparatus. The oxalate concentration in the saturated solutions was determined by titration against 0.01 N $KMnO_4$ solution.

Source and Purity of Materials:
$Th(C_2O_4)_2\cdot6H_2O$ was prepared according to Ref. 2. Source and purity of chemicals were not specified.

Estimated Error:
Temperature: precision ±0.3 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] C. W. Davies, J. Chem. Soc 2093 (1938).
[2] A. A. Grinberg and G. I. Pertzhak, Trudy Radiev. Inst. Akad. Nauk SSSR **7**, 50 (1956).

Components:
(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Hydrogen chloride; HCl; [7647-01-0]
(4)Water; H_2O; [7732-18-5]

Original Measurements:
M. Colani, Compt. Rend. **156**, 1075–6 (1913); **156**, 1907–9 (1913).

Variables:
T/K: 276, 280, and 323
$100w_2$ /mass %: 0.02–10.9
$100w_3$ /mass %: 1.2–35.0

Prepared by:
J. Hála

Experimental Data

Solubility at three different temperatures of $Th(C_2O_4)_2$ in $C_2H_2O_4-HCl$ solutions

Temperature (°C)	HCl ($100w_2$ /mass %)	$C_2H_2O_4$ ($100w_3$ /mass %)	Th (mass %)	Solid phase[a]
13	34.8	0.31	0.30	B
	34.9	0.56	0.18	B
	35.0	0.79	0.11	B
	34.9	1.52	0.05	B
	35.0	1.81	0.04	B
17	1.2	0.71	0.0013	A
	4	0.71	0.0020	A
	8.5	0.71	0.0018	A
	13.2	0.71	0.0022	A
	13.2	1.44	0.0014	A
	13.3	2.63	0.0013	A
50	12.4	0.024	0.033	A
	12.3	0.14	0.012	A
	12.4	0.28	0.0054	A
	12.4	0.43	0.0048	A
	12.4	1.37	0.0033	A
	12.4	2.06	0.0025	A
	12.3	2.76	0.0026	A
	12.4	5.49	0.0026	A
	12.3	10.9	0.0017	A
	32.6	0.43	0.63	B
	32.8	0.82	0.37	B
	32.6	1.34	0.26	B
	32.9	2.30	0.14	B
	32.5	4.46	0.086	B
	32.0	6.64	0.070	B

[a] (A) $Th(C_2O_4)_2\cdot6H_2O$, [16788-62-8]; (B) $Th_4(C_2O_4)_6Cl_4\cdot20H_2O$, [ ].

Auxiliary Information

Method/Apparatus/Procedure:
Isothermal method used. No details given except that at 17 °C 3 months were necessary to bring the solution into equilibrium with the solid phase A. Experiments at >30 mass % HCl were carried out using B as the starting solid phase. The composition of B as the equilibrium solid phase was confirmed by chemical analysis.

Source and Purity of Materials:
Source and purity of chemicals used were not specified.

Estimated Error:
Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

4.9.6. Evaluation of the $Th(C_2O_4)_2+C_2H_2O_4+HNO_3+H_2O$ System

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Nitric acid; HNO_3; [7697-37-2]
(4) Water; H_2O; [7732-18-5]

Evaluator:

J. Hála, Department of Inorganic Chemistry, Masaryk University, 611 37 Brno, Czech Republic, February 2000

Critical Evaluation:

This system has been studied in four references.[1–4] Although quite a number of experimental results are available their comparison is difficult since the solubilities have been reported in various units, and the authors used various approaches to studying this system. In spite of all this, even a rough, comparison reveals considerable inconsistency among the published data. Thus in Refs. 1 and 3, one series of experiments was run with both HNO_3 and $C_2H_2O_4$ concentrations being varied at the same time. Neglecting various units used and temperature of the measurements (mol kg^{-1} solution at 298.15 K in Ref. 1 and mol dm^{-3} at 296.15 in Ref. 3), one can find experiments with similar HNO_3 and $C_2H_2O_4$ concentrations but widely differing in $Th(C_2O_4)_2$ solubilities in both series, e.g.,

8.94 mol HNO_3 kg^{-1} solution/0.52 mol $C_2H_2O_4$ kg^{-1} solution/1.965×10^{-3} mol Th kg^{-1} solution[1]
8.2 mol dm^{-3} HNO_3/0.50 mol dm^{-3} $C_2H_2O_4$/3.23×10^{-5} mol dm^{-3} Th,[3] or
3.44 mol HNO_3 kg^{-1} solution/0.57 mol $C_2H_2O_4$ kg^{-1} solution/6.5×10^{-5} mol Th kg^{-1} solution[1]
3.2 mol dm^{-3} HNO_3/0.54 mol dm^{-3} $C_2H_2O_4$/9.91×10^{-6} mol dm^{-3} Th.[3]

Such differences are much greater than could result from the differences in concentrations. Smaller differences can be observed between the results in Refs. 2 and 4 where always the concentration of one component was kept constant while varying the other one. Here comparison can be done more easily since identical concentration unit, mol dm^{-3}, was used. Neglecting the differences in temperature, i.e., 298.15 K in Ref. 2 and 293.15 K in Ref. 4, one can find the following data:

1.0 mol dm^{-3} HNO_3/0.5 mol dm^{-3} $C_2H_2O_4$/5×10^{-7} mol dm^{-3} $Th(C_2O_4)_2$[2]
1.0 mol dm^{-3} HNO_3/0.5 mol dm^{-3} $C_2H_2O_4$/1.9×10^{-6} mol dm^{-3} $Th(C_2O_4)_2$[4]
1.48 mol dm^{-3} HNO_3/0.05 mol dm^{-3} $C_2H_2O_4$/2.4×10^{-6} mol dm^{-3} $Th(C_2O_4)_2$[2]
1.5 mol dm^{-3} HNO_3/0.05 mol dm^{-3} $C_2H_2O_4$/4.31×10^{-6} mol dm^{-3} $Th(C_2O_4)_2$[4]
2.49 mol dm^{-3} HNO_3/0.05 mol dm^{-3} $C_2H_2O_4$/7.2×10^{-6} mol dm^{-3} $Th(C_2O_4)_2$[2]
2.5 mol dm^{-3} HNO_3/0.05 mol dm^{-3} $C_2H_2O_4$/6.47×10^{-6} mol dm^{-3} $Th(C_2O_4)_2$[4]

In addition, the paper by Bryzgalova *et al.*[2] shows discrepancies even between two series of experiments of that same document where two data for the solubility of $Th(C_2O_4)_2$ in the system 1.0 mol dm^{-3} HNO_3/0.05 mol dm^{-3} $C_2H_2O_4$ differ by a factor of 4. The same is found in the system 1.0 mol dm^{-3} HNO_3/0.01 mol dm^{-3} $C_2H_2O_4$.

It can thus be concluded that although the solubility data published for $Th(C_2O_4)_2$ in the $C_2H_2O_4-HNO_3-H_2O$ system offer good approximation, none of them can be recommended as preferred values. The discrepances may partly be due to differences in equilibrium time (6–7 days in Refs. 1,3 and several hours in Refs. 2, 4), partly to different precision of the methods used for thorium determination (colorimetry and radiometry).

References:

[1] A. G. Kurnakova and L. K. Shubochkin, Zh. Neorg. Khim. **8**, 1249 (1963).
[2] R. V. Bryzgalova, Yu. M. Rogozin, and I. V. Chernitskaya, Radiokhimiya **12**, 286 (1970).
[3] P. R. Monson and R. Hall, USDOE Report DP-1576, 1981.
[4] E. M. Pazukhin, E. A. Smirnova, A. S. Krivochatskii, Yu. L. Pazukhina, and S. M. Kochergin, Radiokhimiya **27**, 606 (1985).

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Nitric acid; HNO_3; [7697-37-2]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

A. G. Kurnakova and L. K. Shubochkin, Zh. Neorg. Khim. **8**, 1249–54 (1963); Russ. J. Inorg. Chem. **8**, 647–50 (1963).

Variables:

T/K: 298
m_2 /mol kg^{-1}: 0.63–1.35
m_3 /mol kg^{-1}: 0–22.96

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $Th(C_2O_4)_2$ in $C_2H_2O_4-HNO_3$[a]

HNO_3 ($100w_3$ / mass %)	HNO_3 (mol kg^{-1})[b]	HNO_3 (m_3 /mol kg^{-1})[c]	$C_2H_2O_4$ ($100w_2$ / mass %)	$C_2H_2O_4$ (mol kg^{-1})[b]	$C_2H_2O_4$ (m_2 /mol kg^{-1})[c]	Th (mg kg^{-1})[b]	Th (10^4 mol kg^{-1})[b]	Th (m_2 / mol kg^{-1})[c]
0	0	0	10.45	1.16	1.30	18	0.78	0.87
4.36	0.69	0.78	7.39	0.82	0.93	18	0.78	0.88
11.78	1.87	2.29	6.60	0.73	0.90	17	0.73	0.90
15.88	2.52	3.22	5.76	0.64	0.82	17	0.73	0.93
21.69	3.44	4.70	5.14	0.57	0.78	15	0.65	0.88
28.03	4.45	6.58	4.40	0.49	0.72	23	0.99	1.47
35.42	5.62	9.25	3.83	0.43	0.70	26	1.12	1.84
37.0	5.89	9.85	3.40	0.38	0.63	41	1.77	2.96
46.89	7.44	14.87	3.07	0.34	0.68	77	3.32	6.63
56.34	8.94	22.96	4.72	0.52	1.35	456	19.65	50.5

[a] The equilibrium solid phases were mixtures of $Th(C_2O_4)_2\cdot6H_2O$, [16788-62-8], and $C_2H_2O_4\cdot2H_2O$, [6153-56-6] in all saturated solutions.
[b] Mol per kg solution.
[c] Calculated by compiler

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Oxalic acid was added to saturated solutions of $Th(C_2O_4)_2\cdot6H_2O$ in HNO_3 solutions of various concentrations, and the mixtures were agitated for 6–7 days. The saturated solutions were analyzed for oxalate content and total acidity by titration with 0.05 N $KMnO_4$ and 0.1 N NaOH, respectively, and the HNO_3 concentration was obtained by difference. The concentration of thorium in the saturated solutions was determined radiometrically. Samples of the saturated solutions were withdrawn onto ashless filter, dried,and β counted. The β activity of the saturated solutions was compared with those of standards prepared from labeled $Th(C_2O_4)_2\cdot6H_2O$. The composition of the equilibrium solid phases was confirmed by optical microscopy and chemical analysis.

Source and Purity of Materials:

$Th(C_2O_4)_2\cdot6H_2O$ was prepared from thorium nitrate of unspecified source and purity. To increase the β activity of thorium for its subsequent radiometric determination, aged $UO_2(NO_3)_2$ in radioactive equilibrium with thorium isotope UX_1 (^{234}Th) was added to thorium nitrate, and $Th(C_2O_4)_2\cdot6H_2O$ was precipitated from hot solution with a stoichiometric amount of oxalic acid. The labeled $Th(C_2O_4)_2\cdot6H_2O$ was filtered, washed ten times with boiling water, and air dried. Freshly distilled 60.4% HNO_3 was used.

Estimated Error:

Temperature: precision ±0.1 K (authors).
Solubility: insufficient data given to allow for error estimate.

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Nitric acid; HNO_3; [7697-37-2]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

P. R. Monson and R. Hall, USDOE Report DP-1576, E. I. Du Pont de Nemours and Co., Savannah River Laboratory, 1981.

Variables:

T/K: 296
c_2 /mol dm^{-3}: 0.18–0.81
c_3 /mol dm^{-3}: 0.28–10.9

Prepared by:

J. Hála

Experimental Data

Solubility at 23 °C of $Th(C_2O_4)_2$ in $C_2H_2O_4$–HNO_3 solutions[a]

$C_2H_2O_4$[b] (c_2 /mol dm^{-3})	HNO_3[b] (c_3 /mol dm^{-3})	Th^{4+} (mg dm^{-3})	$Th(C_2O_4)_2$ (10^6 c_1 /mol dm^{-3})[c]
0.41	10.9	320	1380
0.50	8.2	7.5	32.3
0.42	5.1	3.7	15.9
0.37	4.1	1.9	8.19
0.54	3.2	2.3	9.91
0.57	1.7	0.7	3.02
0.18	0.58	1.6	6.90
0.81	0.28	1.8	7.76

[a] Equilibrium solid phases not investigated
[b] Initial (total) concentration.
[c] Calculated by compiler.

Additional Information:
When plotted against the ratio $[C_2H_2O_4]/[HNO_3]^2$ (proportional to $[C_2O_4^{2-}]/K_{a1}K_{a2}$, where K_{a1} and K_{a2} are dissociation constants of oxalic acid), the solubility of $Th(C_2O_4)_2$ passed through a shallow minimum at $[C_2H_2O_4]/[HNO_3]^2$ of approximately 0.2–0.4. The minimum solubility was explained by the authors as corresponding to the situation where the sparingly soluble $Th(C_2O_4)_2$ complex predominated in the solution. The increase in solubility at lower or higher $[C_2H_2O_4]/[HNO_3]^2$ values then corresponded to the formation in the solution of the cationic $Th(C_2O_4)^{2+}$ or anionic $Th(C_2O_4)_3^{2-}$ and $Th(C_2O_4)_4^{4-}$ complexes,[1] respectively.

Auxiliary Information

Method/Apparatus/Procedure:

Two modifications of isothermal method were used. In the first one, thorium oxalate was equilibrated with $C_2H_2O_4$–HNO_3 solutions of the desired composition for 6–7 days, which was known to be sufficient to reach the equilibrium.[2] In the second method, thorium oxalate was precipitated directly by addition of $C_2H_2O_4$ in a 20%–40% excess to a $Th(NO_3)_4$ solution in 0.5–8.0 mol dm^{-3} HNO_3 solutions. These solutions were equilibrated for 10–14 h. It has not been mentioned if the solutions were thermostated during equilibration, or which results were obtained by which of the two methods used. Thorium was determined in the saturated solutions spectrophotometrically by the arsenazo(III) method modified for HNO_3 solutions[3] (sulfamic acid was used to remove HNO_2 which destroys the reagent and its thorium complex).

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

References:

[1] A. I. Moskvin and L. N. Essen, Russ. J. Inorg. Chem. **12**, 359 (1967).
[2] A. G. Kurnakova and L. K. Shubochkin, Russ. J. Inorg. Chem **8**, 647 (1963).
[3] E. W. Baumann, USDOE Report DP-1560, 1980.

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Nitric acid; HNO_3; [7697-37-2]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

R. V. Bryzgalova, Yu. M. Rogozin, and I. V. Chernitskaya, Radiokhimiya **12**, 286–91 (1970).

Variables:

T/K: 298
c_2 /mol dm^{-3}: 0–0.5
c_3 /mol dm^{-3}: 0.995–2.49

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $Th(C_2O_4)_2$ in $C_2H_2O_4$ /HNO_3 solutions[a]

HNO_3 (c_3 /mol dm^{-3})	$C_2H_2O_4$ (c_2 /mol dm^{-3})	$C_2O_4^{2-}$ [b] (10^7 mol dm^{-3})	$Th(C_2O_4)_2$ (10^6 c_1 /mol dm^{-3})
1.0	—	—	160
1.0	0.0010	0.133	16
1.0	0.0025	0.330	4.2
1.0	0.0050	0.665	2.5
1.0	0.010	1.33	1.1
1.0	0.025	3.30	0.75
1.0	0.050	6.65	0.5
1.0	0.10	13.3	0.5
1.0	0.35	46.5	0.4
1.0	0.50	66.5	0.5
0.995	0.01	1.35	4.0
1.43	0.01	0.50	8.1
2.0	0.01	0.24	21
2.49	0.01	0.156	53
0.995	0.05	6.7	1.9
1.48	0.05	2.5	2.4
2.0	0.05	1.2	3.8
2.49	0.05	0.78	7.2

[a] Equilibrium solid phases were not investigated. The compiler assumes this to be the hexahydrate, $Th(C_2O_4)_2 \cdot 6H_2O$, [16788-62-8], which has been reported to be stable in acidic solutions.[1]
[b] Dissociation constants of oxalic acid used in calculating the oxalate ion concentration were not reported.

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Nitric acid; HNO_3; [7697-37-2]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

E. M. Pazukhin, E. A . Smirnova, A. S. Krivokhatskii, Yu. L. Pazukhina, and S. M. Kochergin, Radiokhimiya **27**, 606–11 (1985).

Variables:

T/K: 293
c_2 /mol dm^{-3}: 0.001–0.5
c_3 /mol dm^{-3}: 0.5–3.0

Prepared by:

J. Hála

Experimental Data

Solubility at 20 °C of $Th(C_2O_4)_2$ in $C_2H_2O_4$–HNO_3 solutions[a]

HNO_3[b] (c_3 /mol dm^{-3})	$C_2H_2O_4$[b] (c_2 /mol dm^{-3})	Total oxalate[c] (mol dm^{-3})	$[C_2O_4^{2-}]$[d] (10^7 mol dm^{-3})	$Th(C_2O_4)_2$ (10^6 c_1 /mol dm^{-3})	HNO_3[e] (m_2 / mol kg^{-1})
0.5	—	0.000 135	0.0884	67.7	0.523
1.0	—	0.000 432	0.0772	216	1.05
1.5	—	0.000 604	0.0495	302	1.56
2.0	—	0.000 984	0.0461	492	2.10
2.5	—	0.001 18	0.0358	590	2.70
3.0	—	0.001 50	0.0318	750	3.29
3.0	0.05		1.06	6.90	
3.0	0.025		0.503	9.91	
2.0	0.2		9.38	2.93	
2.0	0.1		4.69	2.37	
2.0	0.025		1.17	7.11	
2.5	0.1		3.03	2.72	
2.5	0.05		1.52	6.47	
2.5	0.025		0.758	7.24	
1.5	0.2		16.4	2.59	
1.5	0.1		8.20	2.37	
1.5	0.025		2.5	4.96	
1.5	0.05		4.10	4.31	
1.35	0.159		16.0	2.07	
1.35	0.1		10.1	1.8	
1.35	0.1		10.1	2.2	
1.325	0.0026		0.270	7.89	
1.307	0.00165		0.176	11.4	
1.288	0.00105		0.116	22.5	
1.27	0.105		11.9	2.20	
1.25	0.175		20.4	2.07	
1.24	0.415		49.1	1.81	
1.00	0.50		89.3	2.16	
0.50	0.10		65.2	1.98	
0.50	0.05		32.6	1.90	

[a] Equilibrium solid phases were not investigated. It can be assumed this to be the hexahydrate, $Th(C_2O_4)_2 \cdot 6H_2O$, [16788-62-8], in all solutions since the authors reported that the initial solid phase did not undergo any change during equilibration.

[b] Initial concentration.

[c] In solutions with initially no oxalic acid added, these values are given by the solubility of $Th(C_2O_4)_2$.

[d] Equilibrium concentration of the $C_2O_4^{2-}$ ion calculated from total oxalate concentration and H^+ ion concentration by using dissociation constants of oxalic acid, $K_{a1} = 1.05 \times 10^{-1}$ and $K_{a2} = 1.88 \times 10^{-5}$ taken from Ref. 1.

[e] Calculated by compiler from densities of HNO_3 solution taken from Ref. 2.

Additional Information:

The solubility of $Th(C_2O_4)_2$ in the $Th(C_2O_4)_2$–$C_2H_2O_4$–HNO_3–H_2O system was shown by the authors to fit the same equation as in the $Th(C_2O_4)_2$–$C_2H_2O_4$–H_2O system, i.e., $\log C_{Th} = 0.2683(\log[C_2O_4^{2-}])^2 + 2.947 \log[C_2O_4^{2-}] + 2.330$.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. 20–100 mg of $Th(C_2O_4)_2 \cdot 6H_2O$ were stirred with a rotary stirrer at 200–600 rpm with 10 mL solution until equilibrium was reached (a few hours). Excess solid was filtered off in a thermostated space at 25 °C. Thorium in the filtrate was determined colorimetrically with arsenazo III.[2] Data reported are average values of 3–4 determinations.

Source and Purity of Materials:

The $Th(C_2O_4)_2 \cdot 6H_2O$ was prepared by precipitation from 0.1 mol dm^{-3} solutions of $Th(NO_3)_4$ and oxalic acid. The precipitate was allowed to stand for 1 day, the mother liquor decanted, and the precipitate stirred with 0.1 mol dm^{-3} HNO_3 for 5–6 h. The washing was repeated until the wash solution contained equivalent concentrations of thorium and oxalic acid. The precipitate was then filtered, washed with water, ethanol, and ether, and air dried at room temperature. The composition of the product as found by analysis was Th:oxalate:H_2O = 1:1.98:6.3.

Estimated Error:

Temperature: precision ±0.2 K (authors).
Thorium concentration: precision ±10% for $C_{Th} > 1.2 \times 10^{-6}$ mol dm^{-3} and ± (20–30) % for $C_{Th} < 1.2 \times 10^{-6}$ mol dm^{-3} (authors). Comparison of the solubilities of $Th(C_2O_4)_2$ obtained for 1.0 mol dm^{-3} HNO_3 at 0.01 and 0.05 mol dm^{-3} oxalic acid with the corresponding values for 0.995 mol dm^{-3} HNO_3 in the second and third series of measurements shows deviations much larger than would follow from the stated precision.

References:

[1] E. M. Pazukhin, E. A. Smirnova, A. S. Krivokhatskii, Yu. L. Pazukhina, and S. M. Kochergin, Radiokhimiya **27**, 606 (1985).
[2] A. A. Nemodruk and N. E. Kochetkova, Zh. Analit. Khim. **17**, 330 (1962).

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess $Th(C_2O_4)_2 \cdot 6H_2O$ was equilibrated in thermostated vessels for 6 h which was found sufficient to reach equilibrium. The equilibrium concentration of oxalate ion in the solutions was varied by varying either acidity at constant oxalate concentration, or total oxalate concentration at a fixed acidity. After equilibration the saturated solutions were centrifuged and the concentration of thorium was determined colorimetrically with arsenazo III.[3] The method for the determination of oxalate was not specified. The authors reported that the initial solid phase did not undergo any change during equilibration.

Source and Purity of Materials:

$Th(C_2O_4)_2 \cdot 6H_2O$ was prepared by precipitation according to Ref. 4.

Estimated Error:

Temperature: precision ± 0.2 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] A. V. Stepanov and E. M. Pazukhin, Zh. Neorg. Khim. **15**, 1483 (1970).
[2] *Physico-Chemical Tables* (Publ. House Tech. Literature, Prague, 1953), Vol. 1, p. 212.
[3] S. B. Savvin, *Arsenazo III* (Atomizdat, Moscow, 1966) (in Russian), p. 107.
[4] D. I. Ryabchikov and E. K. Golbraikh, *Analytical Chemistry of Thorium* (Publ. House Acad. Sci. USSR, Moscow, 1960) (in Russian), p. 33.

Components:

(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Perchloric acid; $HClO_4$; [7601-90-3]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

A. I. Moskvin and L. N. Essen, Zh. Neorg. Khim. **12**, 688–93; (1967) Russ. J. Inorg. Chem., **12**, 359–62 (1967).

Variables:

T/K: 298
c_2 /mol dm^{-3}: 0.08–0.555
c_3 /mol dm^{-3}: 1.0

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $Th(C_2O_4)_2$ in $C_2H_2O_4$–$HClO_4$ solutions[a]

$C_2H_2O_4$ (c_2 /mol dm^{-3})	$Th(C_2O_4)_2$ (10^4 c_1 /mol dm^{-3})
0.080	0.060
0.158	0.940
0.238	1.00
0.317	1.30
0.397	1.60
0.476	1.70
0.555	1.86

[a] All solutions contained 1.0 mol dm^{-3} $HClO_4$. Solid phases were not investigated. The compiler assumes this to be the hexahydrate, $Th(C_2O_4) \cdot 6H_2O$, [16788-62-8], which precipitates from acidic solutions containing oxalic acid.[1]

Additional information:
The solubility data were used to obtain the solubility product of $Th(C_2O_4)_2$ in two different ways. Graphical treatment according to Refs. 2 and 3 of the data yielded the value of $K_{sp} = 1 \times 10^{22}$ mol^3 dm^{-9}. Another approach considered the increasing solubility of $Th(C_2O_4)_2$ in $C_2H_2O_4$–$HClO_4$ solutions. Assuming that $Th(C_2O_4)_2$ and $Th(C_2O_4)_3^{2-}$ only contributed to the solubility of $Th(C_2O_4)_2$ in these solutions, the solubility was expressed as
$S = [Th(C_2O_4)_2] + [Th(C_2O_4)_3^{2-}] = \beta_2[Th^{4+}][C_2O_4^{2-}]^2 + \beta_3[Th^{4+}][C_2O_4^{2-}]^3 = \beta_2 K_{s0} + \beta_3 K_{s0}[C_2O_4^{2-}]$

where β_2 and β_3 are overall stability constants of the corresponding complexes. The solubility product was then obtained by graphical extrapolation of S to zero oxalic acid concentration as 4.1×10^{-22} mol^3 dm^{-9}. Taking then into consideration the value K_{sp} obtained in the $Th(C_2O_4)_2$–$HClO_4$–NH_4ClO_4–H_2O system, an average value of $K_{sp} = (4.2 \pm 0.1) \times 10^{-22}$ mol^3 dm^{-9} was given which was recalculated to $K_{sp}^0 = 1.1 \times 10^{-25}$ mol^3 dm^{-9} by using the Davies' equation.[4]

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method was used. Excess $Th(C_2O_4)_2 \cdot 6H_2O$ was stirred with 1.0 mol dm^{-3} solutions of $HClO_4$ containing various amounts of oxalic acid for 4 h in a thermostated apparatus. The concentration of thorium in the saturated solutions was determined by an unspecified gravimetric method.

Source and Purity of Materials:

$Th(C_2O_4)_2 \cdot 6H_2O$ was prepared according to Ref. 5. Source and purity of chemicals were not specified.

Estimated Error:

Temperature: precision ± 0.3 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] R. V. Bryzgalova, Yu. M. Rogozin, and I. V. Chernitskaya, Radiokhimiya **12**, 286 (1970).
[2] A. I. Moskvin and A. D. Gelman, Zh. Neorg. Khim. **3**, 956 (1958).
[3] F. A. Zakharova and A. I. Moskvin, Zh. Neorg. Khim. **5**, 1228 (1960).
[4] C. W. Davies, J. Chem. Soc. 2093 (1938).
[5] A. A. Grinberg and G. I. Pertzhak, Trudy Radiev. Inst. Akad. Nauk SSSR **7**, 50 (1956).

4.9.7. $Th(C_2O_4)_2$+$Th(CO_3)_2$+$Na_2C_2O_4$+Na_2CO_3+H_2O System

Components:

Th^{4+},$Na^+\|CO_3^{2-}$,$C_2O_4^{2-}-H_2O$
(1) Thorium bis(oxalate); $Th(C_2O_4)_2$; [2040-52-0]
(2) Thorium carbonate; $Th(CO_3)_2$; [19024-62-5]
(3) Sodium oxalate; $Na_2C_2O_4$; [62-76-0]
(4) Sodium carbonate; Na_2CO_3; [497-19-8]
(1) Water; H_2O; [7732-18-5]

Original Measurements:

I. S. Kovaleva and N. P. Luzhnaya, Zh. Neorg. Khim. **7**, 1693–8 (1962).

Variables:

T/K:298
composition

Prepared by:

J. Hála

Experimental Data

Composition of solutions saturated at 25 °C

$Th(C_2O_4)_2$ (100 w_1 / mass %)	$Th(C_2O_4)_2$ ($m_1/10^3$ mol kg^{-1})[b]	Na_2CO_3 (100w_4 / mass %)	Na_2CO_3 (m_4/ 10^2 mol kg^{-1})[b]	$Th(CO_3)_2$ (100w_2 / mass %)	$Th(CO_3)_2$ (m_2 /mol kg^{-1})[b]	$Na_2C_2O_4$ (100w_3 / mass %)	$Na_2C_2O_4$ ($m_3/10^2$ mol kg^{-1})[b]	Solid phase[a]
0.28	0.8941	22.68	27.37	—	—	—	—	A+B
0.45	1.395	19.86	23.26	0.63	2.263	—	—	B+C
0.45	1.394	19.82	23.19	0.60	2.154	—	—	B+C
1.06	3.086	14.25	15.68	0.53	1.789	—	—	B+C
0.98	2.822	13.25	14.42	0.67	2.236	—	—	B+C
1.06	3.037	12.70	13.75	0.704	2.338	—	—	B+C
1.10	3.129	12.04	12.94	0.704	2.321	—	—	B+C
1.43	4.017	10.52	11.17	0.81	2.637	—	—	B+C
1.96	5.466	9.96	10.50	0.21	0.6788	—	—	B+C
2.98	8.163	7.21	7.463	0.35	1.111	—	—	B+C
0.98	2.660	6.06	6.216	2.68	8.432	—	—	C
6.28	18.13	8.64	9.231	0.39	1.305	—	—	C+X
5.92	17.08	8.44	9.202	0.704	2.354	—	—	C+X
4.53	12.81	7.40	7.907	1.41	4.622	—	—	C+X
5.63	16.69	9.46	10.60	2.25	7.732	—	—	C+X
5.92	16.92	7.82	8.448	—	—	0.54	0.4701	B+X
3.84	10.46	5.30	5.455	—	—	0.88	0.7299	B+X
2.08	5.500	3.05	3.048	—	—	2.20	1.772	B+X
1.92	5.057	2.69	2.678	—	—	2.36	1.893	B+X
1.47	3.831	1.34	1.320	—	—	3.16	2.508	B+X
3.22	8.660	1.48	1.504	—	—	4.18	3.423	B+X
2.65	7.089	0.89	0.8996	—	—	4.85	3.951	B+D
2.86	7.654	1.29	1.305	—	—	4.29	3.497	X+X
1.22	3.158	0.34	0.3326	—	—	3.78	2.980	D+X
1.02	2.635	0.49	0.4783	—	—	3.62	2.848	D+X
1.14	2.913	0.28	0.2704	—	—	2.68	2.086	D+X
0.86	2.181	0.04	0.0383	—	—	2.44	1.884	D+E
1.63	4.144	traces	traces	—	—	2.01	1.557	D+E
5.96	16.96	3.84	4.129	—	—	4.07	3.527	X
0.82	2.14	2.50	2.448	—	—	2.09	1.649	B
0.041	0.1017	0.25	0.2402	—	—	3.32	2.570	B
—	—	22.70	27.50	0.86	3.196	—	—	A+C
—	—	22.93	27.63	—	—	0.21	0.2039	A+B
1.59	4.139	—	—	—	—	4.27	3.385	B+D
2.09	5.354	—	—	—	—	2.25	1.755	C+E
0.73	2.338	22.30	26.99	0.45	1.670	—	—	A+B+C

[a] (A) $Na_2CO_3\cdot10H_2O$, [6132-02-1]; (B) $Na_2C_2O_4$, [62-76-0]; (C) $Na_6Th(CO_3)_5\cdot12H_2O$, [12386-47-9]; (D) $Na_4Th(C_2O_4)_4\cdot6H_2O$, []; (E) $Th(C_2O_4)_2\cdot6H_2O$, [16788-62-8]; (X) unidentified solid phase.

[b] Calculated by compiler.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. The measurements were carried out in stirred vessels equipped with an oil sealing. Starting from solutions corresponding to invariant points, increasing amounts of the third component were added. Equilibrium was attained in one day for systems rich in Na_2CO_3 or 4 days for systems rich in sodium or thorium oxalates. Samples of the saturated solutions were analyzed for oxalate content with $KMnO_4$ titration, and gravimetrically for CO_2 and thorium (as ThO_2). Sodium was determined by difference, in some cases also gravimetrically as Na_2SO_4. Composition of the solid phases was investigated by the method of wet residues and checked by optical microscopy and x-ray diffraction.

Source and Purity of Materials:

$Th(C_2O_4)_26H_2O$ was obtained from $Th(NO_3)_4$, its source and purity not specified. For measurements with thorium carbonate solid phases, the solid used was $Na_6Th(CO_3)_5\cdot12H_2O$, prepared according to Ref. 1. Other chemicals used were reagent grade products.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

References:

[1] I. I. Chernyaev, V. A. Golovnia, and A. K. Molodkin, Proceedings 2nd International Conference Peaceful Uses At. Energy, Geneva, 1958, pp. 28, 203.

4.10. Ammonium Tetrakis(oxalato)thorate

Components:

(1) Ammonium tetrakis(oxalato)thorate; $(NH_4)_4Th(C_2O_4)_4$; [ ]
(2) Ammonium oxalate; $(NH_4)_2C_2O_4$; [1113-38-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

B. Brauner, J. Chem. Soc. **73**, 951–85 (1898).

Variables:

m_2 /mol kg^{-1}:0.733

Prepared by:

J. Hála

Experimental Data

The solubility of $(NH_4)_4Th(C_2O_4)_4$, at unspecified room temperature, was determined to be 90.3 g$(NH_4)_4Th(C_2O_4)_4 \cdot 4H_2O$ in 100 g water. The solution also contained 9.3 g$(NH_4)_2C_2O_4$ per 100 g water since the complex salt is unstable towards hydrolysis in pure water. The solubility was calculated by the author from analysis of one sample (2.8235 g) of the saturated solution which produced a residue of 1.3740 g on drying at 105 °C, which further produced 0.4822 g ThO_2 on ignition. From these data the compiler calculated the solubility of $(NH_4)_4Th(C_2O_4)_4$ to be 80.464 g/100 g water (1.226 mol kg^{-1}) in the presence of 90.97 g $(NH_4)_2C_2O_4$ /kg water (0.733 mol kg^{-1}). The figure 90.3 g salt/100 g water given by the author obviously refers to the tetrahydrate (89.29 g/100 g water, compiler).

Auxiliary Information

Method/Apparatus/Procedure:

The solubility was determined by analyzing the saturated mother liquor obtained in the course of the preparation of $(NH_4)_4Th(C_2O_4)_4 \cdot 4H_2O$. Thorium was determined gravimetrically as ThO_2.

Source and Purity of Materials:

Pure thorium oxalate, prepared from a thorium preparation purified from lanthanides by precipitation of the Na/Th sulfate, was heated with water to boiling, and ammonium oxalate was added until half of the thorium oxalate dissolved. After cooling, the solution was filtered and the filtered concentrated until, when allowed to cool, needle-shaped crystals of the tetrahydrate began to form.

4.11. Thorium Oxobis(*o*-hydroxybenzoate)

Components:

(1) Thorium oxobis(hydroxybenzoate); $ThO(C_7H_5O_3)_2$;[ ]
(2) Ammonium hydroxybenzoate (salicylate); $NH_4(C_7H_5O_3)$; [ ]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

O. E. Zvyagintsev and B. N. Sudarikov, Zh. Neorg. Khim. **2**, 128–37 (1957).

Variables:

T/K: 293–369
c_2 /mol dm^{-3}: 0–1.76

Prepared by:

J. Hála

Experimental Data

Solubility of $ThO(C_7H_5O_3)_2$ in water and in solutions of $NH_4(C_7H_5O_3)$ at different temperatures[a]

Temperature (°C)	Th (mg dm^{-3})	$ThO(C_7H_5O_3)_2$ (10^6 c_1 /mol dm^{-3})[b]	Temperature (°C)	Th (mg dm^{-3})	$ThO(C_7H_5O_3)_2$ (10^6c_1 /mol dm^{-3})[b]
Solubility of $ThO(C_7H_5O_3)_2$ in water as a function of temperature					
20	0.3	0.415	70	1.1	1.52
30	0.4	0.554	80	1.4	1.94
40	0.5	0.692	90	1.7	2.35
50	0.7	0.969	96	2.6	3.60
60	0.9	1.25			

pH	Th (mg dm^{-3})	$ThO(C_7H_5O_3)_2$ (10^6 c_1 /mol dm^{-3})[b]	pH	Th (mg dm^{-3})	$ThO(C_7H_5O_3)_2$ (10^6 c_1 /mol dm^{-3})[b]
Solubility of $ThO(C_7H_5O_3)_2$ in water as a function of pH[c]					
1.2	20.0	27.7	5.6	0.3	0.415
2.2	3.7	5.12	6.8	1.1	1.52
3.0	1.2	1.66	7.9	1.3	1.80
4.2	0.5	0.692	8.5	1.2	1.66

$NH_4(C_7H_5O_3)$ (g dm^{-3})	$NH_4(C_7H_5O_3)$ (c_2 /mol dm^{-3})[b]	Th (mg dm^{-3})	$ThO(C_7H_5O_3)_2$ (10^6c_1 /mol dm^{-3})	$NH_4(C_7H_5O_3)$ (g dm^{-3})	$NH_4(C_7H_5O_3)$ (c_2 /mol dm^{-3})[b]	Th (mg dm^{-3})	$ThO(C_7H_5O_3)_2$ (10^6c_1 / mol dm^{-3})
Solubility at 30 °C of $ThO(C_7H_5O_3)_2$ in $NH_4(C_7H_5O_3)$ solutions[d]							
0	0	1.4	1.94	50	0.196	0.1	0.138
10	0.0392	0.1	0.138	100	0.392	1.4	1.94
20	0.0784	0.1	0.138	200	0.784	1.7	2.35
30	0.118	0.1	0.138	450	1.763	30.2	41.8

$NH_4(C_7H_5O_3)$ (g dm^{-3})	$NH_4(C_7H_5O_3)$ (c_2 /mol dm^{-3})[b]	Th (mg dm^{-3})	$ThO(C_7H_5O_3)_2$ (10^6c_1 /mol dm^{-3})	$NH_4(C_7H_5O_3)$ (g dm^{-3})	$NH_4(C_7H_5O_3)$ (c_2 /mol dm^{-3})[b]	Th (mg dm^{-3})	$ThO(C_7H_5O_3)_2$ (10^6c_1 / mol dm^{-3})
Solubility at 96 °C of $ThO(C_7H_5O_3)_2$ in $NH_4(C_7H_5O_3)$ solutions[d]							
0	0	2.6	3.60	60	0.235	0.5	0.692
10	0.0392	0.2	0.277	100	0.392	1.8	2.49
20	0.0784	0.1	0.138	150	0.588	3.6	4.98
30	0.118	0.1	0.138	200	0.784	5.4	7.48
40	0.157	0.1	0.138	250	0.980	7.2	9.97
50	0.196	0.2	0.277	300	1.176	9.0	12.5

[a] Equilibrium solid phases were not investigated.
[b] Calculated by compiler.
[c] pH adjusted by additions of HCl or NH_3 solutions.
[d] pH=5; 4 h stirring.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess of ^{234}Th-labeled $ThO(C_7H_5O_3)_2$ was stirred for 1–4 h with the solutions under the desired conditions. In most cases, 1–2 h stirring was sufficient for equilibrium to be reached. Then an aliquot of the saturated solution was withdrawn, evaporated, and the concentration of thorium was determined by β counting of ^{234}Th using a Geiger counter.

Source and Purity of Materials:

$ThO(C_7H_5O_3)_2$ labeled with ^{234}Th was prepared by precipitation of a radiochemically pure, boiling $Th(NO_3)_4$ solution with salicylic acid at pH 4–5[1] in the presence of $UO_2(NO_3)_2$. The precipitate of $ThO(C_7H_5O_3)_2$ was thoroughly washed with water from U(VI) salicylate, and reprecipitated. The Th/salicylate ratio in the product was 1:2. Specific activity of the product was 10^4-10^5 counts mg^{-1} min^{-1}.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

References:

[1] O. E. Zvyagintsev and B. N. Sudarikov, Zh. Neorg. Khim. **1**, 241 (1956).

4.12. Thorium (5-nitro)Barbiturate

Components:	**Original Measurements:**
(1) Thorium tetrakis {(5-nitro)barbiturate}; $Th(C_4H_2N_3O_5)_4$ or $C_{16}H_8N_{12}O_{20}Th$; [ ] (2) Water; H_2O; [7732-18-5]	M. W. Goheen and R. J. Robinson, Analyt. Chim. Acta **31**, 175–9 (1964).
Variables:	**Prepared by:**
T/K: 297	J. Hála

Experimental Data

The solubility in water of thorium tetrakis{(5-nitro)barbiturate} is reported to be 1.4×10^{-4} mol dm^{-3} at 24 °C.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess salt was stirred with water for several hours, and then allowed to stand for several days in the saturated solution. An aliquot of the saturated solution was then evaporated by water pump desiccation, and the residue was weighed.

Source and Purity of Materials:

$Th(C_4H_2N_3O_5)_4\cdot 20H_2O$ was prepared by treating an aqueous 0.1 mol dm^{-3} $Th(NO_3)_4$ solution (reagent grade, Baker and Adamson) with a stoichiometric amount of 5-nitrobarbituric acid in the form of 0.05 mol dm^{-3} solution in 50% ethanol. The precipitate was allowed to stand for 1 day, then it was filtered and washed with water and 95% ethanol.

Additional Information:

Except for the water of crystallization, composition of the salt was not reported in the original document. It was deduced by the compiler from the reported thermogravimetric curve which showed that ignition of the air-dried hydrated salt to ThO_2 yielded a residue of 20% of the initial sample mass.

4.13. Thorium 8-Hydroxyquinolinate

Components:

(1) Thorium tetrakis(8-hydroxoquinolinate); $C_{24}H_{36}N_4O_4Th$ or $Th(C_6H_9NO)_4$; [18153-67-8]
(2) Hydrogen chloride; HCl; [7647-01-0]
(3) Sodium chloride; NaCl; [7647-14-5]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

I. M. Korenman and V. V. Korolikhin, Trudy. Khim. Khim. Tekhnol. **4**, 304–6 (1961).

Variables:

T/K: 298
c_2 /mol dm^{-3}: 0.001–0.025
(c_2+c_3)/mol dm^{-3}: 0.5

Prepared by:

J. Hála

Experimental Data

Solubility product of $Th(C_6H_9NO)_4$ in (H+Na)Cl solutions at ionic strength of 0.5 mol dm^{-3} and 25 °C[a]

HCl[b] (c_2 /mol dm^{-3})	pH[c]	$[R]_{tot}$[d] (10^3 mol dm^{-3})	K_{sp}[e,f] (10^{45} mol^5 dm^{-15})
0.0010	4.0	0.57–0.63	4.9–8.0
0.0025	3.8	1.14–1.25	6.6–8.6
0.005	3.55	3.0–3.2	6.3–8.7
0.010	3.4	5.8–5.9	11.4–12.5
0.025	3.1	14.0–14.1	3.8–3.9

[a] It was not stated explicitly whether the equilibrium solid phase was the anhydrous salt or the dihydrate.
[b] Initial concentration.
[c] pH of the saturated solutions.
[d] Total 8-hydroxoquinoline concentration in the saturated solution. Using these data, concentration of free 8-hydroxoquinolinate anion, or R^-, was calculated using dissociation constants of 8-hydroxoquinoline, $K_1=[H^+][R^-][HR]^{-1}=1.54\times10^{-10}$ and $K_2=[HR][H^+]\times[H_2R^+]^{-1}=9.61\times10^{-6}$.[1]
[e] The average value of $K_{sp}=[Th^{4+}][R^-]^4$ was reported to be $(7\pm2)\times10^{-45}$ mol^5 dm^{-15}. Individual K_{sp} values were obtained assuming the Th^{4+} concentration in the saturated solutions was equal to $[R]_{tot}/4$.
[f] The range covers the results of parallel measurements.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess $Th(C_6H_9NO)_4\cdot 2H_2O$ was shaken with the solutions of the desired composition. Equilibration time was 36 h although a period of 4–6 h was found as sufficient for equilibrium to be reached. The saturated solutions were filtered, and the content of 8-hydroxoquinolinol was determined titrimetrically with $KBrO_3$ solution. For each HCl concentration, 5–7 parallel experiments were performed.

Source and Purity of Materials:

$Th(C_6H_9NO)_4\cdot 2H_2O$ was prepared by precipitation according to Ref. 2. The precipitate was boiled with the mother liquor for 1 h to avoid contamination with 8-hydroxoquinoline. The product was characterized by elemental analysis. Calculated/found for the dihydrate: Th 27.49/27.5, 8-hydroxoquinoline 60.24/68.0, H_2O 4.27/4.5, in mass %.

Estimated Error:

Temperature: precision ±0.1 K (authors).
Solubility: the reported range of 8-hydroxoquinolinate concentration suggests precision of <5% for the titrimetric method.

References:

[1] A. E. Klygina and N. S. Kolyada, Zh. Neorg. Khim. **3**, 2767 (1958).
[2] F. J. Welcher, *Organic Analytical Reagents* (NJ, 1948), Vol. 1, p. 265.

4.14. Thorium Phthalocyaninate

Components:

(1) Bis(phthalocyaninato)thorium; $C_{64}H_{32}N_{16}Th$ or $Th(C_{32}H_{16}N_8)_2$; [12581-78-1]
(2) Solvents

Original Measurements:

P. N. Moskalev, G. N. Shapkin, and Yu. S. Misko, Radiokhimiya **20**, 343–4 (1978).

Variables:

Prepared by:

J. Hála

Experimental Data

Solubility of $Th(C_{32}H_{16}N_8)_2$ in two solvents[a]

Solvent	$Th(C_{32}H_{16}N_8)_2$ (g dm^{-3})	$Th(C_{32}H_{16}N_8)_2$ (10^4c_1 /mol dm^{-3})[b]
1-chloronaphthalene; $C_{10}H_7Cl$; [90-13-1]	0.56	7.52
Benzene; C_6H_6; [71-43-2]	0.039	0.524

[a] Temperature not specified. The solubilities were reported to be independent of temperature over the range from 13 to 50 °C.
[b] Calculated by compiler.

Additional Information:
The solubility of $Th(C_{32}H_{16}N_8)_2$ in dimethylformamide (C_3H_7NO, [68-12-2]) was reported to be less than 0.001 g dm^{-3}. The compound was found to practically insoluble in methanol (CH_4O, [67-56-1]) and ethanol (C_2H_6O, [64-17-5]).

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. The solid was equilibrated with the desired solvent in ground glass stoppered cylinders in a thermostated bath until equilibrium was attained. The saturated solutions were filtered through a glass filter, an aliquot was diluted to $\sim10^{-5}$ mol dm^{-3} with dimethylformamide containing 1% $N_2H_4\cdot H_2O$, and the concentration of phthalocyanine was determined spectrophotometrically.

Source and Purity of Materials:

$Th(C_{32}H_{16}N_8)_2$ was prepared according to Ref. 1. Its chemical composition and purity was checked by chemical analysis and x-ray diffraction. Reagent grade solvents were used without further purification.

Estimated Error:

Solubility: insufficient data given to allow for error estimate.

References:

[1] F. Lux, D. Dempf, and D. Grow, Angew. Chem. **80**, 792 (1968).

5. The Solubility of Uranium Compounds

5.1. Uranium Dioxo Carbonate

5.1.1. Evaluation of the UO_2CO_3–CO_3^2–Na_2CO_3–H_2O System

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Components:

(1) Uranium(VI) dioxo carbonate; UO_2CO_3; [12274-95-2]
(2) Carbon dioxide; CO_2; [124-38-9]
(3) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(4) Water; H_2O; [7732-18-5]

Evaluator:

J. Hála, Department of Inorganic Chemistry, Masaryk University, 61137 Brno, Czech Republic, June 2000

Critical Evaluation:

Great attention has been paid to the solubility of UO_2CO_3, and also of $UO_3 \cdot xH_2O$, due to the importance of solid/liquid equilibria of these compounds in relation to ecological risk potential stemming from uranium mines, mill tailings, and rockpiles, and to transfer of uranium from these facilities into the biosphere. Solubility of UO_2CO_3 in water or in aqueous solutions is not accessible to experimental measurements at normal atmospheric conditions, i.e., at partial pressure of CO_2 of 0.03%, since UO_2CO_3 is thermodynamically stable only at higher partial pressures of CO_2. (At partial pressure of $CO_2 < 1\%$, $UO_3 \cdot xH_2O$ is the thermodynamically stable phase.[8]) Therefore the solubility of UO_2CO_3 has been measured in the UO_2CO_3–CO_2–H_2O and UO_2CO_3–CO_2–$NaClO_4$–H_2O systems under higher partial pressures of CO_2 or in the atmosphere of pure CO_2. Several sets of data are available for the solubility of UO_2CO_3 in these systems. Some authors[1–3,5–7,9] reported numerical data while others[8,10] published their data in graphical form or reported the solubility product of UO_2CO_3 only.[4] There is general agreement among the published data in that the solubility of UO_2CO_3 is at its minimum, and constant, at approximately $10^{-8.3}$–$10^{-7.0}$ mol dm^{-3} equilibrium carbonate ion concentration.[5,6,9] Within this $[CO_3^{2-}]$ interval, the solubility of UO_2CO_3 has been reported to be between $10^{-4.2}$ $10^{-4.6}$ (Refs. 6, 9) or approximately $10^{-5.0}$ (Ref. 5) mol dm^{-3}, with rather a large scatter of solubility data in some studies. At lower or higher $[CO_3^{2-}]$ values the solubility of UO_2CO_3 increases. At lower CO_3^{2-} concentrations, particularly in acidic solutions, the enhanced solubility is caused by the action of H_3O^+ ion on UO_2CO_3 while the formation of anionic carbonatocomplexes of U(VI) in the saturated solutions is responsible at higher CO_3^{2-} concentrations. In nearly all studies the authors computer fitted their experimental data with models considering UO_2CO_3 as the solid phase and various U(VI) solution species, with the aim at calculating the solubility product of UO_2CO_3 and equilibrium or stability constants of various aqueous U(VI) species. The table summarizes the available values for the solubility product of UO_2CO_3 at or close to 298.1 K.

T/K	p_2/%	$NaClO_4$ (c_3 /mol dm^{-3})	$-\log K_{sp}$[c]	Reference
298±0.5	100	<0.02[a]	14.25	1
298±0.1	110–120[b]	0	14.05±0.08	2
298±0.02	9–98	0	14.4±0.1[d]	3
		0.5	13.21±0.06	3
		3.0	13.94±0.06	3
297±2	100	0.1	13.89±0.11	4
298±0.1	100	0.1	14.18±0.03	5
298	100	0.1	13.29±0.11	6
295±1	100	0.1	13.35±0.14	7
		0	14.21±0.14[d]	7
298±2	8	0.1	14.05±0.09	8
		0	14.91±0.10[d]	8
298±1	100	0.1	14.10±0.14	10

[a] Estimated by evaluator.
[b] Overpressure of CO_2 of 0.1–0.2 atm.
[c] Concentration unit for K_{sp} is mol dm^{-6}.
[d] K_{sp}^0; calculated by the authors from their K_{sp} values.

The data obtained for ionic strength of 0.1 mol dm^{-3} are generally in good agreement but some uncertainty still persists even though high precision solubility measurements, conducted as pH titrations, have been used in the more recent studies.[3–8] In these measurements, equilibration time of several weeks up to 6 months was used to ensure attainment of steady state at pH<6.5 where the equilibrium solid phase is UO_2CO_3, the solid phases were characterized continuously during the experiments, and high-precision procedures for pH measurement were used. In some cases the measurements were performed starting from both undersaturated and supersaturated solutions. Neglecting minor differences in temperature at which measurements were performed, the values of the solubility product of UO_2CO_3 reported for 0.1 mol dm^{-3} $NaClO_4$ in Refs. 6, 7 agree excellently but are approximately five times higher than the two values reported in Refs. 4, 5, 8. The latter authors repeated their measurements reported in Refs. 4, 5 after several years[8] with excellent reproducibility. The reason for this difference among K_{sp} values obtained by different authors is not clear since nearly identical experimental conditions and procedures at pH<6.5 were used in all studies. It seems likely that the scatter in the solubility data reported in individual studies is due to systematic errors inherent to experimental procedures used, and the difference in K_{sp} values then, at least partly, also to the choice of the aqueous U(VI) species (see below) considered in computer treatment of solubility data. It has been suggested recently[11] that the differences in the solubility encountered in this system are probably not due to the size of UO_2CO_3 crystals or to differences in UO_2CO_3 crystallinity. Neither are the differences in solubility caused by the procedure used to calculate the equilibrium carbonate ion concentration. The latter is obtained from the measured pH and a set of CO_2 solution equilibria

$$CO_{2(g)} \overset{K_H}{\leftrightarrows} CO_{2(aq)} \overset{K^*}{\leftrightarrows} H_2CO_3 \overset{K_{a1}}{\leftrightarrows} HCO_3^- \overset{K_{a2}}{\leftrightarrows} CO_3^{2-}$$

as $\log[CO_3^{2-}] = \log K + \log p(CO_2) + 2\,\mathrm{pH}$, with $\log K = \log(K_H K^* K_{a1} K_{a2})$. The constant K, either determined by some authors or taken from literature sources, shows a very small scatter ($-\log K$: 17.65,[7] 17.64,[12] 17.62,[13] 17.68,[14] 17.65;[15] all in 0.1 mol dm^{-3} $NaClO_4$).

Logically, similar situation is observed with the K_{sp}^0 values. These were obtained either experimentally at very low ionic strength,[1,2] or calculated from the values obtained at higher ionic strengths by applying specific ion interaction theory.[3,7,8] The average value from those reported in Refs. 1, 2, 3, 7 is $10^{-(14.2\pm0.2)}$ mol^2 dm^{-6} with somewhat higher value obtained in Ref. 8. Based on these K_{sp}^0 values it can be concluded that the value $10^{-10.73}$ mol^2 dm^{-6} obtained earlier[16] from the solubility of $UO_2(OH)_2$ in Na_2CO_3 solutions is erroneous.

There is less agreement as to the equilibrium U(VI) solution species existing in the UO_2CO_3–CO_2–$NaClO_4$–H_2O and/or UO_2CO_3–CO_2–H_2O systems. While aiming at obtaining the best fit of their experimental data with a model, the authors have considered a variety of species and their combinations: UO_2^{2+} and UO_2CO_3;[1] UO_2^{2+}, UO_2OH^+, $UO_2(OH)_2$, and $U_2O_5^{2+}$;[2] UO_2^{2+}, UO_2CO_3, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, and $(UO_2)_3(CO_3)_6^{6-}$;[3] UO_2^{2+}, UO_2CO_3, $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$;[9] UO_2CO_3, $UO_2(CO_3)_2^{2-}$,$UO_2(CO_3)_3^{-4}$, $(UO_2)_2(OH)_2^{2+}$, and $(UO_2)_3(OH)_6^+$;[5] UO_2CO_3, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$.[6] These species contribute to the total U(VI) concentration in the saturated solutions that are in equilibrium with UO_2CO_3, and their relative importance is dependent on pH and/or $[CO_3^{2-}]$. While there is general agreement in that the enhanced solubility of UO_2CO_3 at higher pH and/or $[CO_3^{2-}]$ values is caused by the formation of anionic carbonatocomplexes of UO_2^{2+}, the importance of various hydrolyzed hydroxo species has not been solved unambiguously. In this respect some more recent studies[8,10] have brought a better insight into the problem by experimentally verifying the existence of some of the solution species. (The UO_2^{2+}–CO_3^{2-}–OH^- solution equilibria have been the subject of study in several more documents where, however, solubility of UO_2CO_3 has not been studied. Consequently, such documents have not been included in this evaluation.)

References:

[1] E. I. Sergeeva, A. A. Nikitin, I. L. Khodakovskii, and G. B. Naumov, Geokhimiya 1340 (1972); Geochem. Internat **9**, 900 (1972).
[2] A. V. Pirozhkov and N. M. Nikolaeva, Izv. Sibirsk. Otdel. Akad. Nauk SSSR, Ser. Khim. **5**, 55 (1976); **6**, 30 (1976).
[3] I. Grenthe, D. Ferri, F. Salvatore, and G. Riccio, J. Chem. Soc. Dalton Trans. 2439 (1984).
[4] G. Meinrath and T. Kimura, Inorg. Chim. Acta **204**, 79 (1993).
[5] G. Meinrath and T. Kimura, J. Alloys Compds **202**, 89 (1993).
[6] U. Kramer-Schnabel, H. Bischoff, R. H. Xi, and G. Marx, Radiochim. Acta **56**, 183 (1992).
[7] I. Pashalidis, W. Runde, and J. I. Kim, Radiochim. Acta **61**, 141 (1993).
[8] G. Meinrath, Y. Kato, T. Kimura, and Z. Yoshida, Radiochim. Acta **75**, 159 (1996).
[9] I. Pashalidis, K. R. Czerwinski, F. Fanghanel, and J. I. Kim, Radiochim. Acta **76**, 55 (1997).
[10] Y. Kato, T. Kimura, Z. Yoshida, and N. Nitani, Radiochim. Acta **74**, 21 (1996).
[11] G. Meinrath, Y. Kato, T. Kimura, and Z. Yoshida, Radiochim. Acta **84**, 21 (1999).
[12] R. M. Smith and A. E. Martell, *Critical Stability Constants* (Plenum, New York, 1976), Vol. 4.
[13] G. Meinrath and J. I. Kim, Radiochim Acta **52/53**, 29 (1991).
[14] L. Maya, Inorg. Chem. **21**, 2895 (1982).
[15] W. Runde, G. Meinrath, and J. I. Kim, Radiochim. Acta **58/59**, 93 (1992).
[16] A. K. Babko and V. S. Kadenskaya, Zh. Neorg. Khim. **5**, 2568 (1960).

Components:

(1) Uranium(VI) dioxocarbonate; UO_2CO_3; [12274-95-2]
(2) Carbon dioxide; CO_2; [124-38-9]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

E. I. Sergeeva, A. A. Nikitin, I. L. Khodakovskii, and G. B. Naumov, Geokhimiya 1340–50 (1972); Geochem. Internat. **9**, 900 (1972).

Variables:

T/K: 298–473
p_2(pressure of CO_2)/atmosphere = 1(9.81×10^4 Pa) at 25 and 50 °C
pH: 3.2–6.2

Prepared by:

J. Hála

Experimental Data

Solubility of UO_2CO_3 in water at partial pressure of CO_2 of 1 atm as a function of temperature[a]

Temperature (°C)	pH	UO_2CO_3 (10^5 m_1 /mol kg^{-1})	Temperature (°C)	pH	UO_2CO_3 (10^5 m_1 /mol kg^{-1})
25	3.22	253.0	50	3.47	120.0
	4.09	17.1		4.88	4.20
	4.33	6.30		5.04	4.50
	4.44	4.31		5.20	4.22
	4.66	4.83		5.28	5.32
	4.87	5.71		6.02	13.0
	5.07	5.36		6.16	70.0
	5.22	4.29			
	5.31	5.17	100[b]	4.10	4.47
	5.55	9.9	150[b]	4.05	4.58
	5.83	14.4	200[b]	3.95	6.09
	6.23	100.0			

[a] Equilibrium solid phase was UO_2CO_3, [12274-95-2], in all solutions.
[b] Pressure of CO_2 not specified.

Additional Information:

The dependence of the UO_2CO_3 solubility on pH, at a constant temperature, was interpreted by the authors by assuming the following equilibria:

at pH<4.4: $UO_2CO_{3(s)}+2H^+_{(aq)} \leftrightarrows UO^{2+}_{2(aq)}+CO_{2(g)}+H_2O$, with equilibrium constant of $(8.0\pm4.0)\times10^3$ at 25 °C and 4.45×10^3 at 50 °C,

at pH 4.4–5.3: $UO_2CO_{3(s)} \leftrightarrows UO_2CO_{3(aq)}$, with equilibrium constant of $(4.1\pm0.7)\times10^{-5}$, $(4.3\pm0.3)\times10^{-5}$, 4.5×10^{-5}, 4.6×10^{-5}, and 6.1×10^{-5} at 25, 50, 100, 150, and 200 °C, respectively,

at pH>5.3: $UO_2CO_{3(s)}+CO_{2(g)}+H_2O \leftrightarrows UO_2(CO_3)^{2-}_{2(aq)}+2H^+_{(aq)}$, with equilibrium constant of $(2.2\pm0.7)\times10^{-16}$ and $(1.0\pm0.5)\times10^{-16}$ at 25 and 50 °C, respectively.

All equilibrium constants refer to zero ionic strength.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Either UO_2CO_3 or $UO_2(OH)_2$ were used as the starting solid. To attain the final desired equilibrium pH, small aliquots of dilute $HClO_4$ or $NaHCO_3$ solution were added to the starting slurry of the solid. In experiments at 25 and 50 °C the solutions containing excess solid were equilibrated in vessels equipped with electrodes and a glass filter,[1] by passing through them a stream of purified CO_2 at CO_2 pressure of 1 atm. The gas was presaturated with water vapor. The equilibration time ranged from 17 to 79 days at 25 °C or from 9 to 31 days at 50 °C. The attainment of equilibrium was checked by uranium and pH determination. The saturated solutions were allowed to stand for 2–14 days before taking samples for analysis. Experiments at higher temperatures were carried out in a steel autoclave[1] electrically heated in an aluminum block. The temperature was checked with thermocouples. After equilibration, the autoclave was rapidly cooled with water, samples were withdrawn with a syringe and ultracentrifuged. pH was measured with a glass electrode under continuous stream of CO_2. The concentration of uranium in the saturated solutions was determined colorimetrically with arsenazo III. The composition of the equilibrium solid phases was checked by x-ray diffraction.

Source and Purity of Materials:

UO_2CO_3 was prepared by passing CO_2 gas through a slurry of $UO_2(OH)_2$.[2] The latter was prepared from $UO_2(NO_3)_2$ by either carbonate[3] or peroxide method. Doubly distilled water was used. $NaHCO_3$ and $HClO_4$ were reagent grade products.

Estimated Error:

Temperature: precision ±0.5 K at 298 and 323 K; ±2.5 K at 373 K and above (authors).
pH: precision ±0.04 pH unit at 298 K; ±0.3 pH unit at 323 K (authors).

References:

[1] A. A. Nikitin, E. I. Sergeeva, I. L. Khodakovskii, and G. B. Naumov, Geokhimiya 297 (1972).
[2] I. I. Chernyayev, V. A. Golovnya, and G. V. Ellert, Zh. Neorg. Khim. **1** 2726 (1956).
[3] R. Wey, I. Lauffenburger, and D. Saehr, Bull. Soc. Chim. France 1874 (1968).

Components:

(1) Uranium(VI) dioxocarbonate; UO_2CO_3; [12274-95-2]
(2) Carbon dioxide; CO_2; [124-38-9]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. V. Pirozhkov and N. M. Nikolaeva, Izv. Sibirsk. Otdel. Akad. Nauk SSSR, Ser. Khim. **5**, 55–9 (1976) N. M. Nikolaeva, *ibid.* **6**, 30–1 (1976).

Variables:

T/K: 298–423

Prepared by:

J. Hála

Experimental Data

Solubility of UO_2CO_3 in water in the presence of CO_2 as a function of temperature[a,b]

Temperature (°C)	CO_2[c] (10^2 mol dm^{-3})	pH	U (10^5 mol dm^{-3})	UO_2CO_3[d] ($c_1/10^5$ mol dm^{-3})	$-\log K_{s0}$[e]		$-\log K_{s0}$[f]
25	4.322	4.06	17.22	10.238	14.03	14.30	14.05±0.08
					14.12	14.15	
50	2.925	3.95	3.23	1.4840	14.74	14.81	14.84±0.06
					14.84	14.95	
75	2.38	4.00	3.42	1.4930	14.99	15.02	15.04±0.04
					15.10		
100	2.52	4.07	6.75	2.4750	15.30	15.17	15.22±0.05
					15.20		
125	1.98	4.18	4.89	1.0880	16.22	16.09	16.14±0.04
					16.11	16.15	
150	0.294	4.69	4.64	0.06748	17.05	17.83	[g]

[a] Solid phases were not investigated. Since the measurements were performed in an atmosphere under CO_2 overpressure the compiler assumes, based on other published data, that the equilibrium solid phase was UO_2CO_3, [12274-95-2], in all solutions.

[b] The authors reported only one measurement arbitrarily chosen out of three to four measurements carried out at each temperature. However, all the calculated values of solubility product were reported.

[c] Total CO_2 concentration, i.e. the sum of the concentrations of CO_2, H_2CO_3, HCO_3^-, and CO_3^{2-}, Determined gravimetrically.

[d] $[UO_2CO_3]$=total concentration of uranium$-([UO_2^{2+}]+[UO_2(OH)^+]+[UO_2(OH)_2]+2[U_2O_5^{2+}])$.

[e] Calculated by the authors from individual measurements.

[f] Average value.

[g] Not calculated because at 150 °C UO_2CO_3 hydrolyzed almost completely to $UO_2(OH)_2$ which resulted in inconsistent K_{s0} values.

Additional Information:

Using literature data for the equilibrium constants of hydrolytic equilibria of the UO_2^{2+} ion and dissociation constants of H_2CO_3, the concentration of the UO_2^{2+}, $UO_2(OH)^+$, $UO_2(OH)_2$, and $U_2O_5^{2+}$ species were calculated, and from these the solubility product of UO_2CO_3 and the stability constant of the UO_2CO_3 complex in the solution were calculated by the authors as a function of temperature. The least squares treatment of the data yielded for the thermodynamic stability constant (activity of ions considered to be equal to concentrations since the saturated solutions were extremely diluted, ionic strength was $\leqslant 3\times10^{-4}$ mol dm^{-3}) $\beta=[UO_2CO_3][UO_2^{2+}]^{-1}[CO_3^{2-}]^{-1}$, the equation

$$\log \beta=-8.988+0.04053T+621959.1/T^2$$

and for the thermodynamic solubility product of UO_2CO_3

$$-\log K_{s0}^0=15.04-0.01756T+5.0269\times10^{-5}T^2$$

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. The measurements were conducted in a teflon autoclave.[1] Slurry of UO_2CO_3 in water was first equilibrated by passing through it a stream of CO_2 gas for 2 h at room temperature at atmospheric pressure. Then an overpressure of CO_2 of 0.1–0.2 atm was applied, and the mixture was heated at the desired temperature under continuous mixing for several days. Attainment of equilibrium was checked by measuring pH and CO_2 pressure until constant values were obtained. Then two samples of the saturated solution were withdrawn by means of teflon filters placed inside the autoclave to determine uranium spectrophotometrically with arsenazo I[2] and CO_2 gravimetrically. Solid phases were not investigated. The pH of the saturated solutions was measured at the desired temperature in the presence of solid UO_2CO_3 with a high temperature glass electrode.

Source and Purity of Materials:

UO_2CO_3 was prepared by prolonged passing through a slurry of UO_3 (reagent grade) in doubly distilled water a stream of purified CO_2 gas.[3] Analysis of the product yielded results which agreed within ±0.1% with the formula UO_2CO_3. Purified CO_2 and doubly distilled water were used.

Estimated Error:

Temperature: precision ± 0.1 K (authors).
pH: precision ± 0.02 pH unit (authors).
Uranium concentration: precision ±3% (authors).
CO_2 concentration: precision ±0.1% (authors).

References:

[1] A. V. Pirozhkov, Izv. Sibirsk. Otdel. Akad. Nauk SSSR, Ser. Khim. **4**, 153 (1976).
[2] *Analytical Chemistry of Uranium* (in Russian), edited by D. I. Ryabchikov and M. M. Senyavin (Nauka, Moscow, 1962), p. 132.
[3] I. I. Chernyayev, V. A. Golovnya, and G. V. Ellert, Zh. Neorg. Khim. **1**, 2726 (1956).

Components:

(1) Uranium(VI) dioxocarbonate; UO_2CO_3; [12274-95-2]
(2) Carbon dioxide; CO_2 ; [124-38-9]
(3) Perchloric acid; $HClO_4$; [7601-90-3]
(4) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(5) Water; H_2O; [7732-18-5]

Original Measurements:

I. Grenthe, D. Ferri, F. Salvatore, and G. Riccio, J. Chem. Soc. Dalton Trans. 2439–43 (1984).

Variables:

T/K: 298
p_2 /atmosphere = 0.0477 – 0.9797
H^+ ion concentration/mol dm^{-3} = 5×10^{-7} – 3.2×10^{-4}
c_4 /mol dm^{-3} = 0.5 and 3.0

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of UO_2CO_3 in $NaClO_4$ solutions[a]

$-\log[H^+]^b$	CO_2 (p_2/atm)	$-\log C_u^{c,d}$	$-\log[H^+]^b$	CO_2 (p_2/atm)	$-\log C_u^{c,e}$
3.980	0.0983	2.938	3.841	0.0975	2.976
4.629	0.0974	4.181	4.066	0.0984	3.458
5.246	0.0982	4.724	6.215	0.0970	3.234
5.918	0.0981	3.807	6.303	0.0978	2.921
6.175	0.0987	2.676	3.621	0.2909	2.987
3.753	0.2900	2.976	4.406	0.2863	4.427
4.349	0.2844	4.042	4.981	0.2910	4.928
4.826	0.2932	4.653	5.916	0.2887	3.554
5.501	0.2932	4.224	6.014	0.2917	3.122
5.885	0.2917	2.937	6.210	0.477	3.887
3.491	0.9797	3.015	3.568	0.9768	4.084
5.008	0.9666	4.638	3.621	0.9713	3.570
5.496	0.9742	3.560	4.113	0.9658	4.372
			4.625	0.9577	4.893
			5.180	0.9599	4.073
			5.652	0.9758	3.505

[a] Equilibrium solid phase was UO_2CO_3, [12274-95-2], in all solutions.
[b] Free hydrogen ion concentration.
[c] Concentration of uranium in mol dm^{-3}.
[d] Concentration of $NaClO_4$ = 0.5 mol dm^{-3}.
[e] Concentration of $NaClO_4$ = 3.0 mol dm^{-3}.

Additional Information:

The variation of UO_2CO_3 solubility with hydrogen ion concentration and CO_2 pressure was interpreted by the authors as being due to the formation of $(UO_2)_p(CO_3)_t^{2(p-t)}$ complex species in the saturated solutions. By combining the solubility measurements with additional chemical information from the studies of homogeneous equilibria in the U(VI)–CO_2–H_2O system[1,2] the solubility product of UO_2CO_3 and the overall stability constants of the complexes formed at 25 °C were obtained:

	3.0 mol dm^{-3} $NaClO_4$	0.5 mol dm^{-3} $NaClO_4$	Water
$CO_{2(g)}+H_2O \leftrightarrows CO_3^{2-}+2H^+$; $\log K_{a2}$:	-17.61 ± 0.03	-17.15 ± 0.03	-18.10 ± 0.05
$UO_2CO_{3(s)} \leftrightarrows UO_2^{2+}+CO_3^{2-}$; $\log K_{sp}$:	-13.94 ± 0.06	-13.21 ± 0.06	-14.4 ± 0.1
$UO_2^{2+}+CO_3^{2-} \leftrightarrows UO_2CO_{3(aq)}$; $\log \beta_{1,1}$:	8.3 ± 0.1	8.3 ± 0.1	9.5 ± 0.2
$UO_2^{2+}+2CO_3^{2-} \leftrightarrows UO_2(CO_3)_2^{2-}$; $\log \beta_{2,1}$:	16.20 ± 0.15	15.36 ± 0.15	16.6 ± 0.2
$UO_2^{2+}+3CO_3^{2-} \leftrightarrows UO_2(CO_3)_3^{4-}$; $\log \beta_{3,1}$:	22.61 ± 0.15	21.46 ± 0.15	21.3 ± 0.2
$3UO_2^{2+}+6CO_3^{2-} \leftrightarrows (UO_2)_3(CO_3)_6^{6-}$; $\log \beta_{6,3}$:	56.2 ± 0.3	53.7 ± 0.3	53.4 ± 0.8

The constants given for water were obtained by the authors by using specific ion–interaction theory.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. The solubility of UO_2CO_3 was measured as a function of the partial pressure of CO_2 and H^+ ion concentration. Through initial $(Na+H)ClO_4$ solutions of constant ionic strength a stream of CO_2 /N_2 gas mixture was passed and the desired concentration of H^+ ion was achieved by coulometric generation of OH^- or H^+ ions. Then excess UO_2CO_3 was added, the mixture was continuously stirred until equilibrium was attained which was indicated when the potential of the glass electrode remained constant within 0.2 mV during several days. Then the total concentration of uranium in the saturated solution was determined spectrophotometrically using the thiocyanate method.[3] The partial pressure of CO_2 was calculated from the known composition of the gas mixture, the measured atmospheric pressure and the vapor pressure of water over a solution containing the respective concentration of $NaClO_4$. The free H^+ ion concentration was determined by the authors' method[1] using a glass electrode. All measurements were carried out in a thermostated apparatus.[4] The pressure was measured with a piezoresistive transducer. The composition of the solid phases in equilibrium with the solutions was checked by x-ray powder photography. No changes of the initial solid were observed upon equilibration.

Source and Purity of Materials:

UO_2CO_3 was precipitated from $UO_2(NO_3)_2$ solution saturated with CO_2 gas, by dropwise adding a solution of $NaHCO_3$. The solid was stirred under the mother liquor in a CO_2 atmosphere in order to avoid losses of CO_2, centrifuged, and washed with $NaClO_4$ solution of the respective concentration saturated with CO_2. The composition of UO_2CO_3 was confirmed by elemental analysis and x-ray diffraction. Commercially available CO_2 /N_2 mixtures were used. The gases were purified by passing them through a H_2SO_4 /$NaClO_4$ solution and a G4 glass filter. Perchloric acid (Merck) was a reagent grade product. $NaClO_4$ was prepared according to Ref. 5. The solution was made to contain about 10^{-3} mol dm^{-3} H^+.

Estimated Error:

Pressure: precision $\pm5.10^{-4}$ atm (authors).
Temperature: precision ±0.02 K (authors).
H^+ concentration: precision ±0.02 mV (authors).

References:

[1] L. Ciavatta, D. Ferri, I. Grenthe, and F. Salvatore, Inorg. Chem. **20**, 463 (1981).
[2] D. Ferri, I. Grenthe, and F. Salvatore, Acta Chem. Scand. **35A**, 165 (1981).
[3] S. Ahrland, Svensk. Kem. Tidskr. **72**, 757 (1960).
[4] L. Ciavatta, D. Ferri, I. Grenthe, F. Salvatore and K. Spahiu, Inorg. Chem. **22**, 2088 (1983).
[5] G. Biedermann, Ark. Kemi **9**, 277 (1956).

Components:

(1) Uranium(VI) dioxocarbonate; UO_2CO_3; [12274-95-2]
(2) Carbon dioxide; CO_2; [124-38-9]
(3) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

G. Meinrath and T. Kimura, Inorg. Chim. Acta **204**, 79–85 (1993).

Variables:

T/K: 297
p_2 (partial pressure of CO_2)/%:100
c_3 /mol dm^{-3}:0.1

Prepared by:

J. Hála

Experimental Data

Solubility product of UO_2CO_3, $K_{s0}=[UO_2^{2+}][CO_3^{2-}]$, was reported to be $10^{-(13.89\pm0.11)}$ at 24 °C and at ionic strength of 0.1 mol dm^{-3} $NaClO_4$. From this value, using single ion activity coefficients of $\log\gamma(UO_2{}^{2+})=-0.40$, $\log\gamma(CO_3^{2-})=-0.46$, and $\log\gamma(H^+)=-0.09$, thermodynamic solubility product, was later obtained as $K^0_{sp}=10^{-(14.75\pm0.10)}$.

Additional Information:

Solubility data were reported in graphical form only. Equilibrium carbonate ion concentration in the saturated solutions was calculated by the authors from the measured pH by using the Henry constant and the dissociation constants of H_2CO_3 in 0.1 mol dm^{-3} $NaClO_4$. At 100% partial pressure of CO_2, the equilibrium solid phase was UO_2CO_3, [12274-95-2] (rutherfordine). At partial pressures of CO_2 of 0.98% (mixtures of CO_2 and N_2) or 0.03%, the solid phase was $UO_3\cdot 2H_2O$, [20593-39-9].

Auxiliary Information

Method/Apparatus/Procedure:

Solubility experiments were conducted as pH titrations in a glass vessel in the pH range from 2.8 to 4.6 in CO_2 atmosphere (100% partial pressure of CO_2). The gas was bubbled through the solution continuously after being moistened in washing flasks. The solid was precipitated from $\sim 2\times10^{-3}$ mol dm^{-3} U(VI) solution by addition of 0.05 mol dm^{-3} Na_2CO_3. The system was allowed to equilibrate for 3 weeks and then pH titration was carried out by stepwise adding either 0.05 mol dm^{-3} Na_2CO_3 or 0.1 mol dm^{-3} $HClO_4$ solution. After each addition, steady pH value was reached within 2 or 3 days. The pH was measured simultaneously with two glass electrodes (ROSS-type, Orion) calibrated with standard buffer solutions. The concentration of U(VI) was determined spectrophotometrically. The spectrophotometer was calibrated by using UO_2^{2+} solutions of known concentrations. Samples of saturated solutions were separated from the solid by ultrafiltration with filters of 0.45 and 0.2 μm pore size. Solid phases were characterized by DTA/TGA, photoacoustic FTIR spectroscopy, UV-VIS photoacoustic spectroscopy and x-ray diffraction.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: precision ±2 K (authors).

References:

[1] G. Meinrath, Y. Kato, T. Kimura, and Z. Yoshida, Radiochim. Acta **75**, 159 (1999).

Components:

(1) Uranium(VI) dioxocarbonate; UO_2CO_3 ; [12274-95-2]
(2) Carbon dioxide; CO_2 ; [124-38-9]
(3) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

G. Meinrath, Y. Kato, T. Kimura, and Z. Yoshida, Radiochim. Acta, **75**, 159–67 (1996).

Variables:

T/K: 298
p_2 (partial pressure of CO_2)/%:8
c_3 /mol dm^{-3}: 0.1

Prepared by:

J. Hála

Experimental Data

The solubility of UO_2CO_3 as a function of pH or CO_3^{2-} ion concentration was reported in graphical form only. Solubility product of UO_2CO_3, $K_{sp}=[UO_2^{2+}][CO_3^{2-}]$, was reported to be $10^{-(14.05\pm0.09)}$ at 25 °C and at ionic strength of 0.1 mol dm^{-3} $NaClO_4$. From this value, using single ion activity coefficients of $\log\gamma(UO_2^{2+})=-0.40$, $\log\gamma(CO_3^{2-})=-0.46$, and $\log\gamma(H^+)=-0.09$, thermodynamic solubility product was obtained as $K^o_{sp}=10^{-(14.91\pm0.10)}$. At partial pressure of CO_2 of 8%, and at pH 2.8–4.6 the equilibrium solid phase was microcrystalline UO_2CO_3, [12274-95-2].

Additional Information:

(1) The following equations were derived to express the concentration of $UO^{2+}_{2(aq)}$ as a function of pH or concentration of CO_3^{2-} ion, respectively, at ionic strength of 0.1 mol dm^{-3} $NaClO_4$, $\log[UO_2^{2+}]=\log K_{sp}(UO_2CO_3)-\Sigma\log K-\log p(CO_2)-2\mathrm{pH}$, and $\log[UO_2^{2+}]=\log K_{sp}(UO_2CO_3)-\Sigma\log[CO_3^{2-}]$.

Equilibrium carbonate ion concentration was calculated by the authors using, as in Refs. 1–3, Henry constant of CO_2 in water (K_H) and dissociation constants of carbonic acid, K_1 and K_2, in 0.1 mol dm^{-3} $NaClO_4$, as $\log[CO_3^{2-}]=\Sigma\log K+\log p(CO_2)+2\mathrm{pH}$, where $\Sigma\log K=\log K_H+\log K_1+\log K_2$ ($\Sigma\log K=-17.67$, Ref. 4).

(2) At partial pressures of CO_2 of 0.3%, and 0.03%, and pH 2.8–4.6, the equilibrium solid phase was identified as $UO_3\cdot 2H_2O$. At $p_2=0.03\%$ and pH>7, the solid phase was an amorphous sodium polyuranate.

Auxiliary Information

Method/Apparatus/Procedure:

Solubility experiments were conducted as pH titrations in the pH range from 2.8 to 4.6 under 8% partial pressure of CO_2. Most of experimental procedure was identical with that in the authors' previous work.[1–3] Solutions for the titration contained 0.05 mol dm^{-3} U(VI) (depleted uranium) and 0.1 mol dm^{-3} $NaClO_4$ to maintain constant ionic strength, and were flushed continuously with a certified N_2 /CO_2 gas mixture moistened in washing flasks. The pH titrations were performed forward and backward by addition of either 0.1 mol dm^{-3} $HClO_4$ or 0.05 mol dm^{-3} Na_2CO_3. Combination glass electrodes (ROSS-type, Orion) used for pH measurement were calibrated against five standard buffer solutions in the pH range of 1.7–10. Phase separation was achieved by ultrafiltration at 0.45 or 0.2 μm pore size. The concentration of U(VI) was determined spectrophotometrically. Solid phases were characterized continuously during solubility studies by DTA/TGA, photoacoustic Fourier transform infrared (FTIR), and ultraviolet-visible (UV-VIS) spectroscopy, and x-ray diffraction.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: precision ± 2 K (authors).
Solubility product: standard deviation see above.

References:

[1] G. Meinrath and T. Kimura, Inorg. Chim. Acta **204**, 79 (1993).
[2] Y. Kato, T. Kimura, Z. Yoshida, and N. Nitani, Radiochim. Acta **74**, 21 (1996).
[3] G. Meinrath and T. Kimura, J. Alloys Compd. **202**, 89 (1993).
[4] G. Meinrath, Y. Kato, T. Kimura, and Z. Yoshida, Radiochim. Acta **84**, 21 (1999).

Components:

(1) Uranium(VI) dioxo carbonate; UO_2CO_3 ; [12274-95-2]
(2) Carbon dioxide; CO_2 ; [124-38-9]
(3) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

I. Pashalidis, K. R. Czerwinski, T. Fanghanel, and J. I. Kim, Radiochim. Acta **76**, 55–62 (1997).

Variables:

T/K: 295
p_2 (partial pressure of CO_2)/%: 100
c_3 /mol dm^{-3}: 0.1

Prepared by:

J. Hála

Experimental Data

Solubility of UO_2CO_3 as a function of carbonate ion concentration in 0.1 mol dm^{-3} $NaClO_4$ at 22 °C[a]

pH	$-\log[CO_3^{2-}]^{b,c}$	$-\log[UO_2^{2+}]^{c}$	pH	$-\log[CO_3^{2-}]^{a,b}$	$-\log[UO_2^{2+}]^{c}$
3.89	9.77	3.43	5.31	6.93	4.46
3.91	9.73	3.47	5.33	6.89	4.37
3.98	9.59	3.62	5.37	6.81	4.46
4.18	9.19	3.84	5.38	6.79	4.08
4.64	8.27	4.38	5.42	6.71	4.37
4.66	8.23	4.46	5.52	6.51	4.39
4.68	8.19	4.29	5.53	6.49	4.10
4.70	8.15	4.21	5.55	6.45	4.02
4.83	7.89	4.24	5.57	6.41	4.09
4.86	7.83	4.52	5.60	6.35	4.01
4.91	7.73	4.52	5.63	6.29	4.01
5.02	7.51	4.21	5.79	5.97	3.70
5.04	7.47	4.59	5.80	5.95	3.77
5.10	7.35	4.47	5.82	5.91	3.74
5.21	7.13	4.19	5.92	5.71	3.46
5.22	7.11	4.33	5.93	5.69	3.35
5.26	7.03	4.18	5.95	5.65	3.36
5.28	6.99	4.22			

[a] Equilibrium solid phase was UO_2CO_3, [12274-95-2], in all solutions.
[b] Equilibrium concentration of the carbonate ion; it was calculated by the authors from the equation $\log[CO_3^{2-}]=\Sigma \log K + \log p(CO_2)+2pH$, where $\Sigma \log K=-17.55(\pm 0.09)$ includes Henry constant for CO_2, and dissociation constants of carbonic acid.
[c] Concentrations in mol dm^{-3}.

Additional information:

From the solubility data reported in this document and in the authors' previous work,[1] and the solubility product of UO_2CO_3 taken from Ref. 1, the overall stability constants for the complexation of the UO_2^{2+} ion with CO_3^{2-} , were calculated. Depending on the equilibrium concentration of the CO_3^{2-} ion the solution species were UO_2^{2+} , UO_2CO_3, $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$. Also evaluated were activity coefficients of all species applying the Pitzer approach. Then, based on the Pitzer interaction parameters, the solubility of UO_2CO_3 in 0.1 mol dm^{-3} $NaClO_4$ was calculated. The calculated values showed a fairly good agreement with the experimental results.

Auxiliary Information

Method/Apparatus/Procedure:

Solubility experiments were conducted as pH titrations in 0.1 mol dm^{-3} $NaClO_4$ under 100% partial pressure of CO_2 in a closed glass vessel. Solutions for the titration contained solid UO_2CO_3. The pH was measured by using combination glass electrodes (ROSS-type, Orion) which were calibrated against six standard buffer solutions in the pH range of 2–8. The concentration of U(VI) was determined spectrophotometrically using arsenazo III reagent.[2] The solid phases were characterized by infrared (IR) spectroscopy, and x-ray diffraction.

Source and Purity of Materials:

To prepare UO_2CO_3, about 1 g $UO_2(NO_3)_2$ was dissolved in 50 mL 0.1 mol dm^{-3} $NaClO_4$, adjusted to pH 3.5, and CO_2 gas was slowly bubbled through the solution for 1 week. The yellowish precipitate was collected, washed with water, and placed in 30 mL 0.1 mol dm^{-3} $NaClO_4$ under CO_2 atmosphere for the pH titration measurement.

Estimated Error:

Temperature: precision ± 2 K (authors).
Error of $\log[UO_2^{2+}]$: ±0.01 to ±0.06 log units (reported separately for every measurement).

References:

[1] I. Pashalidis, W. Runde, and J. I. Kim, Radiochim. Acta **61**, 141 (1993).
[2] J. Borak, Z. Slovak, and J. Fischer, Talanta **17**, 215 (1970).

Components:

(1) Uranium(VI) dioxocarbonate; UO_2CO_3 ; [12274-95-2]
(2) Carbon dioxide; CO_2 ; [124-38-9]
(3) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

Y. Kato, T. Kimura, Z. Yoshida, and N. Nitani, Radiochim. Acta **74**, 21–5 (1996).

Variables:

T/K: 298
p_2 (partial pressure of CO_2)/%: 0.03; 100
c_3 /mol dm^{-3}: 0.1

Prepared by:

J. Hála

Experimental Data

Solubility product of UO_2CO_3, $K_{sp}=[UO_2^{2+}][CO_3^{2-}]$, was reported to be $10^{-(14.10\pm0.14)}$ mol^2 dm^{-6} at 25 °C and at ionic strength of 0.1 mol dm^{-3} $NaClO_4$. This value was obtained from the solubility measurements under partial pressure of CO_2 of 100%. Under such conditions the equilibrium solid phase was UO_2CO_3, [12274-95-2]. The solubility data were presented in graphical form only, and calculation of K_{sp} was performed using the same procedure as in the authors' previous work.[1,2]

Auxiliary Information

Method/Apparatus/Procedure:

Solubility experiments were conducted as pH titrations in a thermostated glass vessel in the pH range from 2.9 to 4.9 in an atmosphere of air (0.03% CO_2) or pure CO_2. The solid phase was precipitated from 0.02 mol dm^{-3} solution of U(VI) by addition of 0.1 mol dm^{-3} $NaHCO_3$, or 0.1 mol dm^{-3} $HClO_4$. The pH was measured by using combination glass electrodes (Horiba) which were calibrated against buffer solutions with pH of 4.01 and 6.86 (both ±0.01). Phase separation was achieved by centrifugation at 3000 rpm and ultrafiltration with a filter of 0.22 μm pore size. The concentration of U(VI) was determined by fluorescence spectrophotometry (Hitachi F-4500) in solutions acidified to 1 mol dm^{-3} $HClO_4$. Solid phases were characterized by photoacoustic UV-VIS and FTIR spectroscopy, and x-ray crystallography (Rigaku RAD-3C). For photoacoustic spectroscopy, about 5–10 mg of air-dried solid phase was used.

Source and Purity of Materials:

Nothing specified except that UO_2^{2+} stock solution was prepared from reagent grade U_3O_8.

Estimated Error:

Temperature: precision±0.1 K (authors).

References:

[1] G. Meinrath and T. Kimura, Inorg. Chim. Acta **204**, 79 (1993).
[2] G. Meinrath and T. Kimura, J. Alloys Compd. **202**, 89 (1993).

Components:

(1) Uranium(VI) dioxocarbonate; UO_2CO_3 ; [12274-95-2]
(2) Carbon dioxide; CO_2 ; [124-38-9]
(3) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

G. Meinrath and T. Kimura, J. Alloys Compd. **202**, 89–93 (1993).

Variables:

T/K: 298
p_2 (partial pressure of CO_2)/%: 100
c_3 /mol dm^{-3}: 0.1

Prepared by:

J. Hála

Experimental Data

Solubility of UO_2CO_3 in 0.1 mol dm^{-3} $NaClO_4$ solutions saturated at 25 °C under CO_2 atmosphere[a]

pH	$-\log C_u$[b]	$-\log C(CO_3^{2-})c$[b]	pH	$-\log C_u$[b]	$-\log C(CO_3^{2-})$[c]
3.08	2.71	11.46	4.50	4.86	8.62
3.11	2.66	11.40	4.75	4.89	8.12
3.15	2.94	11.32	5.16	4.89	7.30
3.17	2.93	11.28	5.28	4.88	7.06
3.28	3.12	11.06	5.33	4.86	6.96
3.41	3.32	10.80	5.55	4.72	6.52
3.77	3.95	10.08	5.61	4.62	6.40
4.10	4.50	9.42	5.75	4.29	6.12
4.15	4.60	9.32	5.77	4.19	6.08
4.15	4.61	9.32	5.97	3.52	5.68
4.22	4.63	9.18	5.98	3.58	5.66
4.31	4.71	9.00	6.13	3.04	5.36
4.33	4.76	8.96	6.16	2.88	5.30
4.40	4.79	8.82	6.17	2.92	5.28
4.47	4.84	8.68	6.19	2.68	5.24

[a] The solid phase at equilibrium was UO_2CO_3, [12274-95-2], in all solutions.
[b] Total uranium(VI) concentration in the saturated solution.
[c] Equilibrium CO_3^{2-} concentration calculated by the authors from the solution equilibria of CO_2 and dissociation constants of H_2CO_3 (1).

Additional Information:

The solubility S of UO_2CO_3 was interpreted by the authors as $S=K_{sp}[CO_3^{2-}]^{-1}(1+\Sigma\beta_n[CO_3^{2-}]^n)$, where $K_{sp}=[UO_2^{2+}][CO_3^{2-}]=10^{-(14.18\pm0.03)}$, and $\beta_n=[UO_2(CO_3)_n^{2-2n}][UO_2^{2+}]^{-1}[CO_3^{2-}]^{-n}$, with $\beta_1=10^{(9.23\pm0.04)}$, $\beta_2=10^{(15.38\pm0.17)}$, and $\beta_3=10^{(21.86\pm0.05)}$, all at ionic strength of 0.1 mol dm^{-3} $NaClO_4$. No significant contribution to the solubility from $UO_2(OH)^+$ was observed. The contribution from $(UO_2)_3(OH)_5^+$ and $(UO_2)_2(OH)_2^{2+}$ species was less than 0.8%. By using single ion activity coefficients of $\log\gamma(UO_2^{2+})=-0.40$, $\log\gamma(CO_3^{2-})=-0.46$, and $\log\gamma(H^+)=-0.09$, thermodynamic solubility product of UO_2CO_3 was later obtained as $K_{sp}^0=10^{-(15.04\pm0.04)}$.

Components:

(1) Uranium(VI) dioxocarbonate; UO_2CO_3; [12274-95-2]
(2) Carbon dioxide; CO_2; [124-38-9]
(3) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

U. Kramer-Schnabel, H. Bischoff, and R. H. Xi, Radiochim. Acta **56**, 183–8 (1992).

Variables:

T/K: 295
p_2 (partial pressure)/%: 100
c_3 /mol dm^{-3}: 0.1

Prepared by:

J. Hála

Experimental Data

Solubility of UO_2CO_3 in 0.1 mol dm^{-3} solution of $NaClO_4$ at 25 °C and 100% partial pressure of CO_2

pH[a]	$-\log[CO_3^{2-}]$[b]	$-\log C_U$[c]	pH[a]	$-\log[CO_3^{2-}]$[b]	$-\log C_U$[c]
3.63	10.38	2.98	4.39	8.86	4.23
3.90	9.84	2.91	4.46	8.72	4.31
3.94	9.76	3.48	4.55	8.54	4.42
4.18	9.28	3.96	4.79	8.06	4.35
4.19	9.26	3.94	4.81	8.02	4.29
4.19	9.25	3.98	4.83	7.98	4.28
4.24	9.15	3.40	4.90	7.84	4.24
4.27	9.10	4.00	5.04	7.56	3.95
4.28	9.08	4.00	5.05	7.54	4.14
4.33	8.99	4.07	5.41	6.82	2.61
4.34	8.96	4.04	5.47	6.70	2.78
4.34	8.96	4.10			

[a] The solubility of UO_2CO_3 was studied in the pH range from 3 to 6 since under these conditions UO_2CO_3, [12274-95-2], was the equilibrium solid phase. The solid changed to a mixed uranyl hydroxocarbonate at pH>6.5, and to $UO_2(OH)_2$ and $Na_2U_2O_7$ at pH >8.

[b] Equilibrium concentration of free carbonate ion; it was calculated from the measured pH, partial pressure of CO_2, and the dissociation constants of carbonic acid.

[c] Total uranium concentration in the saturated solution.

Additional Information:

The solubility data were fitted to various models which took into consideration different U(VI) species. The best fit was found for a model considering UO_2CO_3 as the solid phase, and solution complexes $UO_2(CO_3)_n^{2-2n}$ $(n=1-3)$ with stability constants $\beta_n = [UO_2(CO_3)_n^{2-2n}][UO_2^{2+}]^{-1}[CO_3^{2-}]^{-n}$. The following constants were obtained: $K_{sp}=[UO_2^{2+}][CO_3^{2-}]=10^{-13.29}$, $\beta_1=10^{8.70}$, $\beta_2=10^{16.33}$, and $\beta_3=10^{23.92}$. The solubility of UO_2CO_3 was also studied isothermally by dissolving it in $NaHCO_3$ solutions. The data obtained agreed basically with those from the titration technique but were not considered for the subsequent calculations since they showed rather large scatter.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Measurements were carried out in CO_2 atmosphere in 0.1 mol dm^{-3} $NaClO_4$ solutions in a thermostated titration vessel. A 0.01 mol dm^{-3} solution of U(VI) labeled with ^{233}U was precipitated at pH ~6 by adding 0.05 mol dm^{-3} Na_2CO_3. Moistened CO_2 was bubbled through the solution continuously. The solution with the precipitate was allowed to stand under CO_2 atmosphere for 3 weeks. During this period, pH and U(VI) concentration were checked repeatedly and when they remained unchanged, the pH of the solution was varied stepwise in the pH range from 3.0 to 6.2 by adding small portions of either 0.1 mol dm^{-3} $HClO_4$ or 0.05 mol dm^{-3} Na_2CO_3. A steady state with stabilized pH value was usually attained within 1–3 days, from both supersaturation and undersaturation. Phase separation was then achieved by ultrafiltration though a 220 nm pore size filter, and the concentration of U(VI) in the solution was measured by liquid scintillation counting of ^{233}U using Tricarb 300 (Packard) spectrometer. The α counting efficiency was determined to be 99.64%, by calibration with an ^{241}Am standard. Combination glass electrodes (Orion) were used for pH measurement after calibration against four standard buffer solutions. Solid phases were characterized using DTA/TGA and x-ray powder diffraction.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: precision ± 0.1 K (authors).
pH: precision ± 0.02 pH units (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] W. Runde, G. Meinrath, and J. I. Kim, Radiochim. Acta **58/59**, 93 (1992).
[2] G. Meinrath, Y. Kato, T. Kimura, and Z. Yoshida, Radiochim. Acta **75**, 159 (1999).

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. The solid was dissolved in solutions of varying initial pH under CO_2 atmosphere. The gas was purified and equilibrated by passing it through 1 mol dm^{-3} H_2SO_4, distilled water, and 0.1 mol dm^{-3} $NaClO_4$ before it entered the reaction vessel. Constant pH (within ±0.02 pH unit) was reached within 3–14 days. Then samples of the saturated solutions were withdrawn and filtered through 450 nm pore size filter. Great care was taken to ensure that during sampling and filtration the contact of the sample with air was as short as possible to avoid CO_2 contamination or loss. The samples were analyzed for U(VI) by liquid scintillation counting using a Beckman LS2800 counter calibrated with U(VI) solutions containing 1×10^{-5}–3×10^{-3} mol dm^{-3} U(VI), or spectrophotometrically (Hitachi 330 spectrophotometer) by using a modified arsenazo III method.[1] The uranium concentrations obtained by these two methods agreed within 3%. The composition of the equilibrium solid phases was investigated by means of x-ray diffraction and ^{14}C-labeled UO_2CO_3.

Source and Purity of Materials:

Solutions of UO_2^{2+} were prepared from $UO_2(NO_3)_2\cdot 6H_2O$ (Merck p.a.). The decay products were removed on the day the experiment started by passing the UO_2^{2+} solution in 9 mol dm^{-3} HCl through Dowex 1×4 ion exchange resin, and eluting (VI) with 1 mol dm^{-3} HCl. The solution was evaporated to dryness, and UO_2CO_3 was prepared by adding saturated $NaHCO_3$ solution to the dry residue at room temperature. (The residue was redissolved for the sake of standardizing it with EDTA titration.) The residue dissolved with the evolution of CO_2 until a pale yellow precipitate formed. Then the reaction vessel was stoppered and allowed to stand overnight, the precipitate was centrifuged, washed with water several times, and characterized by x-ray diffraction. It was identified as UO_2CO_3 by comparing the diffraction pattern with literature data.[2,3] The precipitate, dried over silica gel, was also analyzed for uranium content: for UO_2CO_3, calculated 3.6%, found 3.1%. Other chemicals were Merck reagent grade products. Doubly distilled deionized water was used for the preparation of the solutions. It was boiled before use to remove all traces of CO_2.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

References:

[1] S. B. Savvin, Talanta **8**, 673 (1961).
[2] J. R. Clark and C. L. Christ, Am. Miner.**41**, 844 (1956).
[3] Powder Diffraction File, Inorganic phases. Int. Center for Diffraction Data, U.S.A.

Components:	**Original Measurements:**
(1) Uranium(VI) dioxocarbonate; UO_2CO_3; [12274-95-2] (2) Carbon dioxide; CO_2; [124-38-9] (3) Sodium perchlorate; $NaClO_4$; [7601-89-0] (4) Water; H_2O; [7732-18-5]	I. Pashalidis, W. Runde, and J. I. Kim, Radiochim. Acta **61**, 141–6 (1993).
Variables:	**Prepared by:**
T/K: 295 p_2 (partial pressure)/%: 100 c_3 /mol dm^{-3}: 0.1	J. Hála

Experimental Data

Solubility of UO_2CO_3 in 0.1 mol dm^{-3} solution of $NaClO_4$ at 25 °C and 100% partial pressure of CO_2[a]

pH	$-\log[CO_3^{2-}]$[b]	$-\log[UO_2^{2+}]$	$-\log K_{sp}$[c]
3.11	11.40	1.81[d]	13.21
3.11	11.40	1.73[e]	13.14
3.26	11.40	2.33[d]	13.43
3.45	10.73	2.61[d]	13.34
3.45	10.73	2.68[e]	13.41
3.45	10.69	2.78[e]	13.47
3.46	10.69	2.76[d]	13.45
3.56	10.51	2.89[d]	13.39
3.69	10.23	3.03[d]	13.27
3.69	10.23	3.19[e]	13.43
3.78	10.06	3.15[d]	13.21
3.78	10.06	3.55[e]	13.61
3.84	9.94	3.23[d]	13.17
4.00	9.61	3.58[d]	13.19
4.00	9.61	3.91[e]	13.52

[a] Equilibrium solid phase was UO_2CO_3, [12274-95-2], in all solutions.
[b] The concentration of free carbonate ion. It was calculated from the measured pH, partial pressure of CO_2, Henry constant, and dissociation constants of carbonic acid.
[c] $K_{sp}=[UO_2^{2+}][CO_3^{2-}]$.
[d] Determined by UV spectroscopy.
[e] Determined by ICP-AES.

Additional Information:

The average value of K_{sp} was reported to be $10^{-(13.35\pm0.14)}$ $mol^2\ dm^{-6}$. By using the specific ion interaction theory procedure, this was recalculated by the authors to zero ionic strength to obtain $K_{sp}^0=10^{-(14.21\pm0.14)}$ $mol^2\ dm^{-6}$.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. A portion of UO_2^{2+} stock solution was diluted with 0.1 mol dm^{-3} $NaClO_4$, neutralized to pH 7 with NaOH, and CO_2 gas was bubbled through the precipitate of UO_2CO_3. The precipitation procedure and subsequent solubility measurements were performed in a closed glass vessel. The pH of the solution in contact with UO_2CO_3 was adjusted stepwise by addition of 0.1 mol dm^{-3} $HClO_4$ or NaOH. The gas was bubbled through the vessel continuously. The pH was measured with a ROSS-type combination electrode containing 3 mol dm^{-3} $NaClO_4$ as a filling solution. The electrode was calibrated against six different buffer solutions. The time of equilibration after each adjustment of pH was not reported. The equilibrium uranium concentration in the saturated solution was determined by ICP-AES to obtain the total uranium concentration, and by UV spectroscopy to obtain the UO_2^{2+} concentration. The solid phases were characterized by x-ray powder diffraction, and IR and UV spectroscopy.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: precision ±1 K (authors).
Solubility: insufficient data given to allow for error estimate.

Components:

(1) Uranium(VI) dioxocarbonate; UO_2CO_3; [12274-95-2]
(2) Sodium carbonate; Na_2CO_3; [593-85-1]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

C. A. Blake, C. F. Coleman, K. B. Brown, D. G. Hill, R. S. Lowrie, and J. M. Schmitt, J. Am. Chem. Soc. **78**, 5978–83 (1956).

Variables:

T/K: 299
c_2 /mol dm^{-3}: 0.094–1.41

Prepared by:

J. Hála

Experimental Data

Solubility of UO_2CO_3 in Na_2CO_3 solutions at 26 °C[a]

Na_2CO_3 (c_2 /mol dm^{-3})	Na_2CO_3 (m_2 /mol kg^{-1})[c]	UO_2CO_3 (c_1 /mol dm^{-3})	UO_2CO_3 (m_1 /mol kg^{-1})[c]	Density[b] (g cm^{-3})
0.094	0.0949	0.087	0.0879	1.029
0.189	0.192	0.174	0.177	1.061
0.337	0.389	0.338	0.349	1.121
0.566	0.593	0.521	0.546	1.188
0.755	0.811	0.742	0.797	1.257
0.943	1.025	0.886	0.963	1.314
1.13	1.268	1.09	1.223	1.373
1.41	1.763	1.35	1.640	1.423

[a] Composition of equilibrium solid phases not reported.
[b] At 25 °C.
[c] Calculated by compiler.

Additional Information:
The authors reported that solubilities up to 32 mass % UO_3 were also measured. No data were reported, however, since the solutions in this region were very viscous, difficult to centrifuge, and in equilibrium with appreciable CO_2 pressure (20 mm). Equilibrium concentrations in these solutions could not be measured because of supersaturation.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Solutions containing excess UO_2CO_3 were equilibrated in Pyrex or polyfluoroethylene bottles for at least 10 days but usually for 3 or more weeks to ensure equilibrium. The agitation was carried out in a constant temperature room. The contents of the bottle was then centrifuged, and both the solid and liquid phases were analyzed for uranium, sodium, and carbonate. Depending on uranium concentration in the saturated solutions, uranium was determined either by potentiometric titration with $FeSO_4$ after reduction of uranium, or colorimetrically with ascorbic acid. Sodium was determined by flame photometry, and carbonate by absorption-gravimetric method.

Source and Purity of Materials:

UO_2CO_3 was prepared by agitating a mixture of UO_3, water and excess of solid CO_2 in a steel bomb for 5 h at 90–105 °C and pressures of 2500 to 3000 ppsi (17.2–20.7 MPa). A pale yellow product with consistently constant U/CO_3 ratio of 1.01–1.03 was obtained. UO_3 used was prepared by precipitating the peroxide $UO_4\cdot xH_2O$ from a solution of $UO_2(NO_3)_2$ at pH 2.5 with subsequent decomposition of the precipitate at 325 °C. Source and purity of $UO_2(NO_3)_2$ not specified. Reagent grade Na_2CO_3 was used.

Estimated Error:

Temperature: precision ±0.2 K (authors).
Solubility: insufficient data given to allow for error estimate.

5.2. Sodium Dicarbonatodioxouranate(VI)(2-)

Components:

(1) Sodium dicarbonatodioxouranate; $Na_2UO_2(CO_3)_2$; [ ]
(2) Water; H_2O; [7732-18-5]

Original Measurements:

M. Bachelet, E. Cheylan, M. Duis, and J. C. Goulette, Bull. Soc. Chim. France 173–9 (1954).

Variables:

T/K: 291

Prepared by:

J. Hála

Experimental Data

The solubility at 18 °C of $Na_2UO_2(CO_3)_2$ in water was reported to be 1415 g salt/L solution (3.26 mol dm^{-3}, compiler).

Auxiliary Information

Method/Apparatus/Procedure:

Nothing specified.

Source and Purity of Materials:

$Na_2UO_2(CO_3)_2$ was prepared by dissolution of $UO_3\cdot 1/2H_2O$ in 1 L of a solution containing stoichiometric amount of $NaHCO_3$ by passing a stream of CO_2 through the slurry. The resulting solution was evaporated at 40 °C. Analysis (found/calculated, in mass %): UO_3 64.7/65.6, Na_2O 14.6/14.22, CO_2 20.7/20.18. Source and purity of materials used not specified.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

5.3. Salts of Tris(carbonato)Dioxouranante(4-)

Components:
(1) Alkali metal tricarbonatodioxouranates(VI)
(2) Water; H_2O; [7732-18-5]

Original Measurements:
(1) M. Bachelet, E. Cheylan, K. Duis, and J. C. Goulette, Bull. Soc. Chim. France 55–60 (1952).
(2) M. Bachelet, E. Cheylan, K. Duis, and J. C. Goulette, Bull. Soc. Chim. France 173–9 (1954).

Variables:
Temperature

Prepared by:
J. Hála

Experimental Data

Solubility of alkali metal tricarbonatodioxouranates(VI) in water[a]

Salt	Temperature (°C)	Salt in the saturated solution (g dm^{-3})	Salt in the saturated solution (mol dm^{-3})[e]
$Na_4UO_2(CO_3)_3$[b]	20	204[d]	0.713
$K_4UO_2(CO_3)_3$[c]	0	47	0.0775
	18	71	0.117
$Rb_4UO_2(CO_3)_3$[c]	20	550	0.695
$Cs_4UO_2(CO_3)_3$[c]	20	1300	1.325

[a] Equilibrium solid phases not investigated.
[b] [12076-52-7]; original measurement in Ref. 1.
[c] Original measurements in Ref. 2.
[d] g UO_3 dm^{-3}.
[e] Calculated by compiler.

Auxiliary Information

Method/Apparatus/Procedure:
Nothing specified.

Source and Purity of Materials:
The salts were prepared by dissolving $UO_3 \cdot 1/2H_2O$ in a solution of the corresponding alkali metal hydrogencarbonate at room temperature. The mole ratio of reactants was 1:4. From the resulting solutions the sodium salt was precipitated at 50 °C, and the other salts were obtained after evaporation of the solutions at room temperature and recrystallization from water. Source and purity of materials used were not specified. Analysis (found/calculated, mass %): K salt—UO_3 47.14/47.20, K_2O 30.38/31.00, CO_2 22.48/21.80;Rb salt—UO_3 35.04/36.10, Rb_2O 47.95/47.20, CO_2 17.01/16.70; Cs salt—UO_3 29.30/29.10, Cs_2O 56.70/57.45, CO_2 14.00/13.46. Analysis of the Na salt was not reported.

Estimated Error:
Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

Components:
(1) Sodium tricarbonatodioxouranate(VI); $Na_4UO_2(CO_3)_3$; [12076-52-7]
(2) Sodium carbonate; Na_2CO_3; [497-19-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
C. A. Blake, C. F. Coleman, K. B. Brown, D. G. Hill, R. S. Lowrie, and J. M. Schmitt, J. Am. Chem. Soc. **78**, 5978–83 (1956).

Variables:
T/K: 299
c_2 /mol dm^{-3}: 0–0.5

Prepared by:
J. Hála

Experimental Data

Solubility of $Na_4UO_2(CO_3)_3$ in Na_2CO_3 solutions at 26 °C[a]

Na_2CO_3 (c_2 /mol dm^{-3})	$Na_4UO_2(CO_3)_3$ (c_1 /mol dm^{-3})
0	0.286
0.3	0.173
0.5	0.130

[a] Composition of equilibrium solid phases was not reported.

Auxiliary Information

Method/Apparatus/Procedure:
Isothermal method used. Solutions containing excess solid were equilibrated in Pyrex or polyfluoroethylene bottles for at least 10 days, but usually for 3 or more weeks to ensure equilibrium. The agitation was carried out in a constant-temperature room. The contents of the bottle were then centrifuged, and both the solid and liquid were analyzed for uranium, sodium, and carbonate. Depending on uranium concentration in the saturated solution, uranium was determined either by potentiometric titration with $FeSO_4$ after reduction of uranium, or colorimetrically with ascorbic acid. Sodium was determined by flame photometry, and carbonate by absorption-gravimetric method.

Source and Purity of Materials:
$Na_4UO_2(CO_3)_3$ was prepared according to Ref. 1. First, sodium uranate was precipitated from $UO_2(NO_3)_2$ solution with NaOH, washed and dissolved in a solution of $NaHCO_3$. The salt was then obtained by evaporating the solution to a low volume while passing CO_2 through the solution. The salt was recrystallized from water to yield a bright yellow product with the CO_3 /U ratio of 3:3.2. Source and purity of materials used were not specified. Na_2CO_3 was a reagent grade product.

Estimated Error:
Temperature: precision ±2 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] W. E. Bunce, N. H. Furnam, and R. T. Mundy, Report M-4238, 1947.

Components:

(1) Sodium tricarbonatodioxouranate(VI); $Na_4UO_2(CO_3)_3$; [12076-52-7]
(2) Sodium chloride; NaCl; [7647-14-5]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

C. A. Blake, C. F. Coleman, K. B. Brown, D. G. Hill, R. S. Lowrie, and J. M. Schmitt, J. Am. Chem. Soc. **78**, 5978–83 (1956).

Variables:

T/K: 299
c_2 /mol dm^{-3}: 1.0–4.0

Prepared by:

J. Hála

Experimental Data

Solubility of $Na_4UO_2(CO_3)_3$ in NaCl solutions at 26 °C[a]

NaCl (c_2 /mol dm^{-3})	$Na_4UO_2(CO_3)_3$ c_1 /mol dm^{-3}
1.0	0.075
1.5	0.034
2.0	0.020
2.5	0.012
3.0	0.006
3.5	0.003
4.0	0.0025

[a] Composition of equilibrium solid phases was not investigated.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Solutions containing excess solid were equilibrated in Pyrex or polyfluoroethylene bottles for at least 10 days, but usually for 3 or more weeks to ensure equilibrium. The agitation was carried out in a constant-temperature room. The contents of the bottle were then centrifuged, and both the solid and liquid were analyzed for uranium, sodium, and carbonate. Depending on uranium concentration in the saturated solution, uranium was determined either by potentiometric titration with $FeSO_4$ after reduction of uranium, or colorimetrically with ascorbic acid. Sodium was determined by flame photometry, and carbonate by absorption-gravimetric method.

Source and Purity of Materials:

$Na_4UO_2(CO_3)_3$ was prepared according to Ref. 1. First, sodium uranate was precipitated from $UO_2(NO_3)_2$ solution with NaOH, washed and dissolved in a solution of $NaHCO_3$. The salt was then obtained by evaporating the solution to a low volume while passing CO_2 through the solution. The salt was recrystallized from water to yield a bright yellow product with the CO_3 /U ratio of 3:3.2. Source and purity of materials used were not specified.

Estimated Error:

Temperature: precision ±2 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] W. E. Bunce, N. H. Furnam, and R. T. Mundy, Report M-4238, 1947.

Components:

(1) Sodium tricarbonatodioxouranate(VI); $Na_4UO_2(CO_3)_3$; [12076-52-7]
(2) Sodium sulfate; Na_2SO_4 ; [7757-82-6]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

C. A. Blake, C. F. Coleman, K. B. Brown, D. G. Hill, R. S. Lowrie, and J. M. Schmitt, J. Am. Chem. Soc. **78**, 5978–83 (1956).

Variables:

T/K: 299
c_2 /mol dm^{-3}: 0.3–3.0

Prepared by:

J. Hála

Experimental Data

Solubility of $Na_4UO_2(CO_3)_3$ in Na_2SO_4 solutions at 26 °C[a]

Na_2SO_4 (c_2 /mol dm^{-3})	$Na_4UO_2(CO_3)_3$ (c_1 /mol dm^{-3})
0.3	0.168
0.5	0.135
1.5	0.045
2.0	0.035
3.0	0.011

[a] Composition of equilibrium solid phases was not investigated.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Solutions containing excess solid were equilibrated in Pyrex or polyfluoroethylene bottles for at least 10 days, but usually for 3 or more weeks to ensure equilibrium. The agitation was carried out in a constant-temperature room. The contents of the bottle were then centrifuged, and both the solid and liquid were analyzed for uranium, sodium, and carbonate. Depending on uranium concentration in the saturated solution, uranium was determined either by potentiometric titration with $FeSO_4$ after reduction of uranium, or colorimetrically with ascorbic acid. Sodium was determined by flame photometry, and carbonate by absorption-gravimetric method.

Source and Purity of Materials:

$Na_4UO_2(CO_3)_3$ was prepared according to Ref. 1. First, sodium uranate was precipitated from $UO_2(NO_3)_2$ solution with NaOH, washed and dissolved in a solution of $NaHCO_3$. The salt was obtained by evaporating the solution to a low volume while passing CO_2 through the solution. The salt was then recrystallized from water to yield a bright yellow product with the CO_3 /U ratio of 3:3.2. Source and purity of materials used were not specified.

Estimated Error:

Temperature: precision ±2 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] W. E. Bunce, N. H. Furnam, and R. T. Mundy, Report M-4238, 1947.

Components:

(1) Sodium tricarbonatodioxouranate(VI); $Na_4UO_2(CO_3)_3$; [12076-52-7]
(2) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

C. A. Blake, C. F. Coleman, K. B. Brown, D. G. Hill, R. S. Lowrie, and J. M. Schmitt, J. Am. Chem. Soc. **78**, 5978–83 (1956).

Variables:

T/K: 299
c_2 /mol dm^{-3}: 0.5–3.5

Prepared by:

J. Hála

Experimental Data

Solubility of $Na_4UO_2(CO_3)_3$ in $NaClO_4$ solutions at 26 °C[a]

$NaClO_4$ (c_2 /mol dm^{-3})	$Na_4UO_2(CO_3)_3$ (c_1 /mol dm^{-3})
0.5	0.134
1.0	0.056
1.5	0.028
2.0	0.015
2.5	0.008
3.0	0.005
3.5	0.002

[a] Composition of equilibrium solid phases was not investigated.

Additional information:

Activity solubility product of $Na_4UO_2(CO_3)_3$ was calculated by the authors from the solubility data using the method of Harned and Owen[1] for highly soluble salts, and reported to be $K^0_{sp}=[Na^+]^4[UO_2(CO_3)_3^{4-}]=0.01$ mol^5 dm^{-15}.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Solutions containing excess solid were equilibrated in Pyrex or polyfluoroethylene bottles for at least 10 days, but usually for 3 or more weeks to ensure equilibrium. The agitation was carried out in a constant-temperature room. The contents of the bottle were then centrifuged, and both the solid and liquid were analyzed for uranium, sodium, and carbonate. Depending on uranium concentration in the saturated solution, uranium was determined either by potentiometric titration with $FeSO_4$ after reduction of uranium, or colorimetrically with ascorbic acid. Sodium was determined by flame photometry, and carbonate by absorption-gravimetric method.

Source and Purity of Materials:

$Na_4UO_2(CO_3)_3$ was prepared according to Ref. 2. First, sodium uranate was precipitated from $UO_2(NO_3)_2$ solution with NaOH, washed and dissolved in a solution of $NaHCO_3$. The salt was then obtained by evaporating the solution to a low volume while passing CO_2 through the solution. The salt was recrystallized from water to yield a bright yellow product with the CO_3/U ratio of 3:3.2. Source and purity of materials used were not specified.

Estimated Error:

Temperature: precision ±2 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions* (Reinhold, New York, 1950), p. 476.
[2] W. E. Bunce, N. H. Furnam, and R. T. Mundy, Report M-4238, 1947.

Components:

(1) Sodium tricarbonatodioxouranate(VI); $Na_4UO_2(CO_3)_3$; [12076-52-7]
(2) Sodium carbonate; Na_2CO_3; [497-19-8]
(3) Sodium chloride; NaCl; [7647-14-5]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

C. A. Blake, C. F. Coleman, K. B. Brown, D. G. Hill, R. S. Lowrie, and J. M. Schmitt, J. Am. Chem. Soc **78**, 5978–83 (1956).

Variables:

T/K: 299
c_2 /mol dm^{-3} = 0.22–1.72
c_3 /mol dm^{-3}: 0.28

Prepared by:

J. Hála

Experimental Data

Solubility at 26 °C of $Na_4UO_2(CO_3)_3$ in Na_2CO_3–NaCl solutions[a]

Na_2CO_3[a] (c_2 /mol dm^{-3})	$Na_4UO_2(CO_3)_3$ (c_1 /mol dm^{-3})
0.22	0.126
0.72	0.063
1.22	0.034
1.72	0.020

[a] Composition of equilibrium solid phases was not investigated. All solutions contained also 0.28 mol dm^{-3} NaCl.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Solutions containing excess solid were equilibrated in Pyrex or polyfluoroethylene bottles for at least 10 days, but usually for 3 or more weeks to ensure equilibrium. The agitation was carried out in a constant-temperature room. The contents of the bottle were then centrifuged, and both the solid and liquid were analyzed for uranium, sodium, and carbonate. Depending on uranium concentration in the saturated solution, uranium was determined either by potentiometric titration with $FeSO_4$ after reduction of uranium, or colorimetrically with ascorbic acid. Sodium was determined by flame photometry, and carbonate by absorption-gravimetric method.

Source and Purity of Materials:

$Na_4UO_2(CO_3)_3$ was prepared according to Ref. 1. First, sodium uranate was precipitated from $UO_2(NO_3)_2$ solution with NaOH, washed and dissolved in a solution of $NaHCO_3$. The salt was then obtained by evaporating the solution to a low volume while passing CO_2 through the solution. The salt was recrystallized from water to yield a bright yellow product with the CO_3/U ratio of 3:3.2. Source and purity of materials used were not specified.
Na_2CO_3 was a regent grade product.

Estimated Error:

Temperature: precision ±2 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] W. E. Bunce, N. H. Furnam, and R. T. Mundy, Report M-4238, 1947.

Components:

(1) Ammonium tricarbonatodioxouranate(VI); $(NH_4)_4UO_2(CO_3)_3$; [18077-77-5]
(2) Water; H_2O; [7732-18-5]

Original Measurements:

F. Giolitti and V. Vecchiarelli, Gazz. Chim. Ital. **35**, 170–81 (1985).

Variables:

T/K: 292–360

Prepared by:

J. Hála

Experimental Data

Composition of solutions of $(NH_4)_4UO_2(CO_3)_3$ saturated at various temperatures

Temperature (°C)	U (g/100 g)[a]	CO_2 (g/100 g)[a]	NH_3 (g/100 g)[a]	$U:CO_2:NH_3$[b]
18.6	2.71	1.54	0.795	1:3.08:4.10
36.5	3.09	2.29	1.188	1:4.01:5.35
48.3	3.03	2.71	1.35	1:4.95:6.35
62.0	—	3.17	1.62	—
87.3	3.95	3.96	2.027	1:5.52:7.15

[a] g/100 g saturated solution.
[b] Mole ratio in the saturated solutions.

Additional information:

The composition of the equilibrium solid phases was not investigated. At 18.6 °C the composition of the saturated solution corresponded to the formula ratio of the salt. The authors reported the solubility of $(NH_4)_4UO_2(CO_3)_3$ at this temperature as 6.04 g salt/100 g saturated solution. Using the authors' value of uranium concentration in the saturated solution, compiler calculated the solubility as 5.95 g salt/100 g solution ($m_1 = 0.121$ mol kg^{-1}). At higher temperatures the salt decomposed in the solution.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. A large excess of the solid was agitated for between 4 and 24 h with water in a thermostated bath at the desired temperature. The clear solution was analyzed for uranium (gravimetrically as U_3O_8), CO_2, and NH_3 (methods not specified).

Source and Purity of Materials:

$(NH_4)_4UO_2(CO_3)_3$ was prepared by addition to a solution of $UO_2(NO_3)_2$ heated to 50 °C concentrated solution of $(NH_4)_2CO_3$ in a twofold excess over the amount necessary to obtain a clear alkaline solution, and then concentrated ammonia solution. Crystals of $(NH_4)_4UO_2(CO_3)_3$ precipitated on cooling. Source and purity of materials used were not specified.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

Components:

(1) Ammonium tricarbonatodioxouranate(VI); $(NH_4)_4UO_2(CO_3)_3$; [18077-77-5]
(2) Sodium tricarbonatodioxouranate(VI); $Na_4UO_2(CO_3)_3$; [12076-52-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

N. N. Elovskikh and A. I. Stabrovskii, Zh. Neorg. Khim. **6**, 1300–1 (1961).

Variables:

T/K: 296
Mole ratio of components (1) and (2)

Prepared by:

J. Hála

Experimental Data

Concentration of uranium in $(NH_4)_4UO_2(CO_3)_3$ /$Na_4UO_2(CO_3)_3$ solutions saturated at 23 °C

$(NH_4)_4UO_2(CO_3)_3$ (g)[a]	$Na_4UO_2(CO_3)_3$ (g)[a]	Mole ratio[b]	U (g dm^{-3})[c]	U (mol dm^{-3})[c,d]
3.97	1.95	1:0.5	126.40	0.531
2.91	3.01	1:1	169.75	0.713
1.93	4.00	1:2	154.71	0.650
1.44	4.49	1:3	142.00	0.597
1.16	4.77	1:4	132.10	0.555
0.96	4.97	1:5	117.23	0.493

[a] Mass of the salt equilibrated with 10 mL water.
[b] Mole ratio of salts in the initial system.
[c] Concentration of uranium in the saturated solutions.
[d] Calculated by compiler.

Additional information:

When mixtures of $(NH_4)_4UO_2(CO_3)_3$ and $Na_4UO_2(CO_3)_3$ were dissolved stable solutions were obtained with uranium concentration higher than that corresponding to the binary salt/water systems, i.e., ~66 g dm^{-3} or 0.28 mol dm^{-3} uranium for $Na_4UO_2(CO_3)_3$, and ~30 g dm^{-3} or 0.13 mol dm^{-3} uranium for $(NH_4)_4UO_2(CO_3)_3$.[1] The effect was ascribed to the formation of a mixed sodium/ammonium tricarbonatodioxouranate. From a solution initially containing both salts in a 1:1 mole ratio the mixed salt $Na_2(NH_4)_2UO_2(CO_3)_3 \cdot H_2O$ could be precipitated with ethanol.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Mixtures of both salts in various mole ratios were equilibrated with 10 mL water for 16 h. Method of uranium determination in the saturated solutions was not reported. Solid phases were not investigated.

Source and Purity of Materials:

No details reported.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

Components:

(1) Magnesium tricarbonatodioxouranate(VI); $Mg_2UO_2(CO_3)_3$;
[ ]
(2) Water; H_2O; [7732-18-5]

Original Measurements:

M. Bachelet, E. Cheylan, M. Douis, and J. C. Goulette, Bull. Soc. Chim. France 565–9 (1952).

Variables:

T/K: 296–325

Prepared by:

J. Hála

Experimental Data

Composition of solutions of $Mg_2UO_2(CO_3)_3$ saturated at various temperatures[a]

Temperature (°C)	U ($g\ dm^{-3}$)	$Mg_2UO_2(CO_3)_3$ ($g\ dm^{-3}$)[b]	$Mg_2UO_2(CO_3)_3$ (c_1 /mol dm^{-3})[b]
23	39.0	81.71	0.1638
32	41.5	86.94	0.1743
42	57.8	121.1	0.2428
52	81.0	169.7	0.3403

[a] Composition of equilibrium solid phases was not investigated.
[b] Calculated by compiler.

Additional information:
$Mg_2UO_2(CO_3)_3$ hydrolyzed above 70 °C.

Auxiliary Information

Method/Apparatus/Procedure:

Nothing specified.

Source and Purity of Materials:

$Mg_2UO_2(CO_3)_3\cdot 18H_2O$ was obtained by passing a stream of CO_2 through a slurry of stoichiometric amounts of $UO_3\cdot 1/2H_2O$ and basic magnesium carbonate for 2–3 days under agitation. The reactants dissolved and the salt was obtained either by crystallization or by precipitation with acetone as strongly efflorescent yellow crystals. Analysis (found/calculated for anhydrous salt obtained at 60 °C, mass %): UO_3 57.35/57.00, MgO 16.15/16.20, CO_2 26.5/26.80. Source and purity of materials used not specified.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

Components:

(1) Calcium tricarbonatodioxouranate(VI); $Ca_2UO_2(CO_3)_3$;
[ ]
(2) Water; H_2O; [7732-18-5]

Original Measurements:

M. Bachelet, E. Cheylan, M. Douis, and J. C. Goulette, Bull. Soc. Chim. France 565–9 (1952).

Variables:

T/K: 273–328

Prepared by:

J. Hála

Experimental Data

Composition of solutions of $Ca_2UO_2(CO_3)_3$ saturated at various temperatures[a]

Temperature (°C)	U ($g\ dm^{-3}$)	$Mg_2UO_2(CO_3)_3$ (c_1 /mol dm^{-3})[b]
0	0.33	0.001386
23	1.34	0.005630
40	3.68	0.01546
55	5.02	0.02108

[a] Composition the the equilibrium solid phases was not investigated.
[b] Calculated by compiler.

Additional information:
$Ca_2UO_2(CO_3)_3$ hydrolyzed above 60 °C.

Auxiliary Information

Method/Apparatus/Procedure:

Nothing specified.

Source and Purity of Materials:

$Ca_2UO_2(CO_3)_3\cdot 10H_2O$ was obtained by passing a stream of CO_2 through a slurry of stoichiometric amounts of $UO_3\cdot 1/2H_2O$ and $CaCO_3$ for 24 h, filtering off the unreacted material and evaporation. Analysis (found/calculated for anhydrous salt obtained by heating the decahydrate at 80 °C, mass %): UO_3 54.40/54.40, CaO 20.8/21.1, CO_2 24.8/24.9. Source and purity of materials used not specified.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

Components:

(1) Strontium tricarbonatodioxouranate(VI); $Sr_2UO_2(CO_3)_3$; [ ]
(2) Water; H_2O; [7732-18-5]

Original Measurements:

M. Bachelet, E. Cheylan, M. Duis, and J. C. Goulette, Bull. Soc. Chim. France 565–9 (1952).

Variables:

T/K: 292

Prepared by:

J. Hála

Experimental Data

The solubility at 19 °C of $Sr_2UO_2(CO_3)_3$ in water was reported to be 1.7 g dm^{-3} salt or 0.655 g uranium/dm^3 solution (using the latter value the compiler calculated $c_1 = 2.75 \times 10^{-3}$ mol dm^{-3}). The composition of the equilibrium solid phase was not investigated.

Auxiliary Information

Method/Apparatus/Procedure:

Nothing specified.

Source and Purity of Materials:

$Sr_2UO_2(CO_3)_3 \cdot 9H_2O$ was prepared either by prolonged passing a stream of CO_2 through a slurry of $UO_3 \cdot 1/2H_2O$ and $SrCO_3$ under agitation, or by double decomposition reaction between $Na_2UO_2(CO_3)_3$ and $SrCl_2$. Analysis (found/calculated for the anhydrous salt, mass %): UO_3 46.75/45.7, SrO 32.70/33.15, CO_2 20.55/21.15. Source and purity of materials used not specified.

Estimated Error:

Temperature: precision not reported.

5.4. Sodium Pentakis(carbonato) Bis{dioxouranate(VI)}(6-)

Components:

(1) Sodium pentacarbonatobis{dioxouranate(VI)}; $Na_6(UO_2)_2(CO_3)_5$; [ ]
(2) Water; H_2O; [7732-18-5]

Original Measurements:

M. Bachelet, E. Cheylan, M. Duis, and J. C. Goulette, Bull. Soc. Chim. France 55–60 (1952).

Variables:

T/K: 293

Prepared by:

J. Hála

Experimental Data

A solution in water of $Na_6(UO_2)_2(CO_3)_5$ saturated at 20 °C was reported to contain 190 g UO_3 /dm^3 solution. From this value the compiler calculated the concentration of uranium to be 0.664 mol dm^{-3}. Composition of the equilibrium solid phase was not investigated.

Additional information:
In Ref. 1, $Na_6(UO_2)_2(CO_3)_5$ was reported to be a mixture of $Na_4UO_2(CO_3)_3$ and $Na_2UO_2(CO_3)_2 \cdot xH_2O$.

Auxiliary Information

Method/Apparatus/Procedure:

Nothing specified.

Source and Purity of Materials:

$Na_6(UO_2)_2(CO_3)_5$ was prepared by prolonged agitation of a slurry of $UO_3 \cdot 1/2H_2O$ and $NaHCO_3$ (mole ratio 1:3) in water by passing through it a stream of CO_2 gas at room temperature. From the resulting solution, the salt was precipitated at 50 °C. Source and purity of materials used not specified.[1]

Estimated Error:

Temperature: precision not reported.

References:

[1] L. A. McClaine, E. P. Bullwinkel, and J. C. Huggins, Proceedings Peaceful Uses Atomic Energy, Geneva, 1955, Vol. **8**, p. 26.

5.5. Uranium(VI) Dioxo Bis(carboxylates)

Components:

(1) Uranium(VI) dioxobis(carboxylates)
(2) Water; H_2O; [7732-18-5]

Original Measurements:

G. Courtois, Compt. Rend. **158**, 1511–4 (1914); **158**, 1688–91 (1914); Bull Soc. Chim. France **33**, 1761–73 (1923).

Variables:

Constant temperature

Prepared by:

J. Hála

Experimental Data

Solubilities of uranium(VI) dioxobis(carboxylates) in water

Dicarboxylate, $UO_2R_y \cdot xH_2O$[a]	Temperature (°C)	Solubility[b] (g salt/100 g saturated solution)
$UO_2(HCO_2)_2 \cdot H_2O$; (formate); [	15	7.20[c]
$UO_2(C_2H_3O_2)_2 \cdot 2H_2O$; (acetate); [6159-44-0]	17	7.73[d]
$UO_2(C_3H_5O_2)_2 \cdot 2H_2O$; (propionate); [	19	8.48
$UO_2(C_4H_7O_2)_2 \cdot 2H_2O$; (butyrate); [	17	10.53
$UO_2(C_4H_7O_2)_2 \cdot 2H_2O$; (iso-butyrate); [	20	4.25
$UO_2(C_5H_9O_2)_2 \cdot 2H_2O$; (valerate); [	14	3.72
$UO_2(CH_2(OH)CO_2)_2$; (glycolate); [	19	15.60[e]
$UO_2(CH_3CH(OH)CO_2)_2$; (lactate); [	18	2.92[f]
$UO_2C_4H_4O_6 \cdot 4H_2O$; (tartrate); [	17	3.82
$UO_2(C_7H_5O_2)_2$; (benzoate); [	18	0.32
$UO_2(C_7H_4(OH)O_2)_2 \cdot 2H_2O$; (salicylate); [	18	0.52

[a] Composition of the initial solid salt. Equilibrium solid phases were not investigated.

[b] For salts prepared as hydrates it was not stated whether the reported solubilities refer to the hydrate or anhydrous salt. Only for the salicylate the solubility was explicitly reported as that of the dihydrate.

[c] Saturated solutions of uranium dioxide formate were unstable; even in the dark a basic salt precipitated out after 24 h.

[d] Saturated solution was unstable in the dark. When exposed to difuse light, a basic salt, $UO_2(C_2H_3O_2)_2 \cdot UO_3 \cdot 4H_2O$, precipitated out.

[e] Saturated solutions were unstable, and a basic salt, $UO_2(CH_2(OH)CO_2)_2 \cdot UO_3 \cdot 4H_2O$, precipitated out in the dark.

[f] Saturated solutions stable in the dark. When exposed to light, a green hydrolytic product precipitated out, and a small quantity of CO_2 was produced.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used, no details reported. Unless stated otherwise (see above), the saturated solutions were stable with respect to hydrolysis when exposed to light.

Source and Purity of Materials:

The salts were prepared by action of the corresponding acid, either in solution or in the form of a suspension in water, on $UO_2(OH)_2$. The salts were recrystallized, and characterized by elemental analysis.

Estimated Error:

Precision of temperature or solubility not reported.

Components:

(1) Uranium dioxobis(formate); $UO_2(CHO_2)_2$; [16984-59-1]
(2) Formic acid; CH_2O_2; [64-18-6]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. Colani, Bull. Soc. Chim. France **45**, 624–6 (1929).

Variables:

T/K:298
100 w_2 /mass%:0.012–93.93

Prepared by:

J. Hála

Experimental Data

Composition of aqueous solutions of formic acid saturated with $UO_2(CHO_2)_2$ at 25 °C

CH_2O_2 (100 w_2 /mass%)	UO_3 (mass %)	$UO_2(CHO_2)_2$ (100 w_1 /mass%)[b]	Solid phase[a]
0.012	0.076		A
0.285	0.368		A
0.806	0.759		A
1.33	1.07		A
4.88	3.06		A
8.23	4.87		A
10.87	6.05	[c]	A+B
12.33	5.71	7.19	B
20.16	4.12	5.19	B
31.57	2.52	3.17	B
44.85	1.15	1.45	B
50.67	0.765	0.963	B
61.32	0.325	0.409	B
72.29	0.116	0.146	B
85.86	0.058	0.073	B
93.93	0.057	0.072	B

[a] A: $UO_2(CHO_2)_2 \cdot UO_3 \cdot 3H_2O$, [ ]; B: $UO_2(CHO_2)_2 \cdot H_2O$, [ ].

[b] Calculated by compiler under the assumption that $UO_2(CHO_2)_2$ is the species existing in these solutions.

[c] For this solution the author reported 7.99 g $UO_2(CHO_2)_2 \cdot H_2O$ per 100 g solution.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. The solid used for experiments was $UO_2(CHO_2)_2 \cdot H_2O$. No further details were reported except that equilibration was carried out in the dark.

Estimated Error:

Precision of temperature measurement or solubility determination not reported.

Components:
(1) Uranium(VI) dioxobis(acetate); $UO_2(C_2H_3O_2)_2$; [541-09-3]
(2) Water; H_2O; [7732-18-5]

Original Measurements:
J. Zehenter, Monatsh. Chem. **21**, 235–55 (1900).

Variables:
T/K: 288

Prepared by:
J. Hala

Experimental Data

The solubility of $UO_2(C_2H_3O_2)_2$ was reported to be 7.694 g salt in 100 g water at 15 °C. Composition of the equilibrium solid phase was not investigated.

Additional Information:
It is not clear from the document whether the reported solubility refers to the anhydrous salt or to the dihydrate, $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$, [6159-44-0]. The reported solubility value is almost identical with that reported in Ref. 1.
It was reported that solutions of $UO_2(C_2H_3O_2)_2$ are fully stable when kept in the dark. When exposed to light, the solutions became turbid, and a sparingly soluble hydrolytic product precipitated.

Auxiliary Information

Method/Apparatus/Procedure:
Isothermal method used, no details specified.

Source and Purity of Materials:
$UO_2(C_2H_3O_2)_2$ was a product of Merck (puriss.).

Estimated Error:
Precision of temperature or solubility measurement not reported.

References:
[1] G. Courtois, Compt. Rend. **158**, 1511 (1914).

Components:
(1) Uranium(VI) dioxobis(acetate); $UO_2(C_2H_3O_2)_2$; [541-09-3]
(2) Acetic acid; $C_2H_4O_2$; [64-19-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
A. Colani, Bull. Soc. Chim. France **41**, 1291–3 (1927).

Variables:
T/K: 298
100 w_2 /mass%: 0.27–97.8

Prepared by:
J. Hála

Experimental Data

Composition of aqueous solutions of acetic acid saturated with $UO_2(C_2H_3O_2)_2$ at 25 °C

$C_2H_4O_2$ (100 w_2 /mass%)	UO_3 (mass %)	$UO_2(C_2H_3O_2)_2$ (100 w_1 /mass%)[b]	Solid phase[a]
0.270	0.544		A
0.499	0.883		A
0.618	1.11		A
0.747	1.28		A
1.20	2.07		A
2.32	4.12		A+B
2.49	4.47		B
2.64	4.89		B+C
2.87	4.54	6.16	C
4.55	4.07	5.52	C
11.3	3.79	5.14	C
24.8	3.30	4.48	C
30.7	3.11	4.22	C
36.9	2.88	3.91	C
41.1	2.65	3.60	C
46.4	2.36	3.20	C
56.7	1.87	2.54	C
65.9	1.38	1.87	C
77.4	0.831	1.13	C
79.9	0.858	1.16	C+D
81.6	0.645	0.875	D
88.2	0.405	0.550	D
97.8	0.306	0.415	D

[a] A: $UO_2(C_2H_3O_2)_2 \cdot 2UO_2(OH)_2$, [ ]; B: $UO_2(C_2H_3O_2)_2 \cdot UO_2(OH)_2 \cdot 3H_2O$, [ ]; C: $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$, [6159-44-0]; D: $UO_2(C_2H_3O_2)_2 \cdot C_2H_4O_2 \cdot 2H_2O$, [ ].

[b] Calculated by compiler under the assumption that $UO_2(C_2H_3O_2)_2$ is the species existing in these solutions.

Auxiliary Information

Method/Apparatus/Procedure:
Excess $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$ or $UO_2(C_2H_3O_2)_2 \cdot 2UO_2(OH)_2$ and the solution of acetic acid of the desired concentration were kept at a temperature close to 100 °C for several hours in order to speed up hydrolytic reactions. The mixture was then thermostated at 25 °C under frequent stirring until equilibrium was reached. Experiments were conducted in flasks protected from light. Equilibration time and methods used to analyze the saturated solutions were not reported.

Source and Purity of Materials:
Nothing specified.

Estimated Error:
Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

Components:

(1) Uranium(VI) dioxobis(acetate); $UO_2(C_2H_3O_2)_2$; [541-09-3]
(2) Phosphoric acid tri-*n*-butyl ester; $C_{12}H_{27}O_4P$; [126-73-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. V. Baluev, A. Yu. Silin, I. G. Suglubova, and A. P. Taranov, Radiokhimiya **30**, 442–7 (1988).

Variables:

T/K:298
100 w_2 /mass%:50.8–71.6
100 w_3 /mass%:0–3.16

Prepared by:

J. Hála

Experimental Data

Composition of binary tri-*n*-butyl phosphate–water solutions saturated with $UO_2(C_2H_3O_2)_2$, and phase diagram of the $UO_2(C_2H_3O_2)_2$–$C_{12}H_{27}O_4P$–H_2O system at 25 °C

$C_{12}H_{27}O_4P$ (100 w_2 /mass%)[b]	H_2O (100 w_3 /mass%)	$UO_2(C_2H_3O_2)_2$ (100 w_1 /mass%)	Solid phase[a]
71.63	3.16	25.21	A
64.35	2.20	33.45	A
58.02	1.63	40.35	B
53.86	1.08	45.12	B+C
50.48	0.36	49.16	C
50.8	0	49.2[c]	C

[a] (A) $UO_2(C_2H_3O_2)_2\cdot 2H_2O$, [6159-44-0]; (B) $UO_2(C_2H_3O_2)_2\cdot H_2O$, [ ]; (C) $UO_2(C_2H_3O_2)_2$, [541-09-3]

[b] Calculated by compiler by difference.

[c] Solubility of anhydrous $UO_2(C_2H_3O_2)_2$ in dry tri-*n*-butylphosphate; $m_1 = 2.50$ mol kg^{-1} (authors).

Phase diagram (Fig. 4) of the $UO_2(C_2H_3O_2)_2$–$C_{12}H_{27}O_4P$–H_2O system at 25 °C:

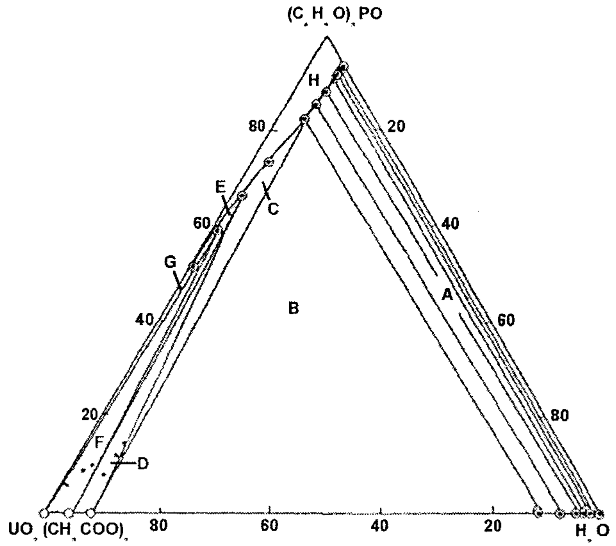

FIG. 4. Uranium (VI) dioxobis(acetate)–tri-*n*-butyl phosphate–water system. Legend to the phase diagram: (A) two-phase region; (B) two liquid phases in equilibrium with $UO_2(C_2H_3O_2)_2\cdot 2H_2O$; (C) saturated solutions in equilibrium with $UO_2(C_2H_3O_2)_2\cdot 2H_2O$; (D) saturated solutions in equilibrium with $UO_2(C_2H_3O_2)_2\cdot 2H_2O$ and $UO_2(C_2H_3O_2)_2\cdot H_2O$; (E) saturated solutions in equilibrium with $UO_2(C_2H_3O_2)_2\cdot H_2O$; (F) saturated solutions in equilibrium with $UO_2(C_2H_3O_2)_2\cdot H_2O$ and $UO_2(C_2H_3O_2)_2$; (G) saturated solutions in equilibrium with $UO_2(C_2H_3O_2)_2$; (H) unsaturated aqueous-organic solutions.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Desired amounts of the salt, tri-*n*-butyl phosphate and water were equilibrated in sealed glass ampoules protected from light in a thermostated bath. The concentration of uranium and water in the equilibrium phases were determined gravimetrically and by Fischer method, respectively. Composition of the equilibrium solid phases was determined by Schreinemakers method. Details of the methods used were identical with those in Ref. 1.

Source and Purity of Materials:

$UO_2(C_2H_3O_2)_2\cdot 2H_2O$ used was a reagent grade product, source was not specified. Monohydrate and anhydrous salt were obtained by vacuum dehydration.

Estimated Error:

Temperature: precision ±0.05 K (authors).
Solubility: precision not reported.

References:

[1] A. V. Baluev, A. A. Lumpov, and I. G. Suglubova, Radiokhimiya **26**, 196 (1984).

5.6. Uranium(VI) Dioxobis(acetate) Dihydrate

Components:

(1) Uranium(VI) dioxobis(acetate) dihydrate; $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$; [6159-44-0]
(2) Solvents

Original Measurements:

M. Szilagy, At. Kozlem. **2**, 49–52 (1960).

Variables:

T/K:298

Prepared by:

J. Hála

Experimental Data

Solubility of $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$ at 25 °C in four solvents

Solvent	$UO_2(C_2H_3O_2)_2 \cdot 2H_2O^a$ (100 w_1 /mass%)
Phthalic acid di-*n*-octyl ester; $C_{24}H_{38}O_4$; [117-84-0] (POE)	0.00087
Phthalic acid di-*n*-butyl ester; $C_{16}H_{22}O_4$; [84-74-2] (PBE)	0.0502
Phosphoric acid tri-*n*-butyl ester; $C_{12}H_{27}O_4P$; [126-73-8] (TBP)	3.17
Phosphoric acid di-*n*-butyl ester; $C_8H_{19}O_4P$; [107-66-4] (DBP)	30.9

[a] Compiler assumed the solubility data referred to the dihydrate. This was not stated explicitly in the original document where the solubility data were reported to refer to ''uranyl acetate.''

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method was used. Solvents were equilibrated with excess solid in a thermostated bath in ground-glass stoppered vessels. Equilibration time was 5, 26, 14, and 70 days for POE, PPE, TBP, and DBP, respectively. The concentration of uranium in the saturated solutions was determined fluorimetrically in case of POE and PBE, or gravimetrically as U_3O_8 in case of TBP and DBP. Saturated solutions did not show any precipitation of a solid or color change over a period of 12 months. Composition of the equilibrium solid phase was not reported.

Source and Purity of Materials:

$UO_2(C_2H_3O_2)_2 \cdot 2H_2O$ was a reagent grade product, source not specified. The solvents were commercial products of unspecified purity with densities (g cm^{-3}) of 0.9825 (POE), 1.0478 (PBE), 1.0551 (TBP), and 0.9732 (DBP).

Estimated Error:

Precision of temperature or solubility measurement not reported.

5.7. Sodium Tris(acetato) Dioxouranate(VI)

Components:

(1) Sodium tris(acetato) dioxouranate(VI); $NaUO_2(C_2H_3O_2)_3$; [14286-13-6]
(2) Sodium acetate; $C_2H_3O_2Na$; [127-09-3]
(3) Acetic acid; $C_2H_4O_2$; [64-19-7]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

B. P. Nikolskii, V. I. Paramonova, L. A. Kotchevanova, and G. G. Pamfilova, Khimiya Transuranovych Oskolochnych Elementov (Chemistry of Transuranium Elements and Fission Products), AN SSSR, Otd. Obsh. Tekh. Khim., 19–26, 1967.

Variables:

T/K: 293
c_2 /mol dm^{-3}: 0.18–4.0

Prepared by:

J. Hála

Experimental Data

Solubility product of $NaUO_2(C_2H_3O_2)_3$ at 20 °C

$C_2H_3O_2Na$ (c_2 /mol dm^{-3})	$K_{sp}{}^a$ (10^3 mol^2 dm^{-6})	pH^b
0.18	5.2	3.9–4.4
0.25	5.9	4.0–4.8
0.5	5.9	4.6–5.2
1.0	5.0	4.4–6.3
2.0	3.3	4.3–6.3
3.0	2.05	5.6–6.7
4.0	1.54	5.5–6.9

[a] $K_{sp} = [Na^+][UO_2(C_2H_3O_2)_3^-]$; it was obtained by the authors as the product of experimentally determined sodium and uranium concentrations in the saturated solutions. The authors assumed that at acetate concentrations used all U(VI) was present as the $UO_2(C_2H_3O_2)_3^-$ ion. The values K_{sp} reported are average values of several determinations carried out in the pH range indicated.

[b] pH range within which K_{sp} remained constant. Concentration of acetic acid used to adjust pH was not specified. At pH higher than those shown, an increase of K_s was observed which was ascribed by the authors to hydrolysis of U(VI). These data were not considered when average K_{sp} was calculated. At pH$<$4 a decrease in K_{sp} was observed due to the presence of higher acetic acid concentration. Neither these data were considered in the calculation of the average K_{sp} values.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. To a given volume of a solution with the desired composition $NaUO_2(C_2H_3O_2)_3$ was added in an amount to obtain a saturated solution containing excess solid. The pH of the solutions was adjusted by additions of acetic acid. The solutions were allowed to stand for several days at room temperature, and then shaken in a thermostated bath for 2 h. Saturated solutions were analyzed for uranium gravimetrically as U_3O_8 after removal of acetate from the sample by repeated evaporation with HNO_3, and for sodium gravimetrically as Na/Zn/UO_2 acetate or Na_2SO_4. The pH was determined with a glass electrode. Attaining equilibrium was confirmed by using other equilibration procedures such as precipitation of $NaUO_2(C_2H_3O_2)_3$ in the desired medium, or by cooling to 20 °C a solution saturated previously at 85 °C.

Source and Purity of Materials:

Nothing specified.

Estimated Error: (authors).
Temperature: precision ±0.2 K.
Concentration of uranium or sodium: precision ±(1–3)%.
pH: precision ±0.05 pH units.
K_{sp} : ±(3–5)%.

Components:

(1) Sodium tris(acetato) dioxouranate(VI); $NaUO_2(C_2H_3O_2)_3$; [14286-13-6]
(2) Sodium acetate; $C_2H_3O_2Na$; [127-09-3]
(3) Acetic acid; $C_2H_4O_2$; [64-19-7]
(4) Salts
(5) Water; H_2O; [7732-18-5]

Original Measurements:

B. P. Nikolskii, V. I. Paramonova, L. A. Kotchevanova, and G. G. Pamfilova, Khimiya Transuranovych Oskolochnych Elementov (Chemistry of Transuranium Elements and Fission Products), AN SSSR, Otd. Obsh. Tekh. Khim., 1967, pp. 19–26.

Variables:

T/K: 293; 323; 348
c_2 /mol dm^{-3}: 1–3
c_3 /mol dm^{-3}: 0.06–2

Prepared by:

J. Hála

Experimental Data

Solubility product of $NaUO_2(C_2H_3O_2)_3$ at various ionic strengths and temperatures

Salt	Salt (c_4 /mol dm^{-3})	$C_2H_3O_2Na$ (c_2 /mol dm^{-3})	$C_2H_4O_2$ (c_3 /mol dm^{-3})	K_{sp}[a] (10^3 mol^2 dm^{-6})
—	—	2.99	0.06–1.3	2.05±0.07
$C_2H_3O_2NH_4$; [631-61-8]	3.00	—	2	3.34±0.03
	2.00	1.00	1	3.3±0.1
$NaClO_4$; [7601-89-0]	2.00	1.00	1	3.9±0.1
$NaNO_3$; [7631-99-4]	2.00	1.00	1	4.1±0.1
NH_4NO_3; [6484-52-2]	1.00	2.00	1	3.54±0.04
	2.00	1.00	1	5.2±0.1

[a] At 20 °C. Average value of two or three measurements in the pH range where K_{sp} was independent of pH.

Salt	Salt (c_4 /mol dm^{-3})	$C_2H_3O_2Na$ (c_2 /mol dm^{-3})	Ionic strength (mol dm^{-3})	K_{sp}[a] (10^3 mol^2 dm^{-6})
$NaNO_3$; [7631-99-4]	1.0	1.0	2.0	4.5
	1.5	1.5	3.0	3.5
	2.0	2.0	4.0	2.8
	2.5	2.5	5.0	2.4
	2.0	1.0	3.0	4.1
	3.0	1.0	4.0	3.4
	4.0	1.0	5.0	2.6
$NaClO_4$; [7601-89-0]	2.0	1.0	3.0	3.9
NH_4NO_3; [6484-52-2]	2.0	1.0	3.0	3.2
$C_2H_3O_2NH_4$; [631-61-8]	2.0	1.0	3.0	3.3

[a] At 20 °C. Average value of two or three measurements in the pH range where K_{sp} was independent of pH. Solutions contained unspecified concentration of acetic acid used to adjust pH.

Temperature (°C)	$C_2H_4O_2$ (c_3 /mol dm^{-3})	pH[a]	K_{sp}[b] (10^3 mol^2 dm^{-6})
20	0.09	5.29	4.2
	0.34	5.01	4.0
	1.04	4.43	4.1
			4.1±0.1[c]
50	0.1	5.58	7.6
	0.5	4.87	7.5
	1.0	4.59	7.9
			7.7±0.1[c]
75	0.1	5.51	15.4
	0.5	4.88	15.7
	1.0	4.47	15.9
			15.7±0.2[c]

[a] pH of the equilibrium solutions.

[b] At 20 °C. All solutions contained 1.00 mol dm^{-3} $C_2H_3O_2Na$ and 2.00 mol dm^{-3} $NaNO_3$.

[c] Average value.

Additional information:
The K_{sp} values obtained in $C_2H_3O_2Na$–$C_2H_4O_2$ and $C_2H_3O_2Na$–$NaNO_3$ ($C_2H_3O_2Na/NaNO_3$ ratio 1:1, ionic strength 2–5 mol dm^{-3}) solutions were used to calculate the K^0_{sp} value as $K^0_{sp} = K_{sp}\gamma^2_{\pm} = (2.7 \pm 0.2) \times 10^{-3}$ mol^2 dm^{-6}. The mean activity coefficient $\gamma_{\pm}$ was calculated according to Ref. 1 using Å and 3.8 Å for the parameter of closest ion approach in $NaUO_2(C_2H_3O_2)_3$ in $C_2H_3O_2Na$–$C_2H_4O_2$ and $C_2H_3O_2Na$–$NaNO_3$ solutions, respectively.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. To a given volume of a solution with the desired composition $NaUO_2(C_2H_3O_2)_3$ was added in an amount to obtain a saturated solution containing excess solid. The pH of the solutions was adjusted by additions of acetic acid. The solutions were allowed to stand for several days at room temperature, and then shaken in a thermostated bath for 2 h. Saturated solutions were analyzed for uranium gravimetrically as U_3O_8 after removal of acetate from the sample by repeated evaporation with HNO_3, and for sodium gravimetrically as Na/Zn/UO_2 acetate or Na_2SO_4. The pH was determined with a glass electrode. Attaining equilibrium was confirmed by using other equilibration procedures such as precipitation of $NaUO_2(C_2H_3O_2)_3$ in the desired medium, or by cooling to 20 °C a solution saturated previously at 85 °C.

Source and Purity of Materials:

Nothing specified.

Estimated Error: (authors).
Temperature: precision ±0.2 K in the first two series of measurements, ±0.1 K in the third series.
Concentration of uranium or sodium: precision ±(1–3)%.
pH: precision ±0.05 pH units.

References:

[1] G. Harned and B. Owen, *The Physical Chemistry of Electrolyte Solutions* (Russian Transl.) (Moscow, 1952), p. 371.

5.8. Sodium Zinc Tris(dioxouranium(VI)) Nonakis(acetate)

Components:

(1) Sodium zinc tris{uranium(VI) dioxo} nonakis(acetate); $NaZn(UO_2)_3(C_2H_3O_2)_9$; [ ]
(2) Ethanol; C_2H_6O; [64-17-5]
(3) Water; H_2O; [7732-18-5]

Original measurements:

G. W. B. van der Lingen, Analyst **57**, 376–7 (1932).

Variables:

T/K: 298
Ethanol/volume %: 50–100

Prepared by:

J. Hála

Experimental Data

Solubility in ethanol–water mixtures of $NaZn(UO_2)_3(C_2H_3O_2)_9$ at 25 °C[a]

C_2H_6O (w_2 /vol. %)	$NaZn(UO_2)_3(C_2H_3O_2)_9$ (g/100 cm^3 solution)
50	0.967
60	0.316
70	0.194
80	0.119
90	0.062
96	0.042
100	0.132

[a] Equilibrium solid phases were not investigated. From aqueous solutions the salt crystallizes as hexahydrate,[1] and it was not mentioned whether it retains the water of crystallization when in equilibrium with ethanol–water mixtures or with neat ethanol.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method was used. The solubility of the salt was determined by evaporating to dryness of an aliquot of the saturated solution, and weighing the residue.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

References:

[1] H. H. Barber and I. M. Kolthoff, J. Am. Chem. Soc. **50**, 1625 (1928).

5.9. Uranium(VI) Dioxo Bis(carboxylates)+Organic Solvent+Water Ternary Systems

Components:

(1) Uranium(VI) dioxo bis(trifluoroacetate); $UO_2(C_2F_3O_2)_2$; [54974-80-0]
(2) Diethyl ether; $C_4H_{10}O$; [60-29-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

V. M. Vdovenko, A. V. Baluev, and I. G. Suglubova, Radiokhimiya, **17**, 62–5 (1975).

Variables:

T/K: 298
100 w_2 /mass %: 17.58–92.03
100 w_3 /mass %: =0.20–5.92

Prepared By:

J. Hála

Experimental Data

Composition of binary diethyl ether–water solutions saturated with $UO_2(C_2F_3O_2)_2$, and phase diagram of the $UO_2(C_2F_3O_2)_2$–$C_4H_{10}O$–H_2O system at 25 °C

$C_4H_{10}O$ (100 w_2 /mass %)[b]	H_2O (100 w_3 /mass %)	$UO_2(C_2F_3O_2)_2$[a] (100 w_1 /mass %)
92.03	0.20	7.77
84.63	0.76	14.61
60.87	2.51	36.62
59.23	2.61	38.16
17.58	5.92	76.50[c]

[a] The equilibrium solid phase was $UO_2(C_2F_3O_2)_2 \cdot 2C_4H_{10}O$ in all solutions.

[b] Calculated by compiler by difference.

[c] In this system the mole ratio $H_2O/UO_2(C_2F_3O_2)_2$ is 2:1, and the system can, according to the authors, be considered to represent molten $UO_2(C_2F_3O_2)_2 \cdot 2H_2O \cdot 1.5\ C_4H_{10}O$. At salt concentrations higher than 77 mass % it was not possible to investigate the solubility isotherm due to high viscosity of the system which prevented the solid phase to separate. For the same reason the solubility of $UO_2(C_2F_3O_2)_2$ in water could not be determined.

Phase diagram (Fig. 5) of the $UO_2(C_2F_3O_2)_2$–$C_4H_{10}O$–H_2O system at 25 °C.

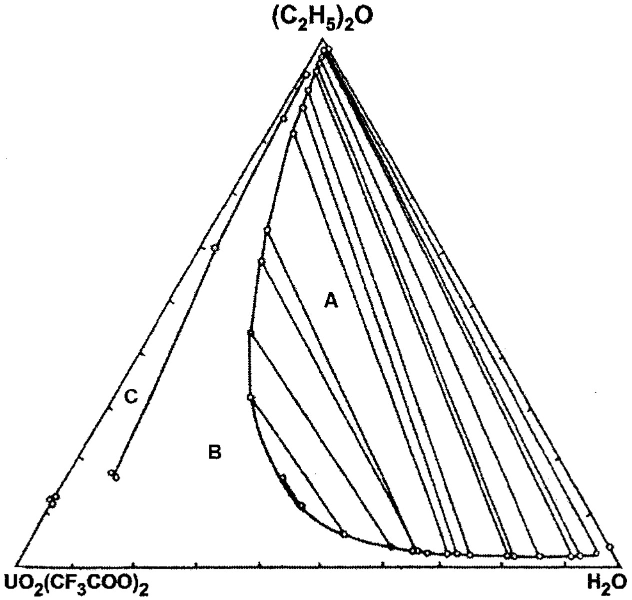

FIG. 5. Uranium (VI) dioxo bis(trifluoroacetate)–diethyl ether–water system. Legend to the phase diagram: (A) two-phase region; (B) unsaturated homogeneous water–diethyl ether solutions; (C) saturated solutions in equilibrium with $UO_2(C_2F_3O_2)_2 \cdot C_4H_{10}O$.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. The phases were brought to equilibrium by shaking them in sealed glass ampoules. The concentration of uranium and water in the equilibrium phases was determined gravimetrically (method not specified) and by Fischer method, respectively. All work was conducted in atmosphere of dry air since the solvate of $UO_2(C_2F_3O_2)_2$ was strongly hygroscopic.

Source and Purity of Materials:

Anhydrous $UO_2(C_2F_3O_2)_2$ and its solvate were prepared according to Ref. 1. Diethyl ether was purified according to Ref. 2, dried over sodium metal, and distilled on a rectification column.

Estimated Error:

Temperature: precision ±0.05 K (authors).
Solubility: precision not reported.

References:

[1] V. M. Vdovenko, A. V. Baluev, and I. G. Suglubova, in *Complex Formation and Extraction of Lanthanides and Actinides* (in Russian) (Nauka, Leningrad, 1974), p. 35.
[2] A. Weisberger, E. Poskauer, J. Riddick, and E. Tups, *Organic Solvents* (Russian Transl.) (IL, Moscow, 1958).

Components:

(1) Uranium (VI) dioxo bis(trifluoroacetate); $UO_2(C_2F_3O_2)_2$; [54974-80-0]
(2) Phosphoric acid tri-*n*-butyl ester; $C_{12}H_{27}O_4P$; [126-73-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. V. Baluev, A. A. Lumpov, and I. G. Suglubova, Radiokhimiya **27**, 274–80 (1985).

Variables:

T/K:298
100 w_2 /mass %:3.95–57.70
100 w_3 /mass %:0–12.67

Prepared by:

J. Hála

Experimental Data

Composition of binary tri-*n*-butyl phosphate–water solutions saturated with $UO_2(C_2F_3O_2)_2$, and phase diagram of the $UO_2(C_2F_3O_2)_2$–$C_{12}H_{27}O_4P$–H_2O system at 25 °C

$C_{12}H_{27}O_4P$ (100 w_2 /mass %)[b]	H_2O (100 w_3 /mass %)	$UO_2(C_2F_3O_2)_2$ (100 w_1 /mass %)	Solid phase[a]
57.70	0	42.30[c]	A
55.68	0.10	44.22	A
55.78	0.31	43.91	A
52.94	1.01	46.05	A+B
51.54	1.47	46.99	B
51.03	1.74	47.23	B
48.70	1.53	49.77	B
47.80	1.97	50.23	B
45.35	1.86	52.79	B
44.73	1.86	53.41	B
43.02	2.61	54.37	B
41.47	2.65	55.88	B
35.96	3.52	60.52	B
35.73	3.26	61.01	B
28.88	5.20	65.92	B+C
27.99	5.00	67.01	B+C
26.93	5.41	67.66	B+C
7.62	10.50	81.88	C
3.95	12.67	83.38	C

[a] (A) $UO_2(C_2F_3O_2)_2$, [54974-80-0]; (B) $UO_2(C_2F_3O_2)_2 \cdot H_2O$, [ ]; (C) unspecified hydrolyzed forms of $UO_2(C_2F_3O_2)_2$.
[b] Calculated by compiler by difference.
[c] Solubility of anhydrous $UO_2(C_2F_3O_2)_2$ in dry tri-*n*-butylphosphate; $m_1 = 1.48$ mol kg^{-1} (compiler).

Phase diagram (Fig. 6) of the $UO_2(C_2F_3O_2)_2$–$C_{12}H_{27}O_4P$–H_2O system at 25 °C:

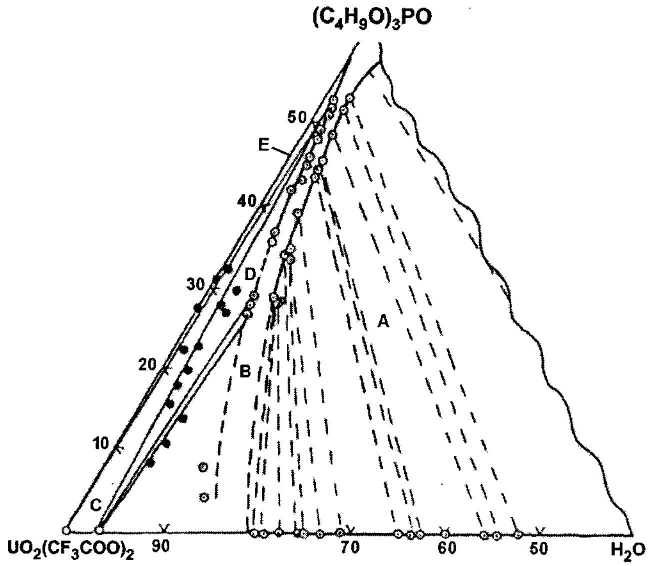

FIG. 6. Uranium (VI) dioxo bis(trifluoroacetate)–tri-*n*-butyl phosphate–water system. Legend to the phase diagram: (A) two-phase region; (b) unsaturated aqueous-organic solutions; (C) saturated solutions in equilibrium with $UO_2(C_2F_3O_2)_2$ and $UO_2(C_2F_3O_2)_2 \cdot H_2O$; (D) saturated solutions in equilibrium with $UO_2(C_2F_3O_2)_2 \cdot H_2O$; (E) saturated solutions in equilibrium with $UO_2(C_2F_3O_2)_2$.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Calculated amounts of the salt, tri-*n*-butyl phosphate and water were equilibrated in sealed glass ampoules protected from light in a thermostated bath for 4 days which was found sufficient for equilibrium to be reached. The phases were separated by centrifugation and analyzed as in Ref. 1. Equilibrium solid phases were identified by Schreinemakers method. It was not possible to obtain the whole solubility curve due to the strong tendency of the salt to hydrolyze in systems containing more than 3%–4% of water, and to high viscosity of concentrated solutions.

Source and Purity of Materials:

$UO_2(C_2F_3O_2)_2$ and its monohydrate were prepared according to Ref. 2. Tri-*n*-butyl phosphate was purified according to Ref. 3, and then distilled at 15 mm Hg pressure. Fraction boiling at 172–175 °C was collected for use.

Estimated Error:

Temperature: precision ±0.05 K (authors).
Solubility: precision not reported.

References:

[1]A. V. Baluev, S. V. Zhdanovskii, and I. G. Suglubova, Radiokhimiya **20**, 68 (1978).
[2]V. M. Vdovenko, A. V. Baluev, and I. G. Suglubova, in *Complex Formation and Extraction of Lanthanides and Actinides* (in Russian) (Nauka, Leningrad, 1974), p. 35.
[3]H. Irving and D. N. Edgington, J. Inorg. Nucl. Chem. **10**, 306 (1959).

Components:	**Original Measurements:**
(1) Uranium (VI) dioxo bis(monochloroacetate); $UO_2(C_2H_2O_2Cl)_2$; [15221-09-7] (2) Diethyl ether; $C_4H_{10}O$; [60-29-7] (3) Water; H_2O; [7732-18-5]	V. M. Vdovenko, A. V. Baluev, and I. G. Suglubova, Radiokhimiya **17**, 65–8 (1975).
Variables:	**Prepared by:**
T/K:298 100 w_2 /mass %:87.97–99.69 100 w_3 /mass %:0–1.30	J. Hála

Experimental Data

Composition of binary diethyl ether–water solutions saturated with $UO_2(C_2H_2O_2Cl)_2$, and phase diagram of the $UO_2(C_2H_2O_2Cl)_2$–$C_4H_{10}O$–H_2O system at 25 °C

$C_4H_{10}O$ (100 w_2 /mass %)[b]	H_2O (100 w_2 /mass %)	$UO_2(C_2H_2O_2Cl)_2$ (100 w_1 /mass %)	Solid phase[a]
99.69	0	0.31[c]	A
98.47	0.11	1.42	A+B
98.47	0.11	1.42	B
96.35	0.25	3.40	B
96.57	0.33	3.10	B
89.29	0.61	10.10	B
87.97	1.30	10.73	B

[a](A) $UO_2(C_2H_2O_2Cl)_2$, [15221-09-7]; (B) $UO_2(C_2H_2O_2Cl)_2 \cdot H_2O$, [ ].
[b]Calculated by compiler by difference.
[c]Solubility of $UO_2(C_2H_2O_2Cl)_2$ in dry diethyl ether; $m_1 = 6.80 \times 10^{-3}$ mol kg^{-1} (compiler).

Additional information:

Due to hydrolysis in mixtures containing higher amount of water it was possible to investigate systems with mole ratios H_2O/salt<3 only. Phase diagram (Fig. 7) of the $UO_2(C_2H_2O_2Cl)_2$–$C_4H_{10}O$–H_2O system at 25 °C.

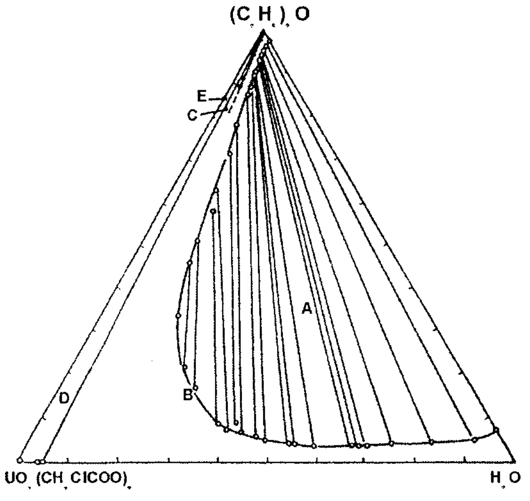

FIG. 7. Uranium (VI) dioxo bis(monochloroacetate)–diethyl ether–water system. Legend to the phase diagram: (A) two liquid phases; (B) unsaturated homogeneous water–diethyl ether solutions; (C) saturated solutions in equilibrium with $UO_2(C_2H_2O_2Cl)_2H_2O$; (D) saturated solutions in equilibrium with $UO_2(C_2H_2O_2Cl)_2$; (E) saturated solutions in equilibrium with $UO_2(C_2H_2O_2Cl)_2$ and $UO_2(C_2H_2O_2Cl)_2 \cdot H_2O$.

Components:

(1) Uranium (VI) dioxo bis(monochloroacetate); $UO_2(C_2H_2O_2Cl)_2$; [15221-09-7]
(2) Phosphoric acid tri-*n*-butyl ester; $C_{12}H_{27}O_4P$; [126-73-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. V. Baluev, A. A. Lumpov, and I. G. Suglubova, Radiokhimiya **27**, 280–8 (1985).

Variables:

T/K:298
100 w_2 /mass %:30.97–60.3
100 w_3 /mass %:0.09–3.50

Prepared by:

J. Hála

Experimental Data

Composition of binary tri-*n*-butyl phosphate–water solutions saturated with $UO_2(C_2H_2O_2Cl)_2$, and phase diagram of the $UO_2(C_2H_2O_2Cl)_2-C_{12}H_{27}O_4P-H_2O$ system at 25 °C

$C_{12}H_{27}O_4P$ (100 w_2 /mass %)[b]	H_2O (100 w_3 /mass %)	$UO_2(C_2H_2O_2Cl)_2$ (100 w_1 /mass %)	Solid phase[a]
30.97	3.50	65.53	A
30.94	2.85	66.21	A
35.29	2.68	62.03	A
41.93	1.12	56.95	A
43.25	1.06	55.69	A
43.28	1.03	55.69	A
44.97	1.30	53.73	A
46.04	1.01	52.95	A
48.03	0.92	51.05	A
50.26	0.92	48.82	A
55.16	0.48	44.36	A+B
59.41	0.12	40.47	B
60.30	0.09	39.61	B

[a] (A) $UO_2(C_2H_2O_2Cl)_2 \cdot H_2O$, [ ]; (B) $UO_2(C_2H_2O_2Cl)_2$ [15221-09-7].
[b] Calculated by compiler by difference.

Additional information:
Composition of the phases reported are average values of two to three measurements. Extrapolated value of the solubility of $UO_2(C_2H_2O_2Cl)_2$ in dry tri-*n*-butylphosphate was reported to be approximately $m_1 = 1.45$ mol kg^{-1}. In a more recent document,[1] $m_1 = 1.43$ mol kg^{-1} was reported.

Phase diagram (Fig. 8) of the $UO_2(C_2H_2O_2Cl)_2-C_{12}H_{27}O_4P-H_2O$ system at 25 °C.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. The phases were brought to equilibrium by shaking them in sealed glass ampoules. The concentration of uranium and water in the equilibrium phases was determined gravimetrically (method not specified) and by Fischer method, respectively.

Source and Purity of Materials:

Anhydrous $UO_2(C_2H_2O_2Cl)_2$ and its hydrate were prepared and analyzed according to Ref. 1. Diethyl ether was purified according to Ref. 2, dried over sodium metal, and distilled on a rectification column.

Estimated Error:

Temperature: precision ±0.05 K (authors).
Solubility: precision not reported.

References:

[1] V. M. Vdovenko, A. V. Baluev, and I. G. Suglubova, *Complex Formation and Extraction of Lanthanides and Actinides* (in Russian) (Nauka, Leningrad, 1974), p. 35.
[2] A. Weisberger, E. Poskauer, J. Riddick, and E. Tups, *Organic Solvents* (Russian Transl.) (IL, Moscow, 1958).

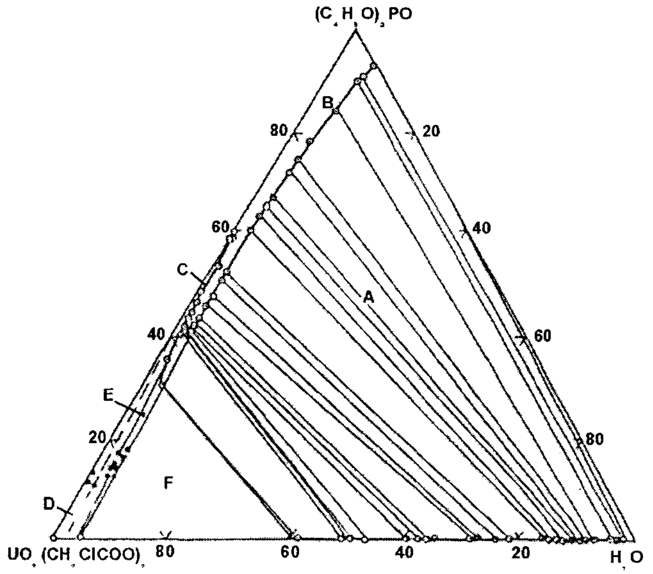

FIG. 8. Uranium (VI) dioxo bis(monochloroacetate)–tri-*n*-butyl phosphate–water system. Legend to the phase diagram: (A) two-phase region; (B) unsaturated aqueous–organic solutions; (C) saturated solutions in equilibrium with $UO_2(C_2H_2O_2Cl)_2$; (D) saturated solutions in equilibrium with $UO_2(C_2H_2O_2Cl)_2$ and $UO_2(C_2H_2O_2Cl)_2 \cdot H_2O$; (E) saturated solutions in equilibrium with $UO_2(C_2H_2O_2Cl)_2 \cdot H_2O$; (F) $UO_2(C_2H_2O_2Cl)_2 \cdot H_2O$ in equilibrium with saturated organic and aqueous solutions.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Calculated amounts of the salt, tri-*n*-butyl phosphate, and water were equilibrated in sealed glass ampoules protected from light in a thermostated bath for 4 days which was found sufficient for equilibrium to be reached. The phases were separated by centrifugation and analyzed as in Ref. 2. Equilibrium solid phases were identified by Schreinemakers method.

Source and Purity of Materials:

$UO_2(C_2H_2O_2Cl)_2$ and its monohydrate were prepared according to Ref. 3. Tri-*n*-butyl phosphate was purified according to Ref. 4, and then distilled at 15 mm Hg pressure. Fraction boiling at 172–175 °C was collected for use.

Estimated Error:

Temperature: precision ±0.05 K (authors).
Solubility: precision not reported.

References:

[1] A. V. Baluev, A. Yu, Silin, I. G. Suglubova, and A. P. Taranov, Radiokhimiya **30**, 442 (1988).
[2] A. V. Baluev, S. V. Zhdanovskii, and I. G. Suglubova, Radiokhimiya **20**, 68 (1978).
[3] V. M. Vdovenko, A. V. Baluev, and I. G. Suglubova, in *Complex Formation and Extraction of Lanthanides and Actinides* (in Russian) (Nauka, Leningrad, 1974), p. 35.
[4] H. Irving, and D. N. Edgington, J. Inorg. Nucl. Chem. **10**, 306 (1959).

Components:

(1) Uranium (VI) dioxo bis(trichloroacetate); $UO_2(C_2O_2Cl_3)_2$; [21740-41-0]
(2) Diethyl ether; $C_4H_{10}O$; [60-29-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

V. M. Vdovenko, A. V. Baluev, and I. G. Suglubova, Radiokhimiya **17**, 58–62 (1975).

Variables:

T/K:298
100 w_2 /mass %:1.3–98.8
100 w_3 /mass %:0.2–19.4

Prepared by:

J. Hála

Experimental Data

Composition of binary diethyl ether–water solutions saturated with $UO_2(C_2O_2Cl_3)_2$, and phase diagram of the $UO_2(C_2O_2Cl_3)_2$–$C_4H_{10}O$–H_2O system at 25 °C

$C_4H_{10}O$ (100 w_2 /mass %)[b]	H_2O (100 w_3 /mass %)	$UO_2(C_2O_2Cl_3)_2$ (100 w_1 /mass %)	Solid phase[a]
1.30	19.40	79.30	A
2.85	17.00	80.15	A
5.70	12.60	81.70	A
5.95	13.15	80.90	A+B
4.53	13.12	82.35	A+B
8.70	12.80	78.50	A+B
10.22	16.43	73.35	B
16.65	20.00	63.35	B+C
19.18	16.95	63.87	B+C
17.30	18.30	64.40	C
25.10	11.70	63.20	C
47.40	4.88	47.72	C
50.98	4.05	44.97	C
60.70	2.50	36.80	C
59.77	1.85	38.38	C+D
69.85	1.60	28.55	D
81.20	0.90	17.90	D
85.23	1.25	13.25	D
86.83	0.60	12.57	D+E
98.80	0.20	1.00	E

[a] (A) $UO_2(C_2O_2Cl_3)_2 \cdot 3H_2O$, [ ]; (B) $UO_2(C_2O_2Cl_3)_2 \cdot 2H_2O \cdot C_4H_{10}O$, [ ]; (C) $UO_2(C_2O_2Cl_3)_2 \cdot 2H_2O \cdot 2C_4H_{10}O$, [ ]; (D) $UO_2(C_2O_2Cl_3)_2 \cdot H_2O \cdot C_4H_{10}O$, [ ]; (E) $UO_2(C_2O_2Cl_3)_2 \cdot C_4H_{10}O$, [ ].
[b] Calculated by compiler by difference.

Phase diagram (Fig. 9) of the $UO_2(C_2O_2Cl_3)_2$–$C_4H_{10}O$–H_2O system at 25 °C.

Components:

(1) Uranium(VI) dioxo bis(trichloroacetate); $UO_2(C_2O_2Cl_3)_2$; [21740-41-0]
(2) Phosphoric acid tri-*n*-butyl ester; $C_{12}H_{27}O_4P$; [126-73-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. V. Baluev, A. A. Lumpov, and I. G. Suglubova, Radiokhimiya **26**, 196–206 (1984).

Variables:

T/K:298
100 w_2 /mass%:6.5–48.1
100 w_3 /mass%:0.01–14.28

Prepared by:

J. Hála

Experimental Data

Composition of binary tri-*n*-butyl phosphate–water solutions saturated with $UO_2(C_2O_2Cl_3)_2$, and phase diagram of the $UO_2(C_2O_2Cl_3)_2-C_{12}H_{27}O_4P-H_2O$ system at 25 °C

$C_{12}H_{27}O_4P$ (100 w_2 /mass%)[b]	H_2O (100w w_3 /mass%)	$UO_2(C_2O_2Cl_3)_2$ (100 w_1 /mass%)	Solid phase[a]
48.09	0.01	51.90	A
46.72	0.75	52.53	A+B
45.76	0.66	53.58	A+B
37.92	1.10	60.98	B
33.66	1.81	64.53	B
29.32	3.65	67.03	B
30.40	2.35	67.25	B
28.35	4.12	67.53	B
26.23	5.33	68.40	B+C
26.42	4.20	69.38	B+C
24.36	5.74	69.90	C
21.43	6.82	71.75	C+D
17.25	8.40	74.35	D
11.18	11.20	77.62	D
4.72	16.68	78.60	D
6.51	14.28	79.21	D

[a] (A) $UO_2(C_2O_2Cl_3)_2$, [21740-41-0]; (B) $UO_2(C_2O_2Cl_3)_2\cdot H_2O$, [ ]; (C) $UO_2(C_2O_2Cl_3)_2\cdot 2H_2O$, [ ]; (D) $UO_2(C_2O_2Cl_3)_2\cdot 3H_2O$, [ ].

[b] Calculated by compiler by difference.

Additional information:

In a more recent reference,[1] the solubility at 25 °C in dry tri-*n*-butylphosphate of $UO_2(C_2O_2Cl_3)_2$ was reported as $m_1 = 1.81$ mol kg^{-1}.

Phase diagram (Fig. 10) of the $UO_2(C_2O_2Cl_3)_2-C_{12}H_{27}O_4P-H_2O$ system at 25 °C.

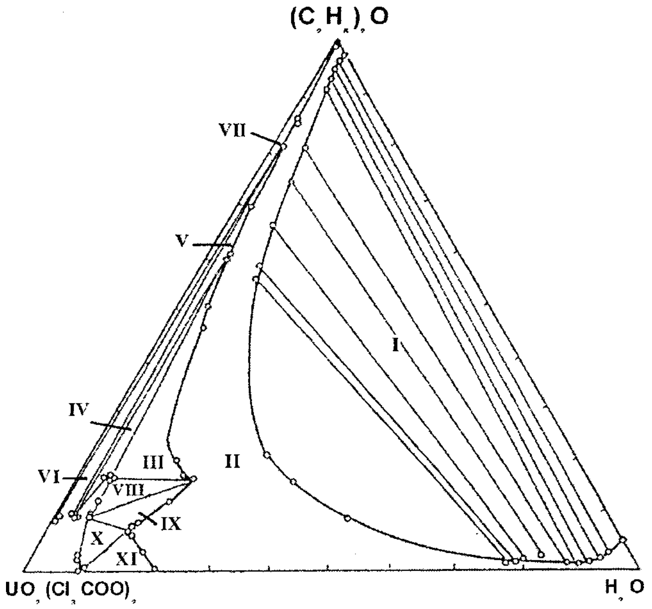

FIG. 9. Uranium (VI) dioxo bis(trichloroacetate)–diethyl ether–water system. Legend to the phase diagram (for notation of solid phases see above): (I) two liquid phases; (II) unsaturated homogeneous water–diethyl ether solutions; region (III)–(XI) represent fields of saturated solutions in equilibrium with the following solid phases: (III) C; (IV) C+D; (V) D; (VI) D+E; (VII) E; (VIII) B+C; (IX) B; (X) A+B; (XI) A.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. The phases were brought to equilibrium by shaking them in sealed glass ampoules. The concentration of uranium and water in the equilibrium phases was determined gravimetrically (method not specified) and by Fischer method, respectively. All work was conducted in the atmosphere of dry air since the hydrates and hydrato-solvates of $UO_2(C_2O_2Cl_3)_2$ are strongly hygroscopic.

Source and Purity of Materials:

Anhydrous $UO_2(C_2O_2Cl_3)_2$ and its hydrate were prepared and analyzed according to Ref. 1. Diethyl ether was purified according to Ref. 2, dried over sodium metal, and distilled on a rectification column.

Estimated Error:

Temperature: precision ±0.05 K (authors).
Solubility: precision not reported.

References:

[1] V. M. Vdovenko, A. V. Baluev, and I. G. Suglubova, in *Complex Formation and Extraction of Lanthanides and Actinides* (in Russian) (Nauka, Leningrad, 1974), p. 35.

[2] A. Weisberger, E. Poskauer, J. Riddick, and E. Tups, *Organic Solvents* (Russian Transl.) (IL, Moscow, 1958).

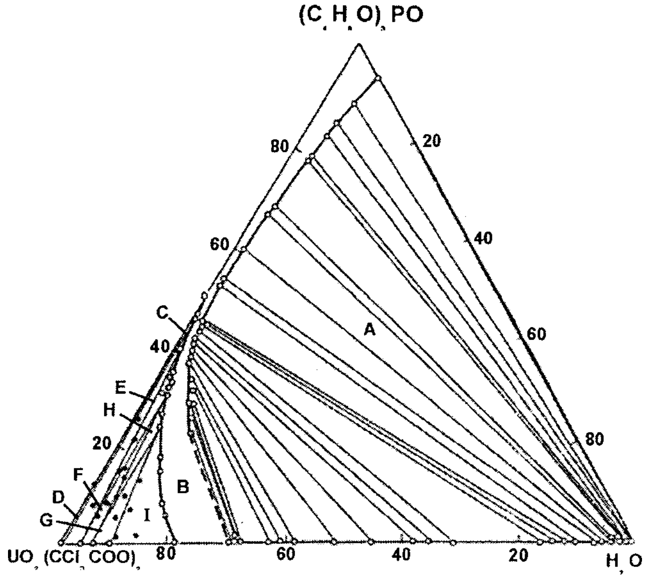

FIG. 10. Uranium (VI) dioxo bis(trichloroacetate)–tri-*n*-butyl phosphate–water system. Legend to the phase diagram: (A) two-phase region; (B) unsaturated aqueous-organic solutions; (C) saturated solutions in equilibrium with $UO_2(C_2O_2Cl_3)_2$; (D) saturated solutions in equilibrium with $UO_2(C_2O_2Cl_3)_2$ and $UO_2(C_2O_2Cl_3)_2 \cdot H_2O$; (E) saturated solutions in equilibrium with $UO_2(C_2O_2Cl_3)_2 \cdot H_2O$; (F) saturated solutions in equilibrium with $UO_2(C_2O_2Cl_3)_2 \cdot H_2O$ and $UO_2(C_2O_2Cl_3)_2 \cdot 2H_2O$; (G) saturated solutions in equilibrium with $UO_2(C_2O_2Cl_3)_2 \cdot 2H_2O$ and $UO_2(C_2O_2Cl_3)_2 \cdot 3H_2O$; (H) saturated solutions in equilibrium with $UO_2(C_2O_2Cl_3)_2 \cdot 2H_2O$; (I) saturated solutions in equilibrium with $UO_2(C_2O_2Cl_3)_2 \cdot 3H_2O$.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Calculated amounts of the salt, tri-*n*-butyl phosphate and water were equilibrated in sealed glass ampoules protected from light in a thermostated bath for 4 days which was found sufficient for equilibrium to be reached. The phases were separated by centrifugation and analyzed as in Ref. 2. Composition of the phases reported are average results of two to three measurements. Equilibrium solid phases were identified by Schreinemakers method. All work was conducted in atmosphere of dry argon since $UO_2(C_2O_2Cl_3)_2$ tends to hydrolyze and is strongly hygroscopic.

Source and Purity of Materials:

$UO_2(C_2O_2Cl_3)_2$ and its hydrates were prepared according to Ref. 3. Tri-*n*-butylphosphate was purified according to Ref. 4, and then distilled at 15 mm Hg pressure. Fraction boiling at 172–175 °C was collected for use.

Estimated Error:

Temperature: precision ± 0.05 K (authors).
Solubility: precision not reported.

References:

[1] A. V. Baluev, A. Yu. Silin, I. G. Suglubova, and A. P. Taranov, Radiokhimiya **30**, 442 (1988).
[2] A. V. Baluev, S. V. Zhdanovskii, and I. G. Suglubova, Radiokhimiya **20**, 68 (1978).
[3] V. M. Vdovenko, A. V. Baluev, and I. G. Sugluboya, in *Complex Formation and Extraction of Lanthanides and Actinides* (in Russian) (Nauka, Leningrad, 1974), p. 35.
[4] H. Irving and D. N. Edgington, J. Inorg. Nucl. Chem. **10**, 306 (1959).

Components:

(1) Uranium(VI) dioxo bis(trichloroacetate); $UO_2(C_2O_2Cl_3)_2$; [21740-41-0]
(2) 4-methyl-2-pentanone (methyl isobutylketone); $C_6H_{12}O$; [108-10-1]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. V. Baluev, M. A. Myagkova-Romanova, and I. G. Suglubova, Radiokhimiya **34**, 59–68 (1992).

Variables:

T/K:298
100 w_2 /mass%:0.09–85.9
100 w_3 /mass%:0.02–20.70

Prepared by:

J. Hála

Experimental Data

Composition of binary 4-methyl-2-pentanone–water solutions saturated with $UO_2(C_2O_2Cl_3)_2$, and phase diagram of the $UO_2(C_2O_2Cl_3)_2$–$C_6H_{12}O$–H_2O system at 25 °C

$C_6H_{12}O$ (100 w_2 /mass%)[b]	H_2O (100 w_3 /mass%)	$UO_2(C_2O_2Cl_3)_2$ (100 w_1 /mass%)	Solid phase[a]
85.88	0.02	14.10	A
66.02	2.10	31.88	A
56.22	3.85	39.93	A
33.65	8.34	58.01	A+B
32.46	8.50	59.04	A+B
29.74	8.90	61.36	B
19.72	10.29	69.99	B
7.79	13.55	78.66	B
3.78	17.40	78.82	B
0.09	20.70	79.21	B

[a] (A) $UO_2(C_2O_2Cl_3)_2 \cdot C_6H_{12}O$, [ ]; (B) $UO_2(C_2O_2Cl_3)_2 \cdot 3H_2O$, [ ]
[b] Calculated by compiler by difference.

Phase diagram (Fig. 11) of the $UO_2(C_2O_2Cl_3)_2$–$C_6H_{12}O$–H_2O system at 25 °C.

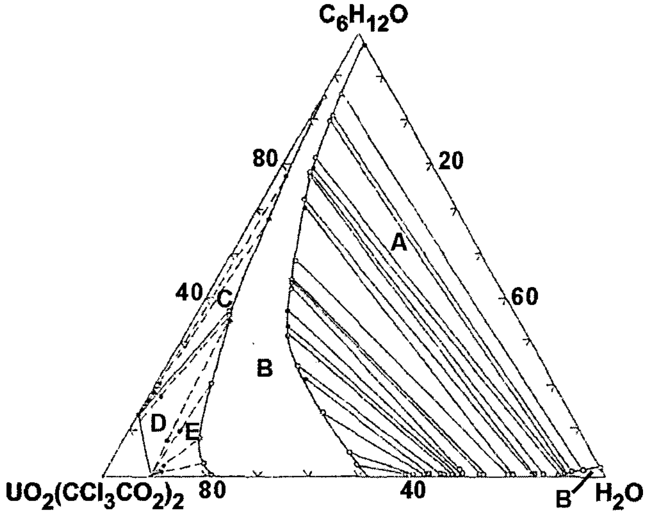

FIG. 11. Uranium (VI) dioxo bis(benzenesulfonate)–tri-*n*-butyl phosphate–water system. Legend to the phase diagram: (A) two-phase region; (B) unsaturated aqueous–organic solutions; (C) saturated solutions in equilibrium with $UO_2(C_2O_2Cl_3)_2 \cdot C_6H_{12}O$; (D) saturated solutions in equilibrium with $UO_2(C_2O_2Cl_3)_2 \cdot C_6H_{12}O$ and $UO_2(C_2O_2Cl_3)_2 \cdot 3H_2O$; (E) saturated solutions in equilibrium with $UO_2(C_2O_2Cl_3)_2 \cdot 3H_2O$

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Calculated amounts of the salt, methyl isobutylketone, and water were equilibrated in sealed glass ampoules protected from light in a thermostated bath. Equilibration time was not reported. The phases were separated by centrifugation and analyzed for the content of the salt and water according to Refs. 1 and 2. Compositions of the phases reported are average results of two to three measurements. By analogy to other authors' work, the compiler assumes that equilibrium solid phases were identified by Schreinemakers method.

Source and Purity of Materials:

$UO_2(C_2O_2Cl_3)_2$ and its hydrates were prepared according to Ref. 3. Methyl isobutylketone was a reagent grade product (source not specified) and was used without further purification.

Estimated Error:

Temperature: precision ± 0.05 K (authors).
Solubility: precision not reported.

References:

[1] V. M. Vdovenko *et al.*, Radiokhimiya **17**, 58 (1975).
[2] A. V. Balue and I. G. Suglubova, in *The Chemistry of Uranium* (in Russian), edited by B. N. Laskorin (Nauka, Moscow, 1989), p. 188.
[3] V. M. Vdovenko, A. V. Baluev, and I. G. Suglubova, in *Complex Formation and Extraction of Lanthanides and Actinides* (in Russian) (Nauka, Leningrad, 1974), p. 35.

5.10. Uranium(VI) Dioxo Bis(benzenesulfonate)+Phosphoric Acid Tri-*n*-Butyl Ester+Water System

Components:

(1) Uranium(VI) dioxo bis(benzenesulfonate); $UO_2(C_6H_5O_3S)_2$; [94667-45-5]
(2) Phosphoric acid tri-*n*-butyl ester; $C_{12}H_{27}O_4P$; [126-73-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. V. Baluev, I. G. Suglubova, and A. P. Taranov, Radiokhimiya **30**, 349–54 (1988).

Variables:

T/K: 298
100 w_2 /mass%: 0–52.64
100 w_3 /mass%: 0–26.06

Prepared by:

J. Hála

Experimental Data

Composition of binary tri-*n*-butyl phosphate–water solutions saturated with $UO_2(C_6H_5O_3S)_2$, and phase diagram of the $UO_2(C_6H_5O_3S)_2$–$C_{12}H_{27}O_4P$–H_2O system at 25 °C

$C_{12}H_{27}O_4P$ (100 w_2 /mass%)[b]	H_2O (100 w_3 /mass%)	$UO_2(C_6H_5O_3S)_2$ (100 w_1 /mass%)	Solid phase[a]
52.64	0	47.36[c]	A
49.94	0.88	49.18	A
45.98	2.01	52.11	A+B
43.87	3.09	53.04	B
34.45	6.02	59.40	B
28.03	9.48	62.49	B
14.71	19.10	66.19	B
2.97	25.76	71.27	B
0	26.06	73.93[d]	B

[a] (A) $UO_2(C_6H_5O_3S)_2$, [94667-45-5]; (B) $UO_2(C_6H_5O_3S)_2 \cdot H_2O$, [ ].
[b] Calculated by compiler by difference.
[c] Solubility at 25 °C of $UO_2(C_6H_5O_3S)_2$ in dry tri-*n*-butyl phosphate; $m_1 = 1.54$ mol kg^{-1} (compiler).
[d] Solubility at 25 °C of $UO_2(C_6H_5O_3S)_2$ in water; $m_1 = 4.85$ mol kg^{-1} (compiler).

Phase diagram (Fig. 12) of the $UO_2(C_6H_5O_3S)_2$–$C_{12}H_{27}O_4P$–H_2O system at 25 °C.

Additional information:

The phase diagram of the $UO_2(C_6H_5O_3S)_2$–H_2O–$C_{12}H_{27}O_4P$ system at 25 °C was studied by the ^{1}H the nuclear magnetic resonance (NMR) method[1] with fairly good agreement with the data reported in the compiled document, except for some differences in the boundary between regions A and B.

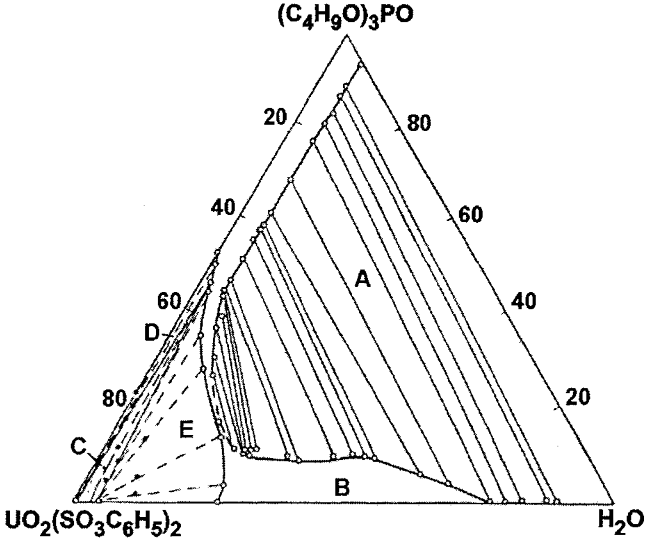

FIG. 12. Uranium (VI) dioxooxalate–sodium oxalate–water system. Legend to the phase diagram: (A) two-phase region; (B) unsaturated aqueous–organic solutions; (C) saturated solutions in equilibrium with $UO_2(C_6H_5O_3S)_2$ and $UO_2(C_6H_5O_3S)_2 \cdot H_2O$; (D) saturated solutions in equilibrium with $UO_2(C_6H_5O_3S)_2$; (E) saturated solutions in equilibrium with $UO_2(C_6H_5O_3S)_2 \cdot H_2O$.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Calculated amounts of the salt, tri-*n*-butylphosphate and water were equilibrated in sealed glass ampoules protected from light in a thermostated bath for 4 days which was found sufficient for equilibrium to be reached. The phases were allowed to separate on standing or by centrifugation, and analyzed for the content of uranium and water by gravimetric (unspecified) and Fischer methods, respectively. By analogy to other authors' work the compiler assumes that the equilibrium solid phases were identified by Schreinemakers' method.

Source and Purity of Materials:

$UO_2(C_6H_5O_3S)_2 \cdot H_2O$ was prepared by dissolving amorphous UO_3 in aqueous solutions of benzenesulfonic acid, and crystallizing the salt. Anhydrous salt was obtained by vacuum dehydration of the hydrate according to Ref. 2. Tri-*n*-butylphosphate was purified according to Ref. 3, and then distilled at 15 mm Hg pressure. Fraction boiling at 172–175 °C was collected for use.

Estimated Error:

Temperature: precision ±0.05 K (authors).
Solubility: precision not reported.

References:

[1] E. O. Ashevskaya, L. L. Scherbakova, and V. A. Scherbakov, J. Radioanal. Nucl. Chem., Articles **143**, 307 (1990).
[2] A. V. Baluev, S. G. Krylov, I. G. Suglubova, and A. P. Taranov, Vest. Leningrad. Gosud. Univ., Phys. Chem. **22**, 36 (1984).
[3] H. Irving, and D. N. Edgington, J. Inorg. Nucl. Chem. **10**, 306 (1959).

5.11. Uranium(IV) Oxalate

5.11.1. Evaluation of the $U(C_2O_4)_2+H_2O$ System

Components:	**Evaluator:**
(1) Uranium(IV) bis(oxalate); $U(C_2O_4)_2$; [2847-15-6] (2) Water; H_2O; [7732-18-5]	J. Hála, Department of Inorganic Chemistry, Masaryk University, 611 37 Brno, Czech Republic, May 2000

Critical Evaluation:

The only extensive study on this system has been carried out by Grinberg and Petrzhak[1] who measured the solubility of $U(C_2O_4)_2 \cdot 6H_2O$ in water at 298 K as a function of specific activity of the salt and equilibration time by two different equilibration techniques, and used three different methods for the determination of uranium in the saturated solutions. They observed rather large scatter of results, and ascribed it to low dissolution rate of the salt and consequently to slow attainment of equilibrium. Moreover, the results obtained when uranium was determined by coprecipitation with LaF_3 (which enabled them to eliminate the influence of UO_2^{2+} produced by oxidation of U(IV)) were consistently much lower than those based on total uranium concentration in the saturated solutions. This indicated that the solubility of $U(C_2O_4)_2$ was rather sensitive to oxidation of U(IV) by traces of oxygen in solutions which could not be eliminated even though the measurements were performed in an inert atmosphere. The dissolution process was further complicated by the fact that during oxidation of $U(C_2O_4)_2$ to $UO_2C_2O_4$, oxalic acid was released, and caused the solubility of $U(C_2O_4)_2$ further to increase. Because of these processes, the authors considered the $U(C_2O_4)_2-H_2O$ system to be a nonequilibrium one. As the most reliable solubility value they proposed that obtained by the LaF_3 method, i.e., 20–25 $mgU(C_2O_4)_2 \cdot 6H_2O$ per dm^3. Taking the average of the two values, the evaluator obtained the solubility of $U(C_2O_4)_2$ in water at 298 K as 4.3×10^{-5} mol kg^{-1}, which is suggested to be used as a tentative value. It is almost identical with that of Zakharova and Moskvin[2] who, in their study of the ternary $U(C_2O_4)_2-HCl-H_2O$ system, obtained the solubility to be 4.27×10^{-5} mol kg^{-1}. These authors, however, did not specify the temperature of the measurement, or comment on the effect of the oxidation of U(IV) in this system. Originally, Grinberg and Petrzhak reported the solubility of $U(C_2O_4)_2$ in water to be 9.7×10^{-5} mol kg^{-1}.[3] In their more recent study[1] they rejected this value as erroneously high due to the interference from oxidation of U(IV).

References:

[1] A. A. Grinberg and G. I. Petrzhak, Radiokhimiya **5**, 319 (1963).
[2] F. A. Zakharova and A. I. Moskvin, Zh. Neorg. Khim. **5**, 1228 (1960).
[3] A. A. Grinberg and G. I. Petrzhak, Zh. Neorg. Khim. **3**, 204 (1958).

Components:
(1) Uranium(IV) bis(oxalate); $U(C_2O_4)_2$; [2847-15-6]
(2) Water; H_2O; [7732-18-5]

Original Measurements:
A. A. Grinberg, G. I. Petrzhak, and L. I. Evteev, Zh. Neorg. Khim. **3**, 204–11 (1958).

Variables:
T/K: 298

Prepared by:
J. Hála

Experimental Data

The solubility in water of $U(C_2O_4)_2 \cdot 6H_2O$ was reported to be 0.051 g salt/kg H_2O or 9.7×10^{-5} mol kg^{-1} at 25 °C

Additional information:
The pH of the saturated solutions was 4.3 on average, and the molar electrical conductivity varied between 451 and 495 Ω^{-1} cm^{-2}. From this the authors concluded that in the saturated solutions $U(C_2O_4)_2$ is fully dissociated according to the equation

$$U(C_2O_4)_2(H_2O)_n + 2H_2O \leftrightarrows U(C_2O_4)(H_2O)_{n+2}^{2+} + C_2O_4^{2-}$$

while the $U(C_2O_4)(H_2O)_{n+2}^{2+}$ ion dissociated by about 70% according to the reaction

$$U(C_2O_4)(H_2O)_{n+2}^{2+} \leftrightarrows U(C_2O_4)(H_2O)_{n+1}(OH)^{+} + H^{+}$$

Auxiliary Information

Method/Apparatus/Procedure:
Nothing specified in the document compiled. By analogy to a more recent authors' paper[1] it can be assumed that isothermal method was used, that the solutions were brought to saturation for 6–8 h under H_2 atmosphere, and that oxalate concentration in the saturated solutions was determined titrimetrically with $KMnO_4$ solution.

Source and Purity of Materials:
Nothing specified.

Estimated Error:
Precision of temperature or solubility measurement not reported.

References:
[1] A. A. Grinberg and G. I. Petrzhak, Radiokhimiya **5**, 319 (1963).

Components:
(1) Uranium(IV) bis(oxalate); $U(C_2O_4)_2$; [2847-15-6]
(2) Water; H_2O; [7732-18-5]

Original Measurements:
A. A. Grinberg and G. I. Petrzhak, Radiokhimiya, **5**, 319–29 (1963).

Variables:
T/K: 298
Specific activity of $U(C_2O_4)_2$

Prepared by:
J. Hála

Experimental Data

Solubility at 25 °C of $U(C_2O_4)_2$ in water

Isothermal method-modification A (see Method section)

$U(C_2O_4)_2 \cdot 6H_2O$ (g)[a]	$U(C_2O_4)_2 \cdot 6H_2O$ (counts min^{-1} mg^{-1})[b]	Equilibration time (h)	$U(C_2O_4)_2 \cdot 6H_2O$ (mg dm^{-3})[c]	$U(C_2O_4)_2 \cdot 6H_2O$ (mg dm^{-3})[d]
0.25	8.75×10^3	9	44	21
0.30	5.92×10^3	9.5	46	15
		13.5	—	24
1.00	5.92×10^3	0.5	45	17
		23.5	56	22
	7.20×10^3	9.5	40	18
		23.5	98	25
		5.5[e]	71	18
		9.5[e]	100	28
0.10	7.20×10^6	4.0	25	14
		7.0	40	16
0.20	4.64×10^6	6	24	8
		16	44	13
		23	75	14
		30	68	15
		37	83	19
		50	97	18
		86	100	19
0.20	4.64×10^6	7	23	9
		11	30	9
		18	45	10
		22	54	15
		26	70	17
1.07	4.64×10^6	5.5	54	7
		11.5	77	10
		24	101	13
		52	140	20
		87	189	31
		122	238	32
		170	274	32

[a] Amount of $U(C_2O_4)_2 \cdot 6H_2O$ used in the experiment.
[b] Specific activity of $U(C_2O_4)_2 \cdot 6H_2O$.
[c] Obtained by direct α counting.
[d] Obtained by coprecipitation with LaF_3.
[e] In the presence of air.

Additional information:
An average solubility value of ~20 mg $U(C_2O_4)_2 \cdot 6H_2O$/dm^3 (~3.8×10^{-5} mol dm^{-3}; compiler) was given by the authors based on the LaF_3 method of uranium determination.

Isothermal method-modification B

$U(C_2O_4)_2\cdot6H_2O$ (counts min^{-1} mg^{-1})[a]	Equilibration time (h)	$U(C_2O_4)_2\cdot6H_2O$ (mg dm^{-3})[b]	$U(C_2O_4)_2\cdot6H_2O$ (mg dm^{-3})[c]	$U(C_2O_4)_2\cdot6H_2O$ (mg dm^{-3})[d]
1.57×10^3[e]	6	86	94	—
1.19×10^3[e]	35	93	97	25
	11	109	—	—
	24	172	188	—
	30	183	189	—
	100	182	179	32
2.89×10^3[f]	9	23	25	—
2.55×10^3[f]	14	74	71	—
	20	69	65	—
	34	72	73	26
	180	113	92	22
	200	109	100	24
	200	111	103	27
4.64×10^3[f]	19	—	97	17
	31	—	100	16
	157	—	100	17

[a] Specific activity of $U(C_2O_4)_2\cdot6H_2O$ used in the experiment.
[b] Obtained by electroplating.
[c] Obtained by direct α counting.
[d] Obtained by coprecipitation onto LaF_3.
[e] Measurements carried out with finely ground $U(C_2O_4)_2\cdot6H_2O$.
[f] Coarse crystalline $U(C_2O_4)_2\cdot6H_2O$ placed in boiling water and cooled in a stream of nitrogen gas.

Additional information:

An average solubility value of ~25 mg dm^{-3} $U(C_2O_4)_2\cdot6H_2O$ ($\sim4.8\times10^{-5}$ mol dm^{-3}; compiler) was given by the authors based on the LaF_3 method of uranium determination.

The authors state that the great scatter of solubility values obtained by the three methods was due to the low dissolution rate of $U(C_2O_4)_2\cdot6H_2O$, and consequently to slow attainment of equilibrium, and—as indicated by the difference in the figures obtained by different analytical methods—also by partial oxidation of uranium(IV). The latter effect was caused by traces of O_2 not removed from the system, and partially by the products of radiolysis of water. The process of $U(C_2O_4)_2\cdot6H_2O$ dissolution was further complicated by the fact that during its oxidation to $UO_2C_2O_4$, oxalic acid was released which increased the solubility of $U(C_2O_4)_2$ and at the same time hindered its oxidation. Because of these processes, the authors characterized the $U(C_2O_4)_2-H_2O$ system as a nonequilibrium one, and concluded the solubility of $U(C_2O_4)_2$ in water given by them in a previous paper[1] to be erroneous.

Auxiliary Information

Source and Purity of Materials:

$U(C_2O_4)_2\cdot6H_2O$ labeled with ^{233}U was prepared by reduction of UO_2^{2+} with rongalite in acidic solutions. Hydrogen gas was freed from oxygen by passing it over palladium-treated asbestos.

Estimated Error:

Temperature: precision ±0.1 K for method A, ± 0.3 K for method B (authors).

References:

[1] A. A. Grinberg, E. I. Petrzhak, and L. I. Evteev, Zh. Neorg. Khim. **3**, 204 (1958).
[2] A. A. Grinberg, L. E. Nikolskaya, G. I. Petrzhak, V. I. Spitsyn, and F. M. Filinov, Zh. Anal. Khim. **12**, 92 (1957).

5.11.2. Evaluation of the $U(C_2O_4)_2+HCl+H_2O$ System

Components:	Evaluator:
(1) Uranium(IV) bis(oxalate); $U(C_2O_4)_2$; [2847-15-6] (2) Hydrogen chloride; HCl; [7647-01-0] (3) Water; H_2O; [7732-18-5]	J. Hála, Department of Inorganic Chemistry, Masaryk University, 611 37 Brno, Czech Republic, May 2000

Critical Evaluation:

The solubility of $U(C_2O_4)_2$ in aqueous HCl solutions was measured as a function of HCl concentration in two documents.[1,2] In the work of Dorough,[1] the measurements were carried out at 298 K, and care was taken to prevent uranium(IV) from oxidation by oxygen dissolved in the solutions measured. No such precautions were taken in the work of Zakharova and Moskvin[2] where, besides this, temperature was not specified. In spite of this, both sets of data fit on one curve when plotted graphically. Owing to the less defined conditions in Ref. 2, however, the evaluator suggests the data of Dorough[1] be given preference.

References:

[1] G. D. Dorough, U. S. At. Energy Comm. Report TID 5290, Book 2, 1958, p. 535.
[2] F. A. Zakharova and A. I. Moskvin, Zh. Neorg. Khim. **5**, 1228 (1960).

Components:

(1) Uranium(IV) bis(oxalate); $U(C_2O_4)_2$; [2847-15-6]
(2) Hydrogen chloride; HCl; [7647-01-0]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

G. D. Dorough, U. S. At Energy Comm., TID 5290, Book 2, 1958, pp. 535–42.

Variables:

T/K: 298
c_2 /mol dm^{-3}: 0.118–6.18

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $U(C_2O_4)_2 \cdot 6H_2O$ in HCl solutions[a]

HCl (c_2 / mol dm^{-3})	U (mg dm^{-3})	$U(C_2O_4)_2$[f] ($10^4 c_1$ / mol dm^{-3})	K[g] (10^{22} mol^4 dm^{-12})	HCl (c_2 / mol dm^{-3})	U (mg dm^{-3})	$U(C_2O_4)_2$[f] ($10^4 c_1$ / mol dm^{-3})	K[g] (10^{22} mol^4 dm^{-12})
0.118	5.15[c]			3.62	142[c]		
	5.51[c]				142[c]		
	5.33[b]	0.224	2.87		142[b]	5.97	0.575
1.049	28.9[c]			6.01	536[c]		
	28.3[c]				462[c]		
	28.6[b]	1.20	1.23		523[d]		
1.18	37.3[c]				465[d]		
	38.3[b]				518[e]		
	37.8[b]	1.59	1.65		458[e]		
3.09	99.3[c]				494[b]	20.8	0.68
	107[c]			6.18	515[d]		
	112[d]				461[d]		
	101[d]				488[b]	20.5	0.508
	105[b]	4.41	0.56				

[a] Equilibrium solid phases were not investigated.
[b] Average value (author).
[c] Determined by plating.
[d] Determined by the filter paper method.
[e] Determined by an unspecified volumetric method.
[f] Calculated by compiler.
[g] Equilibrium constant for the reaction $U(C_2O_4)_2(H_2O)_{(s)} \leftrightarrows U(OH)^{3+} + 2C_2O_4^{2-} + H^+$, calculated by the author as $K = [U(OH)^{3+}] \times [C_2O_4^{2-}]^2[H^+]$ by using mean ionic activity coefficients of HCl as interpolated from the data in Ref. 1, and the dissociation constants of oxalic acid, $K_{a1} = 5.9 \times 10^{-2}$ and $K_{a2} = 6.4 \times 10^{-5}$ (source not given).

Additional information:

Based on the value of the constant K, the author concluded that nearly complete hydrolysis of U(IV) to $U(OH)^{3+}$ took place in HCl solutions saturated with $U(C_2O_4)_2$.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Great care was taken to prevent oxidation of U(IV) oxalate since $UO_2C_2O_4$ is relatively quite soluble. Prior to solubility determination, the solutions were boiled to remove dissolved O_2 and then kept under N_2 atmosphere. A sample of UO_2^{2+}-free U(IV) oxalate was washed a number of times with the solution in which the solubility was to be measured and shaken with the same solution in a glass-stoppered flask under N_2 atmosphere in a thermostated bath. After 24 h the saturated solution was withdrawn through a suction filter apparatus, and analyzed for uranium content by α counting. Two methods were used to prepare the samples for counting. In the electroplating method, the samples of the saturated solutions were converted to UO_2SO_4 by fuming with concentrated H_2SO_4, diluted with water, and electrodeposited on a platinum cathode as UF_4 from sodium fluoride solution. The cathode was then ignited and α counted. In the filter paper method, the samples of the saturated solutions were converted to UO_2SO_4, an aliquot was placed on a filter paper, which was then mounted on a copper disk, dried, and counted. No differences were note in samples prepared by approaching equilibrium from above and below the equilibrium temperature. All measurements were made on $U(C_2O_4)_2$ samples 3 days old, since freshly precipitated $U(C_2O_4)_2$ was reported to have a considerably higher solubility.[2]

Source and Purity of Materials:

$U(C_2O_4)_2 \cdot 6H_2O$ was prepared from UO_3. The latter was dissolved in HCl (1:1), and the resulting solution of UO_2Cl_2 was reduced electrolytically to U(IV), which was precipitated with oxalic acid. The precipitate was filtered, washed with boiled 3 mol dm^{-3} HCl, and shaken with oxygen-free 3 mol dm^{-3} HCl vigorously for 3 h in N_2 atmosphere. The last operation was repeated three times. Source and purity of chemicals used not specified.

Estimated Error:

Uranium concentration: standard deviation of the mean =1.1%–6% (author).

References:

[1] G. N. Lewis and M. Randall, *Thermodynamics* (McGraw–Hill, New York, 1923), p. 336.
[2] E. L. Wagner, The Solubility and Solubility Product of U(IV) Oxalate, Report RL-4.6.321.

Components:

(1) Uranium(IV) bis(oxalate); $U(C_2O_4)_2$; [2847-15-6]
(2) Hydrogen chloride; HCl; [7647-01-0]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

F. A. Zakharova and A. I. Moskvin, Zh. Neorg. Khim. **5**, 1228–33; Russ. J. Inorg. Chem. **5**, 592–5 (1960).

Variables:

c_2 /mol dm^{-3}: 0–3.0

Prepared by:

J. Hála

Experimental Data

Solubility at °C of $U(C_2O_4)_2\cdot 6H_2O$ in HCl solutions[a]

HCl (c_2 /mol dm^{-3})	$U(C_2O_4)_2\cdot 6H_2O$ (10^2g dm^{-3})[b]	$U(C_2O_4)_2\cdot 6H_2O$ (10^4c_1 /mol dm^{-3})[c]	K_{sp}[d] (10^{22} mol^3 dm^{-9})	K_{sp}[e] (10^{25} mol^3 dm^{-9})
0	2.23	0.427	—	—
0.1	1.26	0.241	—	—
0.3	1.71	0.328	6.6	2.1
0.5	2.19	0.419	2.8	0.5
1.0	5.00	0.958	3.2	0.8
2.0	14.00	2.86	—	—
3.0	23.56	4.51	—	—
			4.3 ± 1.6[f]	1.1 ± 0.7[f]

[a] Measurements were conducted at unspecified temperature. Equilibrium solid phases were not investigated.

[b] Average value of three measurements.

[c] Calculated by compiler.

[d] Calculated by authors as $K_{sp}=[U^{4+}][C_2O_4^{2-}]^2$ by using the U^{4+} and $C_2O_4^{2-}$ concentrations obtained from equilibrium constants for the reactions $U(C_2O_4)_2+2H^+\leftrightarrows U(C_2O_4)^{2+}+C_2H_2O_4$, and $U(C_2O_4)_2+4H^+\leftrightarrows U^{4+}+2C_2H_2O_4$ determined from the solubility data, and the dissociation constants of oxalic acid taken from Ref. 1. Hydrolysis of U^{4+} and the formation of the UCl^{3+} complex were considered using the appropriate data from Ref. 2.

[e] Source of activity coefficients not reported.

[f] Average value (authors).

Additional information:

In another approach, the equilibrium constant for the reaction $U(C_2O_4)_2+4H^+\leftrightarrows U^{4+}+2C_2H_2O_4$ was obtained as $K=1.5\times10^{-11}$ mol^{-2} dm^6, and from this the solubility product of $U(C_2O_4)_2$ was obtained as $K_{s0}=K(K_{a1}K_{a2})^2=7.0\times10^{22}$ mol^3 dm^{-9} with dissociation constants of oxalic acid taken from Ref. 1.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Solutions containing excess solid were equilibrated for 4–6 h which was sufficient for equilibrium to be reached. Uranium in the saturated solutions was determined by α counting.

Source and Purity of Materials:

$U(C_2O_4)_2\cdot 6H_2O$ was prepared from ^{233}U-labeled $UO_2(NO_3)_2$ solution by reduction with rongalite. U(IV) oxalate was dissolved in $(NH_4)_2C_2O_4$ solution,the solution was centrifuged, and the oxalato complex decomposed with HCl. $U(C_2O_4)_2\cdot 6H_2O$ precipitated was centrifuged, washed to remove excess oxalic acid, and air dried. Source and purity of chemicals not reported.

Estimated Error:

α counting: precision ±5% (authors).

References:

[1] L. E. Drabkina, A. I. Moskvin, and A. D. Gelman, Zh. Neorg. Khim. **3**, 1934 (1958).[2] K. A. Kraus and F. Nelson, J. Am. Chem. Soc. **72**, 3901 (1950).

Components:

(1) Uranium(IV) bis(oxalate); $U(C_2O_4)_2$; [2847-15-6]
(2) Sulfuric acid; H_2SO_4; [7664-93-9]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

G. D. Dorough, U. S. At Energy Comm., TID 5290, Book 2, 1958, pp. 535–542.

Variables:

T/K: 298
c_2 /mol dm^{-3}: 0.515

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $U(C_2O_4)_2\cdot 6H_2O$ in 0.515 mol dm^{-3} H_2SO_4 solution[a]

H_2SO_4 (c_2 /mol dm^{-3})	U (mg dm^{-3})	$U(C_2O_4)_2$[c] (10^4c_1 /mol dm^{-3})
0.515	160	
	174	
	167[b]	7.02

[a] Equilibrium solid phases were not investigated.

[b] Average value (author).

[c] Calculated by compiler.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Great care was taken to prevent oxidation of U(IV) oxalate since $UO_2C_2O_4$ is relatively quite soluble. Prior to solubility determination, the solutions were boiled to remove dissolved O_2 and then kept under N_2 atmosphere. A sample of UO_2^{2+}-free U(IV) oxalate was washed a number of times with the solution in which the solubility was to be measured and shaken with the same solution in a glass-stoppered flask under N_2 atmosphere in a thermostated bath. After 24 h the saturated solution was withdrawn through a suction filter apparatus, and analyzed for uranium content by α counting. Samples of the saturated solutions were converted to UO_2SO_4 by fuming with concentrated H_2SO_4, diluted with water, and electrodeposited on a platinum cathode as UF_4 from sodium fluoride solution. The cathode was then ignited and α counted. All measurements were made on $U(C_2O_4)_2$ samples 3 days old, since freshly precipitated $U(C_2O_4)_2$ has a considerably higher solubility.[1]

Source and Purity of Materials:

$U(C_2O_4)_2\cdot 6H_2O$ was prepared from UO_3. The latter was dissolved in HCl (1:1), and the resulting solution of UO_2Cl_2 was reduced electrolytically to U(IV), which was precipitated with oxalic acid. The precipitate was filtered, washed with boiled 3 mol dm^{-3} HCl, and shaken with oxygen-free 3 mol dm^{-3} HCl vigorously for 3 h in N_2 atmosphere. The last operation was repeated three times. Source and purity of chemicals used not specified.

Estimated Error:

Temperature: precision not reported.
Uranium concentration: standard deviation of the mean=4% (author).

References:

[1] E. L. Wagner, The Solubility and Solubility Product of U(IV) Oxalate, Report RL-4.6.321.

Components:

(1) Uranium(IV) bis(oxalate); $U(C_2O_4)_2$; [2847-15-6]
(2) Perchloric acid; $HClO_4$; [7601-90-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

N. M. Nikolaeva, Izv. Sibirsk. Otdel. Akad. Nauk SSSR, Ser. Khim. Nauk. **6**, 64–9 (1979).

Variables:

T/K: 298–363
c_2 /mol dm^{-3}: 0.1 and 0.735

Prepared by:

J. Hála

Experimental Data

Solubility in HCl solutions of $U(C_2O_4)_2 \cdot 6H_2O$ as a function of temperature[a]

$HClO_4$ (c_2 /mol dm^{-3})	Temperature (°C)	U ($10^5 c_1$ /mol dm^{-3})	$HClO_4$ (c_2 /mol dm^{-3})	Temperature (°C)	U ($10^5 c_1$ /mol dm^{-3})
0.1005	25	1.5	0.735	25	3.75
	40	1.8		40	6.35
	50	2.0		50	9.20
	60	3.4		60	15.2
	70	4.6		70	21.6
	80	6.8		80	30.8
	90	10.7		90	40.6

[a] Equilibrium solid phases were not investigated.

Additional Information:

The author described the solubility of $U(C_2O_4)_2 \cdot 6H_2O$ in 0.1 mol dm^{-3} HCl by the reaction

$$U(C_2O_4)_2 \cdot 6H_2O_{(s)} \leftrightarrows U(C_2O_4)_{2(aq)}$$

In 0.735 mol dm^{-3} HCl the following reaction was reported to take place in the solution:

$$U(C_2O_4)_{2(aq)} + 2H^+ \leftrightarrows U(C_2O_4)^{2+} + H_2C_2O_4$$

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess $U(C_2O_4)_2 \cdot 6H_2O$ was equilibrated with 50 mL solution of the desired composition in a thermostated teflon vessel. Agitation of the mixture was carried out by means of a stream of argon gas. Equilibrium was reached within 4–5 h. Saturated solutions were analyzed for uranium content either photometrically with arsenazo III in 4 mol dm^{-31} or, at higher uranium concentrations, titrimetrically with standard $KMnO_4$ solution.

Source and Purity of Materials:

$U(C_2O_4)_2 \cdot 6H_2O$ was prepared by adding hot (90 °C) solution of oxalic acid saturated at room temperature to a boiling solution of U(IV) obtained by electrolytic reduction of UO_2Cl_2. Pale green hexahydrate was kept on water bath for 30 min, filtered, and washed three or four times with hot water. The product was analyzed gravimetrically for uranium (as U_3O_8), and titrimetrically for oxalate content. It contained 2% free oxalic acid.

Estimated Error:

Temperature: precision ± 0.1 K (author).
Solubility: insufficient data given to allow for error estimate.

References:

[1] D. I. Ryabchikov and M. M. Senyavina, Eds., *Analytical Chemistry of Uranium* (in Russian) (Acad. Sci. USSR, 1962), p. 134.

Components:

(1) Uranium(IV) bis(oxalate); $U(C_2O_4)_2$; [2847-15-6]
(2) Sodium oxalate; $C_2O_4Na_2$; [62-76-0]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

N. M. Nikolaeva, Izv. Sibirsk. Otdel. Akad. Nauk SSSR, Ser. Khim. Nauk. **6**, 64–9 (1979).

Variables:

T/K:298–363
c_2 /mol dm^{-3}:0.01

Prepared by:

J. Hála

Experimental Data

Solubility in 0.01 mol dm^{-3} $C_2O_4Na_2$ solutions of $U(C_2O_4)_2 \cdot 6H_2O$ as a function of temperature[a]

Temperature (°C)	$U(C_2O_4)_2$ ($10^3 c_1$ /mol dm^{-3})
25	5.52
40	5.95
50	6.21
60	6.51
70	6.68
80	7.25
90	7.71

[a] Equilibrium solid phases were not investigated.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess $U(C_2O_4)_2 \cdot 6H_2O$ was equilibrated with 50 ml 0.01 mol dm^{-3} $C_2O_4Na_2$ solution in a thermostated teflon vessel. Agitation of the mixture was carried out by means of a stream of argon gas. Equilibrium was reached within 4–5 h. Saturated solutions were analyzed for uranium content either photometrically with arsenazo III in 4 mol dm^{-31} or, at higher uranium concentrations, titrimetrically with standard $KMnO_4$ solution.

Source and Purity of Materials:

$U(C_2O_4)_2 \cdot 6H_2O$ was prepared by adding hot (90 °C) solution of oxalic acid saturated at room temperature to a boiling solution of U(IV) obtained by electrolytic reduction of UO_2Cl_2. Pale green hexahydrate was kept on water bath for 30 min, filtered, and washed three or four times with hot water. The product was analyzed gravimetrically for uranium (as U_3O_8), and titrimetrically for oxalate content. It contained 2% free oxalic acid.

Estimated Error:

Temperature: precision ±0.1 K (author). Solubility: insufficient data given to allow for error estimate.

References:

[1] D. I. Ryabchikov and M. M. Senyavina, Eds., *Analytical Chemistry of Uranium* (in Russian) (Acad. Sci. USSR, 1962), p. 134.

Components:

(1) Uranium(IV) bis(oxalate); $U(C_2O_4)_2$; [2847-15-6]
(2) Oxalic acid; $C_2O_4H_2$; [144-62-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. A. Grinberg and G. I. Petrzhak, Radiokhimiya **5**, 319–29 (1963).

Variables:

T/K:298
c_2 /mol dm^{-3}:0.0004–0.75

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $U(C_2O_4)_2$ in oxalic acid solutions[a]

$C_2O_4H_2$ (c_2 /mol dm^{-3})[a]	$U(C_2O_4)_2 \cdot 6H_2O$ (mg dm^{-3})	Method of U(IV) determination[b]	$U(C_2O_4)_2$ ($10^4 c_1$ /mol dm^{-3})[c]
0.0004	29 39	D	0.661
	39 35	E	
	33 32	P	
0.0005	38 41 36 35 43 44 43 43 46 42 45 39	D	0.779
	40	E	
	35	P	
0.005	53 49 52 54 58 56 60 57 61 60	E	1.07
0.042	67 72 66	D	1.36
	71 71 71	E	
	69 77 73	P	
0.05	84 80 81 81 88 91 87 89 85 83 74 76	D	1.60
	85 91	E	
	76 78	P	
0.125	116 114 118 116 114 115 117	D	2.22
0.21	140	D	2.76
	141	E	
	152	P	
0.25	154 151 149 145 151 154 142	D	2.95
	156 171 161	E	
	156 156 154	P	
0.335	167 162 166	D	3.16
0.50	201 190 122[d] 187 176 181 172 181 183	D	3.57
	189 190	E	
	194 190	P	
0.75	202 214 216 221 218 215 218 225 201 204	D	4.09

[a] Equilibrium solid phases were not investigated.
[b] (D) direct α counting; (E) α counting of electrodeposited uranium; (P) precipitation of U(IV) with La(III).
[c] Calculated by compiler by using the average value of authors' data of uranium concentration in the saturated solutions.
[d] This value was not considered when taking the average value.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method was used. First, the usual approach was tried in which excess $U(C_2O_4)_2 \cdot 6H_2O$ was stirred with solutions of oxalic acid in a thermostated vessel for 8–10 h until equilibrium was reached. To prevent oxidation of uranium(IV) by O_2 during the saturation process, electrolytically produced H_2 was bubbled through the solution. Samples of the saturated solutions were taken with a pipette with a cotton wad and α counted on a platinum target. When high oxalic acid concentration was present, the samples were first evaporated and ignited in a porcelain crucible to remove oxalic acid, the dry residue was then dissolved in 1.5 mol dm^{-3} HNO_3, and mounted onto a platinum target. Solubility data so obtained were ill reproducible, fluctuating within up to 30%–50% because of turbidity in some saturated solutions, which could not be removed by filtration. The following modification of the method yielded good results. 20–40 mg of $U(C_2O_4)_2 \cdot 6H_2O$ and a solution of oxalic acid were placed in a test tube, and a stream of N_2 was passed through for 5–10 min. Without interrupting the flow of gas the test tube was sealed, and then agitated for 30–360 h in an air-thermostated apparatus. Three samples for uranium determination were taken from each test tube, and uranium was determined by different methods in each one: (i) by direct α counting on a platinum target either with or without oxalic acid removal, (ii) α counting of uranium deposited electrolytically on platinum from HNO_3 solutions at pH 3 with current density of 0.5 A cm^{-2}, (iii) by coprecipitation of uranium(IV) with LaF_3 (0.5 mg La(III) used). The last method made it possible to judge the change in valency of uranium during the process of saturation. Since it yielded solubility data consistent with the other two methods, the authors concluded that oxidation of $U(C_2O_4)_2$ did not take place in oxalic acid solutions.

Source and Purity of Materials:

$U(C_2O_4)_2 \cdot 6H_2O$ labeled with ^{233}U was prepared by reduction of UO_2^{2+} with rongalite[1] in acidic solutions. H_2 and N_2 gases were freed from oxygen by passing them over palladium-treated asbestos or through alkaline solution of pyrogallol, respectively.

Estimated Error:

Temperature: precision ±0.3 K for measurements in sealed test tubes (authors). Solubility: insufficient data given to allow for error estimate.

References:

[1] A. A. Grinberg, L. E. Nikolskaya, G. I. Petrzhak, V. I. Spitsyn, and F. M. Filinov, Zh. Anal. Khim. **12**, 92 (1957).

Components:
(1) Uranium(IV) bis(oxalate); $U(C_2O_4)_2$; [2847-15-6]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Hydrogen chloride; HCl; [7647-01-1]
(4) Water; H_2O; [7732-18-5]

Original Measurements:
G. D. Dorough, U. S. At. Energy Comm., TID 5290, Book 2, 1958, pp. 535–42.

Variables:
T/K:298
$100w_2$ /mass%:0.26
c_3 /mol dm^{-3}:3.08 and 6.05

Prepared by:
J. Hála

Experimental Data

Solubility at 25 °C of $U(C_2O_4)_2 \cdot 6H_2O$ in $C_2H_2O_4$–HCl solutions[a]

HCl (c_3 /mol dm^{-3})	$C_2H_2O_4$ (100 w_2 /mass%)	U (mg dm^{-3})	$U(C_2O_4)_2$[c] (10^6 c_1 /mol dm^{-3})
3.084	0.26	1.4	
		1.64	
		1.52[b]	6.39
6.05	0.268	13.6	
		15.4	
		14.5[b]	60.9

[a] Equilibrium solid phases were not investigated.
[b] Average value (author).
[c] Calculated by compiler.

Additional information:

Attempts made by the author to calculate the solubility product of $U(C_2O_4)_2$ were unsuccessful because of unknown extent of hydrolysis and complexation of U(IV).

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Great care was taken to prevent oxidation of U(IV) oxalate since $UO_2C_2O_4$ is relatively quite soluble. Prior to solubility determination, the solutions were boiled to remove dissolved O_2 and then kept under N_2 atmosphere. A sample of UO_2^{2+}-free U(IV) oxalate was washed a number of times with the solution in which the solubility was to be measured and shaken with the same solution in a glass-stoppered flask under N_2 atmosphere in a thermostated bath. After 24 h the saturated solution was withdrawn through a suction filter apparatus, and analyzed for uranium content. Samples of the saturated solutions were converted to UO_2SO_4 by fuming with concentrated H_2SO_4, diluted with water, and electrodeposited on a platinum cathode as UF_4 from sodium fluoride solution. The cathode was then ignited and α counted. All measurements were made on $U(C_2O_4)_2$ samples 3 days old, since freshly precipitated $U(C_2O_4)_2$ was reported to have a considerably higher solubility.[1]

Source and Purity of Materials:

$U(C_2O_4)_2 \cdot 6H_2O$ was prepared from UO_3. The latter was dissolved in HCl (1:1), the resulting solution of UO_2Cl_2 was reduced electrolytically to U(IV), which was then precipitated with oxalic acid. The precipitate was filtered, washed with boiled 3 mol dm^{-3} HCl, and shaken with oxygen-free 3 mol dm^{-3} HCl vigorously for 3 h in N_2 atmosphere. The last operation was repeated three times. Source and purity of chemicals used not specified.

Estimated Error:

Uranium concentration: standard deviation of the mean $=(6-9)\%$ (author). Solubility: insufficient data given to allow for error estimate.

References:

[1] E. L. Wagner, The Solubility and Solubility Product of U(IV) Oxalate, Report RL-4.6.321.

Components:
(1) Uranium(IV) bis(oxalate); $U(C_2O_4)_2$; [2847-15-6]
(2) Ammonium oxalate; $(NH_4)_2C_2O_4$; [1113-38-8]
(3) Hydrogen chloride; HCl; [7647-01-0]
(4) Water; H_2O; [7732-18-5]

Original Measurements:
F. A. Zakharova and A. I. Moskvin, Zh. Neorg. Khim. **5**, 1228–33 (1960); Russ. J. Inorg. Chem. **5**, 592–5 (1960).

Variables:
c_2 /mol dm^{-3}:0.07–0.24
c_3 /mol dm^{-3}:0.5

Prepared by:
J. Hála

Experimental Data

Solubility of $U(C_2O_4)_2 \cdot 6H_2O$ in $(NH_4)_2C_2O_4$ solutions containing 0.5 mol dm^{-3} HCl[a]

$(NH_4)_2C_2O_4$ (c_2 /mol dm^{-3})	$U(C_2O_4)_2$ ($10^4 c_1$ /mol dm^{-3})
0.070	2.15
0.105	2.30
0.140	2.66
0.158	2.90
0.176	3.10
0.193	4.30
0.211	6.28
0.228	10.8
0.241	15.9

[a] Measurements were conducted at unspecified temperature. Composition of equilibrium solid phases was not investigated.

Additional information:

The increasing solubility of $U(C_2O_4)_2$ with increasing $(NH_4)_2C_2O_4$ concentration was ascribed by the authors to the formation of U(IV) oxalato complexes in the saturated solutions. From their solubility data the authors obtained overall instability constants of the $U(C_2O_4)_x^{4-2x}$ $(x=1-4)$ complexes.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Solutions containing excess solid were equilibrated for 4–6 h which was sufficient for equilibrium to be reached. Uranium in the saturated solutions was determined by α counting.

Source and Purity of Materials:

$U(C_2O_4)_2 \cdot 6H_2O$ was prepared from ^{233}U-labeled $UO_2(NO_3)_2$ solution by reduction with sodium sulfoxylate, and subsequent precipitation. U(IV) oxalate was dissolved in $(NH_4)_2C_2O_4$ solution, the solution was centrifuged, and the oxalato complex decomposed with HCl. $U(C_2O_4)_2 \cdot 6H_2O$ precipitated was centrifuged, washed to remove excess oxalic acid, and air dried. Source and purity of chemicals not reported.

Estimated Error:

α counting: precision ±5% (authors).

5.11.3. Potassium Tetrakis(Oxalato) Uranate(IV)

Components:
(1) Potassium tetrakis(oxalato)uranate(IV); $K_4U(C_2O_4)_4$; [ ]
(2) Water; H_2O; [7732-18-5]

Original Measurements:
N. A. Orlov, Zh. Russ. Fiz. Khim. Obsh. (J. Russ. Phys. Chem. Soc.) **34**, 375–80 (1902).

Variables:
T/K: 290

Prepared by:
J. Hála

Experimental Data

The solubility in water of $K_4U(C_2O_4)_4$ was reported to be 21.73 g salt in 100 g H_2O at 17 °C. This value was obtained from an experiment where 4.9878 g saturated solution yielded 0.8903 g dry residue after evaporation. The composition of the residue was not specified. Assuming the residue to be the hexahydrate, $K_4U(C_2O_4)_4 \cdot 6H_2O$, the compiler calculated the solubility of $K_4U(C_2O_4)_4$ to be $m_1 = 0.247$ mol kg^{-1}.

Auxiliary Information

Method/Apparatus/Procedure:
Isothermal method, no details reported.

Source and Purity of Materials:
$K_4U(C_2O_4)_4 \cdot 6H_2O$ was prepared as green crystals by dissolving $U(C_2O_4)_2 \cdot 6H_2O$ in concentrated solution of $K_2C_2O_4$, and allowing the solution to crystallize. The composition of the product was confirmed by chemical analysis: the product yielded 63.17% $K_2U_2O_7+K_2CO_3$ upon ignition, and 83.91% $UO_2SO_4+K_2SO_4$ upon fuming with concentrated H_2SO_4. Calculated for the hexahydrate: 63.27% and 83.63%, respectively.

5.11.4. Uranium(VI) Dioxo(oxalate)

5.11.5. Evaluation of the $UO_2C_2O_4+H_2O$ System

Components:
(1) Uranium(VI) dioxo(oxalate); $UO_2C_2O_4$; [2031-89-2]
(2) Water; H_2O; [7732-18-5]

Evaluator:
J. Hála, Department of Inorganic Chemistry, Masaryk University, 611 37 Brno, Czech Republic, May 2000

Critical Evaluation:

The most extensive study of the solubility of $UO_2C_2O_4$ in water is that of Colani[1] who reported solubilities over the temperature interval from 284.1 to 373.1 K. Other data have been published by Bolshakov *et al.*[2–4] in their studies of various ternary systems. While their value at 298.1 K (100 $w_1=0.58$ mass %; $m_1=0.0163$ mol kg^{-1})[2,3] is in excellent agreement with that of Colani,[1] their value at 273.1 K (100 $w_1=0.21$ mass %; $m_1=0.005\,88$ mol kg^{-1})[4] falls below the Colani's solubility/temperature curve. It is, therefore, recommended to use the data of Colani as tentative values. The two measurements at 287.1 and 373.1 K reported by Ebelmen[5] are somewhat dubious since it is not clear whether they refer to the anhydrous salt or to the trihydrate, $UO_2C_2O_4 \cdot 3H_2O$. Assuming the original data refer to the trihydrate which was reported to be the equilibrium phase in aqueous HNO_3 solutions containing less than 31 mass % HNO_3,[1,2] the solubility of the anhydrous salt at 373.1 K is found to be 100 $w_1=3.06$ mass % or $m_1=0.088$ mol kg^{-1}, which is in excellent agreement with Colani's measurements. The Ebelmen's value at 287.1 K seems to be erroneously high.

References:
[1] M. Colani, Bull. Soc. Chim. France **37**, 856 (1925).
[2] K. A. Bolshakov and S. S. Korovin, Trudy Mosk. Inst. Tonkoi Khim. Tekhnol. **7**, 165 (1958).
[3] K. A. Bolshakov and S. S. Korovin, Zh. Neorg. Khim. **2**, 1940 (1957).
[4] K. A. Bolshakov, V. E. Plyushchev, and T. A. Ermakova, Zh. Neorg. Khim. **2**, 222 (1957).
[5] M. Ebelmen, Ann. Chim. Phys. **5**, 189 (1842).

Components:
(1) Uranium(VI) dioxooxalate; $UO_2C_2O_4$; [2031-89-2]
(2) Water; H_2O; [7732-18-5]

Original Measurements:
M. Ebelmen, Ann. Chim. Phys. **5**, 189–223 (1842).

Variables:
T/K: 287; 373

Prepared by:
J. Hála

Experimental Data

The solubility in water of $UO_2C_2O_4$ was reported to be 0.8 and 3.4 g salt in 100 g H_2O at 14 and 100 °C, respectively.

Note: It it not clear whether these figures refer to the trihydrate, $UO_2C_2O_4 \cdot 3H_2O$, [18860-43-0], or to the anhydrous salt. Assuming that they refer to the trihydrate, the compiler calculated the solubility of the anhydrous salt as $w_1 = 0.69$ and 3.06 mass %, respectively.

Auxiliary Information

Method/Apparatus/Procedure:
Nothing specified.

Source and Purity of Materials:
$UO_2C_2O_4 \cdot 3H_2O$ was prepared by precipitation from a concentrated solution of $UO_2(NO_3)_2$ with a hot concentrated solution of oxalic acid. A viscous product was obtained which turned into a yellow crystalline powder after some time. It was purified by recrystallization.

Components:
(1) Uranium(VI) dioxooxalate; $UO_2C_2O_4$; [2031-89-2]
(2) Water; H_2O; [7732-18-5]

Original Measurements:
M. Colani, Bull. Soc. Chim. France **37**, 856–61 (1925).

Variables:
T/K: 284–373

Prepared by:
J. Hála

Experimental Data

Solubility of $UO_2C_2O_4$ in water as a function of temperature[a]

Temperature (°C)	$UO_2C_2O_4$ (100 w_1 /mass %)	$UO_2C_2O_4$ (mol kg^{-1})[b]
11	0.45	0.0126
15	0.47	0.0132
20	0.50	0.0140
50	1.00	0.0282
75	1.65	0.0469
100	3.06	0.0882

[a] The equilibrium solid phase was $UO_2C_2O_4 \cdot 3H_2O$, [18860-43-0] in all solutions.
[b] Calculated by compiler.

Auxiliary Information

Method/Apparatus/Procedure:
Nothing specified.

Source and Purity of Materials:
Nothing specified.

Estimated Error:
Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

5.11.6. Evaluation of the $UO_2C_2O_4+HNO_3+H_2O$ System

Components:
(1) Uranium(VI) dioxo(oxalate); $UO_2C_2O_4$; [2031-89-2]
(2) Nitric acid; HNO_3; [7697-37-2]
(3) Water; H_2O; [7732-18-5]

Evaluator:
J. Hála, Department of Inorganic Chemistry, Masaryk University, 611 37 Brno, Czech Republic, May 2000

Critical Evaluation:

The solubility of $UO_2C_2O_4$ in aqueous HNO_3 solutions was studied in four documents. In Refs. 1–3 the solubility of $UO_2C_2O_4$ was measured as a function of HNO_3 concentration, in mass %, at 293.1 K,[1,2] or 298.1 and 323.1 K,[3] while Moskvin and Zakharova[4] measured the solubility as a function of concentration of HNO_3 in mol dm^{-3} at 293.1 K. The two series of measurements performed at 293.1 K[1,2] do not coincide. The data of Amphlett and Davidge[2] are lower than those of Colani,[1] the difference being more pronounced with increasing HNO_3 concentration. The reason for this discrepancy is not clear since Colani[1] did not report any details of the procedure used. Another discrepancy exists between the data of Colani[1] and those of Bolshakov and Korovin.[3] While in the latter document the solubility of $UO_2C_2O_4$ was reported to increase with increasing temperature, the data obtained at 298.1 K[3] seem to be somewhat lower than those of Colani[1] taken at 293.1 K. The data of Moskvin and Zakharova[4] cannot be compared with those in Refs. 1–3 because of different concentration units used. For these reasons none of the published data can be given preference, and each set of data can be used as tentative one for the specific conditions for which they were obtained.

As for the equilibrium solid phases, Colani[1] and Bolshakov and Korovin[3] agree in that the trihydrate, $UO_2C_2O_4\cdot3H_2O$, [18860-43-0], exists in solutions containing less than 31 mass % HNO_3. However, at >48.5 mass % HNO_3, Bolshakov and Korovin[3] reported the solid phase to be the monohydrate, $UO_2C_2O_4\cdot H_2O$, [ ], while Amphlett and Davidge[2] reported the anhydrous salt, $UO_2C_2O_4$, [2031-89-2] to be in equilibrium with 58.9 mass % HNO_3.

References:
[1] M. Colani, Bull. Soc. Chim. France **37**, 856 (1925).
[2] C. B. Amphlett and O. T. Davidge, J. Chem. Soc. 2938 (1952).
[3] K. A. Bolshakov and S. S. Korovin, Trudy Mosk. Inst. Tonkoi Khim. Tekhnol. **7**, 165 (1958).
[4] A. I. Moskvin and E. A. Zakharova, Zh. Neorg. Khim. **4**, 2151 (1959).

Components:
(1) Uranium(VI) dioxooxalate; $UO_2C_2O_4$; [2031-89-2]
(2) Nitric acid; HNO_3; [7697-37-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
C. B. Amphlett and O. T. Davidge, J. Chem. Soc. 2938–9 (1952).

Variables:
T/K: 293
100 w_2 /mass %: 15.1–69.5

Prepared by:
J. Hála

Experimental Data

Composition of HNO_3 solutions saturated with $UO_2C_2O_4$ at 20 °C[a]

HNO_3 (100 w_2 /mass %)	HNO_3 (mol kg^{-1} of the HNO_3 /H_2O solvent)[b]	$UO_2C_2O_4$ (g/100 g of the HNO_3 /H_2O solvent)	$UO_2C_2O_4$ (100 w_1 /mass %)[b]	$UO_2C_2O_4$ (mol kg^{-1} of the HNO_3 /H_2O solvent)[b]
15.1	2.40	1.63	1.60	0.0455
26.8	4.25	1.88	1.85	0.0525
27.9	4.43	1.87	1.84	0.0522
35.8	5.68	2.19	2.14	0.0612
41.5	6.59	2.68	2.61	0.0749
42.0	6.67	2.84	2.76	0.0793
46.5	7.38	3.48	3.36	0.0972
58.9	9.35	4.04[b]	3.88	0.113
69.5	11.03	3.99	3.84	0.111

[a] Equilibrium solid phase at this HNO_3 concentration is the anhydrous salt, $UO_2C_2O_4$, [2031-89-2]; at lower HNO_3 concentrations it was the trihydrate, $UO_2C_2O_4\cdot3H_2O$, [18860-43-0].
[b] Calculated by compiler.

Auxiliary Information

Method/Apparatus/Procedure:
Isothermal method used. Excess solid was shaken with HNO_3 solutions for several days in flasks with securely waxed stoppers. 2 days sufficed to ensure saturation. The rate of oxalic acid decomposition was found to be too low to cause any displacement of equilibrium. The saturated solutions were analyzed for uranium and, after removal of uranium as peroxide, for free acid content. Methods of analysis were not specified. Attempts to determine the composition of the solid phase by direct analysis were only partly successful, owing to the difficulties encountered in removing adsorbed liquid from the solid without washing. One good duplicated determination was obtained for 58.9% HNO_3 system.

Source and Purity of Materials:
$UO_2C_2O_4\cdot3H_2O$ was prepared by precipitation from aqueous $UO_2(NO_3)_2$ solution with sodium oxalate. The precipitate was filtered, washed free from NO_3^-, and dried at 60 °C. Analysis for uranium and oxalate content corresponded to the trihydrate. Source and purity of materials used not specified.

Estimated Error:
Temperature: precision ±1 K (authors).
Solubility: insufficient data given to allow for error estimate.

Components:
(1) Uranium(VI) dioxooxalate; $UO_2C_2O_4$; [2031-89-2]
(2) Nitric acid; HNO_3; [7697-37-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
M. Colani, Bull. Soc. Chim. France **37**, 856–61 (1925).

Variables:
T/K: 293
100 w_2 /mass%: 1.84–31.0

Prepared by:
J. Hála

Experimental Data

Composition of HNO_3 solutions saturated with $UO_2C_2O_4$ at 20 °C[a]

HNO_3 (100 w_2 /mass %)	$UO_2C_2O_4$ (100 w_1 /mass %)	$UO_2C_2O_4$ (mol kg^{-1} of the HNO_3 /H_2O solvent)[b]
1.84	0.79	0.0222
5.34	1.19	0.0336
12.14	1.56	0.0443
17.60	1.76	0.0500
21.47	1.88	0.0535
31.00	2.28	0.0652

[a] The equilibrium solid phase was $UO_2C_2O_4 \cdot 3H_2O$, [18860-43-0], in all solutions.
[b] Calculated by compiler.

Auxiliary Information

Method/Apparatus/Procedure:
Nothing specified.

Source and Purity of Materials:
Nothing specified.

Estimated Error:
Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

Components:
(1) Uranium(VI) dioxooxalate; $UO_2C_2O_4$; [2031-89-2]
(2) Nitric acid; HNO_3 ; [7697-37-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
K. A. Bolshakov and S. S. Korovin, Trudy Mosk. Inst. Tonkoi Khim. Tekhnol. **7**, 165–70 (1958).

Variables:
T/K: 298; 323
100w_2 /mass %: 0–77

Prepared by:
J. Hála

Experimental Data

Composition of HNO_3 solutions saturated with $UO_2C_2O_4$ at 25 and 50 °C

HNO_3[a] (100 w_2 /mass %)	$UO_2C_2O_4$[a] (100 w_1 /mass %)	Solid phase[c]	HNO_3[b] (100 w_2 /mass %)	$UO_2C_2O_4$[b] (100 w_1 /mass %)	Solid phase[c]
0	0.58	A	0	1.00	A
3.98	0.85	A	4.38	1.49	A
5.70	1.12	A	6.48	1.73	A
6.68	1.11	A	11.49	2.34	A
9.50	1.16	A	20.36	2.81	A
10.20	1.20	A	30.37	3.85	A
13.19	1.59	A	34.90	4.68	A
16.50	1.71	A	43.24	6.91	A
19.75	1.73	A	47.20	10.35	[e]
20.70	1.95	A	61.0	8.42	[e]
30.70	2.08	A	65.10	7.26	[e]
39.12	2.83	A	73.83	7.55	[e]
48.50	4.76	A+B			
51.20	4.32	B			
53.86	3.90	B			
60.13	3.70	B			
62.72	3.80	B			
67.10	4.10	B+C[d]			
75.96	2.39	B+C[d]			
77.10	2.12	B+C[d]			

[a] At 25 °C.
[b] At 50 °C.
[c] A: $UO_2C_2O_4 \cdot 3H_2O$, [18860-43-0]; B:$UO_2C_2O_4 \cdot H_2O$,[ ]; C: $UO_2(NO_3)_2$, [10102-06-4].
[d] The authors explained the presence of $UO_2(NO_3)_2$ in the solid phase by the reaction $UO_2C_2O_4+2HNO_3 \leftrightarrows UO_2(NO_3)_2+C_2H_2O_4$, since the equilibrium saturated solutions contained more oxalate than would correspond to the stoichiometry of $UO_2C_2O_4$.
[e] The solid phase contained less than 3 mole H_2O/mole $UO_2C_2O_4$; the exact composition of the hydrate could not be determined.

Auxiliary Information

Method/Apparatus/Procedure:
Isothermal method used. Excess $UO_2C_2O_4 \cdot 3H_2O$ was equilibrated with HNO_3 solutions of the desired composition in thermostated vessels equipped with a stirrer and a hydraulic mercury seal. Equilibrium time was not reported. Samples of the saturated solutions were withdrawn using a pipette equipped with a glass wool filter, and weighed. In the samples, uranium was determined by potentiometric titration with $KMnO_4$, and NO_3^- by the Kjeldahl method. Equilibrium solid phases were identified by the method of inert component (NO_3^-) and by chemical analysis.

Estimated Error:
Temperature: precision ±0.1 K (authors).
Solubility: insufficient data given to allow for error estimate.

Components:

(1) Uranium(VI) dioxooxalate, $UO_2C_2O_4$; [2031-89-2]
(2) Nitric acid; HNO_3; [7697-37-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. I. Moskvin and E. A. Zakharova, Zh. Neorg. Khim. **4**, 2151–60 (1959).

Variables;

T/K: 293
c_2 /mol dm^{-3}:0.5–3.0

Prepared by:

J. Hála

Experimental Data

Solubility at 20 °C of $UO_2C_2O_4$ in HNO_3 solutions[a]

HNO_3 (c_2 /mol dm^{-3})	$UO_2C_2O_4$ (c_1/10^2 mol dm^{-3})	K_s[b] (10^9 mol^2 dm^{-6})
0.5	2.67	4.9
1.0	3.54	3.4
1.5	4.17	2.5
2.0	4.53	3.4
2.5	5.22	2.9
3.0	5.61	2.3
		3.2±1.3[c]

[a] Equilibrium solid phases were not investigated.

[b] Solubility product $K_s=[UO_2^{2+}][C_2O_4^{2-}]$. It was obtained by the authors from the solubility of $UO_2C_2O_4$, and the equilibrium concentration of oxalate ion. The latter was calculated by using dissociation constants of oxalic acid ($K_{a1}=0.108$, $K_{a2}=6.4\times10^{-5}$; source not reported), and assuming equilibrium concentration of H^+ ion was equal to the $HClO_4$ concentration used. Complexation of UO_2^{2+} with NO_3^- was not taken into account which, according to the authors, was the reason for K_s being higher in HNO_3 solutions than in $HClO_4$ solutions.

[c] Average value (authors).

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess $UO_2C_2O_4\cdot3H_2O$ was stirred with the solutions of the desired composition for 6 h. Preliminary experiments showed that this was sufficient to reach equilibrium. Concentration of uranium in the saturated solutions was determined gravimetrically as U_3O_8 after evaporating and igniting an aliquot of the saturated solution.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: precision ±1 K (authors).
Uranium concentration: precision ±2.5% (authors).

Components:

(1) Uranium(VI) dioxooxalate; $UO_2C_2O_4$; [2031-89-2]
(2) Perchloric acid; $HClO_4$; [7601-90-3]
(3) Water;H_2O; [7732-18-5]

Original Measurements:

A. I. Moskvin and E. A. Zakharova, Zh. Neorg. Khim. **4**, 2151–60 (1959).

Variables:

T/K:293
c_2 /mol dm^{-3}: 0.5–3.0

Prepared by:

J. Hála

Experimental Data

Solubility at 20 °C of $UO_2C_2O_4$ in $HClO_4$ solutions[a]

$HClO_4$ (c_2 /mol dm^{-3})	$UO_2C_2O_4$ (c_1/10^2 mol dm^{-3})	K_s[b] (10^9 mol^2 dm^{-6})
0.5	2.31	2.8
1.0	2.77	1.55
1.5	3.12	2.8
2.0	3.44	2.0
2.5	3.66	1.4
3.0	3.69	1.0
		2.0±0.9[c]

[a] Equilibrium solid phases were not investigated.

[b] Solubility product $K_s=[UO_2^{2+}][C_2O_4^{2-}]$. It was obtained by the authors from the solubility of $UO_2C_2O_4$, and the equilibrium concentration of the oxalate ion. The latter was calculated by using dissociation constants of oxalic acid ($K_{a1}=0.108$, $K_{a2}=6.4\times10^{-5}$; source not reported), and assuming the equilibrium concentration of H^+ ion was equal to the $HClO_4$ concentration used.

[c] Average value (authors).

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess $UO_2C_2O_4\cdot3H_2O$ was stirred with the solutions of the desired composition for 6 h. Preliminary experiments showed that this was sufficient to reach equilibrium. Concentration of uranium in the saturated solutions was determined gravimetrically as U_3O_8 after evaporating and igniting an aliquot of the saturated solution.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: precision ± 1 K (authors).
Uranium concentration: precision ±2.5% (authors).

Components:
(1) Uranium(VI) dioxooxalate; $UO_2C_2O_4$; [2031-89-2]
(2) Phosphoric acid; H_3PO_4; [7664-38-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
M. Colani, Bull. Soc. Chim. France **37**, 856–61 (1925).

Variables:
T/K:293
$100w_2$ /mass %: 0.77–15.76

Prepared by:
J. Hála

Experimental Data

Solubility at 20 °C of $UO_2C_2O_4$ in H_3PO_4 solutions[a]

H_3PO_4 (100 w_2 /mass %)	$UO_2C_2O_4$ (100 w_1 /mass %)
0.77	2.10
1.51	3.56
2.67	5.66
4.94	9.25
8.75	15.14
15.76	25.74

[a] The equilibrium solid phase was $UO_2C_2O_4\cdot3H_2O$, [18860-43-9 0], in all solutions.

Auxiliary Information

Method/Apparatus/Procedure:
Nothing specified.

Source and Purity of Materials:
Nothing specified.

Estimated Error:
Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

Components:
(1) Uranium(VI) dioxooxalate; $UO_2C_2O_4$; [2031-89-2]
(2) Hydrogen chloride; HCl; [7647-01-0]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
M. Colani, Bull. Soc. Chim. France **37**, 856–61 (1925).

Variables:
T/K:284
100 w_2 /mass %: 3.6–17.65

Prepared by:
J. Hála

Experimental Data

Solubility at 11 °C of $UO_2C_2O_4$ in HCl solutions[a]

HCl (100 w_2 /mass %)	$UO_2C_2O_4$ (100 w_1 /mass %)
3.60	1.14
8.20	2.00
11.49	2.91
14.99	4.90
17.65	8.82

[a] The equilibrium solid phase was $UO_2C_2O_4\cdot3H_2O$, [18860-43-0], in all solutions.

Auxiliary Information

Method/Apparatus/Procedure:
Nothing specified.

Source and Purity of Materials:
Nothing specified.

Estimated Error:
Temperature: precision not specified.
Solubility: insufficient data given to allow for error estimate.

Components:
(1) Uranium(VI) dioxooxalate; $UO_2C_2O_4$; [2031-89-2]
(2) Sulfuric acid; H_2SO_4; [7664-93-9]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
M. Colani, Bull. Soc. Chim. France **37**, 856–61 (1925).

Variables:
T/K: 293
100 w_2 /mass %: 0.82–29.67

Prepared by:
J. Hála

Experimental Data

Solubility at 20 °C of $UO_2C_2O_4$ in H_2SO_4 solutions[a]

H_2SO_4 (100 w_2 /mass %)	$UO_2C_2O_4$ (100 w_1 /mass %)
0.82	0.85
2.59	1.34
3.05	1.61
5.53	2.04
15.07	3.85
19.88	4.93
25.58	5.98
27.31	6.46
29.67	7.49

[a] The equilibrium solid phase was $UO_2C_2O_4 \cdot 3H_2O$, [18860-43-0], in all solutions.

Auxiliary Information

Method/Apparatus/Procedure:
Nothing specified.

Source and Purity of Materials:
Nothing specified.

Estimated Error:
Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

Components:
(1) Uranium(VI) dioxo oxalate; $UO_2C_2O_4$; [2031-89-2]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
K. A. Bolshakov, S. S. Korovin, V. E. Plyushchev, and T. A. Ermakova, Zh. Neorg. Khim **2**, 222–8 (1957).

Variables:
T/K: 273–343
100 w_2 /mass %

Prepared by:
J. Hála

Experimental Data

Solubility of $UO_2C_2O_4$ in oxalic acid solutions as a function of temperature

Temperature (°C)	$C_2H_2O_4$ (100 w_2 /mass %)	$C_2H_2O_4$ (m_2 /mol kg^{-1})[a]	$UO_2C_2O_4$ (100 w_1 /mass %)	$UO_2C_2O_4$ (m_1 /mol kg^{-1})[a]
0	0	0	0.21	0.00588
	0.74	0.0837	1.03	0.0293
	1.51	0.172	1.25	0.0359
	2.89	0.335	1.38	0.0403
	3.45	0.403	1.40	0.0411[b]
	3.42	0.397	0.91	0.0266
	3.41	0.394	0.45	0.0131
	3.41	0.392	0	0
25	0	0	0.58	0.0162
	0.66	0.0748	1.37	0.0376
	1.73	0.199	1.80	0.0521
	2.58	0.300	2.02	0.0591
	4.01	0.474	2.10	0.0625
	7.80	0.964	2.34	0.0727
	8.70	1.086	2.34	0.0735
	9.70	1.123	2.40	0.0763
	9.90	1.254	2.44	0.0777[b]
	10.00	1.267	2.33	0.0742
	10.12	1.267	1.17	0.0368
	10.20	1.267	0.40	0.0125
	10.17	1.257	0	0
40	0	0	0.83	0.0234
	0.99	0.113	1.80	0.0517
	2.23	0.259	2.22	0.0649
	3.91	0.464	2.53	0.0755
	9.02	1.137	2.84	0.0900
	12.40	1.626	2.91	0.0960
	15.64	2.129	2.75	0.0941
	17.22	2.387	2.64	0.0920[b]
	17.42	2.399	1.93	0.0668
	17.64	2.412	1.14	0.0392
	17.80	2.420	0.51	0.0174
	17.71	2.390	0	0
50	0	0	1.00	0.0282
	1.34	0.155	2.35	0.0681
	1.90	0.220	2.50	0.0730
	4.64	0.557	2.81	0.0848
	6.37	0.781	3.07	0.0947
	7.90	0.986	3.10	0.0973
	9.72	1.24	3.14	0.101
	10.56	1.36	3.19	0.103

	11.50	1.50	3.22	0.105
	13.45	1.79	3.07	0.103
	15.29	2.08	2.87	0.0979
	18.53	2.62	2.79	0.0990
	23.40	3.51	2.51	0.0946
	23.70	3.567	2.50	0.0946[b]
	23.72	3.566	2.40	0.0907
	23.85	3.581	2.18	0.0823
	24.0	3.563	1.19	0.0444
	23.95	3.50	0	0
70[c]	0	0	1.60	0.0454
	1.03	0.119	2.67	0.0774
	1.82	0.212	2.93	0.0859
	2.63	0.311	3.40	0.101
	2.92	0.348	3.76	0.113
	5.23	0.639	3.84	0.118
	7.52	0.943	3.96	0.125
	10.72	1.40	4.12	0.135
	11.94	1.58	4.13	0.137
	13.51	1.82	4.02	0.136
	14.62	1.99	3.98	0.137
	16.91	2.37	3.93	0.131
	22.19	3.31	3.30	0.124
	27.78	4.44	2.68	0.108
	29.96	4.92	2.36	0.0974
	36.68	6.61	1.64	0.0743
	37.86	6.95	1.66	0.0766
	37.92	6.94	1.40	0.0644
	38.24	6.98	0.88	0.0404
	37.92	6.78	0	0

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[a] Calculated by compiler.

[b] Two solid phases, i.e., $UO_2C_2O_4 \cdot 3H_2O$, [18860-43-0] (A) and $C_2H_2O_4 \cdot 2H_2O$, [6153-56-6] (B), were in equilibrium with this solution. In solutions containing lower and higher oxalic acid concentrations, the equilibrium solid phases were A and B, respectively.

[c] For measurements at this temperature the solid phases were not reported.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Mixtures were stirred in a thermostated vessel equipped with a hydraulic seal. The vessel was protected against sunlight to avoid reduction of UO_2^{2+} to U(IV). Equilibrium was reached in 4–5 days at 25 °C, and in 10–11 h at 70 °C. At temperatures above 25 °C samples of the saturated solutions were withdrawn by using preheated pipets. Saturated solutions and the solid phases were analyzed for oxalate by direct titration with standard $KMnO_4$ solution, and for uranium (the sample was evaporated, ignited at 600–700 °C to decompose the oxalate, U_3O_8 was converted to UO_2SO_4, and UO_2^{2+} was reduced with Cd metal to U(IV) which was titrated with 0.02–0.04 N $KMnO_4$ with potentiometric, end-point detection). Composition of the solid phases was also determined by Schreinemakers method.

Source and Purity of Materials:

$UO_2C_2O_4$ was obtained as trihydrate by precipitation of a concentrated $UO_2(NO_3)_2$ solution with a saturated solution of oxalic acid. The gelatinous precipitate was thoroughly washed with water and air dried to obtain trihydrate powder. Source and purity of materials used not specified.

Estimated Error:

Temperature: precision ±0.05 K at 0 and 25 °C, ±0.1 K at higher temperatures (authors).

Uranium concentration: <±0.5% (authors).

Components:

(1) Uranium(VI) dioxooxalate; $UO_2C_2O_4$; [2031-89-2]
(2) Sodium oxalate; $Na_2C_2O_4$; [62-76-0]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. Colani, Compt. Rend. Acad. Sci. **165**, 111–3 (1917).

Variables:

T/K: 288; 323
100 w_2 /mass %: 0–4.9 and 0–9, respectively

Prepared by:

J. Hála

Experimental Data

Phase diagram of the $UO_2C_2O_4-Na_2C_2O_4-H_2O$ system at 15 and 50 °C, and compositions of the saturated solutions at significant points

Temperature (°C)	Significant point[a]	$Na_2C_2O_4$ (100 w_2 /mass %)	$Na_2C_2O_4$ (m_2 /mol kg^{-1})[b]	$UO_2C_2O_4$ (100 w_1 /mass %)	$UO_2C_2O_4$ (m_1 /mol kg^{-1})[b]	Solid phase[c]
15	a	0	0	0.47	0.0132	I
	b	0.80	0.0460	2.65	0.0767	I+II
	c	1.80	0.107	5.01	0.150	II+III
	d	4.93	0.298	3.14	0.0954	III+IV
	e	3.09	0.177	0	0	IV
50	A	0	0	1.00	0.0282	I
	B	1.01	0.0588	3.58	0.105	I+II
	C	3.60	0.231	9.84	0.317	II+V
	D	4.62	0.309	12.33	0.414	V+III
	E	9.03	0.649	13.69	0.495	III+IV
	F	4.28	0.248	0	0	IV

[a] See Fig. 13

[b] Calculated by compiler.

[c] (I) $UO_2C_2O_4 \cdot 3H_2O$, [18860-43-0]; (II) $Na_2(UO_2)_4(C_2O_4)_5 \cdot 11H_2O$, [ ]; (III) $Na_2UO_2(C_2O_4)_2 \cdot 5H_2O$, [ ]; (IV) $Na_2C_2O_4$; [62-76-0]; (V) $Na_2(UO_2)_2(C_2O_4)_3 \cdot 5H_2O$, [ ].

Phase diagram (Fig. 13) of the $UO_2C_2O_4-Na_2C_2O_4-H_2O$ system at 15 and 50 °C.

Components:	**Original Measurements:**
(1) Uranium(VI) dioxooxalate; $UO_2C_2O_4$; [2031-89-2] (2) Ammonium oxalate; $(NH_4)_2C_2O_4$; [1113-38-8] (3) Water; H_2O; [7732-18-5]	A. Colani, Compt. Rend. Acad. Sci. **165**, 234–6 (1917).
Variables:	**Prepared by:**
T/K: 288; 323 100 w_2 /mass %: 0–6.4 and 0–15.9, respectively	J. Hála

Experimental Data

Phase diagram of the $UO_2C_2O_4-(NH_4)_2C_2O_4-H_2O$ system at 15 and 50 °C, and compositions of the saturated solutions at significant points

Temperature (°C)	Significant point[a]	$(NH_4)_2C_2O_4$ (100 w_2 /mass %)	$(NH_4)_2C_2O_4$ (m_2 /mol kg^{-1})[b]	$UO_2C_2O_4$ (100 w_1 /mass %)	$UO_2C_2O_4$ (m_1 /mol kg^{-1})[b]	Solid phase[c]
15	a	0	0	0.47	0.0132	I
	b	2.14	0.190	7.19	0.221	I+II
	c	2.99	0.273	8.78	0.228	II+III
	d	6.43	0.618	9.66	0.322	III+IV
	e	3.69	0.309	0	0	IV
50	A	0	0	1.00	0.0282	I
	B	1.36	0.110	5.11	0.153	I+V
	C	8.52	0.959	19.89	0.776	V+VI
	D	15.90	2.16	23.82	1.10	VI+IV
	E	9.36	0.832	0	0	IV

[a] See Fig. 14

[b] Calculated by compiler.

[c] (I) $UO_2C_2O_4 \cdot 3H_2O$, [18860-43-0]; (II) $(NH_4)_2(UO_2)_2(C_2O_4)_3 \cdot 3H_2O$, [ ]; (III) $(NH_4)_2UO_2(C_2O_4)_2 \cdot 2H_2O$, [ ]; (IV) $(NH_4)_2C_2O_4 \cdot H_2O$, [ ]; (V) $(NH_4)_2(UO_2)_2(C_2O_4)_3$, [ ]; (VI) $(NH_4)_2UO_2(C_2O_4)_2$, [ ].

Additional information:

At 75 °C, $(NH_4)_4UO_2(C_2O_4)_3$, [ ], was identified as the solid phase in solutions containing 18.70 and 21.17 mass % $(NH_4)_2C_2O_4$.

Phase diagram (Fig. 14) of the $UO_2C_2O_4-(NH_4)_2C_2O_4-H_2O$ system at 15 and 50 °C.

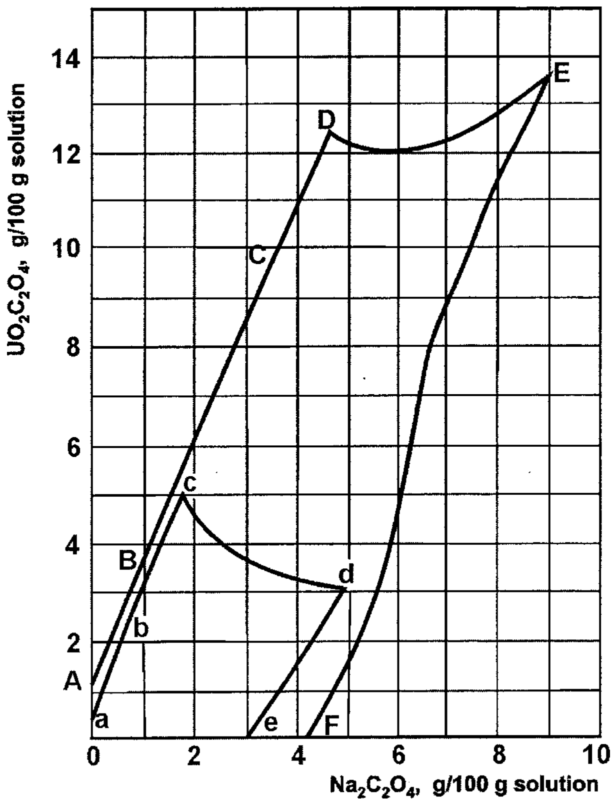

FIG. 13. Uranium (VI) dioxooxalate–ammonium oxalate–water system.

Auxiliary Information

Method/Apparatus/Procedure:	**Source and Purity of Materials:**
No details reported.	No details reported. **Estimated Error:** Temperature: precision not reported.

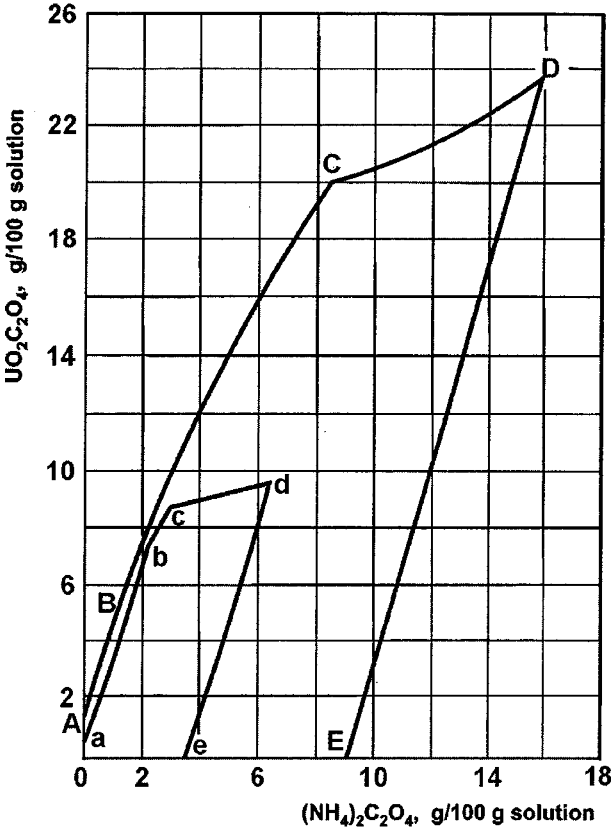

FIG. 14. Uranium (VI) dioxooxalate–potassium oxalate–water system.

Auxiliary Information

Method/Apparatus/Procedure:

No details reported.

Source and Purity of Materials:

No details reported.

Estimated Error:

Temperature: precision not reported.

Components:

(1) Uranium(VI) dioxooxalate; $UO_2C_2O_4$; [2031-89-2]
(2) Potassium oxalate; $K_2C_2O_4$; [583-52-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. Colani, Compt. Rend. Acad. Sci. **163**, 123–5 (1916).

Variables:

T/K: 288;323
100 w_2 /mass %: 0–24.3 and 0–32.75, respectively

Prepared by:

J. Hála

Experimental Data

Phase diagram of the $UO_2C_2O_4$–$K_2C_2O_4$–H_2O system at 15 and 50 °C, and compositions of the saturated solutions at significant points

Temperature (°C)	Significant point[a]	$K_2C_2O_4$ (100 w_2 /mass %)	$K_2C_2O_4$ (m_2 /mol kg^{-1})[b]	$UO_2C_2O_4$ (100 w_1 /mass %)	$UO_2C_2O_4$ (m_1 /mol kg^{-1})[b]	Solid phase[c]
15	a	0	0	0.47	0.0132	I
	b	0.42	0.0257	1.34	0.0381	I+II
	c	1.83	0.117	3.89	0.115	II+III
	d	1.85	0.118	3.76	0.111	III+IV
	e	24.30	1.94	0.10	0.00368	IV+V
	f	24.09	1.91	0	0	V
50	A	0	0	1.00	0.0282	I
	B	1.11	0.0700	3.45	0.101	I+II
	C	4.83	0.340	9.82	0.321	II+III
	D	5.61	0.398	9.52	0.314	III+IV
	E	32.65	2.97	1.22	0.0515	IV+V
	F	32.75	2.93	0	0	V

[a] See Fig. 15.

[b] Calculated by compiler.

[c] (I) $UO_2C_2O_4 \cdot 3H_2O$, [18860-43-0]; (II) $K_2(UO_2)_2(C_2O_4)_3 \cdot 4H_2O$, [ ]; (III) $K_2UO_2(C_2O_4)_2 \cdot 3.5H_2O$, [ ]; (IV) $K_6(UO_2)_2(C_2O_4)_5 \cdot 10H_2O$, [ ]; (V) $K_2C_2O_4 \cdot H_2O$, [6487-48-5].

Phase diagram (Fig. 15) of the $UO_2C_2O_4$–$K_2C_2O_4$–H_2O system at 15 and 50 °C.

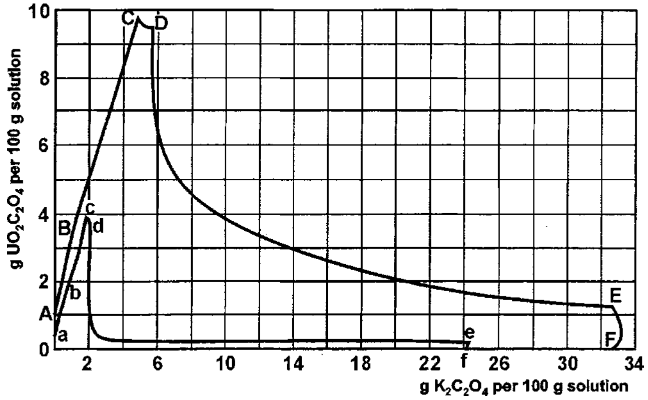

FIG. 15. Sodium carbonato dioxoneptunate (V)–sodium perchlorate–carbon dioxide–water system.

Auxiliary Information

Method/Apparatus/Procedure:

No details reported.

Source and Purity of Materials:

No details reported.

Estimated Error:

Temperature: precision not reported.

Components:

(1) Uranium(VI) dioxooxalate; $UO_2C_2O_4$; [2031-89-2]
(2) Calcium oxalate; CaC_2O_4; [563-72-4]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. Colani, Bull. Soc. Chim. France **1**, 1376–9 (1934); Compt. Rend. Acad. Sci. **198**, 1510–2 (1934).

Variables:

T/K: 288; 323
$100w_2$ /mass %: 0–0.079 and 0–0.044, respectively

Prepared by:

J. Hála

Experimental Data

Composition of the saturated solutions in the $UO_2C_2O_4-CaC_2O_4-H_2O$ system at 15 and 50 °C

Temperature (°C)	CaC_2O_4 (100 w_2 /mass %)	CaC_2O_4 (10^3 m_2 /mol kg^{-1})[a]	$UO_2C_2O_4$ (100 w_1 /mass %)	$UO_2C_2O_4$ (m_1 /mol kg^{-1})[a]	Solid phase[b]
15	0	0	0.470	0.0132	A
	0.012	0.941	0.469	0.0132	A+B
	0.011	0.861	0.260	0.00728	B
	0.079	6.18	0.137	0.00383	B
	0.075	5.86	0.088	0.00246	B
50	0	0	1.00	0.0282	A
	0.022	1.74	0.996	0.0281	A
	0.044	3.47	1.07	0.0302	A+B
	0.038	3.00	1.04	0.0294	B
	0.037	2.92	0.924	0.0261	B
	0.017	1.33	0.239	0.00669	B

[a] Calculated by compiler.
[b] (A) $UO_2C_2O_4\cdot 3H_2O$, [18860-43-0]; (B) $CaC_2O_4\cdot H_2O$, [5794-28-5].

Additional information:
A rough sketch only was given for the phase diagram of the $UO_2C_2O_4-CaC_2O_4-H_2O$ system.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. To a given volume of water, the desired quantities of $UO_2C_2O_4$ and CaC_2O_4 were added. The mixtures were agitated until equilibrium was reached. This took a long, though unspecified period of time. Then the clear supernatant solution was analyzed gravimetrically (methods not specified).

Source and Purity of Materials:

No details reported.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

Components:

(1) Uranium(VI) dioxooxalate; $UO_2C_2O_4$; [2031-89-2]
(2) Strontium oxalate; SrC_2O_4; [814-95-9]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

[1]A. Colani, Bull. Soc. Chim. France **1**, 1376–9 (1934);
[2]A Colani, Compt. Rend. Acad. Sci. **198**, 1510–2 (1934).

Variables:

T/K: 288; 323
100 w_2 /mass %: 0–0.16 and 0–0.52, respectively

Prepared by:

J. Hála

Experimental Data

Composition of the saturated solutions in the $UO_2C_2O_4-SrC_2O_4-H_2O$ system at 15 and 50 °C

Temperature (°C)	SrC_2O_4 (100 w_2 /mass %)	SrC_2O_4 (10^3 m_2 /mol kg^{-1})[a]	$UO_2C_2O_4$ (100 w_1 /mass %)	$UO_2C_2O_4$ (m_1 /mol kg^{-1})[a]	Solid phase[b]
15	0	0	0.470	0.0132	A
	0.093	5.33	0.616	0.0173	A
	0.164	9.42	0.711	0.0200	A+B
	0.158	9.07	0.742	0.0209	B
	0.160	9.19	0.701	0.0197	B
	0.163	9.35	0.549	0.0154	B+C
	0.147	8.42	0.481	0.0135	C
	0.086	4.91	0.266	0.00746	C
	0.033	1.88	0.087	0.00243	C
50	0	0	1.00	0.0282	A
	0.121	6.98	1.23	0.0348	A
	0.343	19.9	1.75	0.0499	A
	0.412	24.0	1.92	0.0549	A
	0.521	30.5	2.10	0.0602	A+B
	0.508	29.7	1.99	0.0570	B
	0.500	29.1	1.82	0.0520	B
	0.477	27.7	1.45	0.0413	B+C
	0.435	25.1	1.32	0.0373	C
	0.189	10.8	0.524	0.0147	C
	0.128	7.32	0.349	0.00979	C
	0.074	4.22	0.176	0.00493	C

[a] Calculated by compiler.
[b] (A) $UO_2C_2O_4\cdot 3H_2O$, [18860-43-0]; (B) $SrUO_2(C_2O_4)_2\cdot 4H_2O$, [ ]; (C) $SrC_2O_4\cdot 4H_2O$, [ ], in original reference,[1] or $SrC_2O_4\cdot 2.5H_2O$, [ ], in original references. [2]

Additional information:
A rough sketch of the phase diagram of the $UO_2C_2O_4-SrC_2O_4-H_2O$ system was reported.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. To a given volume of water, the desired quantities of $UO_2C_2O_4$ and SrC_2O_4 were added. The mixtures were agitated until equilibrium was reached. This took a long, though unspecified period of time. Then the clear supernatant solution was analyzed gravimetrically (methods not specified).

Source and Purity of Materials:

No details reported.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

Components:

(1) Uranium(VI) dioxooxalate; $UO_2C_2O_4$; [2031-89-2]
(2) Barium oxalate; BaC_2O_4; [516-02-9]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. Colani, Bull. Soc. Chim. France **1**, 1376–9 (1934).

Variables:

T/K: 288; 323
100 w_2 /mass %: 0–0.077 and 0–0.37, respectively

Prepared by:

J. Hála

Experimental Data

Composition of the saturated solutions in the $UO_2C_2O_4-BaC_2O_4-H_2O$ system at 15 and 50 °C

Temperature (°C)	BaC_2O_4 (100 w_2 /mass %)	BaC_2O_4 (10^4 m_2 /mol kg^{-1})[a]	$UO_2C_2O_4$ (100 w_1 /mass %)	$UO_2C_2O_4$ (m_1 /mol kg^{-1})[a]	Solid phase[b]
15	0	0	0.470	0.0132	A
	0.0137	6.11	0.453	0.0127	A
	0.0252	11.2	0.460	0.0129	A
	0.0772	34.5	0.563	0.0158	B
	0.0706	31.5	0.525	0.0148	B
	0.0640	28.5	0.422	0.0118	B
	0.0600	26.7	0.166	0.00465	B
	0.0592[c]	26.3	0.140	0.00392	B
	0.0479	21.3	0.0777	0.00217	C
	0.0353	15.7	0.0548	0.00153	C
	0.0306	13.6	0.0449	0.00126	C
	0.0315	14.0	0.0432	0.00122	D
	0.0209	9.28	0.0221	0.000617	D
50	0	0	1.00	0.0282	A
	0.193	86.9	1.30	0.0366	A
	0.343	155	1.58	0.0450	A
	0.370	167	1.62	0.0462	A+B
	0.354	160	1.54	0.0438	B
	0.315	142	0.911	0.0258	B
	0.251	112	0.648	0.0193	B
	0.211	94.3	0.443	0.0125	B+C
	0.186	83.0	0.368	0.0103	C
	0.130	57.8	0.239	0.00669	C+E
	0.102	45.4	0.166	0.00465	E
	0.0366	16.3	0.0461	0.00129	E

[a] Calculated by compiler.
[b] (A) $UO_2C_2O_4\cdot 3H_2O$, [18860-43-0]; (B) $BaUO_2(C_2O_4)_2\cdot 5H_2O$, [ ]; (C) $Ba_2UO_2(C_2O_4)_3\cdot 7H_2O$, [ ], (D) $BaC_2O_4\cdot 2H_2O$, [18581-91-4]; (E) $BaC_2O_4\cdot 0.5H_2O$, [18581-89-0].
[c] In Ref. 1, this composition is reported to be that of the eutonic point with solid phases B and C at equilibrium. Also, composition of two more eutonic points is reported which do not agree with the data reported in this compiled document.

Additional information:
A rough sketch of the phase diagram of the $UO_2C_2O_4-BaC_2O_4-H_2O$ system was reported.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. To a given volume of water, the desired quantities of $UO_2C_2O_4$ and BaC_2O_4 were added. The mixtures were agitated until equilibrium was reached. This took a long, though unspecified period of time. Then the clear supernatant solution was analyzed gravimetrically (methods not specified).

Source and Purity of Materials:

No details reported.

Estimated Error:

Temperature: precision not specified.
Solubility data: insufficient data given to allow for error estimate.

References:

[1]A. Colani, Compt. Rend. **198**, 1510 (1934).

Components:

(1) Uranium(VI) dioxooxalate; $UO_2C_2O_4$; [2031-89-2]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Perchloric acid; $HClO_4$; [7601-90-3]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

A. I. Moskvin and E. A. Zakharova, Zh. Neorg. Khim. **4**, 2151–60 (1959).

Variables:

T/K: 293
c_2 /mol dm^{-3}: 0.08–0.637
c_3 /mol dm^{-3}: 0.5 and 1.0

Prepared by:

J. Hála

Experimental Data

Solubility at 20 °C of $UO_2C_2O_4$ in $C_2H_2O_4$–$HClO_4$ solutions[a]

$HClO_4$ (c_3 /mol dm^{-3})	$C_2H_2O_4$ (c_2 /mol dm^{-3})	$UO_2C_2O_4$ (10^2 c_1 /mol dm^{-3})
0.5	0.080	1.63
	0.159	1.71
	0.238	1.88
	0.318	2.14
	0.476	2.32
	0.636	2.56
1.0	0.080	1.65
	0.158	1.59
	0.316	1.35
	0.476	1.29
	0.636	1.16

[a] Equilibrium solid phases were not investigated.

Additional information:
From the increasing solubility of $UO_2C_2O_4$ with increasing oxalic acid concentration in 0.5 mol dm^{-3} $HClO_4$, the authors calculated stability constants of the $UO_2C_2O_4$ and $UO_2(C_2O_4)_2^{2-}$ complexes. In 1.0 mol dm^{-3} $HClO_4$, the decreasing solubility of $UO_2C_2O_4$ with increasing oxalic acid concentration was taken as an evidence for the absence of complex formation between UO_2^{2+} and $C_2O_4^{2-}$ ion in these solutions. Solid phases were not investigated.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess $UO_2C_2O_4 \cdot 3H_2O$ was stirred with solutions of the desired composition for 6 h. Preliminary experiments showed that this was sufficient for equilibrium to be reached. Concentration of uranium in the saturated solutions was determined gravimetrically as U_3O_8 after evaporating and igniting an aliquot of the solution.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: precision ±1 K (authors).
Concentration of uranium: ±2.5% (authors).

Components:

(1) Uranium(VI) dioxooxalate; $UO_2C_2O_4$; [2031-89-2]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Nitric acid; HNO_3; [7697-37-2]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

A. I. Moskvin and E. A. Zakharova, Zh. Neorg. Khim. **4**, 2151–60 (1959).

Variables:

T/K: 293
c_2 /mol dm^{-3}: 0.08–0.63 for 0.5 and 2.0 mol dm^{-3} HNO_3;
0.08–0.47 for 3.0 mol dm^{-3} HNO_3
c_3 /mol dm^{-3}: 0.5; 2.0; 3.0

Prepared by:

J. Hála

Experimental Data

Solubility 20 °C of $UO_2C_2O_4$ in $C_2H_2O_4$–HNO_3 solutions[a]

HNO_3 (c_3 /mol dm^{-3})	$C_2H_2O_4$ (c_2 /mol dm^{-3})	$UO_2C_2O_4$ (10^2 c_1 /mol dm^{-3})
0.5	0.080	1.83
	0.158	2.07
	0.238	2.28
	0.318	2.43
	0.476	2.68
	0.636	2.98
2.0	0.080	2.48
	0.158	1.92
	0.237	1.66
	0.316	1.50
	0.476	1.30
	0.636	1.32
3.0	0.080	2.91
	0.158	2.08
	0.237	1.50
	0.318	1.29
	0.394	1.12
	0.476	1.07

[a] Equilibrium solid phases were not investigated.

Additional information:
From the increasing solubility of $UO_2C_2O_4$ with increasing oxalic acid concentration in 0.5 mol dm^{-3} $HClO_4$, the authors calculated stability constants of the $UO_2C_2O_4$ and $UO_2(C_2O_4)_2^{2-}$ complexes. In 2.0 and 3.0 mol dm^{-3} $HClO_4$, the decreasing solubility of $UO_2C_2O_4$ with increasing oxalic acid concentration was taken as an evidence for the absence of complex formation between UO_2^{2+} and $C_2O_4^{2-}$ ions in these solutions.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess $UO_2C_2O_4 \cdot 3H_2O$ was stirred with solutions of the desired composition for 6 h. Preliminary experiments showed that this was sufficient for equilibrium to be reached. Concentration of uranium in the saturated solutions was determined gravimetrically as U_3O_8 after evaporating and igniting an aliquot of the solution.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: precision ±1 K (authors).
Concentration of uranium: ±2.5% (authors).

Components:

(1) Uranium(VI) dioxooxalate; $UO_2C_2O_4$; [2031-89-2]
(2) Ammonium oxalate; $(NH_4)_2C_2O_4$; [1113-38-8]
(3) Nitric acid; HNO_3; [7697-37-2]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

A. I. Moskvin and E. A. Zakharova, Zh. Neorg. Khim. **4**, 2151–60 (1959).

Variables:

T/K: 293
c_2 /mol dm^{-3}: 0.07–0.28
c_3 /mol dm^{-3}: 0.5 and 1.0

Prepared by:

J. Hála

Experimental Data

Solubility at 20 °C of $UO_2C_2O_4$ in $(NH_4)_2C_2O_4-HNO_3$ solutions[a]

HNO_3 (c_3 /mol dm^{-3})	$(NH_4)_2C_2O_4$ (c_2 /mol dm^{-3})	$UO_2C_2O_4$ (10^2 c_1 /mol dm^{-3})	HNO_3 (c_3 /mol dm^{-3})	$(NH_4)_2C_2O_4$ (c_2 /mol dm^{-3})	$UO_2C_2O_4$ (10^2 c_1 /mol dm^{-3})
0.5	0.070	2.12	1.0	0.070	2.09
	0.105	2.61		0.105	2.13
	0.140	3.48		0.140	2.18
	0.170	4.44		0.170	2.37
	0.210	6.12		0.210	2.70
	0.245	7.87		0.245	2.78
	0.280	9.71		0.280	3.18

[a] Equilibrium solid phases were not investigated.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess $UO_2C_2O_4 \cdot 3H_2O$ was stirred with solutions of the desired composition for 6 h. Preliminary experiments showed that this was sufficient for equilibrium to be reached. Concentration of uranium in the saturated solutions was determined gravimetrically as U_3O_8 after evaporating and igniting an aliquot of the solution.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: precision ±1 K (authors).
Concentration of uranium: ±2.5% (authors).

Components:

(1) Uranium(VI) dioxooxalate; $UO_2C_2O_4$; [2031-89-2]
(2) Ammonium oxalate; $(NH_4)_2C_2O_4$; [1113-38-8]
(3) Perchloric acid; $HClO_4$; [7601-90-3]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

A. I. Moskvin and E. A. Zakharova, Zh. Neorg. Khim. **4**, 2151–60 (1959).

Variables:

T/K: 293
c_2 /mol dm^{-3}: 0.07–0.28
c_3 /mol dm^{-3}: 0.5, 1.0, and 3.0

Prepared by:

J. Hála

Experimental Data

Solubility at 20 °C of $UO_2C_2O_4$ in $(NH_4)_2C_2O_4-HClO_4$ solutions[a]

$HClO_4$ (c_3 /mol dm^{-3})	$(NH_4)_2C_2O_4$ (c_2 /mol dm^{-3})	$UO_2C_2O_4$ (10^2 c_1 /mol dm^{-3})	$HClO_4$ (c_3 /mol dm^{-3})	$(NH_4)_2C_2O_4$ (c_2 /mol dm^{-3})	$UO_2C_2O_4$ (10^2 c_1 /mol dm^{-3})
0.5	0.070	1.96	3.0	0.070	1.16
	0.105	2.43		0.140	1.13
	0.140	3.21		0.175	0.960
	0.170	4.26		0.210	0.878
	0.210	5.91		0.245	0.780
	0.245	7.50		0.280	0.759
	0.280	9.09			
1.0	0.070	1.54			
	0.105	1.56			
	0.140	1.60			
	0.170	1.70			
	0.210	2.00			
	0.245	2.36			
	0.280	2.65			

[a] Equilibrium solid phases were not investigated.

Additional information:

Decreasing solubility of $UO_2C_2O_4$ with increasing ammonium oxalate in 3.0 mol dm^{-3} $HClO_4$ solutions concentration was taken as an evidence for the absence of complex formation between UO_2^{2+} and $C_2O_4^{2-}$ ions in these solutions. Solid phases were not investigated.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess $UO_2C_2O_4 \cdot 3H_2O$ was stirred with solutions of the desired composition for 6 h. Preliminary experiments showed that this was sufficient for equilibrium to be reached. Concentration of uranium in the saturated solutions was determined gravimetrically as U_3O_8 after evaporating and igniting an aliquot of the solution.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: precision ±1 K (authors).
Concentration of uranium: ±2.5% (authors).

Components:

(1) Uranium(VI) dioxooxalate; $UO_2C_2O_4$; [2031-89-2]
(2) Uranium(VI) dioxo dinitrate; $UO_2(NO_3)_2$; [10102-06-4]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

K. A. Bolshakov and S. S. Korovin, Zh. Neorg. Khim. **2**, 1940–50 (1957).

Variables:

T/K: 298
100 w_2 /mass %: 0–56.23

Prepared by:

J. Hála

Experimental Data

Composition of solutions saturated at 25 °C

$UO_2(NO_3)_2$ (100 w_2 /mass %)	$UO_2(NO_3)$ (m_2 /mol kg^{-1})[a]	$UO_2C_2O_4$ (100 w_1 /mass %)	$UO_2C_2O_4$ (m_1 /mol kg^{-1})[a]	Solid phase[b]
0	0	0.58	0.0163	A
1.26	0.0326	0.58	0.0165	A
5.18	0.140	0.60	0.0178	A
9.55	0.270	0.63	0.0196	A
12.66	0.371	0.63	0.0203	A
18.76	0.591	0.62	0.0215	A
20.40	0.655	0.60	0.0212	A
23.64	0.792	0.58	0.0214	A
31.03	1.15	0.54	0.0220	A
43.39	1.96	0.44	0.0219	A
51.78	2.75	0.35	0.0204	A
55.50	3.19	0.31	0.0196	A+B
55.85	3.23	0.26	0.0166	B
56.00	3.24	0.12	0.00764	B
56.23	3.26	0	0	B

[a] Calculated by compiler.
[b] (A) $UO_2C_2O_4 \cdot 3H_2O$, [18860-43-0]; (B) $UO_2(NO_3)_2 \cdot 6H_2O$, [13520-83-7].

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Mixtures of the desired compositions were equilibrated for 3–6 days. The time necessary for reaching equilibrium increased with increasing concentration of $UO_2(NO_3)$. The vessels used were protected from light to prevent the formation of basic oxalates of U(IV). Saturated solutions were analyzed for uranium, oxalate, and nitrate. Uranium and oxalate were determined by titration with $KMnO_4$ solution, nitrate was determined by the Kjeldahl method after reducing NO_3^- with Deward alloy. Composition of the equilibrium solid phases was determined by the method of indifferent component (NO_3^-), in some cases also by chemical analysis and optical microscopy.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

Components:

(1) Uranium(VI) dioxo oxalate; $UO_2C_2O_4$; [2031-89-2]
(2) Uranium(VI) dioxo dinitrate; $UO_2(NO_3)_2$; [10102-06-04]
(3) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(4) Nitric acid; HNO_3 ; [7697-37-2]
(5) Water; H_2O; [7732-18-5]

Original Measurements:

K. A. Bolshakov and S. S. Korovin, Zh. Neorg. Khim. **2**, 1940–50 (1957).

Variables:

T/K: 298
composition

Prepared by:

J. Hála

Experimental Data

Composition of solutions saturated at 25 °C, and corresponding to selected sections of the quarternary system UO_2^{2+} ,$H^+ \| C_2O_4^{2-}$,NO_3^-

$UO_2(NO_3)_2$ (100 w_2 mass %)	HNO_3 (100 w_4 mass %)	$UO_2C_2O_4$ (100 w_1 mass %)	Solid phase[f]	HNO_3 (100 w_4 mass %)	$UO_2(NO_3)_2$ (100 w_2 mass %)	$UO_2C_2O_4$ (100 w_1 mass %)	Solid phase[f]
47.50[a]	6.06	0	A	22.22[c]	26.52	0.47	B
47.10	6.00	0.43	A+B	22.31	23.38	0.42	B
39.90	5.11	0.38	B	23.56	18.73	0.40	B
28.31	3.55	0.46	B	22.42	16.01	0.41	B
21.21	—	0.54	B	22.37	10.23	0.48	B
14.42	—	0.57	B	22.60	5.46	0.70	B
7.58	—	0.53	B	22.51	1.81	1.26	B
42.93[a]	11.16	0	A				
41.06	10.66	0.46	A+B	$C_2H_2O_4$	HNO_3	$UO_2C_2O_4$	Solid phase[f]
40.13	10.35	0.44	B	(100 w_3	(100 w_4	(100 w_1	
35.28	9.15	0.37	B	mass %)	mass %)	mass %)	
31.97	—	0.43	B				
22.80	—	0.47	B	1.73[d]	0	1.80	B
14.90	—	0.55	B	1.74	2.17	0.94	B
8.83	—	0.57	B	1.72	9.00	0.64	B
8.83	—	0.57	B	1.73	11.87	0.62	B
8.83	—	0.57	B	1.69	27.16	0.97	B
			1.68	31.01	1.29	B	
31.96[a]	23.08	0	A	1.68	35.50	1.45	B
31.44	22.66	0.83	A+B	1.52	39.86	1.82	B
31.06	21.05	0.55	B	1.51	45.30	2.28	B
27.06	17.70	0.38	B	1.75	46.12	2.58	B
22.31	13.93	0.37	B	1.74	47.02	2.93	B+D
17.44	—	0.42	B	1.50	50.55	2.60	D
16.63	10.94	0.44	B	1.51	64.57	1.36	D
10.62	—	0.47	B				
6.27	—	0.55	B				

$C_2H_2O_4$ (100 w_3 mass %)	HNO_3 (100 w_4 mass %)	$UO_2C_2O_4$ (100 w_1 mass%)	Solid phase[f]	$C_2H_2O_4$ (100 w_3 mass %)	HNO_3 (100 w_4 mass %)	$UO_2C_2O_4$ (100 w_1 mass %)	Solid phase[f]
9.30[b]	2.17	0	C	9.90[e]	0	2.44	B+C
8.98	2.17	1.31	C+B	8.98	2.17	1.51	B+C
8.33	—	1.68	B	7.81	5.10	0.78	B+C
7.05	1.33	1.80	B	7.32	6.47	0.61	B+C
6.14	1.25	1.67	B	6.65	9.09	0.49	B+C
4.45	—	1.98	B	6.58	10.52	0.40	B+C
1.06	—	1.35	B	5.99	13.89	0.38	B+C
				4.63	21.54	0.35	B+C
8.34[b]	5.32	0	C	4.13	26.25	0.41	B+C
7.81	5.10	0.78	C+B	3.43	35.53	0.66	B+C
6.97	4.62	1.31	B	3.47	39.15	0.89	B+C
4.22	2.67	1.22	B	3.34	45.74	1.94	B+C
2.04	—	1.32	B	3.28	47.04	2.14	B+C+D
1.19	—	1.24	B	3.22	51.47	1.86	B+D
0.73	—	1.21	B	4.26	62.30	1.30	B+D
7.02[b]	9.52	0	C				
6.65	9.09	0.49	C+B				
6.48	8.60	0.73	B				
4.59	5.68	0.72	B				
2.30	—	0.80	B				
1.74	2.17	0.94	B				
1.08	—	0.90	B				

[a] Section with constant ratio of $UO_2(NO_3)_2$ and HNO_3 concentrations.
[b] Section with constant ratio of $C_2H_2O_4$ and HNO_3 concentrations.
[c] Section with constant HNO_3 concentration.
[d] Section with constant $C_2H_2O_4$ concentration.
[e] Eutonic points for $UO_2C_2O_4$ and $C_2H_2O_4$.
[f] (A) $UO_2(NO_3)_2 \cdot 6H_2O$, [13520-83-7]; (B) $UO_2C_2O_4 \cdot 3H_2O$, [18860-43-0]; (C) $C_2H_2O_4 \cdot 2H_2O$, [6153-56-6]; (D) $UO_2C_2O_4 \cdot H_2O$, [ ].

Additional information:
In solutions containing >25 mass % $UO_2(NO_3)_2$ and >30 mass % HNO_3, $UO_2C_2O_4$ showed a tendency toward formation of supersaturated solutions. Thus for 28.95 mass % $UO_2(NO_3)_2$ and 38.45 mass % HNO_3, the concentration of $UO_2C_2O_4$ reached 8.23 mass %, while the corresponding equilibrium solubility was only 2.72 mass %: Metastable solutions were formed only when dry $UO_2C_2O_4 \cdot 3H_2O$ was added to a solution of $UO_2(NO_3)_2$ in HNO_3.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Mixtures of the desired composition were equilibrated for 3–6 days. The time necessary for reaching equilibrium increased with increasing concentration of $UO_2(NO_3)_2$. The vessels used were protected from light to prevent the formation of basic U(IV) oxalates. Saturated solutions were analyzed for uranium, oxalate, and nitrate. Uranium and oxalate were determined by titration with $KMnO_4$ solution, nitrate was determined by the Kjeldahl method after reducing NO_3^- with Deward alloy. Composition of the equilibrium solid phases was determined by the method of indifferent component (NO_3^-), in some cases also by chemical analysis and optical microscopy.

Source and Purity of Materials:

No details reported.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

5.11.7. Uranium(VI) Dioxo(oxalate) N,N′-Dimethyl Formamide Monosolvate

Components:

(1) Uranium(VI) dioxo oxalate N, N′-dimethyl formamide monosolvate; $UO_2C_2O_4 \cdot C_3H_7NO$; [83835-49-8]
(2) N, N′-dimethyl formamide; C_3H_7NO; [68-12-2]
(3) Nitric acid; HNO_3; [7697-37-2]
(4) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(5) Water; H_2O; [7732-18-5]

Original Measurements:

D. N. Bykhovskii, M. A. Kuzmina, and G. I. Petrzhak, Radiokhimiya **25**, 45–7 (1983).

Variables:

T/K: 298
c_2 /mol dm^{-3}: 0–5.0
c_3 /mol dm^{-3}: 1.0
c_4 /mol dm^{-3}: 0.15

Prepared by:

J. Hála

Experimental Data

Solubility of $UO_2C_2O_4 \cdot C_3H_7NO$ at 25 °C in solutions containing 1.0 mol dm^{-3} HNO_3 and 0.15 mol dm^{-3} oxalic acid as a function of C_3H_7NO concentration[a]

C_3H_7NO (c_2 /mol dm^{-3})	$UO_2C_2O_4 \cdot C_3H_7NO$ (10^3c_1 /mol dm^{-3})	C_3H_7NO (c_2 /mol dm^{-3})	$UO_2C_2O_4 \cdot C_3H_7NO$ (10^3c_1 /mol dm^{-3})
0	15.7±0.7	1.5	0.30±0.01
0.10	2.35±0.21	2.0	0.30±0.01
0.25	1.15±0.07	3.0	0.30±0.02
0.50	0.58±0.01	4.0	0.33±0.01
0.75	0.45±0.02	5.0	0.41±0.02
1.0	0.37±0.02		

[a] Equilibrium solid phases were not investigated.

Additional information:
Also reported was, in graphical form, solubility of $UO_2C_2O_4 \cdot C_3H_7NO$ as a function of oxalic acid concentration, in 1.0 mol dm^{-3} HNO_3/0.5 mol dm^{-3} C_3H_7NO or 1.0 mol dm^{-3} HNO_3/2.0 mol dm^{-3} C_3H_7NO solutions.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess solid was equilibrated with solutions of the desired composition for 30 h while equilibrium was attained after 6 h. Concentration of uranium in the saturated solutions was determined spectrophotometrically with arsenazo III.[1]

Source and Purity of Materials:

The $UO_2C_2O_4 \cdot C_3H_7NO$ complex was prepared by precipitation with 0.8 mol dm^{-3} oxalic acid of a solution which was 0.1 mol dm^{-3} in uranium and 0.6 mol dm^{-3} in C_3H_7NO.[2] The crystalline solid was washed with water, ethanol and ether, and was characterized by chemical analysis and x-ray diffraction.

Estimated Error:

Temperature: precision ±0.2 K (authors).
Solubility: see authors' data above.

References:

[1] S. A. Nikitina, A. A. Lipovskii, and T. A. Demyanova, Radiokhimiya **20**, 900 (1978).
[2] D. N. Bykhovskii, M. A. Kuzmina, L. V. Solncev, and A. G. Tutov, Radiokhimiya **24**, 468 (1982).

Components:

(1) Uranium(VI) dioxo oxalate N, N′-dimethyl formamide monosolvate; $UO_2C_2O_4 \cdot C_3H_7NO$; [83835-49-8]
(2) N,N′-dimethyl formamide; C_3H_7NO; [68-12-2]
(3) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

D. N. Bykhovskii, M. A. Kuzmina, and G. I. Petrzhak, Radiokhimiya **25**, 45–7 (1983).

Variables:

T/K: 298
c_2 /mol dm^{-3}: 0.05–5.0
c_3 /mol dm^{-3}: 0.1

Prepared by:

J. Hála

Experimental Data

Solubility of $UO_2C_2O_4 \cdot C_3H_7NO$ in 0.1 mol dm^{-3} $NaClO_4$ solutions at 25 °C as a function of C_3H_7NO concentration[a]

C_3H_7NO (c_2 /mol dm^{-3})	$UO_2C_2O_4 \cdot C_3H_7NO$ (10^3 c_1 /mol dm^{-3})	C_3H_7NO (c_2 /mol dm^{-3})	$UO_2C_2O_4 \cdot C_3H_7NO$ (10^3 c_1 /mol dm^{-3})
0.050	3.11±0.07	1.0	0.31±0.01
0.10	1.68±0.10	1.5	0.27±0.02
0.15	1.18±0.04	2.0	0.25±0.01
0.20	0.99±0.12	2.5	0.24±0.01
0.25	0.70±0.08	3.0	0.25±0.01
0.35	0.60±0.01	4.0	0.26±0.02
0.50	0.46±0.02	5.0	0.31±0.02
0.75	0.32±0.01		

[a] Equilibrium solid phases were not investigated.

Additional information:
The authors assumed of the existence of $UO_2C_2O_4(C_3H_7NO)$ and $UO_2C_2O_4(C_3H_7NO)_2$ species in the saturated solutions.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess solid was equilibrated with solutions of the desired composition for 30 h while equilibrium was attained after 6 h. Concentration of uranium in the saturated solutions was determined spectrophotometrically with arsenazo III.[1] Solid phases were not investigated.

Source and Purity of Materials:

The $UO_2C_2O_4 \cdot C_3H_7NO$ complex was prepared by precipitation with 0.8 mol dm^{-3} oxalic acid of a solution which was 0.1 mol dm^{-3} in uranium and 0.6 mol dm^{-3} in C_3H_7NO.[2] The crystalline solid was washed with water, ethanol, and ether, and was characterized by chemical analysis and x-ray diffraction.

Estimated Error:

Temperature: precision ±0.2 K (authors).
Solubility: see authors' data above.

References:

[1] S. A. Nikitina, A. A. Lipovskii, and T. A. Demyanova, Radiokhimiya **20**, 900 (1978).
[2] D. N. Bykhovskii, M. A. Kuzmina, L. V. Solncev, and A. G. Tutov, Radiokhimiya **24**, 468 (1982).

5.12. Ammonium Tris(*o*-hydroxybenzoato) Dioxouranate (VI)

Components:

(1) Ammonium tris(hydroxybenzoato) dioxouranate(VI); $NH_4[UO_2(C_7H_5O_3)_3]$; [ ]
(2) Ammonium hydroxybenzoate (salicylate); $NH_4(C_7H_5O_3)$; [ ]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

O. E. Zvyagintsev and B. N. Sudarikov, Zh. Neorg. Khim. **2**, 128–37 (1957).

Variables:

T/K: 291–369
$NH_4(C_7H_5O_3)$/g kg^{-1} saturated solution: 0–230

Prepared by:

J. Hála

Experimental Data

Solubility of $NH_4[UO_2(C_7H_5O_3)_3]$ in water and in solutions of $NH_4(C_7H_5O_3)$ at different temperatures[a]

Solubility of $NH_4[UO_2(C_7H_5O_3)_3]$ in water as a function of temperature

Temperature (°C)	U (g kg^{-1})[b]	$NH_4[UO_2(C_7H_5O_3)_3]$ (10^2 m_1 /mol kg^{-1})[c]
18	1.40	0.590
50	3.73	1.58
75	5.72	2.44
96	7.96	3.42

Solubility at 18 °C of $NH_4[UO_2(C_7H_5O_3)_3]$ as a function of $NH_4(C_7H_5O_3)$ concentration[d]

$NH_4(C_7H_5O_3)$ (g kg^{-1})[b]	U (g kg^{-1})[b]	$NH_4[UO_2(C_7H_5O_3)_3]$ (10^3 mol kg^{-1})[b,c]
0	1.40	5.88
20	0.29	1.22
50	0.11	0.462
100	0.08	0.336
230	0.12	0.504

Solubility at 40 °C of $NH_4[UO_2(C_7H_5O_3)_3]$ as a function of $NH_4(C_7H_5O_3)$ concentration[d]

$NH_4(C_7H_5O_3)$ (g kg^{-1})[b]	U (g kg^{-1})[b]	$NH_4[UO_2(C_7H_5O_3)_3]$ (10^3 mol kg^{-1})[b,c]
0	3.09	13.0
100	1.24	5.21
230	0.56	2.35

Solubility of $NH_4[UO_2(C_7H_5O_3)_3]$ in solutions containing 230 g kg^{-1} $NH_4(C_7H_5O_3)$

Temperature (°C)	U (g kg^{-1})[b]	$NH_4[UO_2(C_7H_5O_3)_3]$ (10^3 mol kg^{-1})[b,c]
18	0.12	0.504
40	0.56	2.35
70	1.05	4.41

Solubility at 18 °C of $NH_4[UO_2(C_7H_5O_3)_3]$ in solutions containing 100 g kg^{-1} $NH_4(C_7H_5O_3)$ as a function of pH

pH	U (g kg^{-1})[b]	$NH_4[UO_2(C_7H_5O_3)_3]$ (10^3 mol kg^{-1})[b,c]
5.10	0.08	0.336
5.43	0.12	0.504
6.02	2.80	11.8
6.25	3.09	13.0

Solubility at 18 °C of $NH_4[UO_2(C_7H_5O_3)_3]$ in solutions containing 200 g kg^{-1} $NH_4(C_7H_5O_3)$ as a function of pH

pH	U (g kg^{-1})[b]	$NH_4[UO_2(C_7H_5O_3)_3]$ (10^3 mol kg^{-1})[b,c]
5.25	0.12	0.504
6.46	3.09	13.0
6.91	11.64	48.9
8.64	12.94	54.4

[a] Equilibrium solid phases were not investigated.
[b] Grams per kg saturated solution.
[c] Calculated by compiler.
[d] pH = 5.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess $NH_4[UO_2(C_7H_5O_3)_3]\cdot 4H_2O$ was stirred for 24 h with the solutions under the desired conditions. In the saturated solutions, uranium was determined gravimetrically; a weighed aliquot of the saturated solution was evaporated to dryness, and the residue was ignited to U_3O_8.

Source and Purity of Materials:

$NH_4[UO_2(C_7H_5O_3)_3]\cdot 4H_2O$ was obtained by precipitation with salicylic acid of a UO_2^{2+} solution at pH 3–6 in the presence of NH_4^+ ions. The salt was obtained as orange crystals. It was recrystallized from hot solution, and dried at 70–75 °C. Analysis, found/calculated for the tetrahydrate (mass %): UO_2^{2+} 34.96/35.02; $C_7H_5O_3^-$ 53.28/53.31; NH_4^+ 2.41/2.33;H_2O 9.75/9.34.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

5.13. Uranium(VI) Dioxo(8-hydroxyquino-linate)

Components:

(1) Uranium(VI) dioxo bis(8-hydroxy-quinolinate)(8-hydroxyquinoline); $UO_2(C_9H_6NO)_2\cdot C_9H_7NO$; or $C_{27}H_{19}N_3O_5U$; [17855-75-3]
(2) 1,4-dioxane; $C_4H_8O_2$; [123-91-1]

Original Measurements:

R. G. Charles and H. Freiser, J. Am. Chem. Soc. **73**, 5223–4 (1951).

Variables:

T/K: 298

Prepared by:

J. Hála

Experimental Data

The solubility of $UO_2(C_9H_6NO)_2\cdot C_9H_7NO$ in 1,4-dioxane at 25 °C is reported to be $x_1 = 0.000\ 51$. From this the compiler calculated $m_1 = 2.76\times 10^{-5}$ mol kg^{-1}.

Auxiliary Information

Method/Apparatus/Procedure:

The solubility was determined by weighing the residue obtained by evaporation of a weighed portion of the saturated solution. The latter was prepared by extracting the solid $UO_2(C_9H_6NO)_2\cdot C_9H_7NO$ in a Soxhlet extractor, and allowing the saturated solution to cool to room temperature.

Source and Purity of Materials:

$UO_2(C_9H_6NO)_2\cdot C_9H_7NO$ was prepared by precipitation with 8-hydroxyquinoline of an aqueous solution of a UO_2^{2+} salt according to Ref. 1. The product was dried at the recommended temperature in a constant temperature oven. 8-hydroxyquinoline used (Lemke Co.) was recrystallized from alcohol and water. 1,4-dioxane (Carbide and Carbon Co.) was purified by the procedure given in Ref. 2, and distilled from sodium before use.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

References:

[1] F. J. Welcher, *Organic Analytical Reagents* (Van Nostrand, New York, 1947), Vol. 1, p. 265.
[2] A. Weissberger and E. Poskauer, *Organic Solvents* (Clarendon, Oxford, 1935).

Components:

(1) Uranium(VI) dioxo bis(8-hydroxy-quinolinate)(8-hydroxyquinoline); $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$; or $C_{27}H_{19}N_3O_5U$; [17855-75-3]
(2) Water; H_2O; [7732-18-5]

Original Measurements:

A. E. Klygin and N. S. Kolyaga, Zh. Neorg. Khim. **3**, 2767–70 (1958).

Variables:

T/K: 298

Prepared by:

J. Hála

Experimental Data

Solubility of $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$ at 25 °C in water[a]

C_9H_7NO[b] (10^3 mol dm^{-3})	U[e] (10^3 mol dm^{-3})	pH[f]	K_{sp}[g] (10^{29} mol^2 dm^{-6})
0.601[c]	0.218	3.90	1.63
2.40[c]	0.797	3.40	1.79
2.95[c]	0.983	3.26	0.87
5.75[c]	1.91	3.07	1.47
18.7[c]	6.19	2.72	3.10
2.24[d]	1.78	3.38	2.60
8.95[d]	5.51	2.84	1.18
16.9[d]	7.31	2.65	1.21
			1.9±0.5[h]

[a] Equilibrium solid phases were not investigated.
[b] Total concentration of 8-hydroxyquinoline in the saturated solution.
[c] Obtained by isothermal procedure. Saturated solutions contained varying concentration of HCl, from 0.00535 to 0.0535 mol dm^{-3}.
[d] Obtained by precipitation procedure. Saturated solutions contained 0.02 mol dm^{-3} NO_3^-, 0.027 mol dm^{-3} Cl^-, and 0.043–0.072 mol dm^{-3} NH_4^+.
[e] Total concentration of uranium in the saturated solution.
[f] pH of the saturated solution.
[g] $K_{sp}=[UO_2^{2+}][R^-]^2[HR]$ (HR stands for C_9H_7NO); calculated by the authors from pH and concentrations of uranium and C_9H_7NO by using authors' values of dissociation constants of 8-hydroxyquinoline, $K_1=[H^+][HR][H_2R^+]^{-1}=8.66\times10^{-6}$ and $K_2=[H^+][R^-][HR]^{-1}=1.76\times10^{-10}$, and the equilibrium constant for the hydrolysis of UO_2^{2+}, $K_h=[UO_2OH^+][H^+][UO_2^{2+}]^{-1}$, taken from Ref. 1.
[h] Average value (authors).

Additional information:

The authors quote Ref. 2, not available to the compiler, where K_{sp} of $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$ was reported to be 3.48×10^{-24} mol^2 dm^{-6}. Klygin and Kolyaga considered this value to be erroneous since in its determination several equilibria such as protonation of C_9H_7NO, complexation of UO_2^{2+} with acetate ion, and hydrolysis of UO_2^{2+} were not taken into consideration.

Auxiliary Information

Method/Apparatus/Procedure:

The solubility product of $UO_2(C_9H_6NO)_2 \cdot (C_9H_7NO)$ was determined by two procedures. In one, 1 g of solid complex was equilibrated for 4 days with 100 mL solution initially containing 0.005 35–0.0535 mol dm^{-3} HCl. In the other one, the complex was precipitated in 100 mL volumetric flasks from 10 mL 0.1 mol dm^{-3} $UO_2(NO_3)_2$ and 25 mL 0.1 mol dm^{-3} C_9H_7NO in 0.107 mol dm^{-3} HCl, and pH of the solution was adjusted by adding varying volumes of ammonia solution. The volumes were filled up to the mark with distilled water, and the flasks were equilibrated for 4 days. Equilibration in both series of measurements was carried out in an air-heated thermostat. The saturated solutions were analyzed for uranium (8-hydroxyquinoline was destroyed by ignition and uranium determined titrimetrically by the HSO_3^-/PO_4^{3-} method[3] or, at low uranium concentrations, colorimetrically with arsenazo,[4] and 8-hydroxyquinoline (titrimetrically with bromate). The pH was measured potentiometrically with a glass electrode.

Source and Purity of Materials:

$UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$ was prepared according to Ref. 5 from 8-hydroxyquinoline purified by sublimation.

Estimated Error:

Temperature: precision±0.2 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] N. P. Komar and Z. A. Tretyak, Zh. Anal. Khim. **10**, 236 (1955).
[2] E. S. Tinovskaya, Nauch. Zap. Kievsk. Univ., Chim. Sbornik **5**, 220 (1949).
[3] N. P. Komar, Zh. Anal. Khim. **7**, 325 (1952).
[4] V. I. Kuznetsov, Dokl. Akad. Nauk SSR **50**, 227 (1945).
[5] R. Berg, *The Use of Quinolinol in Analytical Chemistry* (Russian translation of German edition), (ONTI, Moscow, 1937).

Components:

(1) Uranium(VI) dioxo bis(8-hydroxy-quinolinate)(8-hydroxyquinoline); $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$; or $C_{27}H_{19}N_3O_5U$; [17855-75-3]
(2) Ammonium carbonate; $(NH_4)_2CO_3$; [506-87-6]
(3) Ammonium chloride; NH_4Cl; [12125-01-8]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

A. E. Klygin and I. D. Smirnova, Zh. Neorg. Khim. **4**, 42–5 (1959).

Variables:

T/K: 298
c_2 /mol dm^{-3}: 0.013–0.32

Prepared by:

J. Hála

Experimental Data

Solubility of $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$ at 25 °C in $(NH_4)_2CO_3$ solutions[a,b]

$(NH_4)_2CO_3$ (c_2 /mol dm^{-3})	C_9H_7NO[c] (10^3 mol dm^{-3})	U[d] (10^3 mol dm^{-3})	$[H^+]$[e] (10^9 mol dm^{-3})
0.01299	0.235	0.312	19.95
0.02598	0.485	0.231	8.71
0.03897	0.415	0.347	5.89
0.06495	1.18	0.563	3.89
0.1299	2.20	0.9997	2.138
0.1949	3.07	1.35	1.349
0.2598	3.80	1.59	0.1514
0.2988	4.60	1.78	0.7763
0.3247	4.325	1.83	0.148

[a] Ionic strength kept at 1.0 mol dm^{-3} by using NH_4Cl.
[b] The authors did not report about the composition of the equilibrium solid phase. The compiler assumed this to be $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$, [17855-75-3].
[c] Total concentration of 8-hydroxyquinoline in the saturated solutions.
[d] Concentration of uranium in the saturated solutions.
[e] pH of the equilibrium saturated solutions.

Additional Information:

From the increase of the solubility of $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$ in the presence of $(NH_4)_2CO_3$, and from the solubility of the former,[1] the authors calculated the instability constant of the $UO_2(CO_3)_3^{4-}$ complex.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess solid complex $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$ was equilibrated in volumetric flasks with solutions containing the desired concentration of $(NH_4)_2CO_3$ at ionic strength of 1.0 mol dm^{-3}. the flasks were shaken in a thermostat for 24 h which was found sufficient to reach equilibrium. The saturated solutions were filtered through a No. 4 sintered glass filter, and analyzed for uranium (8-hydroxyquinoline was destroyed by ignition and uranium determined titrimetrically or, at low concentrations, colorimetrically with arsenazo), and 8-hydroxyquinoline (titrimetrically with bromate). The pH was measured potentiometrically with a glass electrode. The concentration of the $(NH_4)_2)CO_3$ stock solution was determined volumetrically based on the volume of CO_2 gas evolved.

Source and Purity of Materials:

$UO_2(C_9H_6NO)_2 .(C_9H_7NO)$ was prepared according to Ref. 2 from 8-hydroxyquinoline purified by sublimation.

Estimated Error:

Temperature: precision ±0.1 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] A. E. Klygin and N. S. Kolyaga, Zh. Neorg. Khim **3**, 2767 (1958).
[2] R. Berg, *The Use of Quinolinol in Analytical Chemistry* (Russian translation of German edition) (ONTI, Moscow, 1937).

Components:
(1) Uranium(VI) dioxo bis(8-hydroxy-quinolinate)(8-hydroxyquinoline); $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$; or $C_{27}H_{19}N_3O_5U$; [17855-75-3]
(2) Ethanol; C_2H_6O; [64-17-5]
(3) Trichloromethane; $CHCl_3$; [67-66-3]

Original Measurements:
S. Oki, Anal. Chim. Acta **44**, 315–22 (1969).

Variables:
100 w_2 /mass%: 0.5

Prepared by:
J. Hála

Experimental Data

Solubility of $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$ in chloroform containing 0.5% ethanol[a]

Solvent	$UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$ (10^4 c_1 /mol dm^{-3})	
$CHCl_3$	8.74 8.74 8.16 8.21 7.89	8.35±0.40[b]
$CHCl_3$+0.5%C_2H_6O	9.48 10.12 9.66 9.48 10.58	9.86±0.48[b]

[a] At unspecified room temperature. Equilibrium solid phases were not investigated.
[b] Average value and standard deviation (compiler).

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Uranium in the saturated solutions was determined, after removal of $CHCl_3$ and 8-hydroxyquinoline by heating the sample to 180 °C, colorimetrically with arsenazo III.[1]

Source and Purity of Materials:

$UO_2(C_9H_6NO)_2 \cdot (C_9H_7NO)$ was prepared by precipitating uranium from 200 mL solution containing 1 g $UO_2(NO_3)_2 \cdot 6H_2O$ with a solution of 1 g 8-hydroxyquinoline in 100 mL 1 mol dm^{-3} HCl. The solution was heated to 70 °C and 2 mol dm^{-3} NH_4OH solution was added dropwise while stirring until no further precipitate appeared. After digestion for 1 h, the precipitate was filtered, washed with hot water, and dried over P_2O_5. 8-hydroxyquinoline, G. R. grade, was used without further purification. The composition of the complex was verified by chemical analysis. $CHCl_3$, G. R. grade, containing 0.5% ethanol was first purified from ethanol by washing it with distilled water twice. It was then dehydrated, first with anhydrous Na_2SO_4, and then by passing it through a column of silica gel.

Estimated Error:
Temperature: precision not reported.
Solubility: see above.

Components:
(1) Uranium(VI) dioxo bis(8-hydroxy-quinolinate); $UO_2(C_9H_6NO)_2$; or $UO_2C_{18}H_{12}N_2O_{4U}$; [ ]
(2) Trichloromethane; $CHCl_3$; [67-66-3]

Original Measurements:
S. Oki, Anal. Chim. Acta **44**, 315–22 (1969).

Variables:

Prepared by:
J. Hála

Experimental Data

The solubility of $UO_2(C_9H_6NO)_2$, at an unspecified room temperature, in chloroform is reported to be $c_1 = 3.99 \times 10^{-4}$ mol dm^{-3}. The complex did not change in composition on dissolution.

Additional information:
In the presence of ethanol or in chloroform saturated with water, the complex decomposed upon dissolution according to the equations

$$3\,UO_2(C_9H_6NO)_{2(s)} + C_2H_5OH \leftrightarrows UO_2(C_9H_6NO)_2 \cdot C_9H_7NO + UO_2(C_9H_6NO)_2 \cdot C_2H_5OH_{(s)}\,, \text{ or}$$

$$2\,UO_2(C_9H_6NO)_{2(s)} + H_2O \leftrightarrows UO_2(C_9H_6NO)_2 \cdot C_9H_7NO + UO_2(C_9H_6NO)(OH)_{(s)}\,,$$

respectively (C_9H_7NO is 8-hydroxyquinoline). Dissolution of $UO_2(C_9H_6NO)_2$ in ethanol containing chloroform resulted in the formation of a dark red solution and a brown solid residue.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Equilibrium was attained in 1–2 days. Uranium in the saturated solutions was determined colorimetrically with arsenazo III[1] after removal of $CHCl_3$ and 8-hydroxyquinoline by heating the sample at 180 °C.

Source and Purity of Materials:

$UO_2(C_9H_6NO)_2$ was prepared according to Ref. 2 by heating the $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$ complex at 260 °C for 1 h. The latter was prepared according to the procedure given in the compilation for the $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$/ethanol/$CHCl_3$ system reported in the same original document. The composition of $UO_2(C_9H_6NO)_2$ was verified by chemical analysis. Chloroform (G. R. grade) containing 0.5% ethanol was first purified from the latter by washing with distilled water twice. It was then dehydrated, first with anhydrous Na_2SO_4, and then by passing it through a column of silica gel.

References:

[1] H. Onishi and Y. Higuchi, Bunseki Kagaku **14**, 1141 (1965).
[2] W. W. Wendlandt, Analyt. Chem. **28**, 499 (1956).

5.14. Uranium(VI) Dioxo(ethylenediaminetetraacetate)

Components:

(1) Uranium(VI) dioxo ethylenediamine tetraacetate; $C_{10}H_{14}N_2O_{10}U$;
(2) Water; H_2O; [7732-18-5]

Original Measurements:

A. E. Klygin, I. D. Smirnova, and N. A. Nikolskii, Zh. Neorg. Khim. **4**, 2623–9 (1959).

Variables:

T/K:298

Prepared by:

J. Hála

Experimental Data

Composition of solutions saturated with $C_{10}H_{14}N_2O_{10}U$ at 25 °C[a]

$[H^+]$ (10^4 mol dm^{-3})	U[b] (10^4 mol dm^{-3})	H_4R[c] (10^2 mol dm^{-3})	K_{sp}[d] (10^6 mol^2 dm^{-6})
8.51	1.72	2.00	2.04
7.94	1.61	2.01	1.96
6.46	1.65	1.99	2.11
5.89	1.71	1.63	1.82
5.29	1.64	1.99	2.18
3.98	1.71	2.04	2.41
1.35	2.44	1.97	3.02
0.257	3.55	2.01	2.01
			2.25±0.18[e]

[a] Equilibrium solid phases were not investigated.
[b] Total concentration of uranium in the saturated solution.
[c] Total concentration of ethylenediamine tetraacetic acid (H_4R) in the saturated solution.
[d] $K_{sp}=[UO_2^{2+}][H_2R^{2-}]$ (H_4R stands for ethylenediamine tetraacetic); calculated by the authors from pH, and total concentrations of uranium and H_4R by using authors' values of the first and second dissociation constant of H_4R, and the equilibrium constant for the hydrolysis of UO_2^{2+}, $K_h=[UO_2OH^+][H^+][UO_2^{2+}]^{-1}$, taken from Ref. 1.
[e] Average value (authors).

Additional information:

From the initial concentrations of $UO_2(NO_3)_2$ and H_4R, and from the stoichiometry of the precipitation reaction, the compiler estimated ionic strength of the saturated solutions to be approximately 0.11 mol dm^{-3}.

Auxiliary Information

Method/Apparatus/Procedure:

The solubility product of UO_2H_2R was determined isothermally at pH 3 to 4.5 since at pH<3 solid H_4R contaminated UO_2H_2R in the equilibrium solid phase while at pH>4.5 the solubility of UO_2H_2R increased considerably due to complex formation in the solution. Measurements were carried out in volumetric flasks, each containing 25 mL 0.1 mol dm^{-3} $UO_2(NO_3)_2$ and 50 mL 0.09 mol dm^{-3} $(NH_4)_2H_2R$. The pH of the solutions was adjusted by adding varying volumes of 0.12 mol dm^{-3} ammonia solution. Equilibrium was reached in 9 days. In the saturated solutions, uranium was determined photometrically with H_2O_2 in alkaline medium,[2] H_4R by titration with $Th(NO_3)_4$ solution,[3] and pH was determined potentiometrically using quinhydrone electrode.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: precision not reported.
Solubility product: see above.

References:

[1] N. P. Komar and Z. A. Tretyak, Zh. Analit. Khim. **10**, 236 (1955).
[2] J. Rodden, in *Analytical Chemistry of the Manhattan Project* (Russian translation) (IL, Moscow, 1956), p. 124.
[3] J. J. Fritz and J. J. Ford, Analyt. Chem. **25**, 1640 (1953).

5.15. Uranium(VI) Dioxo [4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionate]

Components:

(1) Uranium(VI) dioxo bis[4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionate]; $C_{16}H_{10}F_6O_6S_2U$ or $UO_2(C_8H_5F_3O_2S)_2$; [184444-18-3]
(2) Solvents

Original Measurements:

K. Akiba, N. Suzuki, and T. Kanno, Kakuriken Kenkyu Hokoku **2**, 150–2 (1969).

Variables:

T/K:298

Prepared by:

T. Tominaga

Experimental Data

Solubility of $C_{16}H_{10}F_6O_6S_2U$ at 25 °C in various solvents[a]

Solvent	$C_{16}H_{10}F_6O_6S_2U$ (10^4 c_1 /mol dm^{-3})
n-hexane, C_6H_{14}, [110-54-3]	0.10
n-heptane, C_7H_{16}, [142-82-5]	0.12
cyclohexane, C_6H_{12}, [110-82-7]	0.14
benzene, C_6H_6, [71-43-2]	200
toluene, C_7H_8, [108-88-3]	150
isopropylbenzene, C_9H_{12}, [98-82-8]	29.0
chlorobenzene, C_6H_5Cl, [108-90-7]	200
o-dichlorobenzene, $C_6H_4Cl_2$, [95-50-1]	100
dichloromethane, CH_2Cl_2, [75-09-2]	700
chloroform, $CHCl_3$, [67-66-3]	270
tetrachloromethane, CCl_4, [56-23-5]	7.8
trichlorobenzene $C_6H_3Cl_3$[b]	32.0

[a] Equilibrium solid phases not investigated.
[b] Isomer not specified.

Additional information:

In a subsequent document,[1] the authors reported, in graphical form, the solubility of $C_{16}H_{10}F_6O_6S_2U$ in *n*-heptane and CCl_4 as a function of the concentration of 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess solute was shaken with the desired solvent for about 100 h in an air thermostat. After centrifugation, γ activity of the supernatant solution was measured. The solubilities were calculated using a calibration curve prepared by means of solutions containing known amounts of $^{237}UO_2^{2+}$.

Source and Purity of Materials:

The of $C_{16}H_{10}F_6O_6S_2U$ complex was prepared by adding stoichiometric amount of the ligand to a warm solution of uranium(VI) dioxide diacetate labeled with ^{237}U. The resultant yellow precipitate was filtered, washed with water and hexane, and dried over P_2O_5 under reduced pressure. Dry solvents were used.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

References:

[1] K. Akiba and N. Suzuki, Kakuriken Kenkyu Kokoku **3**, 144 (1970).

5.16. Uranium(IV) Phthalocyaninate

Components:

(1) Uranium(IV) bis(phthalocyaninate); $C_{64}H_{32}H_{16}U$ or $U(C_{32}H_{16}N_8)_2$; [ ]
(2) Solvents

Original Measurements:

P. N. Moskalev, G. N. Shapkin, and Yu. S. Misko, Radiokhimiya **20**, 343–4 (1978).

Variables:

T/K: 298

Prepared By:

J. Hála

Experimental Data

Solubility of $C_{64}H_{32}N_{16}U$ in two solvents[a]

Solvent	$C_{64}H_{32}N_{16}U$ (g dm^{-3})	$C_{64}H_{32}N_{16}U$ (10^4 c_1 /mol dm^{-3})[b]
benzene, C_6H_6, [71-43-2]	0.031	0.413
1-chloronaphthalene, $C_8H_{10}Cl$, [90-13-1]	0.31	4.13

[a] The solubility was independent of temperature over the range of 13–50 °C. Equilibrium solid phases were not investigated.
[b] Calculated by compiler.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. The solid was equilibrated with the desired solvent in ground glass stoppered cylinders in a themostated bath until equilibrium was attained. The saturated solutions were filtered through a glass filter, an aliquot was diluted to $\sim 10^{-5}$ mol dm^{-3} with dimethylformamide containing 1% hydrazine hydrate, and the concentration of phthalocynaine was determined spectrophotometrically.

Source and Purity of Materials:

$C_{64}H_{32}N_{16}U$ was prepared according to Ref. 1. Chemical composition and purity of the solute were checked by chemical analysis and x-ray diffraction. Reagent grade solvents were used without further purification.

Estimated Error:

Solubility: insufficient data given to allow for error estimate.

References:

[1] I. S. Kirin, A. B. Kolyadin, and P. N. Moskalev, Zh. Neorg. Khim. **16**, 2731 (1971).

6. The Solubility of Neptunium Compounds

6.1. Neptunium(VI) Dioxocarbonate

Components:

(1) Neptunium(VI) dioxocarbonate; NpO_2CO_3 ; [ ]
(2) Carbon dioxide; CO_2; [124-38-9]
(3) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

Y. Kato, T. Kimura, Z. Yoshida, and N. Nitani, Radiochim. Acta **82**, 63–8 (1998).

Variables:

T/K: 298
p_2 (partial pressure of CO_2)/%: 80
c_3 /mol dm^{-3}=0.1

Prepared By:

J. Hála

Experimental Data

Solubility of NpO_2CO_3 at 25 °C as a function of carbonate ion concentration in 0.1 mol dm^{-3} $NaClO_4$ solutions[a]

pH	$-\log[CO_3^{2-}]$	$-\log$ Np[(VI)]	pH	$-\log[CO_3^{2-}]$	$-\log$ Np[(VI)]	pH	$-\log[CO_3^{2-}]$	$-\log$ Np[(VI)]
2.79	12.27	2.37	3.24	11.37	2.71	2.87	12.11	2.01
2.88	12.09	2.06	3.25	11.35	2.76	3.14	11.57	2.66
2.92	12.01	2.46	3.64	10.57	3.28	3.15	11.55	2.04
3.05	11.75	2.36	3.64	10.57	3.10	3.42	11.01	3.03
3.14	11.57	2.80	5.81	6.23	5.11	3.81	10.23	3.47
3.15	11.55	2.52	5.90	6.05	4.86	6.29	5.27	4.36
3.15	11.55	2.49	5.91	6.03	4.94	6.34	5.17	4.33
3.37	11.11	2.51	5.93	5.99	5.06	6.35	5.15	4.42
3.73	10.39	3.80	5.99	5.87	5.03	6.36	5.13	4.34
3.81	10.23	3.74	6.03	5.79	4.71	6.43	4.99	3.66
4.04	9.77	3.89	6.04	5.77	4.93	6.44	4.97	3.71
4.05	9.77	4.02	6.14	5.57	4.80	6.46	4.93	4.04
4.18	9.49	4.26	6.17	5.51	4.76	6.47	4.91	3.65
4.28	9.29	4.22	6.20	5.45	4.25	6.50	4.85	3.41
4.39	9.07	4.81	6.26	5.33	4.10	6.53	4.79	3.56
4.62	8.61	4.86	6.28	5.29	3.97	6.54	4.77	3.22
4.68	8.49	4.88	6.28	5.29	3.81	6.66	4.53	2.88
4.88	8.09	5.13	6.30	5.25	3.75	6.71	4.43	2.51
5.05	7.75	4.96	6.42	5.01	3.47	6.72	4.41	2.50
5.19	7.47	5.10	6.47	4.91	2.90	6.75	4.35	2.47
5.20	7.45	5.18	6.50	4.85	2.78	6.76	4.33	2.42
5.94	5.97	4.73	6.52	4.81	2.71	6.77	4.31	2.48
5.97	5.91	4.62	6.54	4.77	2.63	6.82	4.21	2.42
			6.63	4.59	2.52			

[a] Solid phase was NpO_2CO_3, [ ], in all solutions.

Additional information:

Free carbonate ion concentration was calculated by the same procedure as in the authors' previous work.[1,2] Using least-squares analysis, the following constants were obtained: solubility product of NpO_2CO_3 ,$K_{sp}=[NpO_2^{2+}][CO_3^{2-}]=10^{-(14.04\pm0.07)}$; stability constants of Np(VI) carbonatocomplexes, $\beta_n=[NpO_2(CO_3)_n^{2-2n}][NpO_2^{2+}]^{-1}[CO_3^{2-}]^{-n}$, $\beta_1=10^{9.20\pm0.10}$, and $\beta_3=10^{20.41\pm0.09}$. For the dicarbonato-complex, the upper limit only was obtained as $\beta_2<10^{14.2}$.

In an earlier paper,[3] the authors reported $K_{sp}=10^{-(14.62\pm0.12)}$ under the same conditions. In this paper, K_{sp} was obtained from six measurements performed at pH<4, and solubility data were presented in graphical form only.

Auxiliary Information

Method/Apparatus/Procedure:

Solubility experiments were conducted as pH titrations in a thermostated glass vessel in the pH range from 2.8 to 6.8 in an atmosphere of 80% CO_2/O_2. The gas was first passed through an ozone generator to produce ozone in the gas and thus stabilize the hexavelant state of Np. The gas was then moistened in washing flasks, and passed continuously through the solution. Ozone was shown to have no effect on the solid/liquid equilibrium. The hexavelant state of Np was checked by measuring the redox potential of working solutions using a Pt–Ag/AgCl combination electrode. The solid phase was precipitated from 0.02 mol dm^{-3} solution of Np(VI) by addition of 0.1 mol dm^{-3} $NaHCO_3$ or 0.1 mol dm^{-3} NaOH, and was left to equilibrate with the solution for 2 weeks or more. Then pH titrations were performed by addition of small aliquots of 0.1 mol dm^{-3} NaOH, 0.1 mol dm^{-3} $NaHCO_3$ or 0.1 mol dm^{-3} $HClO_4$. The pH was measured by using combination glass electrodes (Horiba) which were calibrated against buffer solutions with pH of 4.01 and 6.86 (both ±0.01). The pH and neptunium concentration were measured once per week, and the solubility data were adopted when the values remained unchanged for 2 weeks within experimental error. Phase separation was achieved by centrifugation at 3000 rpm and ultrafiltration with a filter of 220 nm pore size. The concentration of Np(VI) was determined by liquid scintillation counting. The oxidation state of Np(VI) was checked by spectrophotometry (Shimadzu, UV-3100S). During solubility experiments, Np(V) concentration was always <2% of the total neptunium concentration. Solid phases were characterized by x-ray crystallography (Rigaku RAD-3C) and photoacoustic UV-VIS and FTIR spectroscopy. For the latter method, about 5–10 mg of air-dried solid phase was used.

Source and Purity of Materials:

Stock solution of NpO_2^{2+} was prepared from highly pure $^{237}NpO_2$ powder (CEA, France). The latter was dissolved in concentrated HNO_3, the resultant solution was fumed to dryness after addition of concentrated $HClO_4$, and the residue was dissolved in 0.1 mol dm^{-3} $HClO_4$.

Estimated Error:

Temperature: precision ±0.1 K (authors).
Solubility product: see above.

References:

[1] G. Meinrath and T. Kimura, Inorg. Chim. Acta **204**, 79 (1993).
[2] G. Meinrath and T. Kimura, J. Alloy Compd. **202**, 89 (1993).
[3] Y. Kato, T. Kimura, Z. Yoshida, and N. Nitani, Radiochim. Acta **74**, 21 (1996).

6.2. Salts of Dioxocarbonato Neptunate(V)(-1)

6.2.1. Evaluation of the $NaNpO_2CO_3+CO_2+NaClO_4+H_2O$ System

Components:

(1) Sodium dioxocarbonato neptunate(V); $NaNpO_2(CO_3)$; [57127-86-3]
(2) Carbon dioxide; CO_2; [124-38-9]
(3) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

J. Hála, Department of Inorganic Chemistry, Masaryk University, 61137 Brno, Czech Republic, June 2000

Critical Evaluation:

The $NaNpO_2CO_3$ is the most important neptunium compound from the point of view of possible leaching neptunium from radioactive waste repositories. Its solubility in carbonate containing solutions has been investigated in several documents. Ueno and Saito[1] measured the solubility as a function of Na_2CO_3 concentration at 293.1 K in solutions with variable ionic strength. Maya[2] measured the solubility at 298.1 K in Na_2CO_3 solutions containing 0.1 mol dm^{-3} $NaClO_4$. Lemire *et al.*[3] used $Na_2CO_3/NaClO_4$ solutions of constant ionic strength of 1.0 mol dm^{-3} at three temperatures. Meinrath[4] carried out his measurements at ionic strength of approximately 0.1 mol dm^{-3} $NaClO_4$ in an atmosphere of nitrogen gas containing 1% CO_2. Grenthe *et al.*[5] used 3.0 mol dm^{-3} ionic strength at 293.1 K, and Neck *et al.*[6] performed their measurements at several ionic strengths and at 298.1 K. In Refs. 2–6, the solubility of $NaNpO_2CO_3$ was reported as a function of equilibrium carbonate ion concentration. The latter was calculated from the measured pH of the saturated solutions, and a set of aqueous equilibria of CO_2, HCO_3^-, and CO_3^{2-} (see Critical Evaluation for the UO_2CO_3–CO_2–$NaClO_4$–H_2O system).

Due to the different conditions used in these documents, and also because Refs. 2–5 presented the solubility data in graphical form only, the possibilities for detailed comparison are rather limited. Nevertheless, some general features of this system have emerged. References 2–6 agree in that the solubility of $NaNpO_2CO_3$, when plotted against equilibrium CO_3^{2-} concentration, passes through a minimum. In the range of minimum solubility of $NaNpO_2CO_3$, the latter is determined predominantly by the solubility product. The table summarizes the approximate minimum solubility data for $NaNpO_2CO_3$, as estimated by the evaluator from the graphical representation of the authors' data:

Minimum $NaNpO_2CO_3$ solubility (mol dm^{-3})	Corresponding $[CO_3^{2-}]$ range (mol dm^{-3})	Ionic strength (mol dm^{-3})	Reference
3×10^{-6}	$3\times10^{-4}-9\times10^{-4}$	1.0	2
1×10^{-6}	$1\times10^{-4}-2.5\times10^{-4}$	1.0	3
2×10^{-5}	$2.5\times10^{-4}-6.3\times10^{-3}$	0.1	4
1.3×10^{-6}	1×10^{-4}	3.0	5
2×10^{-5}	$1.5\times10^{-4}-2\times10^{-3}$	0.1	6
3.2×10^{-6}	$1.5\times10^{-4}-1\times10^{-3}$	1.0	6
1×10^{-6}	1.5×10^{-4}	3.0	6
2×10^{-7}	1×10^{-4}	5.0	6

From the most extensive study of Neck *et al.*[6] it follows that the magnitude of the minimum solubility of $NaNpO_2CO_3$, as well as the carbonate ion concentration range where it appears, are dependent on ionic strength ($NaClO_4$). Taking this into account there appears to be a good agreement among the published data. There is also an agreement in Refs. 2–6 in that at $[CO_3^{2-}]$ concentrations higher than $10^{-3}-10^{-2}$ mol dm^{-3} the solubility of $NaNpO_2CO_3$ increases with increasing carbonate ion concentration. This effect is particularly pronounced at high carbonate ion concentrations,[1] and has been explained[2–6] in terms of the formation of carbonatocomplexes $NpO_2(CO_3)_n^{1-2n}$ in the saturated solutions. The number of complexes existing depends on the $[CO_3^{2-}]$ range used. Thus, while Meinrath[4] reported the complexes with $n=1$ and 2 at $[CO_3^{2-}]<10^{-2}$ mol dm^{-3}, the existence of the third complex ($n=3$) has been confirmed at higher carbonate ion concentrations.[5,6]

A consistent set of solubility product values of $NaNpO_2CO_3$ has been reported with particularly excellent agreement for K_{sp} values obtained at 298.1 K and 0.1 and 1.0 mol dm^{-3} $NaClO_4$ in Refs. 4, 6 and 2, 6, respectively. The available K_{sp} values are summarized in the following table:

$-\log K_{sp}$	Temperature (K)	Ionic strength (mol dm^{-3})	Reference
11.00±0.07	298.1	0	6
10.22±0.02	298.1	0.1(NaClO$_4$)	4
10.28±0.04	298.1	0.1(NaClO$_4$)	6
10.14±0.04	298.1	1.0(NaClO$_4$)	2
10.10±0.03	298.1	1.0(NaClO$_4$)	6
10.7±0.1	303.1	1.0(NaClO$_4$+Na$_2$CO$_3$)	3
11.0±0.1	323.1	1.0(NaClO$_4$+Na$_2$CO$_3$)	3
10.45±0.04	298.1	3.0(NaClO$_4$)	6
10.56	293.1	3.0	5
11.06±0.06	298.1	5.0(NaClO$_4$)	6

The solubility product of $NaNpO_2CO_3$ at different ionic strengths has also been obtained by calculation using the Pitzer method, with very good agreement with experimental data.[7,9,10]

The equilibrium solid phase is the hydrated salt, $NaNpO_2CO_3 \cdot 3.5H_2O$. This hydrate was first reported by Volkov *et al.*,[8] and since then reconfirmed as the equilibrium solid phase in the solubility studies by several authors.[2,5,9] Lemire[3] reported the solid phase to be the trihydrate, $NaNpO_2CO_3 \cdot 3H_2O$, at 303.1 and 323.1 K. This is in agreement with the finding of Volkov *et al.*[8] who reported that $NaNpO_2CO_3 \cdot 3.5H_2O$ turned into the trihydrate on heating at 303.1 K. Since the solid phase exists as a hydrate, the solubility product may, to a certain extent, depend on the number of crystal water molecules, particularly at high ionic strength where the decrease of water activity is not negligible.[7] At higher carbonate ion concentrations, $NaNpO_2CO_3 \cdot 3.5H_2O$ is thermodynamically unstable, and its slow transformation to $Na_3NpO_2(CO_3)_2 \cdot xH_2O$ takes place.[3,6]

Note: As a part of nuclear waste storage project at Yucca Mountain, Nevada, Tucker *et al.*[11] measured the solubility of $NaNpO_2CO_3$ in ground water from one well. This document has not been compiled for this volume since the composition of the ground water was not defined. The authors obtained $-\log K_{sp} = 10.3 \pm 0.5$ at 333.1 K and at ionic strength of 0.14±0.05 mol dm^{-3}. The measurements were performed at pH 6.0–8.5, and the equilibrium solid phase was identified as $NaNpO_2CO_3 \cdot H_2O$.

References:

[1] K. Ueno and A. Saito, Radiochem. Radioanal. Lett. **22**, 127 (1975).
[2] L. Maya, Inorg. Chem. **22**, 2093 (1983).
[3] R. J. Lemire, G. D. Boyer, and A. B. Campbell, Radiochim. Acta **61**, 57 (1993).
[4] G. Meinrath, J. Radioanal. Nucl. Chem. Lett. **186**, 257 (1994).
[5] I. Grenthe, P. Robouch, and P. Vitorge, J. Less-Common Metals **122**, 225 (1986).
[6] V. Neck, W. Runde, J. I. Kim, and B. Kanellakopulos, Radiochim. Acta **65**, 29 (1994); J. Alloys Compds. **225**, 295 (1995).
[7] V. Neck, T. Fanghänel, G. Rudolf, and J. I. Kim, Radiochim. Acta **69**, 39 (1995).
[8] Yu. F. Volkov, G. I. Visyashcheva, and I. I. Kapshukov, Radiokhimiya **19**, 319 (1977); Sov. Radiochem. **19**, 263 (1977).
[9] W. Runde, M. P. Neu, and D. L. Clark, Geochim Cosmochim. Acta **60**, 2065 (1996).
[10] C. F. Novak and K. E. Roberts, Mater. Res. Soc. Symp. Proc. **353**, 1119 (1995).
[11] D. B. Tucker, E. M. Standifer, H. Nitsche, and R. J. Silva, Lanthanide Actinide Res. **2**, 279 (1988).

6.3. Salts of Dioxo Bis(carbonato) Neptunate(V)(-3)

Components:	Original Measurements:
(1) Sodium carbonato dioxoneptunate(V); $NaNpO_2CO_3$; [57127-86-3] (2) Sodium carbonate; Na_2CO_3; [497-19-8] (3) Water; H_2O; [7732-18-5]	K. Ueno and A. Saito, Radiochem. Radioanal. Lett. **22**, 127–33 (1995).
Variables:	**Prepared By:**
T/K: 293 c_2 /mol dm^{-3}: 0.05–1.6	J. Hála

Experimental Data

Solubility of $NaNpO_2CO_3$ at 20 °C in Na_2CO_3 solutions[a]

Na_2CO_3 (c_2 /mol dm^{-3})	$NaNpO_2CO_3$ (10^4 c_1 /mol dm^{-3})
0.05	0.688
0.07	0.795
0.1	1.18
0.15	2.44
0.2	8.53
0.3	20.4
0.4	32.3
0.6	97.0
1.2	160.0
1.6	161.0

[a] Equilibrium solid phase was $NaNpO_2CO_3$, [57127-86-3], in all solutions.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Portions of a slightly acidic solution containing 5–30 mg Np(V) were added to 5–10 mL Na_2CO_3 solution of the desired concentration. The neptunium concentration was small enough not to change the carbonate concentration. A white precipitate of $NaNpO_2CO_3$ was obtained and allowed to stand for 1–2 days with occasional mixing to attain equilibrium. The saturated solutions were centrifuged, and the neptunium concentration determined radiometrically. The solid phases were analyzed for Np, Na, and carbonate. Saturated solutions and the solid phases contained pentavalent neptunium after equilibration.

Source and Purity of Materials:

A HNO_3 solution of ^{237}Np purified by anion exchange was heated for several hours to oxidize Np(IV) to Np(V)/Np(VI), and then evaporated to dryness. The residue was dissolved in $NH_2OH \cdot HCl$ solution to ensure the pentavalent state of neptunium, which was checked spectrophotometrically. The sodium carbonate used was a reagent grade product.

Estimated Error:

Temperature: precision ±2 K (authors).
Solubility: insufficient data given to allow for error estimate.

Components:
(1) Sodium carbonato dioxoneptunatev(V); $NaNpO_2CO_3$; [57127-86-3]
(2) Sodium carbonate; Na_2CO_3; [497-19-8]
(3) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(4) Water; H_2O; [7732-18-5]

Original Measurements:
L. Maya, Inorg. Chem. **22**, 2093–5 (1983).

Variables:
T/K: 298
c_2 /mol dm^{-3} (CO_3^{2-}): $1.5\times10^{-6}-0.093$
c_3 /mol dm^{-3}: 1.0

Prepared by:
J. Hála

Experimental Data

Solubility of $NaNpO_2CO_3$ at 25 °C in Na_2CO_3 solutions[a]

$-\log[CO_3^{2-}]^b$	$-\log[H^+]^b$	$-\log[Np]^b$	$-\log[CO_3^{2-}]^{b,c}$	$-\log[H^+]^{b,c}$	$-\log[Np]^{b,c}$
5.80	8.08	4.32	5.52[c]	6.96	4.87
5.71	8.21	4.36	4.63[c]	7.21	5.21
4.44	8.99	5.22	4.06[c]	7.51	5.41
3.98	9.31	5.40	3.52[c]	7.79	5.52
3.54	9.62	5.48	2.95[c]	8.08	5.42
3.05	9.94	5.52	4.06[c]	7.51	5.41
2.71	10.15	5.38	3.52[c]	7.79	5.52
2.39	10.37	5.13	2.95[c]	8.08	5.42
2.09	10.55	4.89			
1.64	10.72	4.55			
1.03	10.99	3.50			

[a] All solutions contained 1.0 mol dm^{-3} $NaClO_4$, and were in equilibrium with $NaNpO_2CO_3\cdot3.5H_2O$, [], as the solid phase.
[b] Equilibrium concentrations, in mol dm^{-3}.
[c] Measurements carried out at partial pressure of CO_2 of $10^{-2.027}$ atm (922 Pa) in order to evaluate possible effect on $NaNpO_2CO_3$ solubility of hydrogencarbonate complexation of Np(V).

Additional information:

The solubility data were analyzed by the authors by using a nonlinear least-squares program considering dissolution of $NaNpO_2CO_3$, hydrolysis of NpO_2^+ to form NpO_2OH, and the formation of carbonato complexes of NpO_2^+. For the dissolution reaction

$$NaNpO_2CO_{3(s)} \leftrightarrows Na^+ + NpO_2^+ + CO_3^{2-}$$

the solubility product is

$$K^o_{sp} = [Na^+][NpO_2^+][CO_3^{2-}]\,\gamma(Na^+)\,\gamma(NpO_2^+)\,\gamma(CO_3^{2-}).$$

Since measurements were performed at constant concentration of Na^+ ions, the constant K^*_{sp} was defined as

$$K^*_{sp} = K^o_{sp}\{[Na^+]\,\gamma(Na^+)\,\gamma(NpO_2^+)\,\gamma(CO_3^{2-})\}^{-1} = [NpO_2^+][CO_3^{2-}],$$

and found to be $10^{-(10.14\pm0.04)}$. The increased solubility of $NaNpO_2CO_3$ at $[CO_3^{2-}] > 3\times10^{-4}$ mol dm^{-3} was interpreted by the authors in terms of the formation of $NpO_2CO_3^-$, $NpO_2(CO_3)_2^{3-}$, and $NpO_2(CO_3)_3^{5-}$ complexes for which the respective overall stability constants were calculated to be $10^{4.49\pm0.06}$, $10^{7.11\pm0.07}$, and $10^{8.53\pm0.09}$. Complexation of NpO_2^+ with HCO_3^- ion was not observed.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. $NaNpO_2CO_3\cdot3.5H_2O$ was prepared *in situ* in tubes by addition of Na_2CO_3 in a 1:1 mole ratio to a NpO_2^+ solution. The tubes were centrifuged, and the supernatant was replaced with 1 mol dm^{-3} $NaClO_4$ solution. The solid was suspended and centrifuged again, and this procedure was repeated two more times. Then aliquots of the carbonate stock solution were introduced to cover a range of concentrations up to 0.1 mol dm^{-3}. The mixtures were equilibrated first for 7 days and then for an additional 4 day period. The latter did not produce significant changes in the Np concentration in the saturated solutions. Some of the tubes were then saturated with N_2 gas containing 1% CO_2, sealed and equilibrated for 10 days. After centrifugation, neptunium was determined in the saturated solutions radiometrically, $[H^+]$ was determined by using a glass electrode filled with a 0.001 mol dm^{-3} H^+ + 1.0 mol dm^{-3}$NaClO_4$ solution. The composition of the solid phases was determined by chemical analysis and x-ray diffraction.

Source and Purity of Materials:

Stock solution, 0.0665 mol dm^{-3}, of Np(V) in 0.1 mol dm^{-3} $HClO_4$ was prepared from high purity NpO_2 (ORNL). The oxide was dissolved in hot concentrated HNO_3, the solution was evaporated to dryness, residue dissolved in concentrated $HClO_4$, the solution evaporated, and residue dissolve in water. From this solution NpO_2OH was precipitated and dissolved in 0.1 mol dm^{-3} $HClO_4$. The sodium carbonate used was a reagent grade product.

Estimated Error:

Temperature: precision ±0.1 K (author).
Solubility product: see above.

Components:

(1) Sodium carbonato dioxoneptunate(V); $NaNpO_2CO_3$; [57127-86-3]
(2) Carbon dioxide; CO_2; [124-38-9]
(3) Sodium hydrogencarbonate; $NaHCO_3$; [144-55-8]
(4) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(5) Water; H_2O; [7732-18-5]

Original Measurements:

I. Grenthe, P. Robouch, and P. Vitorge, J. Less-Common Metals **122**, 225–31 (1986).

Variables:

T/K: 293
partial pressure of CO_2 /atm(kPa): 0.11–0.15 (10.8–14.7) and 0.97 (95.15)
c_3 /mol dm^{-3}: 3.0

Prepared by:

J. Hála

Experimental Data

Solubility of $NaNpO_2CO_3$ at 20 °C as a function of equilibrium CO_3^{2-} ion concentration

The results were reported in graphical form only (see Fig. 16).

Additional information:

The solubility of $NaNpO_2CO_3$ in carbonate containing 3.0 mol dm^{-3} solutions of $NaClO_4$ were interpreted by the authors by considering NpO_2^+, $NpO_2CO_3^-$, $NpO_2(CO_3)_2^{3-}$, and $NpO_2(CO_3)_3^{5-}$ as solution species, and hydrated $NaNpO_2CO_3$ and $Na_3NpO_2(CO_3)_2$ as the equilibrium solid phases. The overall stability constants of the carbonatocomplexes of Np(V) were reported to be $10^{5.09}$, $10^{8.15}$, and $10^{10.46}$, respectively, and the solubility products of $NaNpO_2CO_3$ and $Na_3NpO_2(CO_3)_2$ as $10^{-10.56}$ and $10^{-12.44}$, respectively.

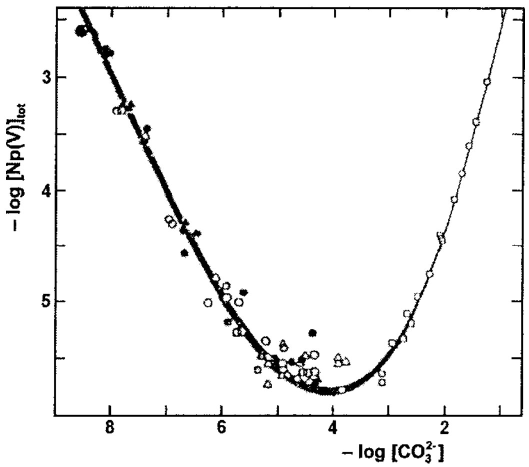

FIG. 16. Sodium carbonato dioxoneptunate (V)–sodium perchlorate–carbon dioxide–water system. Legend to the figure: (squares) measurements carried out by controlling total carbonate concentration; (circles and triangles) measurements carried out at partial pressure of CO_2 of 0.97 and 0.11–0.15 atm, respectively.

Auxiliary Information

Method/Apparatus/Procedure:

Experimental technique used was not described. The compiler assumes that measurements were carried out in a manner similar to that used by the authors in the study of the solubility of UO_2CO_3[1] and PuO_2CO_3.[2]

Source and Purity of Materials:

No details reported.

Estimated Error:

Temperature: precision not reported.

References:

[1] I. Grenthe, D. Ferri, F. Salvatore, and G. Riccio, J. Chem. Soc., Dalton Trans. 2439 (1984).
[2] P. Robouch and P. Vitorge, Inorg. Chim. Acta **140**, 239 (1987).

Components:

(1) Sodium carbonato dioxoneptunate(V); $NaNpO_2CO_3$; [57127-86-3]; or sodium bis(carbonato) dioxoneptunate(V); $Na_3NpO_2(CO_3)_2$; [64438-44-4]
(2) Sodium carbonate; Na_2CO_3; [497-19-8]
(3) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

R. J. Lemire, G. D. Boyer, and A. B. Campbell, Radiochim. Acta **61**, 57–63 (1993).

Variables:

T/K: 303, 323, and 348
Equilibrium concentration of the CO_3^{2-} ion/mol dm^{-3}:10^{-6}–0.1
c_3 /mol dm^{-3}: varying concentration to maintain ionic strength of 1.0 mol dm^{-3} in Na_2CO_3–$NaClO_4$ solutions

Prepared by:

J. Hála

Experimental Data

Solubility of $NaNpO_2CO_3$ or $Na_3NpO_2(CO_3)_2$ at three different temperatures as a function of equilibrium CO_3^{2-} ion concentration

The solubility of $NaNpO_2CO_3$ or $Na_3NpO_2(CO_3)_2$ as a function of equilibrium CO_3^{2-} ion concentration was reported in graphical form only. The authors analyzed the solubility data by a least-squares procedure considering two models differing in the solid phases, i.e., either hydrated $NaNpO_2CO_3$ (model A) or a mixture of hydrated $NaNpO_2CO_3$ and $Na_3NpO_2(CO_3)_2$ (model B). Neptunium species in the saturated solutions were considered to be NpO_2^+, $NpO_2CO_3^-$, $NpO_2(CO_3)_2^{3-}$, and $NpO_2(CO_3)_3^{5-}$, while $NpO_2(OH)_{(aq)}$ was not found to be a significant species. The constant

$$K_{sp}^{*}=[NpO_2^+][CO_3^{2-}]=K_{sp}[Na^+]\gamma(Na^+)\gamma(CO_3^{2-})\gamma(NpO_2^+)$$

was calculated for different temperatures and models. At 30 and 50 °C, K_{sp}^{*} was calculated to be $10^{-(10.7\pm0.1)}$ and $10^{-(11.0\pm0.1)}$, respectively, irrespective of the model used. At 75 °C, K_{sp}^{*} was calculated to be $10^{-(10.7\pm0.2)}$ (model A with $NpO_2CO_3^-$ as solution species), $10^{-(10.8\pm0.2)}$ (model B with $NpO_2CO_3^-$ and $NpO_2(CO_3)_3^{5-}$ as solution species), and $10^{-(11.3\pm052)}$ (model B with $NpO_2CO_3^-$ and $NpO_2(CO_3)_2^{3-}$ as solution species).

Additional information:
At 30 °C, the minimum neptunium solubility ($\sim10^{-6}$ mol dm^{-3}) occurs at free carbonate concentration of about 10^{-3} mol dm^{-3}. For initial carbonate concentration between 0.01 and 0.1 mol dm^{-3} the initial solid, either hydrated $NaNpO_2CO_3$ or hydrated $Na_3NpO_2(CO_3)_2$, was recovered as the primary solid after having been contacted with the solutions for more than 1 month. In a few experiments using hydrated $Na_3NpO_2(CO_3)_2$ as the initial solid, at least partial conversion of the solid occurred:

$$Na_3NpO_2(CO_3)_2\cdot xH_2O\leftrightarrows NaNpO_2CO_3\cdot yH_2O+2Na^++CO_3^{2-}+(y-x)H_2O$$

At 50 °C, $Na_3NpO_2(CO_3)_2$ predominated as the solid phase. Also at 75 °C and at 1.0 mol dm^{-3} Na^+, the stable solid had a ratio of Na:Np>1. Generally, for total carbonate concentration >0.005 mol dm^{-3}, only hydrated $Na_3NpO_2(CO_3)_2$ was identified by x-ray diffraction, although $Na_8(NpO_2)_2(CO_3)_5$ was present in some samples.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. The solubilities were measured in Na_2CO_3 /$NaClO_4$ solutions with initial ionic strength of 1.0 mol dm^{-3}. The solutions were prepared using CO_2-free water which was prepared by boiling and purging with argon. Excess solid was equilibrated with solutions of the desired composition in glass tubes sealed with a rubber gasket. The tubes were submerged in a thermostated bath for periods of time ranging from 2 to 4 weeks. No evaporation losses were detected even after several weeks at 75 °C. After equilibration, hydrogen ion concentration was determined at the temperature of the experiment using a micro pH probe with 4.0 mol dm^{-3} NaCl saturated with AgCl as filling solution. The probe was calibrated at each temperature against solutions of known H^+ or OH^- ion concentration in 1.0 mol dm^{-3} $NaClO_4$. Aliquots of the saturated solutions were withdrawn with a syringe equipped with a 0.2 μm filter, and the concentration of neptunium was determined radiometrically. To this aim, Np(V) was reduced to Np(IV) by Fe(II) sulfamate, the solution was acidified to 6 mol dm^{-3} HCl, Np(IV) was extracted into 10% alamine 336 in xylene, and back extracted into 0.1 mol dm^{-3} HCl. Samples were then evaporated to dryness and α counted. Recovery of Np in this procedure was at least 95%. Solid phases were identified by x-ray diffraction.

Source and Purity of Materials:

Hydrated $NaNpO_2CO_3$ and $Na_3NpO_2(CO_3)_2$ were prepared according to Refs. 1 and 2. Powder x-ray diffraction pattern of the solids were in agreement with those reported for $NaNpO_2CO_3\cdot3H_2O$ and $Na_3NpO_2(CO_3)_2\cdot xH_2O$.

Estimated Error:

Temperature: precision not reported.
Solubility product: see above.

References:

[1] Yu. F. Volkov, G. I. Visyashcheva, and I. I. Kapshukov, Radiokhimiya **19**, 319 (1977).
[2] Yu. F. Volkov, G. I. Visyashcheva, S. V. Tomilin, I. I. Kapshukov, and A. G. Rykov, Radiokhimiya **23**, 248 (1981).

Components:

(1) Sodium carbonato dioxoneptunate(V); $NaNpO_2CO_3$; [57127-86-3]
(2) Carbon dioxide; CO_2; [124-38-9]
(3) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

G. Meinrath, J. Radioanal. Nucl. Chem. Lett. **186**, 257–72 (1994).

Variables:

T/K: 298
p_2 (partial pressure)/%: 1
c_3 /mol dm^{-3}: 0.1 (ionic strength)

Prepared by:

J. Hála

Experimental Data

Solubility of $NaNpO_2CO_3$ at 25 °C as a function of pH

The solubility of $NaNpO_2CO_3$ at 25 °C and at ionic strength of 0.1 mol dm^{-3} ClO_4^- and 1% partial pressure of CO_2 as a function of pH was reported in graphical form (see Fig. 17). Under the conditions used, i.e., pH$<$9 and maximum equilibrium carbonate ion concentration of about 10^{-2} mol dm^{-3}, the author obtained for the solubility of $NaNpO_2CO_3$ the equation

$$S=K_{sp}[Na^+]^{-1}[CO_3^{2-}]^{-1}\{1+\beta_1[CO_3^{2-}]+\beta_2[CO_3^{2-}]^2\}$$

where $K_{sp}=[Na^+][NpO_2^+][CO_3^{2-}]=10^{-(10.22\pm0.02)}$, and β_1 and β_2 are overall stability constants of the $NpO_2CO_3^-$ and $NpO_2(CO_3)_2^{3-}$ complexes which were calculated to be $10^{-(4.52\pm0.02)}$ and $<10^{-6.60}$, respectively.

Additional information:

Equilibrium carbonate ion concentration was obtained from the Henry constant, dissociation constants of carbonic acid, and the measured pH. Hydrolysis of Np(V) was found to be insignificant under the conditions used.

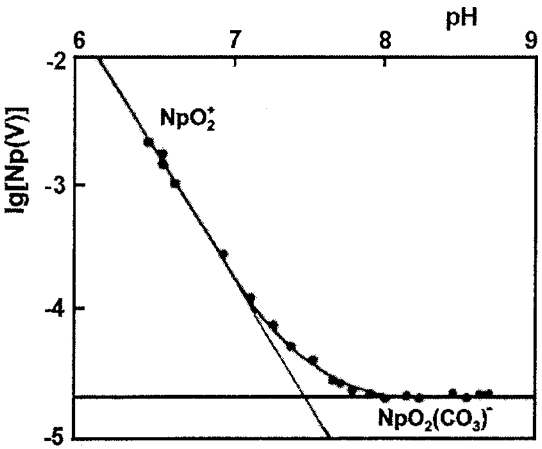

FIG. 17. Sodium carbonato dioxoneptunate (V)–sodium perchlorate–carbon dioxide–water system.

Auxiliary Information

Method/Apparatus/Procedure:

The solubility was measured by radiometric pH titration in a closed thermostated glass vessel. The solid phase was precipitated in the vessel from a 0.02 mol dm^{-3} NpO_2^+ solution in 0.1 mol dm^{-3} $HClO_4$ by addition of 0.05 mol dm^{-3} Na_2CO_3. The solution with the precipitate was allowed to stand for about 3 weeks. Then pH was adjusted by adding solutions of either 0.1 mol dm^{-3} $HClO_4$ or 0.05 mol dm^{-3} Na_2CO_3. The solid–liquid phase equilibrium at a given pH was established within 1–3 days. Equilibrium solubility was attained from both super- and undersaturated solutions to ensure that a reproducible steady state had been established in the investigated pH range of 6–9. A defined atmosphere was maintained by a continuous flow of a certified gas mixture of N_2 containing 1% CO_2 through the solution after moistening the gas in washing flasks. Samples from the liquid phase were withdrawn after ultrafiltration through a 200 nm pore size filter (Advantec). Determination of Np(V) in the saturated solutions was carried out by α spectrometry, liquid scintillation counting, and spectrophotometrically at 981.3 nm. The pH was determined according to Ref. 1. Solid phases were investigated by using x-ray powder diffraction.

Source and Purity of Materials:

Isotopically pure ^{237}Np (CEA, France) was used.

Estimated Error:

Temperature: precision ±0.2 K (author).
Solubility product: see above.

References:

[1] G. Meinrath and J. I. Kim, Radiochim. Acta **52/53**, 29 (1991).

Components:

(1) Sodium carbonato dioxoneptunate(V); $NaNpO_2CO_3$; [57127-86-3]; or sodium bis(carbonato) dioxoneptunate(V); $Na_3NpO_2(CO_3)_2$; [64438-44-4]
(2) Carbon dioxide; CO_2; [124-38-9]
(3) Sodium perchlorate; $NaClO_4$; [7601-89-0]; or Sodium chloride; NaCl; [7647-14-5]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

V. Neck, W. Runde, J. I. Kim, and B. Kanellakopulos, Radiochim. Acta **65**, 29–37, (1994), J. Alloys Compds. **225**, 295–302 (1995).

Variables:

T/K: 298
p_2 (partial pressure)/%: 0.03 (31 Pa) in $NaClO_4$ solutions; 1.0 (1.03 kPa) in NaCl solutions
c_3 /mol dm^{-3}: 0.1–5.0 ($NaClO_4$); 5.0 (NaCl)

Prepared By:

J. Hála

Experimental Data

Solubility of $NaNpO_2CO_3$ and $Na_3NpO_2(CO_3)_2$ at 25 °C as a function of carbonate ion concentration at different ionic strengths

The solubility of $NaNpO_2CO_3$ and $Na_3NpO_2(CO_3)_2$ as a function of equilibrium carbonate ion concentration was reported in graphical form (see Fig. 18). By using nonlinear least-squares analysis, the following values were obtained for the solubility products of $NaNpO_2CO_3$ and $Na_3NpO_3(CO_3)_2$, and the overall stability constants of the $NpO_2(CO_3)_n^{1-2n}$ complexes:

Ionic strength (mol dm^{-3})	log $K_{sp,1}$[a]	log $K_{sp,3}$[a]	log β_1	log β_2	log β_3
0	-11.00 ± 0.07[b]	-14.32 ± 0.15[b]			
0.1($NaClO_4$)	-10.28 ± 0.04		4.58 ± 0.04	6.60 ± 0.07	(<6.8)
1.0($NaClO_4$)	-10.10 ± 0.03	-12.23 ± 0.15	4.50 ± 0.04	6.96 ± 0.06	8.67 ± 0.09
3.0($NaClO_4$)	-10.45 ± 0.04	-12.59 ± 0.10	4.76 ± 0.04	7.69 ± 0.07	10.30 ± 0.09
5.0($NaClO_4$)	-11.06 ± 0.06	-13.57 ± 0.11	5.00 ± 0.05	8.29 ± 0.09	11.47 ± 0.08
5.0 (NaCl)[c]	-10.63 ± 0.11	-12.48 ± 0.23			

[a] $K_{sp,1}=[Na^+][NpO_2^+][CO_3^{2-}]$; $K_{sp,3}=[Na^+]^3[NpO_2^+][CO_3^{2-}]^2$.

[b] Thermodynamic solubility product, obtained by the authors from the specific interaction theory. Corrected for the formation of Np(V) chlorocomplexes.

Additional information:

The increase in the $NaNpO_2CO_3$ solubility at higher carbonate ion concentrations or pH was ascribed by the authors to the formation of the $NpO_2(CO_3)_n^{1-2n}$ complexes. In 0.1 mol dm^{-3} $NaClO_4$, $NaNpO_2CO_3$ was found to be the stable solid phase over the whole CO_3^{2-} concentration range studied. In 1.0 mol dm^{-3} $NaClO_4$ at $[CO_3^{2-}]>0.5$ mol dm^{-3}, and in 3.0 and 5.0 mol dm^{-3} $NaClO_4$, as well as in 5.0 mol dm^{-3} NaCl, and at $[CO_3^{2-}]>(10^{-1.9}-10^{-1.5})$ mol dm^{-3}, the equilibrium solid phase was $Na_3NpO_2(CO_3)_2$, [64438-44-4]. The initial solid used for measurements was $NaNpO_2CO_3$, and in solutions with higher ionic strength and containing higher CO_3^{2-} concentration, it was converted to $Na_3NpO_2(CO_3)_2$ within 10 days. In evaluating the solubility data, the measured pH values at ionic strengths >0.1 mol dm^{-3} were corrected for liquid junction potentials, and apparent protolysis constant of water was then calculated from the corrected values and from literature values of water activity. The equilibrium concentration of CO_3^{2-} ion was evaluated from the Henry constant and dissociation constants of carbonic acid which were determined by potentiometric titration for each particular ionic strength.

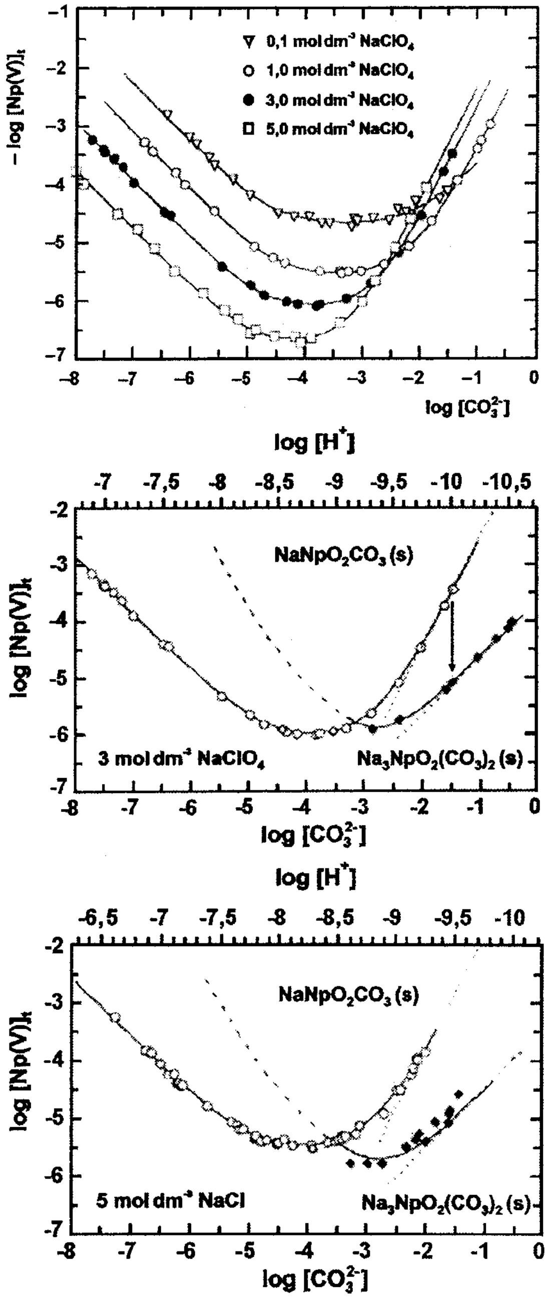

FIG. 18. Sodium carbonato dioxoneptunate (V)–sodium chloride–carbon dioxide–water system.

Auxiliary Information

Method/Apparatus/Procedure:

The solubility measurements were performed in a closed thermostated glass vessel filled with argon gas containing 0.03 or 1% CO_2. The gas mixture was allowed to pass through the vessel during the sampling and pH adjustment while during standing periods the vessel was filled with the gas mixture and closed. In each experiment, some 50 mg Np(V) (~0.002 mol dm^{-3}) was used in 50 mL $HClO_4$ /$NaClO_4$ or HCl/NaCl solution (pH 3) at the desired ionic strength. The oxidation state of Np(V) in the starting solution was confirmed spectrophotometrically in the visible and near IR region. The pH of each solution was raised to 8.0–8.5 by adding $NaHCO_3$ /$NaClO_4$ or $NaHCO_3$ /NaCl solution to precipitate $NaNpO_2CO_3$ which was then left for several days for equilibration. Then the solubility measurements were performed by adjusting the desired pH in the range from 5.9 to 9.9, by stepwise adding either $HClO_4$ /$NaClO_4$ or $NaHCO_3$ /$NaClO_4$ solution, or HCl/NaCl or $NaHCO_3$ /NaCl solution. The equilibrium at each pH was confirmed by determining pH and Np concentration in the solution until constant values were reached. This was attained within 1–3 days depending on pH and ionic strength. After filtration through a 200 nm pore size filter, the Np(V) concentration in the saturated solution was determined radiometrically by liquid scintillation counting, discriminating the ^{237}Np α activity from the overlapping tailing β activity of the ^{233}Pa daughter. A combination glass electrode (ROSS, Orion) was used for pH measurements. The electrode was calibrated regularly against pH buffer standards (Merck). The original junction electrolyte of the electrode was replaced by 3.0 mol dm^{-3} NaCl to avoid precipitation of $KClO_4$. The solid phases were characterized by x-ray powder diffraction.

Source and Purity of Materials:

^{237}Np used was purified from ^{238}Pu. No other details reported.

Estimated Error:

Temperature: precision not reported.
Solubility product: see above.

Components:

(1) Sodium carbonato dioxoneptunate(V); $NaNpO_2CO_3$; [57127-86-3]
(2) Carbon dioxide; CO_2 ; [124-38-9]
(3) Sodium chloride; NaCl; [7647-14-5]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

W. Runde, M. P. Neu, and D. L. Clark, Geochim. Cosmochim. Acta **60**, 2065–73 (1996).

Variables:

T/K: 296
p_2 (partial pressure)/atm: 0.01 (981 Pa)
c_3 /mol dm^{-3}: 0.1 and 3.0

Prepared By:

J. Hála

Experimental Data

Solubility of $NaNpO_2CO_3$ at 23 °C as a function of carbonate ion concentration in NaCl solutions

The solubility of $NaNpO_2CO_3$ as a function of equilibrium carbonate ion concentration, in the range of $[CO_3^{2-}]$ from 10^{-7} to 10^{-1} mol dm^{-3}, was reported in graphical form only. By using nonlinear least-squares analysis, the following values were obtained for the solubility product of $NaNpO_2CO_3$, and the overall stability constants (β_n) of the $NpO_2(CO_3)_n^{1-2n}$ complexes:

NaCl (c_3 /mol dm^{-3})	log K_{sp}[a]	log β_1	log β_2	log β_3
0.1	−10.4±0.2	4.8±0.1		
3.0	−9.4±0.2	4.3±0.1	7.1±0.2	9.2±0.2

[a] $K_{sp}=[Na^+][NpO_2^+][CO_3^{2-}]$.

Additional information:

The solid phases were found to be $NaNpO_2CO_3 \cdot xH_2O$ and $Na_3NpO_2(CO_3)_2 \cdot xH_2O$ at $[CO_3^{2-}]<10^{-3}$ and $>10^{-3}$ mol dm^{-3}, respectively.

Auxiliary Information

Method/Apparatus/Procedure:

The solubility measurements were performed in a closed thermostated glass vessel filled with argon gas containing 0.03 or 1% CO_2. The solids were prepared by addition of 0.1 mol dm^{-3} Na_2CO_3 to an acidic 0.01 mol dm^{-3} NpO_2^+ solution containing the desired concentration of NaCl. The solid phases were allowed to age for several weeks in contact with the solution until pH and the Np(V) concentration in the solution did not change. The pH of each solution was adjusted by adding Na_2CO_3 /NaCl or $NaHCO_3$ /NaCl solution, and was measured using a combination glass electrode (Orion, ROSS) which was calibrated against five standard buffer solutions and eight NaCl solutions of known H^+ or OH^- concentration. After filtration through a 450 nm pore size filter, the Np(V) concentration in the saturated solution was determined radiometrically by liquid scintillation counting, discriminating the ^{237}Np α activity from the overlapping tailing β activity of the ^{233}Pa daughter, and spectrophotometrically. The solid phases were characterized by x-ray powder diffraction.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: precision not reported.
Solubility product: see above.

Components:

(1) Sodium bis(carbonato) dioxoneptunate(V); $Na_3NpO_2(CO_3)_2$; [64438-44-4]
(2) Sodium carbonate; Na_2CO_3 ; [497-19-8]
(3) Sodium nitrate; $NaNO_3$; [7631-99-4]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

G. A. Simakin, Radiokhimiya **19**, 518–21 (1977).

Variables:

T/K: 298
c_2 /mol dm^{-3}: 0.25–1.0

Prepared By:

J. Hála

Experimental Data

Solubility of $Na_3NpO_2(CO_3)_2$ at 25 °C in $Na_2CO_3-NaNO_3$ solutions at ionic strength of 3.0 mol dm^{-3}

The solubility of $Na_3NpO_2(CO_3)_2$ was determined at 25 °C as a function of Na_2CO_3 concentration at pH 12.0 and constant ionic strength of 3.0 mol dm^{-3} maintained by using $NaNO_3$. The results were reported in graphical form only (see Fig. 19). The equilibrium solid phase was $Na_3NpO_2(CO_3)_2 \cdot xH_2O$ in all solutions, the solution Np(V) species was the $NpO_2(CO_3)_3^{5-}$ ion.

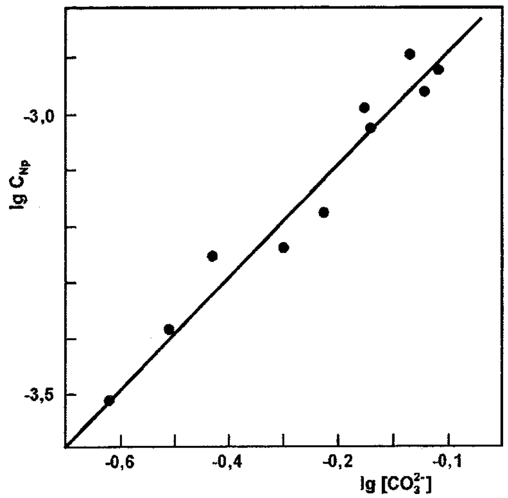

FIG. 19. Sodium bis(carbonato) dioxoneptunate (V)–sodium carbonate–sodium nitrate–carbon dioxide–water system.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess solid was equilibrated with solutions of the desired composition under occasional stirring for 3 days which was found sufficient for equilibrium to be reached. An aliquot of the suspension was then withdrawn, centrifuged, and the Np concentration in the saturated solution was determined by coulometric titration.[1] The solid phase was characterized by x-ray diffraction.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: precision ±0.5 K (author).

References:

[1] G. A. Simakin, P. F. Baklanova, G. F. Kuznetsov, and B. V. Chernev, Zh. Analit. Khim. **29**, 1585 (1974).

Components:

(1) Sodium bis(carbonato) dioxoneptunate(V); $Na_3NpO_2(CO_3)_2$; [64438-44-4]
(2) Sodium carbonate; Na_2CO_3 ; [497-19-8]
(3) Sodium chloride; NaCl; [7647-14-5]
(4) Potassium chloride; KCl; [7447-40-7]
(5) Water; H_2O; [7732-18-5]

Original Measurements:

I. Al Mahamid, C. F. Novak, K. A. Beckraft, S. A. Carpenter, and N. Hakem, Radiochim. Acta. **81**, 93–101 (1998).

Variables:

T/K: 295
m_2 /mol kg^{-1}: 0.009–95–1.00
m_3 /mol kg^{-1}: 5.00
m_4 /mol kg^{-1}: 0.10

Prepared by:

J. Hála

Experimental Data

Solubility of $Na_3NpO_2(CO_3)_2$ at 22 °C as a function of Na_2CO_3 concentration in solutions containing NaCl and KCl[a]

Na_2CO_3 (m_2 /mol kg^{-1})	Np(V)[b] (10^4 mol dm^{-3})
0.00995[c]	0.140±0.045
0.0454[c]	3.55±0.13
0.215[c]	4.09±0.13
1.00[d]	3.47±0.11

[a] All solutions contained 5.00 mol kg^{-1} NaCl and 0.100 mol kg^{-1} KCl.
[b] Total Np(V) concentration in the saturated solution.
[c] Solid phase was $Na_3NpO_2(CO_3)_2$, [64438-44-4].
[d] Unidentified solid phase.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. The solid was equilibrated with solutions of the desired composition in polyetheretherketone vessels (Cadillac Plastics). The equilibration time was 170 days with steady state being achieved within 107 days. All experiments were conducted under argon atmosphere. Samples of the saturated solutions were filtered through 4.1 nm Centricon filters (Amicon Corp.). The pH was measured using a Ross combination glass electrode calibrated in each of the $Na^+/K^+/Cl^-$ solution to account for the liquid junction potential. The Np(V) concentration was measured radiometrically by means of a high purity Ge detector using the 29.4 keV γ line of ^{237}Np. Total inorganic carbon content in the saturated solutions was determined by using Shimadzu TOC-5050 carbon analyzer. No changes in total carbon were observed.

Source and Purity of Materials:

$Na_3NpO_2(CO_3)_2$ was prepared by adding 1 mol dm^{-3} Na_2CO_3 to the Np(V) stock solution to obtain a final carbonate concentration of about 0.5 mol dm^{-3}. A white precipitate was formed. Purity of the Np(V) stock solution, including oxidation state purity, was verified as in the authors' previous work.[1]

Estimated Error:

Temperature: precision ±1 K (authors).
Solubility: see above.

References:

[1] C. F. Novak, I. Al Mahamid, K. A. Beckraft, S. A. Carpenter, N. Hakem, and T. Prussin, J. Solution Chem. **26**, 681 (1997).

Components:

(1) Potassium carbonato dioxoneptunate(V); $KNpO_2CO_3$; [54955-63-4]
(2) Potassium carbonate; K_2CO_3; [584-08-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

G. I. Visyasheva, Yu. F. Volkov, G. A. Simakin, I. I. Kapshukov, A. S. Bevz, and G. N. Yakovlev, Radiokhimiya, **16**, 853–9 (1974).

Variables:

T/K: 293 and 353
c_2 /mol dm^{-3}: 0.1

Prepared by:

J. Hála

Experimental Data

Solubility of $KNpO_2CO_3$ at 20 and 80 °C in 0.1 mol dm^{-3} K_2CO_3 solution[a]

Temperature (°C)	$KNpO_2CO_3$ (mg dm^{-3})	$KNpO_2CO_3$[b] ($10^5 c_1$ /mol dm^{-3})
20	1	0.422
80	40	16.9

[a] Solid phase was $KNpO_2CO_3$, [54955-63-4], in both measurements. It was reported to be stable in solutions containing <0.2 mol dm^{-3} K_2CO_3.

[b] Calculated by compiler for $A_r(Np) = 237.0482$.

Additional information:

In Ref. 1, the solubility of $KNpO_2CO_3$ in K_2CO_3 /KCl solutions of ionic strength of 1.0 mol dm^{-3} was reported to decrease with increasing temperature. The data in Ref. 1 showed rather a great scatter and were presented in graphical form only. For this reason no compilation was prepared from Ref. 1 for this volume.

Auxiliary Information

Method/Apparatus/Procedure:

Nothing specified.

Source and Purity of Materials:

Specpure $^{237}NpO_2$ was dissolved in concentrated HNO_3, and Np(V) was prepared by electrochemical reduction of NpO_2^{2+} at platinum electrode. The final solution was adjusted to contain 0.05 mol dm^{-3} Np(V) and <0.1 mol dm^{-3} HNO_3. On adding 0.1–0.2 mol dm^{-3} K_2CO_3 solution, $KNpO_2CO_3 \cdot xH_2O$ ($x<2$) was obtained as a green precipitate. Analysis (found/calculated for the dihydrate, in mass %): K 9.3/9.67, NpO_2 67.3/66.57, CO_3 14.9/14.85, H_2O (3.2; 5.8)/8.91. K_2CO_3 was a chemically pure product and was recrystallized from water.

Estimated Error:

Temperature: precision ±2 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] R. J. Lemire, G. D. Boyer, and A. B. Campbell, Radiochim. Acta **61**, 57 (1993).

Components:

(1) Potassium carbonato dioxoneptunate(V); $KNpO_2CO_3$; [54955-63-4]
(2) Potassium carbonate; K_2CO_3; [584-08-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

C. F. Novak, I. Al Mahamid, K. A. Beckraft, S. A. Carpenter, N. Hakem, and T. Prussin, J. Solution Chem. **26**, 681–97 (1997).

Variables:

T/K: 295
c_2 /mol kg^{-1}: 0.01–4.83

Prepared by:

J. Hála

Experimental Data

Solubility of $KNpO_2CO_3$ at 22 °C in K_2CO_3 solutions

K_2CO_3 (c_2 /mol kg^{-1})	Np(V)[a,c] (mol dm^{-3})	Solid phase[d]	K_2CO_3 (c_2 /mol kg^{-1})	Np(V)[b,c] (mol dm^{-3})	Solid phase[d]
0.011	$(2.47\pm0.27)\times10^{-7}$	A	0.030	$(3.30\pm0.29)\times10^{-7}$	A
0.030	$(3.00\pm0.30)\times10^{-7}$	A	0.070	$(6.27\pm0.59)\times10^{-7}$	A
0.050	$(3.65\pm0.34)\times10^{-7}$	A	0.130	$(1.79\pm0.14)\times10^{-6}$	A
0.070	$(6.18\pm0.54)\times10^{-7}$	A	0.171	$(3.78\pm0.29)\times10^{-6}$	A
0.100	$(1.26\pm0.09)\times10^{-6}$	A	0.230	$(9.94\pm0.59)\times10^{-6}$	A[e]
0.249	$(1.13\pm0.06)\times10^{-5}$	B	0.300	$(1.65\pm0.10)\times10^{-5}$	A[e]
0.501	$(1.84\pm0.06)\times10^{-5}$	C	0.401	$(3.58\pm0.16)\times10^{-5}$	A[e]
0.739	$(1.99\pm0.06)\times10^{-5}$	C	4.83	$(1.35\pm0.06)\times10^{-4}$	B
0.993	$(2.95\pm0.12)\times10^{-5}$	C			
0.993	$(3.04\pm0.11)\times10^{-5}$	C			
0.993	$(2.82\pm0.09)\times10^{-5}$	C			
1.50	$(4.67\pm0.18)\times10^{-5}$	C			
1.98	$(6.79\pm0.24)\times10^{-5}$	C			
4.81	$(1.25\pm0.04)\times10^{-4}$	B			

[a] Experiments performed with NpO_2OH as the initial solid phase.

[b] Experiments performed with $KNpO_2CO_3$ as the initial solid phase.

[c] Total Np(V) concentration in the saturated solution. The authors did not report on the meaning of the error.

[d] (A) $KNpO_2CO_3$; [54955-64-5]; (B) $K_3NpO_2(CO_3)_2$, α modification, [ ]; (C) $K_3NpO_2(CO_3)_2$, β-modification, [ ]. The authors did not examine the nature of the difference between the two modifications. They assumed it pertained to the water of hydration associated with the solid phases.

[e] From the comparison with measurements using NpO_2OH as the initial solid phase the authors concluded that in these solutions, i.e., in 0.2–0.4 mol dm^{-3} K_2CO_3, $KNpO_2CO_3$ was metastable.

Additional information:

Equilibrium constants for the dissolution reactions $KNpO_2CO_{3(s)} \leftrightarrows K^+ + NpO_2^+ + CO_3^{2-}$ and $K_3NpO_2(CO_3)_{(s)} \leftrightarrows 3K^+ + NpO_2^+ + 2CO_3^{2-}$ were calculated to be $10^{-(13.6\pm0.1)}$ and $10^{-(15.9\pm0.1)}$, respectively. Thermodynamic analysis of the solubility data using the Pitzer ion interaction approach was also given.

Components:

(1) Potassium carbonato dioxoneptunate(V); $KNpO_2CO_3$; [54955-63-4]
(2) Potassium carbonate; K_2CO_3 ; [584-08-7]
(3) Sodium carbonate; Na_2CO_3 ; [497-19-8]
(4) Potassium chloride; KCl; [7447-40-7]
(5) Sodium chloride; NaCl; [7647-14-5]
(6) Water; H_2O; [7732-18-5]

Original Measurements:

I. Al Mahamid, C. F. Novak, K. A. Beckraft, S. A. Carpenter, and N. Hakem, Radiochim. Acta. **81**, 93–101 (1998).

Variables:

T/K: 295
m_2 /mol kg^{-1}: 0.001–1.07
m_3 /mol kg^{-1}: 0.00035–0.00995
m_4 /mol kg^{-1}: 0.0034–3.20
m_5 /mol kg^{-1}: 5.00

Prepared by:

J. Hála

Experimental Data

Solubility of $KNpO_2CO_3$ at 22 °C as a function of K_2CO_3 or Na_2CO_3 concentration in solutions of varying composition[a]

KCl (m_4 /mol kg^{-1})	K_2CO_3 (m_2 /mol kg^{-1})	Na_2CO_3 (m_3 /mol kg^{-1})	NaCl (m_5 /mol kg^{-1})	Np(V)[b] (10^4 mol dm^{-3})
0.0034	0.0010	—	—	$(1.21\pm0.08)\times10^{-6}$
0.0032	0.0101	—	—	$(6.61\pm0.57)\times10^{-7}$
0.0323	0.0010	—	—	$(5.89\pm0.28)\times10^{-7}$
0.0320	0.0101	—	—	$(3.47\pm0.24)\times10^{-7}$
0.0321	0.100	—	—	$(2.50\pm0.32)\times10^{-6}$
0.320	0.0010	—	—	$(2.32\pm0.24)\times10^{-7}$
0.320	0.0101	—	—	$(3.92\pm0.38)\times10^{-7}$
0.320	0.100	—	—	$(3.71\pm0.25)\times10^{-6}$
3.20	0.0010	—	—	$(1.94\pm0.24)\times10^{-7}$
3.20	0.0101	—	—	$(2.24\pm0.32)\times10^{-7}$
3.20	0.100	—	—	$(1.46\pm0.12)\times10^{-5}$
1.00	0.996	—	—	$(1.68\pm0.10)\times10^{-5}$
1.08	1.07	—	—	$(1.82\pm0.12)\times10^{-5}$
0.100	—	0.000 35	5.00	$(1.04\pm0.41)\times10^{-6}$
0.100	—	0.001 00	5.00	$(1.15\pm0.42)\times10^{-6}$
0.100	—	0.003 10	5.00	$(2.11\pm0.99)\times10^{-6}$
0.100	—	0.009 95	5.00	$(6.32\pm0.23)\times10^{-5}$

[a] Solid phase was $KNpO_2CO_3$, [54955-63-4], in all solutions.
[b] Total Np(V) concentration in the saturated solution. The authors did not report on the meaning of the error, or on how the error was estimated.

Additional information:
The authors also measured the solubility of $KNpO_2CO_3$ in three different synthetic Na–K–Mg–Cl brines in the presence of CO_2 gas.[2] A few measurements of the solubility of $KNpO_2CO_3$ were reported, in graphical form, by Lemire *et al.*[3] The measurements were performed at 30 and 75 °C in K_2CO_3–KCl solutions containing 10^{-4}–10^{-1} mol dm^{-3} equilibrium carbonate ion concentration and 1.0 mol dm^{-3} K^+ ions.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used with either NpO_2OH or $KNpO_2CO_3$ as the starting solid. The solid was added to K_2CO_3 solutions of the desired concentration in polyetheretherketone vessels (Cadillac Plastics), and allowed to equilibrate for up to 200 days. Steady-state Np(V) concentration in the solutions was reached in 150 days or less. Samples from the saturated solutions were filtered through 4.1 nm Centricon filters (Amicon Corp.) that had been pretreated with 500 μL of the solution to be analyzed. No adsorption of Np on the filter was observed. Neptunium in the saturated solutions was determined radiometrically by measuring the 29.4 keV γ ray of ^{237}Np using a high purity Ge detector. In samples containing $<10^{-6}$ mol dm^{-3}Np it was necessary to remove the overlap from the daughter ^{233}Pa peak at 28.6 keV. This was achieved by spectra deconvolution. The solid phases were characterized by x-ray diffraction.

Source and Purity of Materials:

NpO_2OH was prepared by addition of a solution of KOH to Np(V) solution in 0.1 mol dm^{-3} HCl. The resulting green solid was washed twice with CO_2-free de-ionized water. The KOH solution was prepared in a CO_2-free glove box. $KNpO_2CO_3$ was prepared by addition of K_2CO_3 solution to the Np(V) stock solution in 0.1 mol dm^{-3} HCl. The carbonate ion concentration was kept below 0.05 mol dm^{-3} to prevent precipitation of $K_3NpO_2(CO_3)_2$. The resulting green solid was washed twice with 0.05 mol dm^{-3} K_2CO_3 to remove any Cl^- ions. The purity of the Np(V) oxidation state in the ^{237}Np stock solution (source not reported) was verified by comparison between spectrophotometric measurements and γ counting. No Np(IV) or Np(VI) were present. KOH (J. T. Baker) and K_2CO_3 (Matheson) used were A. R. grade.

Estimated Error:

Temperature: precision ±1 K (authors).
Solubility: see above.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. The solid was equilibrated with solutions of the desired composition in polyetheretherketone vessels (Cadillac Plastics). The equilibration time was 170 days with steady state being achieved within 107 days. All experiments were conducted under argon atmosphere. Samples of the saturated solutions were filtered through 4.1 nm Centricon filters (Amicon Corp.). The pH was measured using a Ross combination glass electrode calibrated in each of the K^+/Cl^- or $Na^+/K^+/Cl^-$ solution to account for the liquid junction potential. The Np(V) concentration was measured radiometrically by means of a high purity Ge detector using the 29.4 keV γ line of ^{237}Np. In samples containing $<10^{-6}$ mol dm^{-3} Np, the overlap from the 28.6 keV γ line of ^{233}Pa was removed by applying spectral deconvolution. Total inorganic carbon content in the saturated solution was determined by using Shimadzu TOC-5050 carbon analyzer. No changes in total carbon were observed.

Source and Purity of Materials:

Method of preparation of $KNpO_2CO_3$ was not reported. Purity of the Np(V) stock solution, including oxidation state purity, was verified as in the authors' previous work.[1]

Estimated Error:

Temperature: precision ±1 K (authors).

Solubility: see above.

References:

[1] C. F. Novak, I. Al Mahamid, K. A. Beckraft, S. A. Carpenter, N. Hakem, and T. Prussin, J. Solution Chem. **26**, 681 (1997).

[2] C. F. Novak, H. Nitsche, H. B. Sibber, K. Roberts, P. C. Torretto, T. Prussin, K. Beckraft, S. A. Carpenter, D. E. Hobart, and I. Al Mahamid, Radiochim. Acta **74**, 31 (1996).

[3] R. J. Lemire, G. D. Boyer, and A. B. Campbell, Radiochim. Acta **61**, 57 (1993).

Components:

(1) Potassium bis(carbonato) dioxoneptunate(V); $K_3NpO_2(CO_3)_2$; [54955-64-5]

(2) Potassium carbonate; K_2CO_3;[584-08-7]

(3) Water; H_2O; [7732-18-5]

Original Measurements:

G. I. Visyasheva, Yu. F. Volkov, G. A. Simakin, I. I. Kapshukov, A. S. Bevz, and G. N. Yakovlev, Radiokhimiya **16**, 853–9 (1974).

Variables:

T/K: 293 and 353

c_2 /mol dm^{-3}: 1.2

Prepared by:

J. Hála

Experimental Data

Solubility of $K_3NpO_2(CO_3)_2$ at 20 and 80 °C in 1.2 mol dm^{-3} K_2CO_3 solution[a]

Temperature (°C)	$K_3NpO_2(CO_3)_2$ (mg dm^{-3})	$K_3NpO_2(CO_3)_2$[b] ($10^5 c_1$ /mol dm^{-3})
20	8	3.37
80	17	7.17

[a] The white salt $K_3NpO_2(CO_3)_2$ was reported to be stable in 0.8 to 1.5 mol dm^{-3} K_2CO_3 solutions. Based on analysis of the starting material, the compiler assumed the equilibrium solid phase to be hydrated $K_3NpO_2(CO_3)_2$. Another modification of $K_3NpO_2(CO_3)_2$, pale yellow to pale green, was obtained by precipitation from solutions containing >1.8 mol dm^{-3} K_2CO_3. Solubility data for this modification were not reported.

[b] Calculated by compiler for $A_r(Np)=237.0482$.

Auxiliary Information

Method/Apparatus/Procedure:

Nothing specified.

Source and Purity of Materials:

Specpure $^{237}NpO_2$ was dissolved in concentrated HNO_3, and Np(V) was prepared by electrochemical reduction of NpO_2^{2+} at platinum electrode. The final solution was adjusted to contain 0.05 mol dm^{-3} Np(V) and <0.1 mol dm^{-3} HNO_3. On adding 0.8–1.5 mol dm^{-3} K_2CO_3 solution, $K_3NpO_2(CO_3)_2 \cdot xH_2O$ ($x<2$) was obtained as a white precipitate. Analysis (found/calculated for the monohydrate, in mass %): K 23.2/22.37, NpO_2 52.2/51.31, CO_3 23.1/22.89, H_2O 1.6/3.43. K_2CO_3 was a chemically pure product and was recrystallized from water.

Estimated Error:

Temperature: precision ±2 K (authors).

Solubility:insufficient data given to allow for error estimate.

6.4. Salts of Dioxo Tris(carbonato) Neptunate(V)(-5)

Components:
(1) Potassium tris(carbonato) dioxoneptunate(V); $K_5NpO_2(CO_3)_3$; [ ]
(2) Potassium carbonate; K_2CO_3; [584-08-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
D. S. Gorbenko and R. A. Zenkova, Zh. Neorg. Khim. **11**, 520–8 (1966).

Variables:
T/K: 293
c_2 /mol dm^{-3}: 0–5.57

Prepared by:
J. Hála

Experimental Data

Solubility of $K_5NpO_2(CO_3)_3$ at 20 °C in water and in K_2CO_3 solutions[a]

K_2CO_3 (10^2 w_2 /mass%)	K_2CO_3 (c_2 /mol dm^{-3})	Np(V) (mg dm^{-3})	Np(V)[b] (10^5 c_1 /mol dm^{-3})
0	0	10.3	4.35
—	0.2	23.0	9.70
50	5.57[b]	38.0	16.0

[a] The nature of the equilibrium solid phases was not investigated.
[b] Calculated by compiler using A_r(NP)=237.0482.
[c] Calculated by compiler using the density of 1.5404 g cm^{-3} for 50 mass % K_2CO_3.[1]

Auxiliary Information

Method/Apparatus/Procedure:
Isothermal method used. 2–7 mg of the dry salt was equilibrated with water or K_2CO_3 solution of the desired concentration for 1 week with occasional stirring. The time necessary to attain equilibrium was not reported. An aliquot of the saturated solution was acidified with HNO_3, and the neptunium concentration was determined radiometrically.

Source and Purity of Materials:
$K_5NpO_2(CO_3)_3$ was prepared by precipitating NpO_2OH from a solution of Np(V) in 1 mol dm^{-3} HNO_3 by action of NH_3 solution, and by subsequent stirring the precipitate formed with excess of 50% K_2CO_3 solution. The pale green–blue precipitate was kept in 50% K_2CO_3 for 1–2 days, filtered, and washed with dilute solution of K_2CO_3 and acetone. Analysis (found/calculated for anhydrous salt, in mass %): K 28.43/30.28, Np 34.95/36.80, CO_3 27.38/27.95. Source and purity of K_2CO_3 was not specified.

Estimated Error:
Temperature: precision ±2 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:
[1] *Physico-Chemical Tables* (SNTL, Prague, 1953), Vol. 1, p. 268.

Components:
(1) Cesium tris(carbonato) dioxoneptunate(V); $Cs_5NpO_2(CO_3)_3$; [ ]
(2) Cesium carbonate; Cs_2CO_3; [534-17-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
D. S. Gorbenko and R. A. Zenkova, Zh. Neorg. Khim. **11**, 520–8 (1966).

Variables:
T/K: 293
c_2 /mol dm^{-3}: 0.2; 100 w_2 /mass %: 50

Prepared by:
J. Hála

Experimental Data

Solubility of $Cs_5NpO_2(CO_3)_3$ at 20 °C in water and in Cs_2CO_3 solutions[a]

Cs_2CO_3 (10^2 w_2 /mass%)	Cs_2CO_3 (c_2 /mol dm^{-3})	Np(V) (mg dm^{-3})	Np(V)[b] (10^4 mol dm^{-3})
0	0	22.7	0.958
—	0.2	87.5	3.69
50	—	492.0	20.8

[a] The nature of the equilibrium solid phases was not investigated.
[b] Calculated by compiler using A_r(Np)=237.0482.

Auxiliary Information

Method/Apparatus/Procedure:
Isothermal method used. 2–7 mg of the dry salt was equilibrated with water or Cs_2CO_3 solution of the desired concentration for 1 week with occasional stirring. The time necessary to attain equilibrium was not reported. An aliquot of the saturated solution was acidified with HNO_3, and the neptunium concentration was determined radiometrically.

Source and Purity of Materials:
$Cs_5NpO_2(CO_3)_3$ was prepared by precipitating NpO_2OH from a solution of Np(V) in 1 mol dm^{-3} HNO_3 by action of NH_3 solution, and by subsequent stirring the precipitate formed with excess of 50% Cs_2CO_3 solution. The pale green–blue precipitate was kept in 50% Cs_2CO_3 for 1–2 days, filtered, and washed with dilute solution of Cs_2CO_3 and acetone. Analysis (found/calculated for anhydrous salt, in mass %): Cs 58.53/59.69, Np 20.68/21.27, CO_3 14.29/16.16. Source and purity of Cs_2CO_3 was not specified.

Estimated Error:
Temperature: precision ±2 K (authors).
Solubility: insufficient data given to allow for error estimate.

Components:
(1) Ammonium carbonato dioxoneptunate(V); $NH_4NpO_2CO_3$; [ ]
(2) Ammonium carbonate; $(NH_4)_2CO_3$; [506-87-6]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
A. I. Moskvin, Radiokhimiya **13**, 674–81 (1971).

Variables:
T/K: 293[a]
c_2 /mol dm^{-3}: 0–2.20

Prepared by:
J. Hála

Experimental Data

Solubility of $NH_4NpO_2CO_3$ at 20 °C in $(NH_4)_2CO_3$ solutions[b]

$(NH_4)_2CO_3$[c] (c_2 /mol dm^{-3})	Np(V)[c] (10^5 mol dm^{-3})
0	1.0[d]
0.20	1.51
0.60	4.51
1.00	6.20
1.25	10.0
1.50	12.3
2.00	10.5
2.20	7.81

[a] Temperature was not specified in the original document. With reference to the author's other paper[1] the compiler assumed the measurements were performed at 20 °C.

[b] The nature of equilibrium solid phases was not investigated. Since the starting material was hydrated $NH_4NpO_2CO_3$, the compiler assumed this was also the equilibrium solid phase in solutions containing 0.2–1.5 mol dm^{-3} $(NH_4)_2CO_3$.

[c] The pH of the saturated solutions varied from 8.8 to 9.0 on going from 0.2 to 2.2 mol dm^{-3} $(NH_4)_2CO_3$.

[d] Extrapolated (author).

Additional information:
The increase in the solubility of $NH_4NpO_2CO_3$ with increasing $(NH_4)_2CO_3$ concentration was ascribed by the author to the formation of the soluble $NpO_2(OH)CO_3^{2-}$ complex. Its overall stability constant was obtained from the solubility data at 0.2–1.5 mol dm^{-3} $(NH_4)_2CO_3$ as $(6.7\pm1.2)\times10^4$ mol^2 dm^{-6}. To explain decrease of $NH_4NpO_2CO_3$ solubility at 2.00 and 2.20 dm^{-3} $(NH_4)_2CO_3$, the author assumed the formation of a sparingly soluble salt, $(NH_4)_5NpO_2(CO_3)_3$.

Auxiliary Information

Method/Apparatus/Procedure:
Isothermal method used. With reference to the author's other work,[1] the compiler assumed that freshly precipitated $NH_4NpO_2CO_3\cdot xH_2O$ was stirred with $(NH_4)_2CO_3$ solutions of the desired concentration for 6–8 h. Neptunium in the saturated solutions was determined radiometrically (method not specified).

Source and Purity of Materials:
$NH_4NpO_2CO_3\cdot xH_2O$ was obtained by precipitation by adding a stoichiometric amount of $(NH_4)_2CO_3$ to a slightly acidic (pH 4–5) solution of NpO_2^+. Source and purity of chemicals used were not specified.

Estimated Error:
Temperature: precision ±1 K (author; in Ref. 1).
Solubility: insufficient data given to allow for error estimate.

References:

[1] A. I. Moskvin, Radiokhimiya **13**, 681 (1971).

Components:
Ammonium tris(carbonato) dioxoneptunate(VI); $(NH_4)_4NpO_2(CO_3)_3$; [ ]
(2) Ammonium carbonate; $(NH_4)_2CO_3$; [506-87-6]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
A. I. Moskvin, Radiokhimiya **13**, 674–81 (1971).

Variables:
T/K: 293[a]
c_2 /mol dm^{-3}: 0–2.20

Prepared by:
J. Hála

Experimental Data

Solubility of $(NH_4)_4NpO_2(CO_3)_3$ at 20 °C in $(NH_4)_2CO_3$ solutions[b]

$(NH_4)_2CO_3$[c] (c_2 /mol dm^{-3})	Np(VI) (10^2 mol dm^{-3})
0	10.6
0.10	6.54
0.50	2.26
0.75	1.60
1.00	1.27
1.25	0.886
1.50	0.831
1.80	0.665
2.20	0.451

[a] Temperature was not specified in the original document. With reference to the author's other paper[1] the compiler assumed the measurements were performed at 20 °C.

[b] The nature of equilibrium solid phases was not investigated.

[c] The pH of the saturated solutions varied from 8.5 to 9.1 on going from 0 to 2.0 mol dm^{-3} $(NH_4)_2CO_3$.

Additional information:
The decreasing solubility of $(NH_4)_4NpO_2(CO_3)_3$ with increasing $(NH_4)_2CO_3$ concentration was explained by the author by the dissociation of the former to the soluble $NpO_2(CO_3)_2^{2-}$ complex. From the solubility data the author obtained the equilibrium constant, $K=83.3$, for the reaction

$$(NH_4)_4NpO_2(CO_3)_{3(s)} \leftrightarrows NpO_2(CO_3)_2^{2-} + CO_3^{2-} + 4NH_4^+$$

Auxiliary Information

Method/Apparatus/Procedure:
With reference to the author's other work,[1] isothermal method used. Freshly precipitated $(NH_4)_4NpO_2(CO_3)_3$ was stirred with $(NH_4)_2CO_3$ solutions of the desired concentration for 6–8 h. Neptunium in the saturated solutions was determined radiometrically (method not specified).

Source and Purity of Materials:
$(NH_4)_4NpO_2(CO_3)_3$ was prepared either by precipitation by adding solid $(NH_4)_2CO_3$ to a solution obtained by dissolving $NpO_2(OH)_2$ in concentrated HNO_3, or by prolonged equilibration of $NpO_2(OH)_2$ with >0.5 mol dm^{-3} $(NH_4)_2CO_3$. Source and purity of chemicals used were not specified.

Estimated Error:
Temperature: precision ±1 K (author, in Ref. 1).
Solubility: insufficient data given to allow for error estimate.

References:
[1] A. I. Moskvin, Radiokhimiya **13**, 681 (1971).

6.5. Hexamminecobalt(III) Salts of Dioxo(carbonate) Neptunates

Components:

(1A) Bis[hexamminecobalt(III)] pentakis(carbonato)aquaneptunate(IV); $[Co(NH_3)_6]_2Np(CO_3)_5H_2O$; [ ];
(1B) Hexamminecobalt(III) bis(carbonato)dioxo neptunate(V); $Co(NH_3)_6NpO_2(CO_3)_2H_2O$; [ ];
(1C) Bis[hexamminecobalt(III) nitrate] tris(carbonato) dioxoneptunate(VI); $\{[Co(NH_3)_6]NO_3\}_2NpO_2(CO_3)_3$; [ ]
(2) Water; H_2O; [7732-18-5]

Original Measurements:

A. Saito and K. Ueno, J. Inorg. Nucl. Chem. **39**, 315–8 (1977).

Variables:

T/K: 293

Prepared by:

J. Hála

Experimental Data

Solubility at 20 °C of bis[hexamminecobalt(III)] carbonate neptunates in water[a]

Compound	Np (mg dm^{-3})	Np (10^6 mol dm^{-3})[b]
1A	0.35	1.48
1B	2.1	8.85
1C	6.8	28.7

[a] The nature of equilibrium solid phases was not investigated.
[b] Calculated by compiler for $A_r(Np)=237.0482$.

Additional information:

Solubility of the compound 1A in $(NH_4)_2CO_3$ solutions, and of 1B and 1C in Na_2CO_3 solutions as a function of carbonate ion concentration were also measured, and presented in graphical form.

Auxiliary Information

Method/Apparatus/Procedure:

No explicit details were reported for the determination of solubilities in water. Judged from the other solubility measurements reported in this document, the solids were allowed to stand with a small volume of water for 1–2 days. After centrifugation, neptunium was determined in the supernatant by α counting of ^{237}Np using a gas flow proportional counter.

Source and Purity of Materials:

From a stock solution of Np(V) obtained from ^{237}Np purified by ion exchange, Np(VI) was prepared by prolonged heating with concentrated HNO_3 while Np(IV) was prepared by reduction, first to Np(III) by zinc amalgam, and subsequent converting Np(III) to Np(IV) by aeration. The valencies of neptunium were checked by means of absorption spectra. $Co(NH_3)_6Cl_3$ was prepared according to Ref. 1. The compounds 1A, 1B, and 1C were precipitated from 0.3, 0.5, and 0.1 mol dm^{-3} carbonate solutions, respectively, by adding $Co(NH_3)_6Cl_3$ to give a 0.04 mol dm^{-3} solution. Their composition, as deduced from chemical analysis, was $[Co(NH_3)_6]_2Np(IV)(CO_3)_5\cdot 4H_2O$, $[Co(NH_3)_6][Np(V)O_2(CO_3)_2]\cdot 1/6[Co(NH_3)_6]_2(CO_3)_3\cdot 5H_2O$, and $\{[Co(NH_3)_6]NO_3\}_2NpO_2(CO_3)_3$, respectively.

Estimated Error:

Temperature: precision ± 2 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] W. Biltz, Z. Anorg. Allgem. Chem. **83**, 177 (1914).

6.6. Neptunium(IV) Oxalate

Components:

(1) Neptunium(IV) bis(oxalate); $Np(C_2O_4)_2$; [20196-48-9]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

P. I. Kondratova and A. D. Gelman, Radiokhimiya **2**, 315–9 (1960).

Variables:

T/K: 298
c(oxalate ion)/mol dm^{-3}: 7.6×10^{-10}–4.0×10^{-5}

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $Np(C_2O_4)_2$ in oxalic acid solutions[a]

$C_2O_4^{2-}$ (mol dm^{-3})[b]	$Np(C_2O_4)_2$ (10^4 c_1 /mol dm^{-3})	$C_2O_4^{2-}$ (mol dm^{-3})[b]	$Np(C_2O_4)_2$ (10^4 c_1 /mol dm^{-3})
7.6×10^{-10}	1.18	8.7×10^{-7}	0.91
1.4×10^{-9}	0.72	1.75×10^{-6}	1.5
3.6×10^{-9}	0.51	3.15×10^{-6}	2.2
3.5×10^{-8}	0.29	2.5×10^{-5}	15.7
1.75×10^{-7}	0.28	3.2×10^{-5}	24
3.5×10^{-7}	0.41	4.0×10^{-5}	30

[a] The nature of equilibrium solid phases was not investigated.
[b] Oxalate ion concentration was calculated by the authors from the concentration of oxalic acid, pH of the solution, and the dissociation constants of oxalic acid (data not reported).

Additional information:

From the solubility of $Np(C_2O_4)_2$ in oxalic acid solutions, the following Np(IV) oxalatocomplexes were identified in the saturated solutions, and their overall instability constants determined: $Np(C_2O_4)^{2+}$, $K_1=(2.9\pm2)\times10^{-9}$; $Np(C_2O_4)_2$, $K_2=(2.9\pm0.05)\times10^{-18}$; $Np(C_2O_4)_3^{2-}$, $K_3=(1.1\pm0.1)\times10^{-24}$; and $Np(C_2O_4)_4^{4-}$, $K_4=4\times10^{-28}$.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Freshly prepared $Np(C_2O_4)_2\cdot 6H_2O$ was stirred with oxalic acid solutions of the desired concentration for 5 h. The mixture was then centrifuged, and neptunium in the saturated solutions was determined spectrophotometrically at 320 nm making use of absorbancy of the Np(IV)–H_2O_2 complex in alkaline medium.

Source and Purity of Materials:

No details reported.

Estimated Error:

Temperature: precision ±2 K (authors).
Solubility: insufficient data given to allow for error estimate.

Components:

(1) Neptunium(IV) bis(oxalate); $Np(C_2O_4)_2$; [20196-48-9]
(2) Hydrogen chloride; HCl; [7647-01-0]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

P. I. Kondratova and A. D. Gelman, Radiokhimiya, **2**, 315–9 (1960).

Variables:

T/K: 289 and 292
c_2 /mol dm^{-3}: 1.56–2.09 at 289 K; 0.41–1.08 at 292 K

Prepared by:

J. Hála

Experimental Data

Solubility at 16 and 19 °C of $Np(C_2O_4)_2$ in hydrochloric acid solutions[a]

Temperature (°C)	HCl (c_2 /mol dm^{-3})	$Np(C_2O_4)_2$ (10^5 c_1 /mol dm^{-3})				$Np(C_2O_4)_2$ (10^5 c_1 /mol dm^{-3})[b]
16	1.56	19.8	19.2	19.2		19.4±0.20
16	2.09	29.7	28.2			29.0±0.75
19	0.41	4.17	3.28	3.37	3.71	3.63±0.20
19	1.08	12.7	14.6			13.7±0.95

[a] The nature of equilibrium solid phases was not investigated.
[b] Mean value and standard deviation of the mean (compiler).

Additional information:

The increasing solubility of $Np(C_2O_4)_2$ with increasing HCl concentration was explained by the authors by considering the reaction $Np(C_2O_4)_2+4H^+\leftrightarrows Np^{4+}+2C_2H_2O_4$. The equilibrium constant of this reaction was obtained as $(6.0\pm1.3)\times10^{-12}$ and $(4.8\pm0.3)\times10^{-12}$ at 19 and 16 °C, respectively, and did not depend on HCl concentration. This indicated that Np^{4+}/Cl^- complexes played a negligible role in this system. From these constants and dissociation constants of oxalic acid, the solubility product of $Np(C_2O_4)_2$ was obtained as $(8.6\pm1.8)\times10^{-23}$ and $(6.9\pm0.4)\times10^{-23}$ at 19 and 16 °C, respectively.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Freshly prepared $Np(C_2O_4)_2\cdot6H_2O$ was stirred with oxalic acid solutions of the desired concentration for 5 h. The mixture was then centrifuged, and neptunium in the saturated solutions was determined spectrophotometrically at 320 nm making use of absorbancy of the $Np(IV)-H_2O_2$ complex in alkaline medium.

Source and Purity of Materials:

No details reported.

Estimated Error:

Temperature: precision ± 2 K (authors for the measurements in the $Np(C_2O_4)_2-C_2H_2O_4-H_2O$ system reported in this same document).

Solubility: based on standard deviations of individual measurements the compiler estimates the precision ±10%.

Components:

(1) Neptunium(IV) bis(oxalate); $Np(C_2O_4)_2$; [20196-48-9]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Nitric acid; HNO_3; [7697-37-2]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

D. W. Luerkens, USDOE Report DP-1655, E. I. Du Pont de Nemours and Comp., Savannah River Lab., Aiken, SC, 1983.

Variables:

T/K: 295, 318 and 333
c_2 /mol dm^{-3}: 0.013–0.80
c_3 /mol dm^{-3}: 0.4–10.0

Prepared by:

J. Hála

Experimental Data

Solubility of $Np(C_2O_4)_2$ in oxalic acid/nitric acid solutions at three temperatures[a,b]

$C_2H_2O_4^{2-}$ (c_2 /mol dm^{-3})[d]	HNO_3 (c_3 /mol dm^{-3})[d]	Np(IV) (mg dm^{-3})	$Np(C_2O_4)_2$ (10^5 c_1 / mol dm^{-3})[g]	$C_2H_2O_4^{2-}$ (c_2 /mol dm^{-3})[e]	HNO_3 (c_3 /mol dm^{-3})[e]	Np(IV) (mg dm^{-3})	$Np(C_2O_4)_2$ (10^4 c_1 / mol dm^{-3})[g]
0.014	0.4	6.1	2.57	0.013	0.4	45.5	1.92
0.078	0.4	8.7	3.67	0.077	0.4	35.5	1.48
0.158	0.4	12.8	5.40	0.157	0.4	94.0	3.97
0.397	0.4	29.2	12.3	0.397	0.4	92.5	3.90
0.80	0.4	37.4	15.8	0.799	0.4	295.0	12.4
0.623	0.5	31.6	13.3	0.623	0.5	133.0	5.61
0.370	0.6	14.0	5.91	0.242	0.7	34.5	1.46
0.243	0.7	9.9	4.18	0.640	0.8	73.5	3.10
0.640	0.8	20.8	8.78	0.046	1.0	22.5	0.949
0.047	1.0	4.0	1.69	0.096	1.0	25.5	1.08
0.097	1.0	5.9	2.49	0.497	1.0	83.5	3.52
0.498	1.0	9.4	3.97	0.016	2.0	38.5	1.62
0.017	2.0	4.4	1.86	0.036	2.0	26.0	1.10
0.037	2.0	4.6	1.94	0.397	2.0	44.0	1.86
0.084	4.0	5.5	2.32	0.023	5.0	162.5	6.86
0.158	4.0	5.1	2.15	0.122	5.0	74.5	3.14
0.123	5.0	7.7	3.25	0.036	6.0	362.5	15.3
0.034	6.0	35.6	15.0	0.242	7.0	101.0	4.26
0.242	7.0	10.6	4.47	0.063	10.0	330.0	13.9
0.062	10.0	35.9	15.1				

$C_2H_2O_4^{2-}$ (c_2 /mol dm^{-3})[f]	HNO_3 (c_3 /mol dm^{-3})[f]	$Np(C_2O_4)_2$ (mg dm^{-3})	$Np(C_2O_4)_2$ (10^5 c_1 / mol dm^{-3})	$C_2H_2O_4^{2-}$ (c_2 /mol dm^{-3})[f]	HNO_3 (c_3 /mol dm^{-3})[f]	$Np(C_2O_4)_2$ (mg dm^{-3})	$Np(C_2O_4)_2$ (10^4 c_1 / mol dm^{-3})
0.013	0.4	74.9	3.16	0.017	2.0	76.2	3.22
0.077	0.4	60.2	2.54	0.036	2.0	54.8	2.31
0.157	0.4	74.5	3.14	0.196	2.0	36.4	1.54
0.390	0.4	172.4	7.27	0.396	2.0	32.4	1.37
0.789	0.4	263.7	11.1	0.456	3.0	36.7	1.55
0.622	0.5	118.9	5.02	0.016	4.0	378.1	16.0
0.367	0.6	106.6	4.50	0.083	4.0	104.6	4.41
0.241	0.7	61.9	2.61	0.156	4.0	53.8	2.27
0.640	0.8	84.9	3.58	0.123	5.0	198.2	8.36
0.046	1.0	68.3	2.88	0.036	6.0	420.1	17.7
0.097	1.0	49.6	2.09	0.242	7.0	104.6	4.41
0.497	1.0	84.4	3.56	0.063	10.0	369.8	15.6

[a] The nature of equilibrium solid phases was not investigated. In interpretation of the results, the author assumed this to be the hexahydrate, $Np(C_2O_4)_2\cdot 6H_2O$, [ ].

[b] All solutions contained an unspecified concentration of hydrazine used to stabilize Np(IV) valency state, and prevent it from oxidation by products of HNO_3 radiolysis.

[c] Initial (total) concentration.

[d] Room temperature (22 °C).

[e] Measurements performed at 45 °C.

[f] Measurements performed at 60 °C.

[g] Calculated by compiler using $A_r(Np)=237.0482$.

Additional information:

Variations in $Np(C_2O_4)_2$ solubility with the concentrations of oxalic and nitric acids were ascribed by the author to the variations of free oxalate ion concentration, which controls the equilibria between Np(IV) oxalate complexes in solutions. Minimum solubility corresponds to the conditions where the formation of the highly insoluble $Np(C_2O_4)_2$ predominates. Increased solubility corresponds to the formation of $Np(C_2O_4)^{2+}$ or $Np(C_2O_4)_3^{2-}$ complexes as the free oxalate concentration decreases or increases, respectively. Based on these assumptions, the solubility of $Np(C_2O_4)_2$ was expressed as

$$[Np(IV)]_{tot}=[Np(C_2O_4)^{2+}]+[Np(C_2O_4)_2]+[Np(C_2O_4)_3^{2-}]=K_1+K_1K_2/R_s+K_1K_3R_s\,,$$

where $K_1=[Np(C_2O_4)_2]$ (equilibrium constant for the reaction $Np(C_2O_4)_2\cdot 6H_2O_{(s)}$ $Np(C_2O_4)_{2(aq)}$), $K_2=[Np(C_2O_4)^{2+}][C_2H_2O_4]\times[Np(C_2O_4)_2]^{-1}[H^+]^{-2}$, $K_3=[Np(C_2O_4)_3^{2-}][H^+]^2[Np(C_2O_4)_2]^{-1}[C_2H_2O_4]^{-1}$, and $R_s=[C_2H_2O_4][H^+]^{-2}=[C_2H_2O_4][HNO_3]^{-2}$. By least squares treatment of experimental data, the author obtained the following constants, always at 22, 45, and 60 °C, respectively: $K_1=4.2\pm 0.7, 14.3\pm 6.5, 41.9\pm 5.3$; $K_1K_2=0.030\pm 0.002, 0.34\pm 0.02, 0.35\pm 0.02$; $K_1K_3=8.2\pm 0.7, 60.1\pm 5.4, 43.9\pm 4.9$.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. At room temperature (22 °C), excess $Np(C_2O_4)_2\cdot 6H_2O$ was equilibrated with $C_2H_2O_4$ /HNO_3 solutions of the desired concentration. In measurements at 45 and 60 °C, Np(IV) oxalate was precipitated from $C_2H_2O_4$ /HNO_3 solutions by addition of Np(IV) nitrate solution. In both methods, the solutions contained N_2H_4 to protect Np(IV) from oxidation due to radiolytic products of HNO_3, and were equilibrated for 24 h. The measurements at room temperature were not thermostated. Saturated solutions were filtered and sampled using a 0.25 μm micropore filter on a syringe. The filtered samples were immediately diluted in strong HNO_3 to prevent precipitation, and Np concentration was determined by α counting.

Source and Purity of Materials:

A stock solution of purified ^{237}Np was prepared by ion exchange.[1] Neptunium(VI) in the eluate was reduced first to Np(V) by heating the eluate to 55 °C in the presence of 0.1 mol dm^{-3} N_2H_4. The solution of Np(V) was cooled to room temperature and reduced to Np(IV) with 0.03 mol dm^{-3} excess ascorbic acid. Solid Np(IV) oxalate was obtained by precipitation of Np(IV) with excess of oxalic acid. The precipitate was filtered and washed with distilled water to remove excess oxalate and nitrate ions. Source and purity of other chemicals, and radiochemical purity of ^{237}Np used were not specified.

Estimated Error:

Temperature: not reported.

Solubility: insufficient data given to allow for error estimate.

References:

[1] G. A. Burney, USAEC, Report DP-689, 1962.

6.7. Neptunium(VI) Dioxo(oxalate)

Components:

(1) Neptunium(VI) dioxooxalate; $NpO_2C_2O_4$; [ ]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Nitric acid; HNO_3 ; [7697-37-2]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

M. P. Mefodeva, N. N. Krot, T. V. Smirnova, and A. D. Gelman, Radiokhimiya **11**, 193–200 (1969).

Variables:

T/K: 287
c_2 /mol dm^{-3}: 0–0.15
c_3 /mol dm^{-3}: 1.0

Prepared by:

J. Hála

Experimental Data

Solubility at 14 °C of $NpO_2C_2O_4$ in oxalic acid solutions containing 1.0 mol dm^{-3}HNO_3[a]

$C_2H_2O_4$[b] (mol dm^{-3})	$C_2H_2O_4$[c] (c_2 /mol dm^{-3})	$NpO_2C_2O_4$ (10^3c_1 /mol dm^{-3})
0	0.0017	15.7
[d]	0.0032	12.8
0.00630	0.0082	8.9
0.0125	0.0137	7.15
0.0250	0.0262	6.25
0.0379	0.0390	5.85
0.0500	0.0512	4.75
0.10	0.101	4.05
0.10	0.102	3.65
0.15	0.151	3.25

[a] The equilibrium solid phase was $NpO_2C_2O_4\cdot 3H_2O$, [ ], in all solutions.

[b] Initial concentration.

[c] Initial concentration corrected for the increase due to the reaction $2NpO_2C_2O_4+2H^+\leftrightarrows 2NpO_2^+ + C_2H_2O_4+2CO_2$.

[d] The concentration reported as 1.0 mol dm^{-3} is obviously a misprint.

Additional information:

[a] From the solubility data, the authors calculated the solubility product of $NpO_2C_2O_4$ as 2.3×10^{-9} mol^2 dm^{-6}.

[b] The solubility of$NpO_2C_2O_4$ was reported to increase with increasing temperature (data reported in graphical form).

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess of freshly precipitated $NpO_2C_2O_4\cdot 3H_2O$ was equilibrated with solutions of the desired concentration in a thermostated bath for 20 min. Then aliquots were withdrawn using a pipette with a filtration adaptor, and the content of neptunium in the saturated solutions was determined spectrophotometrically. The absorption band of Np(V) at 981 nm was used which made it possible to determine Np(V) and Np(VI) simultaneously, and thus correct the total Np concentration in the solution for Np(V) formed during equilibration. The solubility of $NpO_2C_2O_4$ was calculated from the Np(VI) concentration.

Source and Purity of Materials:

$NpO_2C_2O_4\cdot 3H_2O$ was prepared by precipitating Np(VI) with oxalic acid from a solution containing 20–40 g dm^{-3} Np, 2–3 mol dm^{-3}HNO_3, and 0.05 mol dm^{-3}$KBrO_3$. The precipitate was washed with 0.2 mol dm^{-3}HNO_3, ethanol and ether, and air dried for 30 min.

Estimated Error:

Temperature: not reported.

Solubility: insufficient data given to allow for error estimate.

7. The Solubility of Plutonium Compounds

7.1. Plutonium(VI) Dioxocarbonate

Components:

(1) Plutonium (VI) dioxocarbonate; PuO_2CO_3 ; [39292-10-9]
(2) Lithium hydrogencarbonate; $LiHCO_3$; [5006-97-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

L. J. Wittenberg and R. H. Steinmeyer, J. Inorg. Nucl. Chem. **24**, 1015–6 (1962).

Variables:

T/K: 297
c_2 /mol dm^{-3}: 0–0.94

Prepared by:

J. Hála

Experimental Data

Solubility at 24 °C of PuO_2CO_3 in $LiHCO_3$ solutions[a]

$LiHCO_3$ (c_2 /mol dm^{-3})	Pu(VI) (g dm^{-3})	PuO_2CO_3 (10^3 c_1 /mol dm^{-3})[b]
0	0.043	0.180
0.05	1.12	4.69
0.05[c,d]	1.37	5.73
0.10	3.01	12.6
0.24	10.2	42.7
0.25	11.4	47.7
0.50	14.6	61.0
0.75[c]	22.3	93.3
0.94	24.2	101.2

[a] The equilibrium solid phases were not investigated.
[b] Calculated by compiler using $Ar_r(Pu)=239.053$.
[c] Equilibration time 10 days.
[d] This measurement seems to indicate that 16 h equilibration may not be sufficient to give the true equilibrium solubility values (compiler).

Additional information:
The dissolution reaction was postulated by the authors as

$$PuO_2CO_{3(s)}+x\,LiHCO_{3(aq)}\leftrightarrows Li_xPuO_2(CO_3)(HCO_3)_{x(aq)}$$

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Portions of PuO_2CO_3 were added to $LiHCO_3$ solutions of the desired concentration. The mixtures were equilibrated with occasional agitation for 16 h, in two measurements equilibration time of 10 days was used. After centrifugation an aliquot of the dark red saturated solution was dried on a stainless steel slide and α counted to determine the plutonium content. The concentration of $LiHCO_3$ in the initial solutions was determined by titration with a standard HCl solution.

Source and Purity of Materials:

PuO_2CO_3 was prepared from Li plutonate. The latter was obtained from a Pu(VI) solution by precipitation with solid LiOH. The precipitate was washed several times with dilute LiOH, slurried in water, and CO_2 gas was bubbled through the slurry until the dark brown precipitate changed to yellow PuO_2CO_3. Source and purity of materials used were not specified.

Estimated Error:

Temperature: precision ± 1 K (authors).
Solubility: insufficient data given to allow for error estimate.

7.1.1. Evaluation of the $PuO_2CO_3+CO_2+NaClO_4+H_2O$ System

Components:

(1) Plutonium(VI) dioxo carbonate; PuO_2CO_3 ; [39292-10-9]
(2) Carbon dioxide; CO_2 ; [124-38-9]
(3) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(4) Water; H_2O; [7732-18-5]

Evaluator:

J. Hála, Department of Inorganic Chemistry, Masaryk University, 61137 Brno, Czech Republic, June 2000

Critical Evaluation:

The most extensive studies on the solubility of PuO_2CO_3 in $NaClO_4$ solutions as a function of equilibrium carbonate ion concentration has been carried out by Pashalidis *et al.*[1,2] The data were obtained at 295.1 K in measurements conducted as pH titrations in 0.1 mol dm^{-3}$NaClO_4$ solutions with careful control of experimental parameters such as pH, partial pressure of CO_2, attaining equilibrium, and characterization of solid phases during solubility measurements. Both sets of measurements[1,2] yielded solubility data with excellent reproducibility (see the corresponding compilation sheets). In Ref. 1, solubility product of PuO_2CO_3 was reported to be $K_{sp}=10-^{(13.98\pm0.12)}$ mol^2 dm^{-6} in 0.1 mol dm^{-3} $NaClO_4$, and $K^0_{sp}=10^{-(14.84\pm0.10)}$ mol^2 dm^{-6} at zero ionic strength. Solubility product $K_{sp}=10^{-(13.5\pm0.3)}$ mol^2 dm^{-6} has been reported for 3.0 mol dm^{-3}$NaClO_4$ solutions. Based on these values obtained using high precision experimental technique, it is suggested that the value $K_{sp}=10^{-12.8}$ mol^2 dm^{-6}, obtained by calculation in Ref. 4 from the solubility of $(NH_4)_2Pu_2O_7$ in $(NH_4)_2CO_3$ solutions, be disregarded as erroneously high.

As for the dependence of the solubility of PuO_2CO_3 on equilibrium carbonate ion concentration the situation resembles that for UO_2CO_3 (see Critical Evaluation). The solubility versus $[CO_3^{2-}]$ plot passes through a minimum where the solubility of PuO_2CO_3 is determined by K_{sp} only, while the increase in the solubility at higher $[CO_3^{2-}]$ values is caused by the formation of anionic carbonato-complexes of Pu(VI) in the saturated solutions. In Ref. 2, minimum solubility of approximately 5×10^{-6} mol dm^{-3} was observed in the $[CO_3^{2-}]$ range from 10^{-8} to 10^{-6} mol dm^{-3}. This is in general agreement with the work of Robouch and Vitorge[3] who observed minimum solubility of about 10^{-5} mol dm^{-3} over approximately the same $[CO_3^{2-}]$ range at ionic strength of 3.0 mol dm^{-3} $NaClO_4$.

References:

[1] I. Pashalidis, W. Runde, and J. I. Kim, Radiochim. Acta **61**, 141 (1993).
[2] I. Pashalidis, K. R. Czerwinski, F. Fanghänel, and J. I. Kim, Radiochim. Acta **76**, 55 (1997).
[3] P. Robouch and P. Vitorge, Inorg. Chim. Acta **140**, 239 (1987).
[4] A. D. Gelman, A. I. Moskvin, and V. P. Zaitseva, Radiokhimiya **4**, 154 (1962).

Components:

(1) Plutonium(VI) dioxocarbonate; PuO_2CO_3; [39292-10-9]
(2) Carbon dioxide; CO_2; [124-38-9]
(3) Sodium hydrogencarbonate; $NaHCO_3$; [144-55-8]
(4) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(5) Water; H_2O; [7732-18-5]

Original Measurements:

P. Robouch and P. Vitorge, Inorg. Chim. Acta **140**, 239–42 (1987).

Variables:

T/K: 293
p_2/(partial pressure of CO_2)/kPa: 9.81, 29.4, and 98.1
c_4 /mol dm^{-3}:3.0

Prepared by:

J. Hála

Experimental Data

Solubility of PuO_2CO_3 at 20 °C as a function of equilibrium CO_3^{2-} ion concentration at three different partial pressures of CO_2 and at ionic strength of 3.0 mol dm^{-3}

The solubility of PuO_2CO_3 in $NaHCO_3$ solutions with ionic strength of 3.0 mol dm^{-3} maintained by using $NaClO_4$ was measured at three different partial pressures of CO_2 of 0.1, 0.3 and 1.0 atm at 20 °C. The equilibrium solid phase was identified as PuO_2CO_3, [39292-10-9]. The results were reported in graphical form only (see Fig. 20).

Additional information:

Free carbonate ion concentration was calculated by the authors from the values of $[H^+]$, partial pressure of CO_2, and dissociation constants of carbonic acid. Since at a constant free carbonate ion concentration the solubility of PuO_2CO_3 did not depend on the hydrogencarbonate ion concentration, pH, or pressure of CO_2, the authors concluded that the dissolution is controlled by the reaction

$$PuO_2CO_{3(s)}+(n-1)CO_3^{2-}\leftrightarrows PuO_2(CO_3)_n^{2-2n} \quad (n=1,2,3)$$

From the solubility data, the authors obtained the overall stability constants of the $PuO_2(CO_3)_n^{2-2a}$ complexes as $\beta_1=10^{8.6\pm0.3}$, $\beta_2=10^{13.6\pm0.7}$, and $\beta_3=10^{18.2\pm0.4}$, and the solubility product of PuO_2CO_3 as $K_{sp}=10^{-(13.5\pm0.3)}$, all at 3.0 mol dm^{-3} ionic strength.

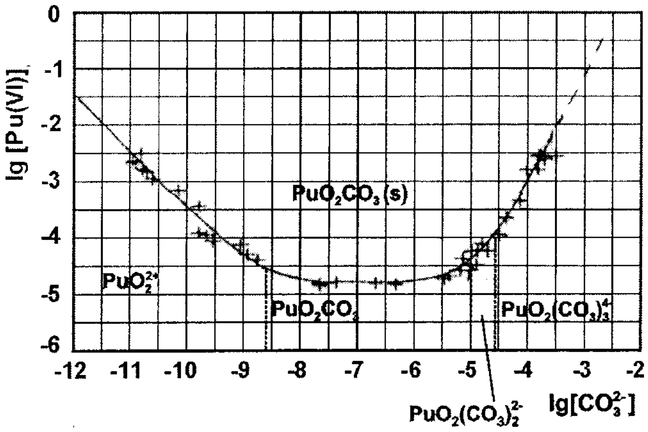

FIG. 20. Plutonium (VI) dioxocarbonate–sodium hydrogen carbonate–sodium perchlorate–carbon dioxide–water system.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal pH titration was used. Freshly precipitated PuO_2CO_3 was dissolved in a 0.1 mol dm^{-3} $NaHCO_3$ +2.9 mol dm^{-3} $NaClO_4$ solution. The green solution obtained (50 mL) was introduced into a cell through which a CO_2/Ar mixture, pre-equilibrated in 3.0 mol dm^{-3} $NaClO_4$, was bubbled at the desired CO_2 pressure. Under constant agitation, pH was measured. When at a given pH the solubility was constant, 3 mol dm^{-3} $HClO_4$ or 1 mol dm^{-3} $NaHCO_3$ was added to vary free carbonate ion concentration. At each constant pH value, the Pu(VI) concentration was determined by acidifying the sample with $HClO_4$, and measuring the light absorption of PuO_2^{2+} spectrophotometrically at 830.4 nm. The concentration of H^+ ions was measured potentiometrically by using a combination glass electrode with a Ag/AgCl reference half cell. The original reference solution was replaced with a 0.01 mol dm^{-3} NaCl+2.99 mol dm^{-3} $NaClO_4$ solution. The electrode was calibrated against a series of buffer solutions. The equilibrium solid phase was characterized by x-ray diffraction several times during the experiment. The pH titration of a given solid were run not longer than 2 weeks in order to avoid radiolytic transformation of the solid into hydrolyzed products.

Source and Purity of Materials:

The Pu(VI) perchlorate solution was prepared from an acid stock solution by evaporation of $HClO_4$ until most of the excess acid had been removed. The concentrated solution was dissolved in 0.1 mol dm^{-3} $HClO_4$ and PuO_2CO_3 was precipitated by addition of $NaHCO_3$. For each pH titration, PuO_2CO_3 was prepared from fresh perchlorate solution to avoid reduction of Pu(VI) by radiolysis.

Estimated Error:

Temperature: ± 1 K (authors).
Solubility: precision not reported.

Components:

(1) Plutonium(VI) dioxocarbonate; PuO_2CO_3; [39292-10-9]
(2) Carbon dioxide; CO_2; [124-38-9]
(3) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

I. Pashalidis, W. Runde, and J. I. Kim, Radiochim. Acta **61**, 141–6 (1993).

Variables:

T/K: 295
p_2(partial pressure)/% = 1 and 100
c_3 /mol dm^{-3}=0.1

Prepared by:

J. Hála

Experimental Data

Solubility of PuO_2CO_3 in 0.1 mol dm^{-3} solution of $NaClO_4$ at 22 °C, and 1% or 100% partial pressure of CO_2[a]

pH	$-\log[CO_3^{2-}]$[b]	$-\log[PuO_2^{2+}]$[c]	$-\log K_{sp}$[e]	pH	$-\log[CO_3^{2-}]$[b]	$-\log[PuO_2^{2+}]$[d]	$-\log K_{sp}$[e]
4.23	11.17	2.94	14.11	3.51	10.60	3.40	14.00
4.24	11.14	2.81	13.95	3.70	10.22	3.77	13.99
4.28	11.06	2.94	13.99	3.84	9.94	3.91	13.85
4.31	10.99	3.067	14.06	3.85	9.92	4.03	13.95
4.33	10.96	3.067	14.02	3.89	9.84	4.03	13.87
4.35	10.93	2.81	13.74	4.01	9.60	4.54	14.14
4.51	10.60	3.25	13.85	4.30	9.02	5.18	14.20
4.53	10.56	3.25	13.81				
4.65	10.32	3.86	14.18				
4.75	10.12	3.88	14.00				
5.22	9.19	4.73	13.92				
5.55	8.52	5.64	14.16				
5.58	8.47	5.47	13.94				
5.60	8.43	5.47	13.89				
5.60	8.41	5.64	14.05				
5.62	8.39	5.47	13.85				

[a] Equilibrium solid phase was PuO_2CO_3, [39292-10-9], in all solutions. The solid was most stable under vacuum. It changed within 2 weeks in HCO_3^- solution, and was not stable at all when in contact with air. Measurements were also performed at 0.03% partial pressure of CO_2. At this pressure slight transformation of PuO_2CO_3 into $PuO_2(OH)_2$ in the surface layer of PuO_2CO_3 crystals took place, as deduced by the authors from the dependence of $\log[PuO_2^{2+}]$ versus pH plots obtained at different partial pressures of CO_2.

[b] Concentration of free carbonate ion (mol dm^{-3}). It was calculated from the measured pH, partial pressure of CO_2, Henry constant, and dissociation constants of carbonic acid.

[c] Measurements at partial pressure of CO_2 of 1%.

[d] Measurements at partial pressure of CO_2 of 100%.

[e] $K_{sp}=[PuO_2^{2+}][CO_3^{2-}]$; the average value from measurements at 1% and 100% partial pressure of CO_2 was reported by the authors as $10^{-(13.98\pm0.12)}$ mol^2 dm^{-6}. This was recalculated by the authors to zero ionic strength by using the specific ion interaction theory procedure, to obtain $K_{sp}^{o}=10^{-(14.84\pm0.10)}$ mol^2 dm^{-6}.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal pH titration was used. A portion of the PuO_2^{2+} stock solution was diluted with 0.1 mol dm^{-3} $NaClO_4$, neutralized to pH 7 with NaOH, and CO_2 gas was bubbled through the solution. A white precipitate of PuO_2CO_3 was formed. The precipitation procedure and subsequent solubility measurements were performed in a closed glass vessel with gas passing through under partial pressure of CO_2 of 1% (CO_2 /Ar mixture) or 100%. The pH of the solution in contact with PuO_2CO_3 was adjusted stepwise by addition of 0.1 mol dm^{-3} $HClO_4$ or NaOH. The gas was bubbled through the vessel continuously. The pH was measured with a ROSS-type combination electrode containing 3 mol dm^{-3} $NaClO_4$ as a filling solution. The electrode was calibrated against six different buffer solutions. The time of equilibration after each adjustment of pH was not reported. The equilibrium plutonium concentration in the saturated solution was determined by liquid scintillation counting to obtain the total plutonium concentration, and by UV spectroscopy to obtain the PuO_2^{2+} concentration. The solid phases were characterized by x-ray powder diffraction, IR, and UV spectroscopy.

Source and Purity of Materials:

^{242}Pu of 99.9% isotopic purity was used. The PuO_2^{2+} stock solution was prepared by fuming with concentrated $HClO_4$ in a platinum crucible, and subsequent treatment with ozone and Ar gas. The valency state of Pu in the stock solution was verified by comparing Pu concentrations as determined by spectrophotometry and liquid scintillation counting.

Estimated Error:

Temperature: precision ±1 K (authors).
Solubility: precision not reported.

Components:

(1) Plutonium(VI) dioxocarbonate; PuO_2CO_3; [39292-10-9]
(2) Carbon dioxide; CO_2; [124-38-9]
(3) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

I. Pashalidis, K. R. Czerwinski, T. Fanghanel, and J. I. Kim, Radiochim. Acta **76**, 55–62 (1997).

Variables:

T/K: 295
p_2(partial pressure of CO_2)/% = 1 and 100
c_3 /mol dm^{-3}=0.1

Prepared by:

J. Hála

Experimental Data

Solubility of PuO_2CO_3 as a function of carbonate ion concentration in 0.1 mol dm^{-3} $NaClO_4$ at 22 °C[a]

pH	$-\log[CO_3^{2-}]$[b,c]	$-\log[PuO_2^{2+}]$[c]	pH	$-\log[CO_3^{2-}]$[b,c]	$-\log[PuO_2^{2+}]$[c]
Measurements at 1% partial pressure of CO_2					
4.22	11.12	2.94	4.99	9.58	4.09
4.23	11.10	2.81	5.21	9.14	4.73
4.27	11.02	2.94	5.57	8.42	5.09
4.30	10.96	3.07	5.57	8.42	5.09
4.32	10.92	3.07	7.06	5.44	4.69
4.34	10.88	2.81	7.06	5.44	4.71
4.50	10.56	3.25	7.40	4.76	4.34
4.52	10.52	3.25	7.42	4.72	4.60
4.64	10.28	3.86	7.47	4.62	4.47
4.69	10.18	3.77	7.53	4.50	4.31
4.70	10.16	3.77	7.54	4.48	4.30
4.74	10.08	3.88	7.63	4.30	3.85
4.81	9.94	3.97	7.64	4.28	4.14
4.83	9.90	3.91	7.72	4.12	3.76
4.84	9.88	4.03	7.81	3.94	3.58
4.85	9.86	3.91	7.82	3.92	3.36
4.88	9.80	4.03	7.87	3.82	3.67
Measurements at 100% partial pressure of CO_2					
3.49	10.58	3.40	3.99	9.58	4.09
3.50	10.56	3.40	4.57	8.42	5.09
3.69	10.18	3.77	4.57	8.42	5.09
3.70	10.16	3.77	5.16	7.24	5.11
3.81	9.94	3.97	5.18	7.20	5.27
3.83	9.90	3.91	5.73	6.10	5.27
3.84	9.88	4.03	5.94	5.68	5.07
3.85	9.86	3.91	6.04	5.48	4.77
3.88	9.80	4.03			

[a] At partial pressure of CO_2 of 1% and 100%, the solid phase was PuO_2CO_3, [39292-10-9], in all solutions.
[b] Equilibrium concentration of the carbonate ion; it was calculated by the authors from the equation $\log[CO_3^{2-}] = \Sigma \log K + \log p(CO_2) + 2\,pH$, where $\Sigma \log K = -17.55(\pm 0.09)$ includes Henry constant for CO_2, and dissociation constants of carbonic acid.
[c] Concentrations in mol dm^{-3}.

Additional information:

Using the reported solubility data, and the solubility product of PuO_2CO_3 from the authors' earlier work of $10^{-(13.98\pm0.12)}$,[1] the overall stability constants for the following carbonatocomplexes of the PuO_2^{2+} ion were calculated: PuO_2CO_3, $\beta_1 = 10^{8.7\pm0.3}$; $PuO_2(CO_3)_2^{2-}$, $\beta_2 = 10^{14.1\pm0.5}$; and $PuO_2(CO_3)_3^{4-}$, $\beta_3 = 10^{17.8\pm0.2}$. By applying the ion interaction Pitzer approach, the thermodynamic solubility product of PuO_2CO_3 was obtained as $K_{sp}^{o} = 10^{-14.85}$ mol^2 dm^{-6}.

Auxiliary Information

Method/Apparatus/Procedure:

Solubility experiments were conducted as pH titrations in 0.1 mol dm^{-3} $NaClO_4$ under 1 (CO_2 /Ar mixture) or 100% partial pressure of CO_2 in a closed glass vessel. A portion of the Pu(VI) stock solution was added to 0.1 mol dm^{-3} $NaClO_4$ solution, the pH was adjusted to 7 with 0.1 mol dm^{-3} NaOH, and CO_2 gas was bubbled through it. A white crystalline precipitate of PuO_2CO_3 was formed. The pH was measured by using combination glass electrodes (ROSS-type, Orion) with 3 mol dm^{-3} $NaClO_4$ as a filling solution, which were calibrated against six standard buffer solutions in the pH range of 2–8. The equilibrium concentration of Pu(VI) at each pH was determined by liquid scintillation counting and absorption spectroscopy at 830.4 nm to obtain total concentration of Pu and concentration of PuO_2^{2+}, respectively. The solid phases were characterized by IR spectroscopy and x-ray diffraction.

Source and Purity of Materials:

^{244}Pu of 99.9% isotopic purity was used to prepare the PuO_2CO_3 solid phase. Plutonium(VI) stock solution (0.01 mol dm^{-3}) was prepared by fuming with concentrated $HClO_4$ in a platinum crucible, and further oxidation by ozone. The purity of the valency state of Pu was verified by comparing of plutonium concentrations as determined by absorption spectroscopy and liquid scintillation counting.

Estimated Error:

Temperature: precision ±2 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] I. Pashalidis, W. Runde, and J. I. Kim, Radiochim. Acta **61**, 141 (1993).

Components:

(1) Plutonium(VI) dioxocarbonate; PuO_2CO_3; [39292-10-9]
(2) Carbon dioxide; CO_2; [124-38-9]
(3) Sodium chloride; NaCl; [7647-14-5]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

M. P. Neu, S. D. Reily, and W. H. Runde, Mater. Res. Soc. Symp. Proc. **465**, 759–65 (1997).

Variables:

T/K: 295
p_2/% (partial pressure): 100
m_3 /mol kg^{-1}: 0.1–5.0

Prepared by:

J. Hála

Experimental Data

Solubility product of PuO_2CO_3 in NaCl solutions at 22 °C and 100% partial pressure of CO_2[a,b]

NaCl (m_3 /mol kg^{-1})	$-\log K_{sp}$[c]
0.1	12.9
0.2	12.4
0.5	12.5
1	12.3
2	12.2
5	12.3

[a] The equilibrium solid phase was confirmed by using various spectroscopic methods to be PuO_2CO_3, [39292-10-9].
[b] Numerical data of PuO_2CO_3 not reported.
[c] $K_{sp}=[PuO_2^{2+}][CO_3^{2-}]$; K_{sp} data reported in mol^2 kg^{-2}. Equilibrium carbonate ion concentration was calculated as $\log[CO_3^{2-}]=\log K+\log p(CO_2)+2\,pH$, where K is the equilibrium constant for the formation of CO_3^{2-} from CO_2 gas in equilibrium with NaCl solutions.

Additional information:

Reduction of Pu(VI) to Pu(V) was observed spectroscopically at low NaCl concentrations. The Pu(V) present in the solution disproportionated to $Pu(VI)_{(aq)}$ and polymeric Pu(IV) hydroxide. On equilibration prolonged up to 4 months, the equilibrium solid phase was PuO_2CO_3. Since equilibration time used in solubility experiments was not reported it is not clear how, and if, this could have affected the K_{sp} data at low NaCl concentrations.

Auxiliary Information

Method/Apparatus/Procedure:

Solubility experiments were performed as pH titration procedure using approximately 50 mg PuO_2CO_3 and 5 mL NaCl solution of the desired concentration contained in a loosely closed vessel, with CO_2 gas bubbling through. Solution pH was adjusted by addition of NaOH/NaCl or HCl/NaCl solutions. The electrode was calibrated against buffer solutions. Equilibration time was not reported. Samples withdrawn from the saturated solutions were filtered using 250 nm pore syringe filters (Millipore), and the Pu(VI) concentration was determined in 25 μL aliquots of the filtrate by liquid scintillation counting.

Source and Purity of Materials:

Plutonium(VI) stock solution was prepared by dissolving ^{239}Pu metal in 7 mol mol dm^{-3} $HClO_4$ and fuming the solution to near dryness with concentrated $HClO_4$. The residue was diluted with water, the Pu concentration was determined by liquid scintillation counting,and plutonium oxidation state purity was verified using absorbance spectroscopy. PuO_2CO_3 was prepared by bubbling CO_2 gas through a stirred acidic stock solution for 3–5 days, washing the resulting precipitate with distilled de-ionized water, redissolving, and repeating precipitation. Ozone was also bubbled through the suspension for the final 2 days to reoxidize any plutonium reduced by radiolysis. The resulting pale tan solid was characterized using powder x-ray diffraction, extended x-ray absorption fine structure (EXAFS), and diffuse reflectance spectroscopy.

Estimated Error:

Temperature: precision ±1 K (authors).
Solubility: error of K_{sp} not reported.

7.2. Ammonium Tris(carbonato) Dioxoplutonate(VI)(-4)

Components:

(1) Ammonium tris(carbonato) dioxoplutonate(VI); $(NH_4)_4PuO_2(CO_3)_3$; [36568-63-5]
(2) Ammonium carbonate; $(NH_4)_2CO_3$; [506-87-6]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

L. E. Drabkina, Radiokhimiya **2**, 377–8 (1960).

Variables:

T/K 293
$100w_2$ /mass%: 5–25

Prepared by:

J. Hála

Experimental Data

Solubility of $(NH_4)_4PuO_2(CO_3)_3$ at 20 °C in $(NH_4)_2CO_3$ solutions[a]

$(NH_4)_2CO_3$ ($100w_2$ /mass%)	Pu (g kg^{-1})[b]		$(NH_4)_4PuO_2(CO_3)_3$ (g kg^{-1})[b,c]
5	3.25	3.80	7.72
10	2.00	1.80	4.16
15	0.973	0.974	2.13
20	0.628	0.693	1.45
25	0.384	0.418	0.877

[a] The nature of equilibrium solid phases was not investigated.
[b] Grams per kg saturated solution.
[c] Calculated by compiler for the average of the two solubility values reported, using $A_r(Pu)=239.053$.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. $(NH_4)_2CO_3$ solutions were stirred with solid $(NH_4)_4NpO_2(CO_3)_3$ for 2 h which was found sufficient to reach equilibrium. Method of analysis of the saturated solutions was not reported.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: precision ±1 K (author).
Solubility: the scatter of the duplicate measurements indicates an error of ±5%–10% (compiler).

Components:

(1) Ammonium tris(carbonato) dioxoplutonate(VI); $(NH_4)_4PuO_2(CO_3)_3$; [36568-63-5]
(2) Ammonium nitrate; NH_4NO_3; [6484-52-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

L. E. Drabkina, Radiokhimiya **2**, 377–8 (1960).

Variables:

T/K: 293
$100w_2$ /mass %:10–64

Prepared by:

J. Hála

Experimental Data

Solubility of $(NH_4)_4PuO_2(CO_3)_3$ at 20 °C in NH_4NO_3 solutions[a]

NH_4NO_3 ($100w_2$ /mass %)	Pu (g kg^{-1})[b]		$(NH_4)_4PuO_2(CO_3)_3$ (g kg^{-1})[b,d]
10	2.32		5.02
20	0.866	0.799	1.803
30	0.423		0.916
40	0.152	0.192	0.372
50	0.070	0.083	0.167
63.9	0.021		0.0455
[c]	0.027		0.0584

[a] The nature of equilibrium solid phases was not investigated.
[b] Grams per kg saturated solution.
[c] Solution saturated with NH_4NO_3; concentration of the latter not reported.
[d] Calculated by compiler using $A_r(Pu)=239.053$. Where two measurements were available, the average value was used.

Additional information:
The author also reported data for the solubility of $(NH_4)_4PuO_2(CO_3)_3$ in solutions containing 5–25 mass % NH_4NO_3 which were saturated with $(NH_4)_2CO_3$. The data are not given here since the concentration of $(NH_4)_2CO_3$ in these solutions was not reported.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. NH_4NO_3 solutions were stirred with solid $(NH_4)_4NpO_2(CO_3)_3$ for 2 h which was found sufficient to reach equilibrium. Method of analysis of the saturated solutions was not reported.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: precision±1 K (author).
Solubility: duplicate measurements at 40 and 50 mass % NH_4NO_3 indicate an error of up to ±10% (compiler).

Components:

(1) Tetraammonium tricarbonatodioxoplutonate(VI); $(NH_4)_4PuO_2(CO_3)_3$; [36568-63-5]
(2) Ammonium carbonate; $(NH_4)_2CO_3$; [506-87-6]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. D. Gelman, A. I. Moskvin, and V. P. Zaitseva, Radiokhimiya **4**, 154–62 (1962).

Variables:

T/K: 298
c_2 /mol dm^{-3}: 0.438–2.19

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $(NH_4)_4PuO_2(CO_3)_3$ in $(NH_4)_2CO_3$ solutions[a]

$(NH_4)_2CO_3$ (c_2 /mol dm^{-3})	$(NH_4)_4PuO_2(CO_3)_3$ (10^3 c_1 /mol dm^{-3})
0.438	21.8
0.876	9.29
1.314	6.65
1.752	4.26
2.190	3.29

[a] The nature of equilibrium solid phases was not investigated.

Additional information:
The authors stated that the $PuO_2(CO_3)_3^{4-}$ ion was unstable in solution, and that in the system studied Pu(VI) existed as $PuO_2(CO_3)_2^{2-}$ in the saturated solutions. The equilibrium constant for the reaction $PuO_2(CO_3)_3^{4-} \leftrightarrows PuO_2(CO_3)_2^{2-} + CO_3^{2-}$ was reported to be $(8.2\pm1.1)\times10^{-3}$ mol dm^{-3}.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess solid $(NH_4)_4PuO_2(CO_3)_3$ was stirred with $(NH_4)_2CO_3$ solutions of the desired concentration for 4–6 h which was found sufficient for equilibrium to be reached. Plutonium concentration in the saturated solutions was determined radiometrically.

Source and Purity of Materials:

$(NH_4)_4PuO_2(CO_3)_3$ was prepared by reacting $(NH_4)_2Pu_2O_7$ with concentrated solution of $(NH_4)_2CO_3$. The salt was obtained as a dark-green solid.

Estimated Error:

Temperature: precision ±1 K (authors).
Solubility: insufficient data given to allow for error estimate.

7.3. Ammonium Hydroxocarbonato Dioxoplutonate(VI)(-1)

Components:

(1) Ammonium hydroxocarbonato-dioxoplutonate(VI); $NH_4PuO_2(CO_3)OH$; [ ]
(2) Ammonium carbonate; $(NH_4)_2CO_3$; [506-87-6]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. D. Gelman, A. I. Moskvin, and V. P. Zaitseva, Radiokhimiya **4**, 154–62 (1962).

Variables:

T/K: 298

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $NH_4PuO_2(CO_3)OH$ in water

The solubility at 25 °C of $NH_4PuO_2(CO_3)OH$ in water was reported to be $c_1 = 1.05 \times 10^{-3}$ mol dm^{-3}. Equilibrium solid phase was not investigated.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess solid was stirred in water for 4–6 h. Plutonium concentration in the saturated solutions was determined radiometrically.

Source and Purity of Materials:

$NH_4PuO_2(CO_3)OH \cdot 3H_2O$ was prepared by dissolving $(NH_4)_2Pu_2O_7$ in 0.17–0.40 mol dm^{-3} $(NH_4)_2CO_3$. From the dark-red solution the complex salt precipitated as a pink solid on addition of an equal volume of 96% ethanol. It was washed several times from excess carbonate with 70%–80% ethanol and ether, and dried over $CaCl_2$. Analysis (found/calculated for the trihydrate, mass %): NH_4 5.3/4.3, Pu 54.12/56.9, CO_2 11.4/10.5. Source and purity of $(NH_4)_2Pu_2O_7$ and $(NH_4)_2CO_3$ not specified.

Estimated Error:

Temperature: precision ±1 K (authors).
Solubility: precision not reported.

7.4. Hexamminecobalt(III) Salt of Pentakis(carbonato)Aquaplutonate(IV)(-6)

Components:

(1) Bis(hexamminecobalt(III)) pentacarbonatoaquaplutonate(IV); $[Co(NH_3)_6]_2[Pu(CO_3)_5H_2O]$; [ ]
(2) Water; H_2O; [7732-18-5] or Ethanol; C_2H_6O; [64-17-5]

Original Measurements:

K. Ueno and M. Hoshi, J. Inorg. Nucl. Chem. **32**, 3817–22 (1970).

Variables:

T/K: 293

Prepared by:

J. Hála

Experimental Data

Solubility at 20 °C of $[Co(NH_3)_6]_2[Pu(CO_3)_5H_2O]$ in water and ethanol[a]

Solvent	Pu (mg/100 g solvent)	$[Co(NH_3)_6]_2[Pu(CO_3)_5H_2O]$ (10^5 c_1 /mol dm^{-3})[b]
water	1.1	2.15
ethanol	0.4	0.431

[a] Equilibrium solid phases were not investigated.
[b] Calculated by compiler using $A_r(Pu) = 239.053$.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess of dry plutonium compound was allowed to stand in the solvent for 24 h. The saturated solution was analyzed radiometrically for plutonium content.

Source and Purity of Materials:

$[Co(NH_3)_6]_2[Pu(CO_3)_5H_2O]$ was prepared by precipitation with $Co(NH_3)_6Cl_3$ from 1 mL2 mol dm^{-3}$(NH_4)_2CO_3$ containing 1 mg Pu(IV). The precipitate was vacuum dried under 10^{-3} mm Hg at room temperature. Analysis: found/calculated for $[Co(NH_3)_6]_2[Th(CO_3)_5H_2O] \cdot 4H_2O$ (mass %): Pu 26.1/25.2, $Co(NH_3)_6$ 33.00/33.9, CO_3 30.0/31.5. Plutonium(IV) solution in 2.5 mol dm^{-3} was prepared by reduction of Pu(VI) with $NaNO_2$. $Co(NH_3)_6Cl_3$ was prepared according to Ref. 1. $(NH_4)_2CO_3$ reagent grade, source not specified. Distilled water and reagent grade ethanol were used.

Estimated Error:

Temperature: precision ±2 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] W. Biltz, Z. Anorg. Allgem. Chem. **83**, 177 (1914).

7.5. Plutonium(III) Formate

Components:

(1) Plutonium(III) tris(formate); $Pu(CHO_2)_3$; [34501-13-8]
(2) Formic acid; CH_2O_2; [64-18-6]
(3) Hydroxyalamine hydrochloride; $NH_2OH\cdot HCl$; [5470-11-1]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

J. D. Navratil, Rockwell Int., Golden, CO (private communication).

Variables:

T/K: 296
c_2 /mol dm^{-3}: 0.5–23.5
c_3 /mol dm^{-3}: 0.05

Prepared by:

J. Hála

Experimental Data

Solubility at 23 °C of $Pu(CHO_2)_3$ in formic acid solutions[a]

CH_2O_2 (c_2 /mol dm^{-3})	$Pu(CHO_2)_3$ (g dm^{-3})	$Pu(CHO_2)_3$ ($10^4 c_1$ /mol dm^{-3})[b]
0.5	1.81	48.8
1.0	1.40	37.7
2	0.76	20.4
5	0.41	11.0
10	0.141	3.79
15	0.052	1.40
23.5	0.015	0.404

[a] The nature of equilibrium solid phases was not investigated. All solution contained 0.05 mol dm^{-3} $NH_2OH\cdot HCl$ to maintain the Pu(III) valency state.

[b] Calculated by compiler using $A_r(Pu)=239.053$.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess $Pu(CHO_2)_3$ was equilibrated with formic acid solutions of the desired concentration for 16 h. It was not stated whether the solutions were thermostated during equilibration. The filtered saturated solutions were analyzed for Pu content by an unspecified method.

Source and Purity of Materials:

$Pu(CHO_2)_3$ was prepared according to Ref. 1. Plutonium metal (99.99%) was dissolved in concentrated HCl, and the solution was filtered through a 0.25 μm Millipore Solvinert filter. In the filtrate the pH was adjusted to 8 by concentrated ammonia solution, and concentrated formic acid was added to dissolve plutonium hydroxide and precipitate $Pu(CHO_2)_3$. The precipitate was aged for 1 h, washed with concentrated formic acid, and dried by aspiration. All chemicals used were reagent grade.

Estimated Error:

Temperature: not reported.
Solubility: values reported were obtained from single determinations; this did not allow for error estimate.

References:

[1] L. R. Crisler, J. Inorg. Nucl. Chem. **34**, 3263 (1972).

Components:

(1) Plutonium(III) tris(formate); $Pu(CHO_2)_3$; [34501-13-8]
(2) Formic acid; CH_2O_2; [64-18-6]
(3) Sodium formate; CHO_2Na; [141-53-7]
(4) Hydroxyalamine hydrochloride; $NH_2OH\cdot HCl$; [5470-11-1]
(5) Water; H_2O; [7732-18-5]

Original Measurements:

J. D. Navratil, Rockwell Int., Golden, CO (private communication).

Variables:

T/K: 296
c_2 /mol dm^{-3}: 0.5–2.0
c_3 /mol dm^{-3}: 0.1–0.5
c_4 /mol dm^{-3}: 0.05

Prepared by:

J. Hála

Experimental Data

Solubility at 23 °C of $Pu(CHO_2)_3$ in CH_2O_2 /CHO_2Na solutions[a]

CH_2O_2 (c_2 /mol dm^{-3})	CHO_2Na (c_2 /mol dm^{-3})	$Pu(CHO_2)_3$ (g dm^{-3})	$Pu(CHO_2)_3$ (10^4 c_1 / mol dm^{-3})[b]	CH_2O_2 (c_2 /mol dm^{-3})	CHO_2Na (c_2 /mol dm^{-3})	$Pu(CHO_2)_3$ (gm dm^{-3})	$Pu(CHO_2)_3$ ($10^4 c_1$ / mol dm^{-3})[b]
0.5	0.1	1.35	56.4	1.5	0.1	0.078	3.27
	0.2	0.39	16.3		0.2	0.040	1.67
	0.3	0.025	1.04		0.3	0.023	0.963
	0.4	0.021	0.879		0.4	0.026	1.09
	0.5	0.020	0.837		0.5	0.028	1.17
1.0	0.1	0.082	3.43	2.0	0.1	0.066	2.76
	0.2	0.024	1.00		0.2	0.034	1.42
	0.3	0.024	1.00		0.3	0.029	1.21
	0.4	0.017	0.714		0.4	0.033	1.38
	0.5	0.027	1.13		0.5	0.034	1.42

[a] The nature of equilibrium solid phases was not investigated. All solution contained 0.05 mol dm^{-3} $NH_2OH\cdot HCl$ to maintain the Pu(III) valency state.

[b] Calculated by compiler using $A_r(Pu)=239.053$.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess $Pu(CHO_2)_3$ was equilibrated with CH_2O_2 /CHO_2Na solutions of the desired concentration for 16 h. It was not stated whether the solutions were thermostated during equilibration. The filtered saturated solutions were analyzed for Pu content by an unspecified method.

Source and Purity of Materials:

$Pu(CHO_2)_3$ was prepared according to Ref. 1. Plutonium metal (99.99%) was dissolved in concentrated HCl, and the solution was filtered through a 0.25 μm Millipore Solvinert filter. In the filtrate the pH was adjusted to 8 by concentrated ammonia solution, and concentrated formic acid was added to dissolve plutonium hydroxide and precipitate $Pu(CHO_2)_3$. The precipitate was aged for 1 h, washed with concentrated formic acid, and dried by aspiration. All chemicals used were reagent grade.

Estimated Error:

Temperature: not reported.
Solubility: values reported were obtained from single determinations; this did not allow for error estimate.

References:

[1] L. R. Crisler, J. Inorg. Nucl. Chem. **34**, 3263 (1972).

Components:

(1) Plutonium(III) tris(formate); $Pu(CHO_2)_3$; [34501-13-8]
(2) Formic acid; CH_2O_2; [64-18-6]
(3) Perchloric acid; $HClO_4$; [7601-90-3]
(4) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(5) Water; H_2O; [7732-18-5]

Original Measurements:

A. V. Ananev and N. N. Krot. Radiokhimiya **26**, 755–8 (1984).

Variables:

T/K: 298
c_2 /mol dm^{-3}: 0.2
c_3 /mol dm^{-3}: 0–0.1
c_4 /mol dm^{-3}: 1.9–2.0

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $Pu(CHO_2)_3$ in CH_2O_2 /$HClO_4$ /$NaClO_4$ solutions

Solubility at 25 °C of $Pu(CHO_2)_3$ was measured in 0.2 mol dm^{-3} solutions of formic acid containing 0–0.1 mol dm^{-3} $HClO_4$, and $NaClO_4$ to maintain ionic strength of 2.0 mol dm^{-3}. The results were reported in graphical form. From the solubility data the solubility product of $Pu(CHO_2)_3$ was calculated to be 5.46×10^{-12} mol^4 dm^{-12} at ionic strength of 2.0 mol dm^{-3}. In these calculations, the existence in the saturated solutions of the $Pu(CHO_2)^{2+}$ and $Pu(CHO_2)_2^{+}$ complexes was taken into account. Their stability constants were also calculated. The equilibrium solid phase was $Pu(CHO_2)_3$, [34501-13-8]. Also reported, in graphical form, was the solubility at 25 °C of $Pu(CHO_2)_3$ in sodium formate–$NaClO_4$ solutions, and the solubility of $Pu(CHO_2)_3$ in water as 7.14×10^{-3} mol dm^{-3}. It was not stated explicitly if the latter value was obtained by calculation or experimentally.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess $Pu(CHO_2)_3$ was equilibrated with solutions of the desired concentration for 10 h in thermostated flasks. Before measurements, the solutions were freed from air by passing through them a stream of argon gas. In the filtered saturated solutions, pH was determined potentiometrically, and the concentration of Pu(III) spectrophotometrically in ~0.6 mol dm^{-3} $HClO_4$ at 603 nm. The pH meter used was callibrated against 2.0 mol dm^{-3} $NaClO_4$. Solid phases were identified by x-ray diffraction.

Source and Purity of Materials:

$^{239}Pu(CHO_2)_3$ was prepared from freshly precipitated $Pu(OH)_3$ and concentrated formic acid according to Refs. 1, 2. The solid product was centrifuged, washed with 10 mol dm^{-3} formic acid and 50% ethanol, and kept over KOH. All other chemicals were reagent grade products. Doubly distilled water was used.

Estimated Error:

Temperature: precision not reported.
Solubility: error not reported.

References:

[1] L. R. Crisler, J. Inorg. Nucl. Chem. **34**, 3263 (1972).
[2] F. Weigel and N. terMeer, Inorg. Nucl. Chem. Lett. **3**, 403 (1967).

7.6. Plutonium(III) Oxalate

Components:

(1) Diplutonium(III) tris(oxalate); $Pu_2(C_2O_4)_3$; [3316-65-2]
(2) Ammonium oxalate; $(NH_4)_2C_2O_4$; [1113-38-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. D. Gelman, N. N. Matorina, and A. I. Moskvin, Dokl. Akad. Nauk SSSR **117**, 88–91; (1957) Sov. J. At. Energy **3**, 115–20 (1957).

Variables:

T/K: 343
c_2 /mol dm^{-3}: 0–0.70

Prepared by:

J. Hála

Experimental Data

Solubility of $Pu_2(C_2O_4)_3$ at 70 °C in water and in $(NH_4)_2C_2O_4$ solutions[a]

$(NH_4)_2C_2O_4$ (c_2 /mol dm^{-3})	$Pu_2(C_2O_4)_3$ (10^4 c_1 /mol dm^{-3})	$(NH_4)_2C_2O_4$ (c_2 /mol dm^{-3})	$Pu_2(C_2O_4)_3$ (10^4 c_1 /mol dm^{-3})
0	0.188	0.41	8.19
0.07	2.02	0.49	9.75
0.13	2.90	0.56	11.40
0.225	4.70	0.62	15.00
0.28	5.66	0.66	20.50
0.35	6.90	0.70	22.50

[a] The nature of the equilibrium solid phases was not investigated. The initial solid used for the measurements is reported to be $Pu_2(C_2O_4)_3\cdot9H_2O$. In Ref. 1 the crystallohydrate of plutonium(III) oxalate was reported to be decahydrate, $Pu_2(C_2O_4)_3\cdot10H_2O$.

Additional information:

From the increase of the solubility of $Pu_2(C_2O_4)_3$ with increasing $(NH_4)_2C_2O_4$ concentration the authors calculated the consecutive instability constants of the $Pu_2(C_2O_4)_n^{(3-2n)}$ complexes. From the solubility of $Pu_2(C_2O_4)_3$ in water the authors obtained the solubility product of the salt as $K_{sp}=[Pu^{3+}]^2[C_2O_4^{2-}]^3=2.53\times10^{-22}$ mol^5 dm^{-15} at 70 °C.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Solutions of the desired concentration were stirred with excess $Pu_2(C_2O_4)_3\cdot9H_2O$ in a thermostated bath for 4–6 h, which was established as sufficient to reach equilibrium. To avoid oxidation of Pu^{3+}, a stream of N_2 gas was passed through the solution during stirring. The concentration of plutonium in the saturated solutions was determined by an unspecified radiometric method.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: not reported.
Solubility: insufficient data given to allow for error estimate.

References:

[1] I. L. Jenkins, F. H. Moore, and M. J. Waterman, J. Inorg. Nucl. Chem. **27**, 77 (1965).

Components:

(1) Diplutonium(III) tris(oxalate); $Pu_2(C_2O_4)_3$; [3316-65-2]
(2) Potassium oxalate; $K_2C_2O_4$; [583-52-8]
(3) Potassium chloride; KCl; [7447-40-7]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

A. D. Gelman, N. N. Matorina, and A. I. Moskvin, Dokl. Akad. Nauk SSSR **117**, 88–91 (1957); Sov. J. At. Energy **3**, 115–20 (1957).

Variables:

T/K: 293
c_2 /mol dm^{-3}: 0–2.41

Prepared by:

J. Hála

Experimental Data

Solubility of $Pu_2(C_2O_4)_3$ at 20 °C in water and in $K_2C_2O_4$ solutions[a,b]

$K_2C_2O_4$ (c_2 /mol dm^{-3})	$Pu_2(C_2O_4)_3$ (10^4 c_1 /mol dm^{-3})	$K_2C_2O_4$ (c_2 /mol dm^{-3})	$Pu_2(C_2O_4)_3$ (10^4 c_1 /mol dm^{-3})
0	0.0432	0.6	10.1
0.01	0.353	0.8	17.1
0.025	0.754	0.9	22.7
0.05	1.00	1.2	34.6
0.075	1.09	1.51	59.1
0.10	1.55	1.81	84.5
0.2	2.7	2.00	106
0.3	4.04	2.41	187

[a] The nature of the equilibrium solid phases was not investigated. The initial solid used for the measurements is reported to be $Pu_2(C_2O_4)_3 \cdot 9H_2O$. In Ref. 1 the crystallohydrate of plutonium(III) oxalate was reported to be the decahydrate, $Pu_2(C_2O_4)_3 \cdot 10H_2O$.
[b] In solutions containing 0.01–1.5 mol dm^{-3} $K_2C_2O_4$ ionic strength was maintained at an unspecified constant value by using KCl.

Additional information:

From the increase of the solubility of $Pu_2(C_2O_4)_3$ with increasing $K_2C_2O_4$ concentration the authors calculated the consecutive instability constants of the $Pu(C_2O_4)_n^{(3-2n)}$ complexes. From the solubility of $Pu_2(C_2O_4)_3$ in water the authors obtained the solubility product of the salt as $K_{sp}=[Pu^{3+}]^2[C_2O_4^{2-}]^3=1.62\times10^{-25}$ mol^5 dm^{-15} at 20 °C.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Solutions of the desired concentration were stirred with excess $Pu_2(C_2O_4)_3 \cdot 9H_2O$ in a thermostated bath for 4–6 h, which was established as sufficient to reach equilibrium. To avoid oxidation of Pu^{3+}, the solutions contained 10–15 g dm^{-3} sodium formaldehyde sulfoxylate, and a stream of N_2 gas was passed through the solutions during stirring. The concentration of plutonium in the saturated solutions was determined by an unspecified radiometric method.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: not reported.
Solubility: insufficient data given to allow for error estimate.

References:

[1] I. L. Jenkins, F. H. Moore, and M. J. Waterman, J. Inorg. Nucl. Chem. **27**, 77 (1965).

7.6.1. Evaluation of the $Pu_2(C_2O_4)_3+C_2H_2O_4+HNO_3+$Ascorbic Acid or Hydrazine$+H_2O$ System

Components:

(1) Diplutonium(III) tris(oxalate); $Pu_2(C_2O_4)_3$; [3316-65-2]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Nitric acid; HNO_3; [7697-37-2]
(4) Ascorbic acid; $C_6H_8O_6$; [50-81-7]; or Hydrazine; N_2H_4; [302-01-2]
(5) Water; H_2O; [7732-18-5]

Evaluator:

J. Hála, Department of Inorganic Chemistry, Masaryk University, 61137 Brno, Czech Republic, June 2000

Critical Evaluation:

The solubility of $Pu_2(C_2O_4)_3$ in oxalic acid–HNO_3 solutions has been studied in three references. Cheneau[1] reported temperature dependence of the solubility at one fixed HNO_3 and oxalic acid concentration while Hasilkar *et al.*[2] and Burney and Porter[3] measured the solubility of $Pu_2(C_2O_4)_3$ as a function of oxalic acid concentration for various HNO_3 concentrations at one temperature, i.e., at 298.1 and 294.1 K, respectively. All measurements were performed in the presence of a reducing agent, either ascorbic acid[2,3] or hydrazine,[1] to ensure the trivalent state of plutonium. The results in Ref. 3 were reported in graphical form only. Although the published data allow for a rather limited comparison, it can clearly be seen from some systems (0.1 mol dm^{-3} $C_2H_2O_4$/2.0 mol dm^{-3} HNO_3; 0.2 mol dm^{-3} $C_2H_2O_4$/1.5 or 2.0 mol dm^{-3} HNO_3) that the data of Burney and Porter[3] are higher than those of Hasilkar *et al.*[2] by a factor of up to 2. It seems that this discrepancy correlates with the equilibration time used, i.e., 16 h in Ref. 3 and 1 h only in Ref. 2. The only measurement of Cheneau[1] that can be compared with those of Refs. 2, 3, i.e., that taken in 0.2 mol dm^{-3} $C_2H_2O_4$/1.45 mol dm^{-3} HNO_3, seems to agree well with that obtained in Ref. 3 for 0.2 mol dm^{-3} $C_2H_2O_4$/1.5 mol dm^{-3} HNO_3, although Cheneau used equilibration time of 30 min only. Uncertainty in temperature may also be important for the published solubility data since Cheneau[1] showed that the solubility of $Pu_2(C_2O_4)_3$ is distinctly temperature dependent. With respect of this it may be relevant to note that it is not clear from the published information whether Burney and Porter[3] performed equilibration in a thermostated apparatus, and that Hasilkar *et al.*[2] described the temperature of their measurements (298.1 K) as approximate room temperature. Moreover, it is apparent from data in Ref. 3 that the solubility of $Pu_2(C_2O_4)_3$ in oxalic acid–HNO_3 solutions was, to some extent, dependent on ascorbic acid concentration. The evaluator assumed this to be due to the formation of soluble Pu(III) complexes with ascorbic acid in the saturated solutions. Taking all this into account, the system would obviously need a thorough reinvestigation with particular emphasis on equilibration time, temperature control, and the type and concentration of the reducing agent used. For this reason, none of the published data can be recommended although the data of Burney and Porter,[3] if digitized from the graphical representation, could serve as a reasonable approximation for the conditions used.

References:

[1] G. Cheneau, Report CEA-R-4109, 1971.
[2] S. P. Hasilkar, N. B. Khedekar, K. Chander, A. V. Jadhav, and H. C. Jain, J. Radioanal. Nucl. Chem. **185**, 119 (1994).
[3] G. A. Burney and J. A. Porter, Inorg. Nucl. Chem. Lett. **3**, 79 (1967).

Components:

(1) Diplutonium(III) tris(oxalate); $Pu_2(C_2O_4)_3$; [3316-65-2]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Nitric acid; HNO_3; [7697-37-2]
(4) Ascorbic acid; $C_6H_8O_6$; [50-81-7]
(5) Water; H_2O;[7732-18-5]

Original Measurements:

G. A. Burney and J. A. Porter, Inorg. Nucl. Chem. Lett. **3**, 79–85 (1967).

Variables:

T/K: 294
c_2 /mol dm^{-3}: 0.09–0.3
c_3 /mol dm^{-3}: 0.5–3.1
c_4 /mol dm^{-3}: 0.05

Prepared by:

J. Hála

Experimental Data

Solubility at 21 °C of $Pu_2(C_2O_4)_3$ in HNO_3–$C_2H_2O_4$–ascorbic acid solutions

The solubility of $Pu_2(C_2O_4)_3$ at 21 °C in HNO_3–$C_2H_2O_4$ solutions containing 0.05 mol dm^{-3} ascorbic acid were presented in graphical form (see Fig. 21). The nature of the equilibrium solid phases was not investigated. Presumably it was the decahydrate, $Pu_2(C_2O_4)_3 \cdot 10H_2O$, [ ], which was reported to precipitate from HNO_3-$C_2H_2O_4$ solutions.[1]

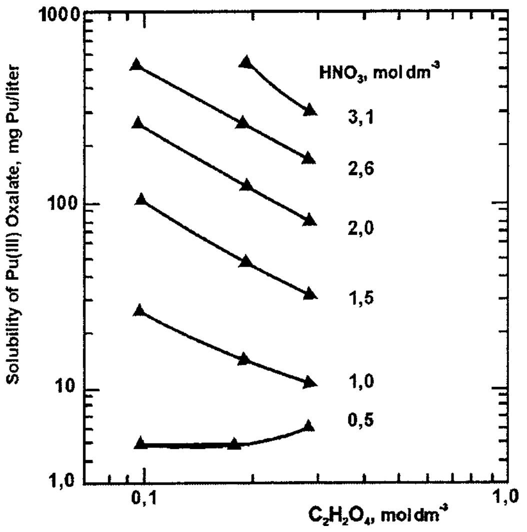

FIG. 21. Diplutonium (III)–tris(oxalate)–oxalic acid–nitric acid–water system.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess $Pu_2(C_2O_4)_3 \cdot 10H_2O$ was added to solutions of the desired composition, and agitated in plastic bottles on a mechanical shaker. Ascorbic acid was used to avoid oxidation of Pu(III). At intervals aliquots of the solutions were withdrawn, filtered, and analyzed for plutonium, acid, and oxalate. Analyses were continued until the system reached equilibrium, which took 16 h. The concentrations of acid and oxalate were determined by titration with NaOH and $KMnO_4$ solutions, respectively. The method for plutonium analysis was not specified.

Source and Purity of Materials:

^{239}Pu(III) oxalate was prepared by dissolving pure Pu metal in sulfamic acid, adding to this solution 0.05 mol dm^{-3} ascorbic acid to stabilize the Pu(III) state, and precipitating Pu(III) oxalate by adding 0.1 mol dm^{-3} oxalic acid solution. The precipitate was filtered, washed with 0.1 mol dm^{-3} oxalic acid, and air dried. The product was the bright blue–green decahydrate. All other chemicals were reagent grade.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

References:

[1] I. L. Jenkins, F. H. Moore, and M. J. Waterman, J. Inorg. Nucl. Chem. **27**, 77 (1965).

Components:

(1) Diplutonium(III) tris(oxalate); $Pu_2(C_2O_4)_3$; [3316-65-2]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Nitric acid; HNO_3; [7697-37-2]
(4) Hydrazine; N_2H_4; [302-01-2]
(5) Water; H_2O; [7732-18-5]

Original Measurements:

G. Cheneau, Center Prod. Plutonium, Marcoule, France, Rapport CEA-R-4109, 1971.

Variables:

T/K: 296–341
c_2 /mol dm^{-3}: 0.20
c_3 /mol dm^{-3}: 1.45
c_4 /mol dm^{-3}: 0.16

Prepared by:

J. Hála

Experimental Data

Solubility of $Pu_2(C_2O_4)_3$ in HNO_3–$C_2H_2O_4$–N_2H_4 solutions as a function of temperature[a]

Temperature (°C)	Pu (mg dm^{-3})	$Pu_2(C_2O_4)_3$ (10^4 c_1 /mol dm^{-3})[b]
23	46	0.949
30	67	1.40
40	121	2.53
50	205	4.29
60	365	7.67
68	547	11.5

[a] The nature of the equilibrium solid phases was not investigated. The initial solid used for the measurements is reported to be $Pu_2(C_2O_4)_3 \cdot 10H_2O$. All solutions contained 1.45 mol dm^{-3} HNO_3, 0.20 mol dm^{-3} oxalic acid, and 0.16 mol dm^{-3} hydrazine.
[b] Calculated by compiler using $A_r(Pu)=239.053$.

Additional information:

Also reported, in graphical form, was the solubility of $Pu_2(C_2O_4)_3$ at 23 °C in HNO_3–$C_2H_2O_4$ solutions containing either 0.1 mol dm^{-3} N_2H_4 or 0.05 mol dm^{-3} ascorbic acid.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Solutions of the desired concentration were stirred with excess $Pu_2(C_2O_4)_3 \cdot 10H_2O$ in a thermostated bath. At intervals aliquots were withdrawn, filtered, and plutonium was determined by α counting. The procedure was repeated until equilibrium was reached, which usually took less then 30 min.

Source and Purity of Materials:

Green $Pu_2(C_2O_4)_3 \cdot 10H_2O$ was obtained by precipitating Pu^{3+} from a solution containing 11 g dm^{-3} Pu, 1.2 mol dm^{-3} HNO_3, and 0.05 mol dm^{-3} ascorbic acid with 0.70 mol dm^{-3} oxalic acid solution. After 30 min stirring, the precipitate was filtered and washed with 0.1 mol dm^{-3} oxalic acid. Source and purity of other chemicals were not specified.

Estimated Error:

Temperature: not reported.
Solubility: insufficient data given to allow for error estimate.

Components:

(1) Diplutonium(III) tris(oxalate); $Pu_2(C_2O_4)_3$; [3316-65-2]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Nitric acid; HNO_3; [7697-37-2]
(4) Ascorbic acid; $C_6H_8O_6$; [50-81-7]
(5) Water; H_2O; [7732-18-5]

Original Measurements:

S. P. Hasilkar, N. B. Khedekar, K. Chander, A. V. Jadhav, and H. C. Jain, J. Radioanal. Nucl. Chem. **185**, 119–25 (1994).

Variables:

T/K: 298
c_2 /mol dm^{-3}: 0.02–0.20
c_3 /mol dm^{-3}: 0.5–2.0
c_4 /mol dm^{-3}: 0.01–0.1

Prepared by:

J. Hála

Experimental Data

Solubility of $Pu_2(C_2O_4)_3$ at 25 °C in HNO_3–$C_2H_2O_4$–$C_6H_8O_6$ solutions[a]

HNO_3 (c_3 /mol dm^{-3})	$C_2H_2O_4$ (c_2 /mol dm^{-3})	Pu (mg dm^{-3})	$Pu_2(C_2O_4)_3$[b] (10^4 c_1 / mol dm^{-3})[c]	HNO_3 (c_3 /mol dm^{-3})	$C_2H_2O_4$ (c_2 /mol dm^{-3})	Pu (mg dm^{-3})	$Pu_2(C_2O_4)_3$[b] (10^4 c_1 / mol dm^{-3})[c]
0.5	0.20	10.7	0.224	1.5	0.20	24.1	0.504
1.0	0.02	123.4	2.58	2.0	0.02	1379.5	28.8
	0.05	51.5	1.08		0.05	417.3	8.73
	0.10	19.9	0.416		0.10	171.7	3.59
	0.20	14.6	0.305		0.20	52.5	1.10
	0.20	10.9	0.228		0.20	44.8	0.937

[a] The nature of the equilibrium solid phases was not investigated. The initial solid used for the measurements is reported to be $Pu_2(C_2O_4)_3 \cdot 10H_2O$.
[b] All solutions contained 0.05 mol dm^{-3} ascorbic acid.
[c] Calculated by compiler using $A_r(Pu)=239.053$.

HNO_3 (c_3 /mol dm^{-3})	$C_6H_8O_6$ (c_4 /mol dm^{-3})	Pu (mg dm^{-3})	$Pu_2(C_2O_4)_3$[b] (10^5 c_1 / mol dm^{-3})[c]	HNO_3 (c_3 /mol dm^{-3})	$C_6H_8O_6$ (c_4 /mol dm^{-3})	Pu (mg dm^{-3})	$Pu_2(C_2O_4)_3$[b] (10^4 c_1 / mol dm^{-3})[c]
1.0	0.01	18.6	3.89	2.0	0.01	63.7	1.33
	0.02	16.2	3.39		0.02	61.5	1.29
	0.05	12.5	2.61		0.05	60.1	1.26
	0.10	13.6	2.85		0.10	58.1	1.22

[b] All solutions contained 0.20 mol dm^{-3} oxalic acid.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. About 450 mg of Pu(III) oxalate powder was equilibrated with 10 mL solution of the desired composition for 1 h in 40 mL equilibration tube using a mechanical shaker. The precipitate was allowed to settle for 1/2 h, and centrifuged. Method of plutonium determination in the saturated solutions not specified.

Source and Purity of Materials:

Plutonium stock solution in 4 mol dm^{-3} HNO_3 was prepared from plutonium freshly purified by ion exchange procedure according to Ref. 1. All other chemicals used were of A.R./G.R. grade. $Pu_2(C_2O_4)_3 \cdot 10H_2O$ was obtained by precipitation. Plutonium at the desired concentration was reduced to Pu^{3+} by means of ascorbic acid so as to maintain 0.05 mol dm^{-3} excess of the latter. Calculated excess over the stoichiometric amount of oxalic was added so that the supernatant contained 0.02–0.2 mol dm^{-3} oxalic acid. The precipitate was allowed to settle for 30 min and then centrifuged.

Estimated Error:

Temperature: temperature reported as approximate value of room temperature; the systems were not thermostated during equilibration.

Solubility: from the duplicate measurements in 0.2 mol dm^{-3} oxalic acid solutions the compiler estimates precision as low as ±15%.

References:

[1] J. L. Rayn and J. Wheelwright, USAEC, Report HW-55893, 1959.

Components:

(1) Diplutonium(III) tris(oxalate); $Pu_2(C_2O_4)_3$; [3316-65-2]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Hydrogen chloride; HCl; [7647-01-0]
(4) Ascorbic acid; $C_6H_8O_6$; [50-81-7]
(5) Water; H_2O; [7732-18-5]

Original Measurements:

S. P. Hasilkar, N. B. Khedekar, K. Chander, A. V. Jadhav, and H. C. Jain, J. Radioanal. Nucl. Chem. **185**, 119–25 (1994).

Variables:

T/K: 298
c_2 /mol dm^{-3}: 0.02–0.20
c_3 /mol dm^{-3}: 0.5–2.0
c_4 /mol dm^{-3}: 0.01–0.1

Prepared by:

J. Hála

Experimental Data

Solubility of $Pu_2(C_2O_4)_3$ at 25 °C in HNO_3–$C_2H_2O_4$–$C_6H_8O_6$ solutions[a]

HCl (c_3 /mol dm^{-3})	$C_2H_2O_4$ (c_2 /mol dm^{-3})	Pu (mg dm^{-3})	$Pu_2(C_2O_4)_3$[b] (10^4 c_1 / mol dm^{-3})[c]	HCl (c_3 /mol dm^{-3})	$C_2H_2O_4$ (c_2 /mol dm^{-3})	Pu (mg dm^{-3})	$Pu_2(C_2O_4)_3$[b] (10^4 c_1 / mol dm^{-3})[c]
0.5	0.20	13.5	0.282	1.5	0.20	32.8	0.686
1.0	0.02	120.8	2.53	2.0	0.02	753.3	15.8
	0.05	35.1	0.734		0.05	291.6	6.10
	0.10	24.1	0.504		0.10	99.5	2.08
	0.20	14.6	0.305		0.20	39.7	0.830
	0.20	10.9	0.305		0.20	61.6	1.29

[a] The nature of the equilibrium solid phases was not investigated. The initial solid used for the measurements is reported to be $Pu_2(C_2O_4)_3 \cdot 10H_2O$.
[b] All solutions contained 0.05 mol dm^{-3} ascorbic acid.
[c] Calculated by compiler using $A_r(Pu)=239.053$.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. About 450 mg of Pu(III) oxalate powder was equilibrated with 10 mL solution of the desired composition for 1 h in 40 mL equilibration tube using a mechanical shaker. The precipitate was allowed to settle for 1/2 h, and centrifuged. Method of plutonium determination in the saturated solutions not specified.

Source and Purity of Materials:

Plutonium stock solution in 4 mol dm^{-3} HNO_3 was prepared from plutonium freshly purified by ion exchange procedure according to Ref. 1. All other chemicals used were of A.R./G.R. grade. $Pu_2(C_2O_4)_3 \cdot 10H_2O$ was obtained by precipitation. Plutonium was reduced to Pu^{3+} by means of ascorbic acid so as to maintain 0.05 mol dm^{-3} excess of the latter. Calculated excess over the stoichiometric amount of oxalic was added so that the supernatant contained 0.02–0.2 mol dm^{-3} oxalic acid. The precipitate was allowed to settle for 30 min, and then centrifuged.

Estimated Error:

Temperature: temperature reported as approximate value of room temperature; the systems were not thermostated during equilibration.

Solubility: from the duplicate measurements in 0.2 mol dm^{-3} oxalic acid solutions the compiler estimates precision as low as ±20%.

References:

[1] J. L. Rayn and J. Wheelwright, USAEC, Report HW-55893, 1959.

7.7. Plutonium(IV) Oxalate

7.7.1. Evaluation of the $Pu(C_2O_4)_2+H_2O$ System

Components:

(1) Plutonium(IV) bis(oxalate); $Pu(C_2O_4)_2$; [13278-81-4]
(2) Water; H_2O; [7732-18-5]

Evaluator:

J. Hála, Department of Inorganic Chemistry, Masaryk University, 611 37 Brno, Czech Republic, May 2000

Critical Evaluation:

Three values for the solubility, in mol dm^{-3}, of $Pu(C_2O_4)_2$ in water have been published, i.e., 4.71×10^{-3} at 298 K,[1] 1.88×10^{-4} at 300 K,[2] and 1.03×10^{-4} at 293 K.[3] There seems to be some uncertainty in these values. First, the value reported by Dawson[1] is higher by more than 1 order of magnitude compared to other two values. The reason for this cannot be identified from the published information. Particularly, missing information on equilibration time in Ref. 1 makes any conclusion difficult. In this respect it is noteworthy that a difference of the same type between Dawson's and other authors' work is also observed for the solubility of $Pu(C_2O_4)_2$ in aqueous solutions of HNO_3 (see Evaluation for the $Pu(C_2O_4)_2-HNO_3-H_2O$ system). Second, it seems that an almost twofold increase in the solubility on going from 293 K[3] to 300 K[2] is rather unusual. For these reasons none of the values published can be given preference.

References:

[1] J. K. Dawson, A.E.R.E. (Harwell), Report C/M 92, 1950.
[2] C. J. Mandleberg, K. E. Francis, and R. Smith, J. Chem. Soc. 2464 (1961).
[3] A. I. Moskvin and A. D. Gelman, Zh. Neorg. Khim. **3**, 956 (1958); A. D. Gelman and A. I. Moskvin, Dokl. Akad. Nauk SSSR **118**, 493 (1958).

Components:

(1) Plutonium(IV) bis(oxalate); $Pu(C_2O_4)_2$; [13278-81-4]
(2) Perchloric acid; $HClO_4$; [7601-90-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. I. Moskvin and A. D. Gelman, Zh. Neorg. Khim, **3**, 956–6 (1958); Dokl. Akad. Nauk SSSR **118**, 493–6 (1958).

Variables:

T/K:293
c_2 /mol dm^{-3}:0–1.0

Prepared by:

J. Hála

Experimental Data

Solubility at 20 °C of $Pu(C_2O_4)_2$ in water and $HClO_4$ solutions[a]

$HClO_4$ (c_2 /mol dm^{-3})	$Pu(C_2O_4)_2\cdot6H_2O$ (mg dm^{-3})	$Pu(C_2O_4)_2$ (10^4 c_1 /mol dm^{-3})	K_{sp}[c] (10^{22} mol^3 dm^{-9})
0	[b]	1.01 1.14 0.96	[b]
0.1	29	0.5	[b]
0.5	53	1.01	7
0.75	[b]	1.29	4
1.0	81	1.57	3

[a] The nature of the equilibrium solid phases was not investigated. The compiler assumes the solid phase is the hexahydrate, $Pu(C_2O_4)_2\cdot6H_2O$, [26588-74-9], which precipitates from acidic solutions.[1]

[b] Not reported.

[c] $K_{sp}=[Pu^{4+}][C_2O_4^{2-}]^2$; calculated by the authors as $K_{sp}=KK_{a1}^2K_{a2}^2$ using the equilibrium constant for the reaction $Pu(C_2O_4)_2\cdot6H_2O_{(s)}+4H^+\leftrightarrows Pu^{4+}+2C_2H_2O_4+6H_2O$, $K=[Pu^{4+}][C_2H_2O_4]^2[H^+]^{-4}=1\times10^{-11}$ mol^{-1} dm^3, and the dissociation constants of oxalic acid $K_{a1}=0.108$ and $K_{a2}=6.4\times10^{-5}$ mol dm^{-3} (source of the constants not reported).

Additional information:

The pH of the saturated solutions of $Pu(C_2O_4)_2$ in water was 4.4± 0.05. By analogy with $U(C_2O_4)_2$,[2] the authors explained this in terms of acid properties of $Pu(C_2O_4)_2$, i.e., by the equilibrium $Pu(C_2O_4)_2(H_2O)_n\leftrightarrows Pu(C_2O_4)(H_2O)_{n-1}+H^++C_2O_4^{2-}$.

Auxiliary Information

Method/Apparatus/Procedure:

The isothermal method[3] was used. Freshly precipitated $Pu(C_2O_4)_2\cdot6H_2O$ was agitated with water or $HClO_4$ solutions of the desired concentration in a thermostated bath for 4–6 h which was found sufficient for equilibrium to be reached. The plutonium concentration in the saturated solutions was determined radiometrically.

Source and Purity of Materials:

$Pu(C_2O_4)_2\cdot6H_2O$ was obtained by precipitation of Pu(IV) with oxalic acid, and washing the precipitate with water.[1]

Estimated Error:

Temperature: ±0.02 K (authors).
Solubility: from the measurements in water the compiler estimates the precision of ±10%.

References:

[1] I. L. Jenkins, F. H. Moore, and M. J. Waterman, J. Inorg. Nucl. Chem. **27**, 81 (1965).
[2] A. A. Grinberg and I. Petrzhak, Trudy Radiev. Inst., Khim. Geokhim., **7**, 50 (1956).
[3] A. I. Moskvin and A. D. Gelman, Zh. Neorg. Khim. **3**, 962 (1958).

7.7.2. Evaluation of the $Pu(C_2O_4)_2+HNO_3+H_2O$ System

Components:	**Evaluator:**
(1) Plutonium(IV) bis(oxalate); $Pu(C_2O_4)_2$; [13278-81-4] (2) Nitric acid; HNO_3; [7697-37-2] (3) Water; H_2O; [7732-18-5]	J. Hála, Department of Inorganic Chemistry, Masaryk University, 611 37 Brno, Czech Republic, May 2000

Critical Evaluation:

Solubility data for this system are available in six documents, and the results of five of them are summarized in Fig. 22. In the papers of Mandleberg *et al.*,[5] and Reas[1] the solubilities were reported for the quarternary system $Pu(C_2O_4)_2-HNO_3$–oxalic acid–H_2O, from which the values for zero concentration of oxalic acid have been extracted for the sake of comparison with other $Pu(C_2O_4)_2-HNO_3-H_2O$ data. Except for two single values for 0.75 mol dm^{-3} HNO_3 reported at 298 K,[1,2] other measurements were carried out at different temperatures. The data published by Indian authors[6] have not been compiled since the authors did not report the temperature of their measurements, and presented the solubility data for $Pu(C_2O_4)_2$ in HNO_3–oxalic acid solutions in graphical form of poor quality. Their values of $Pu(C_2O_4)_2$ solubility in 1 and 2 mol dm^{-3} HNO_3 are higher by roughly 1 order of magnitude than those of Ref. 5.

For the evaluation of the solubility in the $Pu(C_2O_4)_2-HNO_3-H_2O$ system, the observation of Reas[1] seems to be of importance. The author considered his solubility value as erroneously high due to oxidation of oxalic acid by HNO_3 under catalytic action of plutonium. This may be the reason for the discrepances among the results obtained by different authors. A fact which seems to support this view is that a qualitative correlation can be found between the solubility data and the respective equilibration time applied. Thus the lowest values were reported by Moskvin and Gelman[3,4] who used 4–6 h equilibration time while Reas[1] and Mandleberg *et al.*[5] equilibrated the systems for 1–2 weeks, and 2–3 weeks, respectively. (Dawson[2] did not report the equilibration time used.) Thus it seems that the $Pu(C_2O_4)_2-HNO_3-H_2O$ system is a nonequilibrium one, and the published data can serve as a qualitative lead only. The catalytic oxidation process could well be of greater improtance than are the differences in temperature used by different authors. Noteworthy in this respect seems also to be the fact that while severeal studies were performed on the solubility of $U(C_2O_4)_2$ in aqueous solutions of hydrochloric, perchloric, and sulfuric acids, no such study has been reported on the $U(C_2O_4)_2-HNO_3-H_2O$ system.

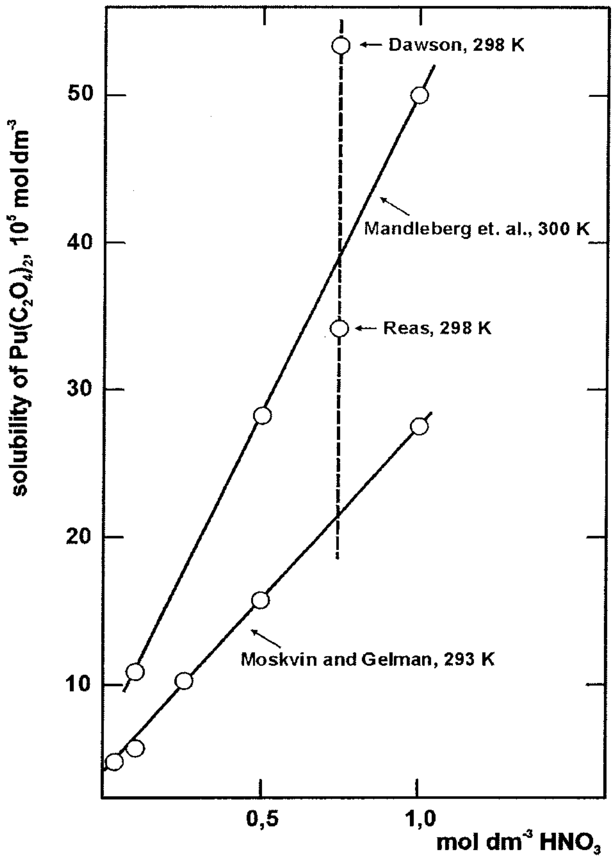

FIG. 22. Plutonium (IV) bis(oxalate)–nitric acid–water system.

References:

[1] W. H. Reas, Natl. Nucl. Energy Ser. Div. IV **14B**, 423 (1949).
[2] J. K. Dawson, A. E. R. E. (Harwell), Report C/M 92, 1950.
[3] A. I. Moskvin and A. D. Gelman, Zh. Neorg. Khim. **3**, 956 (1958).
[4] A. D. Gelman and A. I. Moskvin, Dokl. Akad. Nauk SSSR **118**, 493 (1958).
[5] C. J. Mandleberg, K. E. Francis, and R. Smith, J. Chem. Soc. 2464 (1961).
[6] G. C. Chapru *et al.*, Proceedings National Chemical Radiochemical Symposium 1981, p. 561 (1983).

Components:

(1) Plutonium(IV) bis(oxalate); $Pu(C_2O_4)_2$; [13278-81-4]
(2) Nitric acid; HNO_3; [7697-37-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. I. Moskvin and A. D. Gelman, Zh. Neorg. Khim, **3**, 956–6 (1958); Dokl. Akad. Nauk SSSR **118**, 493–6 (1958).

Variables:

T/K:293
c_2 /mol dm^{-3}:0.025–1.0

Prepared by:

J. Hála

Experimental Data

Solubility at 20 °C of $Pu(C_2O_4)_2$ in HNO_3 solutions[a]

HNO_3 (c_2 /mol dm^{-3})	$Pu(C_2O_4)_2\cdot 6H_2O$ (mg dm^{-3})	$Pu(C_2O_4)_2$ (10^5 c_1 /mol dm^{-3})
0.025	25	4.8
0.1	30	5.7
0.25	54	10.3
0.5	72	13.8
1.0	144	27.5

[a] The nature of the equilibrium solid phases was not investigated. The compiler assumes the solid phase be the hexahydrate, $Pu(C_2O_4)_2\cdot 6H_2O$, [26588-74-9] which precipitates from acidic solutions.[1]

Auxiliary Information

Method/Apparatus/Procedure:

The isothermal method[2] was used. Freshly precipitated $Pu(C_2O_4)_2\cdot 6H_2O$ was agitated with water or $HClO_4$ solutions of the desired concentration in a thermostated bath for 4–6 h which was found sufficient for equilibrium to be reached. The plutonium concentration in the saturated solutions was determined radiometrically.

Source and Purity of Materials:

$Pu(C_2O_4)_2\cdot 6H_2O$ was obtained by precipitation of Pu(IV) with oxalic acid, and washing the precipitate with water.[1]

Estimated Error:

Temperature: ±0.02 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] I. L. Jenkins, F. H. Moore, and M. J. Waterman, J. Inorg. Nucl. Chem. **27**, 81 (1965).
[2] A. I. Moskvin and A. D. Gelman, Zh. Neorg. Khim. **3**, 962 (1958).

Components:

(1) Plutonium(IV) bis(oxalate); $Pu(C_2O_4)_2$; [13278-81-4]
(2) Nitric acid; HNO_3; [7697-37-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

J. K. Dawson, Report A. E. R. E., Harwell, C/M 92, 1960.

Variables:

T/K:298
c_2 /mol dm^{-3}:0.75

Prepared by:

J. Hála

Experimental Data

The solubility of $Pu(C_2O_4)_2$ in 0.75 mol dm^{-3} HNO_3 is reported to be 0.13 g dm^{-3} Pu (5.33×10^{-4} mol dm^{-3}; compiler). The composition of the equilibrium solid phase was not reported but presumably it is the hexahydrate, $Pu(C_2O_4)_2\cdot 6H_2O$, [26588-74-9], which precipitates out from acid solutions.[1]

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method was used. Glass stoppered container containing the acid solution and excess Pu(IV) oxalate was placed in a metal container to exclude light, and this in turn was suspended in a thermostated bath. The container was shaken manually from time to time. The actual equilibration time was not reported. The saturated solution was centrifuged, and aliquots were taken for the determination of Pu by α counting. An argon proportional chamber with 35% geometry or an electroscope were used for counting.

Source and Purity of Materials:

Pu(IV) oxalate was prepared by adding oxalic acid crystals to an almost neutral solution of Pu(IV) nitrate. The precipitate was centrifuged and washed twice with water. Analysis of the product was not reported.

Estimated Error:

Temperature: not reported.
Solubility: ±5% (author).

References:

[1] I. L. Jenkins, F. H. Moore, and M. J. Waterman, J. Inorg. Nucl. Chem. **27**, 81 (1965).

Components:

(1) Plutonium(IV) bis(oxalate); $Pu(C_2O_4)_2$; [13278-81-4]
(2) Sulfuric acid; H_2SO_4; [7664-93-9]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. I. Moskvin and A. D. Gelman, Zh. Neorg. Khim. **3**, 956–61 (1958); Dokl. Akad. Nauk SSSR **118**, 493–6 (1958).

Variables:

T/K:293
c_2 /mol dm^{-3}:0.0125–0.50

Prepared by:

J. Hála

Experimental Data

Solubility at 20 °C of $Pu(C_2O_4)_2$ in H_2SO_4 solutions[a]

H_2SO_4 (c_2 /mol dm^{-3})	$Pu(C_2O_4)_2\cdot 6H_2O$ (mg dm^{-3})	$Pu(C_2O_4)_2$ (10^4 c_1 /mol dm^{-3})
0.0125	68	1.3
0.05	97	1.9
0.25	200	5.0
0.50	418	8.0

[a] The nature of the equilibrium solid phases was not investigated. The compiler assumes the solid phase be the hexahydrate, $Pu(C_2O_4)_2\cdot 6H_2O$, [26588-74-9], which precipitates from acidic solutions.[1]

Auxiliary Information

Method/Apparatus/Procedure:

The isothermal method[2] was used. Freshly precipitated $Pu(C_2O_4)_2\cdot 6H_2O$ was agitated with H_2SO_4 solutions of the desired concentration in a thermostated bath for 4–6 h which was found sufficient for equilibrium to be reached. The plutonium concentration in the saturated solutions was determined radiometrically.

Source and Purity of Materials:

$Pu(C_2O_4)_2\cdot 6H_2O$ was obtained by precipitation of Pu(IV) with oxalic acid, and washing the precipitate with water.[1]

Estimated Error:

Temperature: ±0.02 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] I. L. Jenkins, F. H. Moore, and M. J. Waterman, J. Inorg. Nucl. Chem. **27**, 81 (1965).
[2] A. I. Moskvin and A. D. Gelman, Zh. Neorg. Khim. **3**, 962 (1958).

Components:

(1) Plutonium(IV) bis(oxalate); $Pu(C_2O_4)_2$; [13278-81-4]
(2) Ammonium oxalate; $(NH_4)_2C_2O_4$; [1113-38-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

J. K. Dawson, Report A. E. R. E., Harwell, C/M 92, 1960.

Variables:

T/K: 298
c_2 /mol dm^{-3}: 0–0.13

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $Pu(C_2O_4)_2$ in water and $(NH_4)_2C_2O_4$ solutions[a]

$(NH_4)_2C_2O_4$ (c_2 /mol dm^{-3})	Pu (g dm^{-3})	$Pu(C_2O_4)_2$ (10^3 c_1 /mol dm^{-3})[b]
0	1.15	4.81
0.02	1.38	5.78
0.073	2.0	8.37
0.13	2.62	10.92

[a] The composition of the equilibrium solid phase was not reported.
[b] Calculated by compiler using $A_r(Pu)=239.053$.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method was used. Glass stoppered container containing the $(NH_4)_2C_2O_4$ solution and excess Pu(IV) oxalate was placed in a metal container to exclude light, and this in turn was suspended in a thermostated bath. The container was shaken manually from time to time. The actual equilibration time was not reported. The saturated solution was centrifuged, and aliquots were taken for the determination of Pu by α counting. An argon proportional chamber with 35% geometry or an electroscope were used for counting.

Source and Purity of Materials:

Pu(IV) oxalate was prepared by adding oxalic acid crystals to an almost neutral solution of Pu(IV) nitrate. The precipitate was centrifuged and washed twice with water. Analysis of the product was not reported.

Estimated Error:

Temperature: precision not reported.
Solubility: ±5% (author).

Components:

(1) Plutonium(IV) bis(oxalate); $Pu(C_2O_4)_2$; [13278-81-4]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Nitric acid; HNO_3; [7697-37-2]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

W. H. Reas, Natl. Nucl. Energy Ser., Div IV **14B**, 423–33 (1949).

Variables:

T/K: 298
c_2 /mol dm^{-3}: 0.001–0.40
c_3 /mol dm^{-3}: 0.75

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $Pu(C_2O_4)_2$ in oxalic acid solutions containing 0.75 mol dm^{-3} HNO_3[a]

$C_2H_2O_4$ (c_2 /mol dm^{-3})	$Pu(C_2O_4)_2$ (10^4 c_1 /mol dm^{-3})	$C_2H_2O_4$ (c_2 /mol dm^{-3})	$Pu(C_2O_4)_2$ (10^4c_1 /mol dm^{-3})
0.00034[b]	3.4[c]	0.0433	0.826
0.001	0.522[d]	0.0941	1.39
0.00316	0.389[e]	0.145	2.04
0.0068	0.421	0.196	2.54
0.0179	0.521	0.400	4.89

[a] The composition of the equilibrium solid phases was not reported. The compiler assumes the solid phase is the hexahydrate, $Pu(C_2O_4)_2\cdot 6H_2O$, [26588-74-9], which precipitates at 25 °C from $C_2H_2O_4$ /HNO_3 solutions.[1]

[b] No oxalic acid was added in this measurement. The author assumed that $Pu(C_2O_4)_2\cdot 6H_2O$ dissolved to produce $Pu(C_2O_4)^{2+}$ and $C_2H_2O_4$, and considered the determined solubility to be equal to the oxalic acid concentration in the solution.

[c] The author considered this value as erroneously high due to oxidation of oxalic acid by HNO_3 under catalytic action of Pu(IV).

[d] Mechanical stirring was used in this experiment. The approach to equilibrium was rapid, and equilibrium solubility could be obtained after less than 2 h equilibration.

[e] Solubility obtained by the author by extrapolation. It could not be obtained experimentally since either catalytic oxidation of oxalic acid or Pu(IV) oxidation by an unknown impurity interfered.

Additional information:

The author interpreted the solubility data in terms of the formation of $Pu(C_2O_4)^{2+}$, $Pu(C_2O_4)_2$ and $Pu(C_2O_4)_3^{2-}$ complexes in the saturated solutions. Equilibrium constants for the reactions $Pu(C_2O_4)^{2+}+C_2H_2O_4 \rightleftarrows Pu(C_2O_4)_2+2H^+$ and $Pu(C_2O_4)_2+C_2H_2O_4 \rightleftarrows Pu(C_2O_4)_3^{2-}+2H^+$ were obtained as 965 and 25.1 mol dm^{-3}, respectively.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess $Pu(C_2O_4)_2\cdot 6H_2O$ was shaken for at least 10 days in a thermostat with solutions of the desired composition. In most cases, one or two aliquots were taken for Pu determination at the end of 1 week, and then again two to four aliquots after about 5 days to ensure that true equilibrium solubility values were obtained. Plutonium was determined by α counting after evaporating the aliquots of the saturated solutions on platinum dishes.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: precision ± 0.05 K (author).

Solubility: from the parallel counting data the compiler estimated the precision to be ±10% in solutions containing 0.0068 and 0.0179 mol dm^{-3} oxalic acid, and ±5% at higher oxalic acid concentrations.

References:

[1] I. L. Jenkins, F. H. Moore, and M. J. Waterman, J. Inorg. Nucl. Chem. **27**, 81 (1965).

Components:

(1) Plutonium(IV) bis(oxalate); $Pu(C_2O_4)_2$; [13278-81-4]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Nitric acid; HNO_3; [7697-37-2]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

C. J. Mandleberg, K. E. Francis, and R. Smith, J. Chem. Soc 2464–8 (1961).

Variables:

T/K: 300
c_2 /mol dm^{-3}: 0–0.6
c_3 /mol dm^{-3}: 0–3.52

Prepared by:

J. Hála

Experimental Data

Solubility at 27 °C of $Pu(C_2O_4)_2$ in $C_2H_2O_4$ /HNO_3 solutions[a]

HNO_3 (c_3 /mol dm^{-3})	$C_2H_2O_4$ (c_2 /mol dm^{-3})	Pu (mg dm^{-3})[b]	$Pu(C_2O_4)_2$ (10^4 c_1 / mol dm^{-3})[c]	HNO_3 (c_3 /mol dm^{-3})	$C_2H_2O_4$ (c_2 /mol dm^{-3})	Pu (mg dm^{-3})[b]	$Pu(C_2O_4)_2$ (10^4 c_1 / mol dm^{-3})[c]
0	0	45.9	1.92	1.18	0.0071	16.3	0.682
0	0.05	334	14.0	1.61	0.002	65.8	2.76
0	0.25	242	10.1	1.61	0.015	15	0.628
0.1	0	26.6	1.11	2.00	0	128	5.36
0.1	0.5	132	5.52	2.00	0.05	9.7	0.406
0.5	0	69.0	2.89	2.00	0.25	15.1	0.632
0.5	0.05	26.6	1.11	2.34	0.01	15.3	0.640
0.5	0.25	97.1	4.06	2.34	0.005	24.9	1.04
0.5	0.60	361	15.1	2.52	0.025	16.7	0.661
0.78	0.40	144	6.02	3.52	0.005	92.1	3.85
1.0	0	122	5.10	3.52	0.01	45.8	1.92
1.0	0.05	13.3	0.556	3.52	0.05	18	0.753
1.0	0.25	36.9	1.54	3.52	0.1	18.2	0.761
1.0	0.60	133	5.56	3.52	0.5	31.4	0.895

[a] The composition of the equilibrium solid phases was not reported. The compiler assumes the solid phase is the hexahydrate, $Pu(C_2O_4)_2\cdot 6H_2O$, [26588-74-9], which precipitates at 25 °C from $C_2H_2O_4$ /HNO_3 solutions.[1]

[b] In the original document the plutonium concentration is reported, obviously by mistake, in g/dm^3. In the graphical representation of the data, however, the authors report the solubilities in mg/dm^3, which also agrees with $Pu(C_2O_4)_2$ solubility as reported by other authors.[2,3]

[c] Calculated by compiler using $A_r(Pu)=239.053$.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Portions of $Pu(C_2O_4)_2\cdot 6H_2O$ were continuously agitated with $C_2H_2O_4$ /HNO_3 solutions of the desired composition in a thermostat. Equilibrium was achieved after agitation for 2–3 weeks. The plutonium concentration in the saturated solutions was determined by pipetting portions of the supernatant liquid onto counting trays, and measuring α activity in a proportional counter.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: precision not reported.

Solubility: the authors stated that the data reported were the results of repeated determinations which agreed within a few percent.

References:

[1] I. L. Jenkins, F. H. Moore, and M. J. Waterman, J. Inorg. Nucl. Chem **27**, 81 (1965).
[2] A. I. Moskvin and A. D. Gelman, Zh. Neorg. Khim **3**, 956 (1958).
[3] W. H. Reas, Natl. Nucl. Energy Ser., Div. IV **14B**, 423 (1949).

Components:

(1) Plutonium(IV) bis(oxalate); $Pu(C_2O_4)_2$; [13278-81-4]
(2) Ammonium oxalate; $(NH_4)_2C_2O_4$; [1113-38-8]
(3) Nitric acid; HNO_3; [7697-37-2]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

(1) A. I. Moskvin and A. D. Gelman, Zh. Neorg. Khim. **3**, 962–74 (1958).
(2) A. I. Moskvin and A. D. Gelman, Zh. Neorg. Khim. **3**, 956–61 (1958).

Variables:

T/K: 293
c_2 /mol dm^{-3}: 0.001–0.35
c_3 /mol dm^{-3}: 1.0; 3.8

Prepared by:

J. Hála

Experimental Data

$(NH_4)_2C_2O_4$ (c_2 /mol dm^{-3})	$Pu(C_2O_4)_2$ (10^4 c_1 /mol dm^{-3})
0.001[b]	0.619
0.002	0.502
0.003	0.458
0.004	0.406
0.005	0.355
0.01	0.43
0.05	0.577
0.14	1.8
0.175	2.38
0.21	3.35
0.233	4.18

Additional information:

The increase in the solubility of $Pu(C_2O_4)_2$ in 1.0 mol dm^{-3} HNO_3 solutions at $(NH_4)_2C_2O_4$ concentrations >0.01 mol dm^{-3} was ascribed by the authors to the formation of oxalatocomplexes of Pu(IV). Their overall instability constants, $K_n=[Pu^{4+}]\times[C_2O_4^{2-}]^n[Pu(C_2O_4)_n^{4-n}]^{-1}$, were obtained from experimental solubilities as $K_1=1.8\times10^{-9}$ mol dm^{-3}, $K_2=1.2\times10^{-17}$ mol^2 dm^{-6}, $K_3=4.0\times10^{-24}$ mol^3 dm^{-9}, and $K_4=3.2\times10^{-28}$ mol^4 dm^{-12}. Also calculated were equilibrium constants for the reactions $Pu(C_2O_4)_2\cdot6H_2O_{(s)}+2H^+\leftrightarrows Pu(C_2O_4)^{2+}+C_2H_2O_4+6H_2O$, $Pu(C_2O_4)_2\cdot6H_2O_{(s)}\leftrightarrows Pu(C_2O_4)_2+6H_2O$, $Pu(C_2O_4)_2\cdot6H_2O_{(s)}+C_2H_2O_4\leftrightarrows Pu(C_2O_4)_3^{2-}+2H^++6H_2O$, and $Pu(C_2O_4)_2\cdot6H_2O_{(s)}+2\ C_2H_2O_4\leftrightarrows Pu(C_2O_4)_4^{4-}+4H^++6H_2O$ as 3.1×10^{-8}, 3.2×10^{-5} mol dm^{-3}, 6.8×10^{-4} mol^2 dm^{-6}, and 7.0×10^{-5} mol^3 dm^{-9}, respectively. In these calculations, the authors used dissociation constants of oxalic acid $K_{a1}=0.108$ mol dm^{-3} and $K_{a2}=6.4\times10^{-5}$ mol dm^{-3}, and calculated equilibrium hydrogen and oxalate ion concentrations as $[H^+]=(1-2[C_2O_4^{2-}]_{tot})+K_{a1}[C_2O_4^{2-}]_{tot}/(1-2[C_2O_4^{2-}]_{tot})$, and $[C_2O_4^{2-}]=[C_2O_4^{2-}]_{tot}/(1+[H^+]K_{a1}^{-1}+[H^+]^2K_{a1}^{-1}K_{a2}^{-1})$, respectively, where $[C_2O_4^{2-}]_{tot}$ is the total oxalate concentration.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method was used. Freshly precipitated $Pu(C_2O_4)_2\cdot6H_2O$ was agitated with solutions of the desired concentration in a thermostated bath for 4–6 h which was found sufficient for equilibrium to be reached. The plutonium concentration in the saturated solutions was determined by an unspecified radiometric method.[1]

Source and Purity of Materials:

$Pu(C_2O_4)_2\cdot6H_2O$ was obtained by precipitation of Pu(IV) with oxalic acid, and washing the precipitate with water.[2]

Estimated Error:

Temperature: ±0.02 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] I. L. Jenkins, F. H. Moore, and M. J. Waterman, J. Inorg. Nucl. Chem. **27**, 81 (1965).
[2] A. A. Grinberg and I. Petrzhak, Trudy Radiev. Inst., Khim. Geokhim. **7**, 50 (1956).

7.8. Plutonium(VI) Dioxo(oxalate)

Components:

(1) Plutonium(VI) dioxooxalate; $PuO_2C_2O_4$; [52689-31-3]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Nitric acid; HNO_3; [7697-37-2]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

[1] L. E. Drabkina, A. I. Moskvin, and A. D. Gelman, Zh. Neorg. Khim. **3**, 1934–6 (1958).
[2] A. D. Gelman and L. E. Drabkina, Zh. Neorg. Khim. **3**, 1105–8 (1958).

Variables:

T/K: 293
c_2 /mol dm^{-3}: 0–0.75 or $100w_2$ /mass %: 0–8
c_3 /mol dm^{-3}: 1.1–3.08

Prepared by:

J. Hála

Experimental Data

Solubility at 20 °C of $PuO_2C_2O_4$ in $C_2H_2O_4$ /HNO_3 solutions[a]

HNO_3[b] (c_3 / mol dm^{-3})	$C_2H_2O_4$[b] (c_2 / mol dm^{-3})	$PuO_2C_2O_4$[b] (10^3c_1 / mol dm^{-3})	K_{sp}[d] (10^{10} mol^3 dm^{-9})	HNO_3[c] (c_3 / mol dm^{-3})	$C_2H_2O_4$[c] ($100w_2$ / mass %)	Pu[c] (g dm^{-3})	$PuO_2C_2O_4$ (10^3c_1 / mol dm^{-3})[e]
1.10	0	13.4	9.3	1.1	0	3.20	13.3
	0.11	4.0			1	0.950	3.97
	0.23	2.69			2	0.642	2.69
	0.45	2.46			4	0.588	2.46
	0.75	2.21			6	0.528	2.21
2.01	0	16.3			8	0.491	2.05
	0.11	5.35	4.2	2.0	0	3.91	16.4
	0.23	3.81			1	1.30 1.26	5.35
	0.45	2.61			2	0.877 0.946	3.82
	0.75	2.40			4	0.623	2.64
3.08	0	28.0			6	0.574	2.40
	0.11	9.83			8	0.487 0.497	2.06
	0.23	5.40	5.5	3.08	0	6.75	28.2
	0.45	3.19			1	2.3 2.41	9.85
	0.75	2.55			2	1.20 1.30 1.36	5.40
					4	0.795 0.724 0.766	3.19
					6	0.617 0.612 0.605	2.66
					8	0.567 0.600 0.589	2.45

[a] The composition of the equilibrium solid phases was not reported. The compiler assumes the solid phase is the trihydrate, $PuO_2C_2O_4\cdot3H_2O$, [ ], which precipitates from acidic solutions by action of oxalic acid.[1]

[b] Data from original document.[1]

[c] Data from original document.[2]

[d] $K_{sp}=[PuO_2^{2+}][C_2O_4^{2-}]$. It was calculated by the authors under the assumption that the concentration of PuO_2^{2+} was equal to the experimental solubility of $PuO_2C_2O_4$ since spectrophotometric measurements did not indicate any complex formation between PuO_2^{2+} and $C_2O_4^{2-}$ ions. Equilibrium oxalate ion concentration was obtained from the total concentration of oxalic acid and dissociation constants of the latter, $K_{a1}=0.108$ mol dm^{-3} (Ref. 2) and $K_{a2}=6.4\times10^{-5}$ mol dm^{-3}.[3]

[e] Calculated by the compiler using $A_r(Pu)=239.053$. Where more than one measurements were reported, calculation was done for the average value.

Components:

(1) Plutonium(VI) dioxooxalate; $PuO_2C_2O_4$; [52689-31-3]
(2) Ammonium oxalate; $(NH_4)_2C_2O_4$; [1113-38-8]
(3) Nitric acid; HNO_3; [7697-37-2]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

[1] A. D. Gelman and L. E. Drabkina, Zh. Neorg. Khim. **3**, 1105–8 (1958).
[2] A. D. Gelman, L. E. Drabkina, and A. I. Moskvin, Zh. Neorg. Khim. **3**, 1546–50 (1958).

Variables:

T/K: 293
$100w_2$ /mass %: 1–6 or c_2 /mol dm^{-3}: 0.07–0.4
c_3 /mol dm^{-3}: 0.5–3.0

Prepared by:

J. Hála

Experimental Data

Solubility at 20 °C of $PuO_2C_2O_4$ in $(NH_4)_2C_2O_4$ /HNO_3 solutions[a]

HNO_3[b] (c_3 /mol dm^{-3})	$(NH_4)_2C_2O_4$[b] (100 w_2 /mass %)	Pu[b] (g dm^{-3})	$PuO_2C_2O_4$ (10^3 c_1 /mol dm−3)[d]	HNO_3[c] (c_3 /mol dm^{-3})	$(NH_4)_2C_2O_4$[c] (c_2 /mol dm^{-3})	$PuO_2C_2O_4$[c] (10^3 c_1 /mol dm^{-3})
0.5	1	0.707	2.96	1.0	0.070	3.76
	2	0.916	3.83		0.140	3.30
	3	1.60	6.69		0.256	3.39
1.0	1	0.900	3.76		0.284	3.60
	2	0.760 0.812	3.29		0.305	3.87
	3	0.789 0.738	3.19		0.355	4.40
	4	0.889 0.845	3.62		0.369	4.60
	6	1.25 1.06	4.81		0.398	4.88
2.0	1	1.66	6.94			
	2	1.19	4.98			
	3	0.807	3.38			
	4	0.709	2.97			
	6	0.634	2.65			
3.0	1	2.51	10.5			
	2	1.44	6.02			
	3	1.17	4.89			
	4	0.931	3.89			
	6	0.761	3.18			

[a] The composition of the equilibrium solid phases was not reported.
[b] Data from original document.[1]
[c] Data from original document.[2]
[d] Calculated by the compiler using $A_r(Pu)=239.053$. Where more than one measurements were reported, calculation was done for the average value.

Additional information:

The increase in the solubility of $PuO_2C_2O_4$ with increasing $(NH_4)_2C_2O_4$ concentration in solutions containing 1.0 mol dm^{-3} HNO_3 was explained by the authors by the formation of the $PuO_2(C_2O_4)_2^{2-}$ complex in the solutions. Using dissociation constants of oxalic acid, $K_{a1}=0.108$ mol dm^{-3} (Ref. 1) and $K_{a2}=6.4\times10^{-5}$ mol dm^{-3},[2] and the solubility product of $PuO_2C_2O_4$, $K_{sp}=5.9\times10^{-10}$ mol^2 dm^{-6} (Ref. 2) for the calculation of equilibrium concentrations of the PuO_2^{2+} and $C_2O_4^{2-}$ ions, the overall instability constants were obtained as $K_1=[PuO_2^{2+}][C_2O_4^{2-}][PuO_2C_2O_4]^{-1}=2.2\times10^{-7}$ mol dm^{-3} and $K_2=[PuO_2^{2+}][C_2O_4^{2-}]^2[PuO_2(C_2O_4)_2^{2-}]^{-1}=4.3\times10^{-12}$ mol^2 dm^{-6}.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess of $PuO_2C_2O_4\cdot3H_2O$ was stirred with solutions of the desired composition in a thermostated apparatus for 2 h which was established as sufficient for equilibrium to be reached. The plutonium concentration in the saturated solutions was determined by an unspecified radiometric method.

Source and Purity of Materials:

Pure Pu solution in HNO_3 was used as a starting material. Plutonium was oxidized to Pu(VI) in 0.5–1.0 mol dm^{-3} HNO_3 by heating the solution with $K_2Cr_2O_7$ or MnO_2 at 90 °C for 1–2 h. The course of oxidation was followed spectrophotometrically. By adding crystalline oxalic acid to the Pu(VI) solution in 1–2 mol dm^{-3} HNO_3, a pink crystalline precipitate was obtained which was shown by gravimetric (Pu, H_2O) and titrimetric (oxalate) analysis to be $PuO_2C_2O_4\cdot3H_2O$.

Estimated Error:

Temperature : ±1 K (authors).
Solubility: based on the duplicate or triplicate measurements as reported in original reference,[2] compiler estimated precision to be $\leqslant$10%.

References:

[1] I. L. Jenkins, F. H. Moore, and M. J. Waterman, J. Inorg. Nucl. Chem. **27**, 77 (1965).
[2] G. Seaborg, J. Katz, and P. Manning., Eds., *The Transuranium Elements* (1949), **1**, p. 423.
[3] B. P. Nikolskii, Ed., *Spravochnik Khimika* (*Chemistry Handbook*) (1952), Vol. **3**, p. 505.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess of $PuO_2C_2O_4 \cdot 3H_2O$ was stirred with solutions of the desired composition in a thermostated apparatus for 2 h, which was established as sufficient for equilibrium to be reached. The plutonium concentration in the saturated solutions was determined by an unspecified radiometric method.

Source and Purity of Materials:

Pure Pu solution in HNO_3 was used as a starting material. Plutonium was oxidized to Pu(VI) in 0.5–1.0 mol dm^{-3} HNO_3 by heating the solution with $K_2Cr_2O_7$ or MnO_2 at 90 °C for 1–2 h. The course of oxidation was followed spectrophotometrically. By adding crystalline oxalic acid to the Pu(VI) solution in 1–2 mol dm^{-3} HNO_3, a pink crystalline precipitate was obtained which was shown by gravimetric (Pu,H_2O) and titrimetric (oxalate) analysis to be $PuO_2C_2O_4 \cdot 3H_2O$.

Estimated Error:

Temperature: ±1 K (authors).
Solubility: from the four duplicate measurements precision of ±(3–8)% can be estimated.

References:

[1] G. Seaborg, J. Katz, and P. Manning., Eds., *The Transuranium Elements* (1945), Vol. **1**, p. 423.
[2] L. E. Drabkina, A. I. Moskvin, and A. D. Gelman, Zh. Neorg. Khim. **3**, 1934 (1958).

7.9. Plutonium(III) *o*-hydroxybenzoate

Components: (1) Plutonium(III) tris(*o*-hydroxybenzoate); $Pu(C_7H_5O_3)_3$; [ ] (2) Solvents	**Original Measurements:** O. E. Zvyagintsev and B. N. Sudarikov, Zh. Neorg. Khim. **3**, 975–85 (1958); Russ. J. Inorg. Chem. **3**, 217–33 (1958).
Variables: T/K: 293	**Prepared by:** J. Hála

Experimental Data

Solubility at 20 °C of $Pu(C_7H_5O_3)_3$ in three solvents[a]

Solvent	Pu^{3+} (g kg^{-1})[b]	$Pu(C_7H_5O_3)_3$ ($10^3 m_1$ /mol kg^{-1})[b]
water; H_2O; [7732-18-5]	0.12	0.502
ethanol; C_2H_6O; [64-17-5]	0.50	2.09
acetone; C_3H_6O; [67-64-1]	3.50	14.9

[a] The composition of the equilibrium solid phase was not reported.
[b] Grams per kg solution.
[c] Calculated by compiler using $A_r(Pu)=239.053$.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method was used. Excess $Pu(C_7H_5O_3) \cdot 1.5H_2O$ was equilibrated by stirring for 1 h with the desired solvent. Plutonium concentration in the saturated solutions was determined by an unspecified radiometric method.

Source and Purity of Materials:

Pu(IV) solution was reduced to Pu(III) by either SO_2 or sodium sulfoxylate, and $Pu(C_7H_5O_3) \cdot 1.5H_2O$ was obtained as a light-blue solid on precipitating with salicylic acid at pH 2.8–3.8. Analysis (found/calculated for the hydrate, mass %): Pu 35.34/35.30, salicylate 60.44/60.71. Source and purity of solvents used was not specified.

Estimated Error:

Temperature: temperature of the measurements was given as approximate value.
Solubility: insufficient data given to allow for error estimate.

7.10. Plutonium(IV) oxo(*o*-hydroxybenzoates)

Components:

(1) Plutonium(IV) oxobis(*o*-hydroxybenzoate); $PuO(C_7H_5O_3)_2$; [ ]
(2) Hydrogen chloride; HCl; [7647-01-0]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

O. E. Zvyagintsev and B. N. Sudarikov, Zh. Neorg. Khim. **3**, 975–85 (1958); Russ. J. Inorg. Chem. **3**, 217–33 (1958).

Variables:

T/K: 298
pH (in HCl solutions): 0.4–5.7

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $PuO(C_7H_5O_3)_2$ in HCl solutions as a function of pH[a]

pH[b]	Pu^{4+} (mg kg^{-1})[c]	$PuO(C_7H_5O_3)_2$ ($10^5\ m_1$ /mol kg^{-1})[c,d]
0.4	71.0	29.7
1.5	50.0	20.9
2.0	6.2	2.59
3.0	1.3	0.544
5.2	0.5	0.209
5.7	0.3	0.125

[a] The composition of the equilibrium solid phase was not reported.
[b] The pH was adjusted by adding HCl. Actual concentration of the latter was not specified.
[c] Grams per kg saturated solution.
[d] Calculated by compiler using $A_r(Pu)=239.053$.

Additional information:
At pH>6, $PuO(C_7H_5O_3)_2$ was reported to hydrolyze to yield a sparingly soluble product, which was identified as $Pu_2O_3(C_7H_5O_3)\cdot xH_2O$.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method was used. Excess $PuO(C_7H_5O_3)_2$ was equilibrated by stirring for 1 h with solutions of the desired pH. Plutonium concentration in the saturated solutions was determined by an unspecified radiometric method.

Source and Purity of Materials:

$PuO(C_7H_5O_3)_2$ was prepared by precipitation of a Pu(IV) solution with salicylic acid at pH 0–5 as a brown precipitate. Analysis (found/calculated for $PuO(C_7H_5O_3)_2$, mass %): Pu 45.50/45.18, salicylate 51.80/51.80.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

Components:

(1) Diplutonium(IV) trioxo(*o*-hydroxybenzoate); $Pu_2O_3(C_7H_5O_3)$; [ ]
(2) Hydrogen chloride; HCl; [7647-01-0]; or Ammonia; NH_3; [7664-41-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

O. E. Zvyagintsev and B. N. Sudarikov, Zh. Neorg. Khim. **3**, 975–85 (1958); Russ. J. Inorg. Chem. **3**, 217–33 (1958).

Variables:

T/K: 283–371
pH (in HCl or NH_3 solutions): 0.7–9.4

Prepared by:

J. Hála

Experimental Data

Solubility of $Pu_2O_3(C_7H_5O_3)$ as a function of temperature and pH[a]

Solubility of $Pu_2O_3(C_7H_5O_3)$ as a function of temperature[b]			Solubility of $Pu_2O_3(C_7H_5O_3)$ as a function of pH[e]		
Temperature (°C)	Pu^{4+} (mg kg^{-1})[c]	$Pu_2O_3(C_7H_5O_3)$ ($10^6\ m_1$ /mol kg^{-1})[d]	pH	Pu^{4+} (mg kg^{-1})[c]	$Pu_2O_3(C_7H_5O_3)$ ($10^6\ m_1$ /mol kg^{-1})[d]
10	0.3	1.25	0.7	23.6	98.7
25	1.3	5.44	2.3	2.4	10.0
50	3.9	16.3	4.2	2.0	8.37
70	6.3	26.4	5.7	1.3	5.44
85	1.0	4.18	7.2	0.3	1.25
98	0.5	2.09	9.4	0.7	2.93

[a] The composition of the equilibrium solid phase was not reported.
[b] The pH of the saturated solutions not reported.
[c] Grams per kg saturated solution.
[d] Calculated by compiler using $A_r(Pu)=239.053$ neglecting the small plutonium concentration in the saturated solutions.
[e] The pH was adjusted by using HCl or NH_3. Actual concentration of HCl or NH_3 was not specified.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method was used. Excess $Pu_2O_3(C_7H_5O_3)\cdot xH_2O$ was equilibrated with the desired solution and/or at the desired temperature by stirring for 1–2 h. Plutonium concentration in the saturated solutions was determined by an unspecified radiometric method.

Source and Purity of Materials:

$Pu_2O_3(C_7H_5O_3)\cdot xH_2O$ was prepared as amorphous gray–yellow to brown solid by boiling solutions of $PuO(C_7H_5O_3)_2$ in ammoniacal solutions of ammonium salicylate or in alkaline solutions of sodium salicylate. The Pu(IV): salicylate ratio in the product was within 2:0.92–2:1.09.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

Components:

(1) Diplutonium(IV) trioxo(*o*-hydrxybenzoate); $Pu_2O_3(C_7H_5O_3)$; [ ]
(2) Ammonium chloride; NH_4Cl; [12125-02-9]; or Ammonium nitrate; NH_4NO_3; [6484-52-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

O. E. Zvyagintsev and B. N. Sudarikov, Zh. Neorg. Khim. **3**, 975–85 (1958); Russ. J. Inorg. Chem. **3**, 217–33 (1958).

Variables:

T/K: 298
m_2 /mol kg^{-1}: 3.42; 8.44 (NH_4Cl); 0–12.5 (NH_4NO_3)

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C and pH 6 of $Pu_2O_3(C_7H_5O_3)$ in NH_4Cl or NH_4NO_3 solutions[a]

Salt	Salt (g kg^{-1})[b]	Salt (m_2 /mol kg^{-1})[c]	Pu^{4+} (mg kg^{-1})[b]	$Pu_2O_3(C_7H_5O_3)$ (10^6 m_1 /mol kg^{-1})[c]
NH_4Cl; [12125-02-9]	157	3.42	0.5	2.48
	315	8.44	0.1	0.611
NH_4NO_3; [6484-52-2]	50	0.658	0.5	2.20
	100	1.39	0.4	1.86
	300	5.35	0.3	1.79
	500	12.5	0.1	0.84

[a] The composition of the equilibrium solid phase was not reported.
[b] Grams per kg saturated solution.
[c] Calculated by compiler. For m_1, $A_r(Pu)=239.053$ was used and the small plutonium concentration in the saturated solutions was neglected.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method was used. Excess $Pu_2O_3(C_7H_5O_3)\cdot xH_2O$ was equilibrated by stirring with solutions of the desired concentration for 1–2 h. Plutonium concentration in the saturated solutions was determined by an unspecified radiometric method.

Source and Purity of Materials:

$Pu_2O_3(C_7H_5O_3)\cdot xH_2O$ was prepared as amorphous gray–yellow to brown solid by boiling solutions of $PuO(C_7H_5O_3)_2$ in ammoniacal solutions of ammonium salicylate or in alkaline solutions of sodium salicylate. The Pu(IV):salicylate ratio in the product was within 2:0.92–2:1.09.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

Components:

(1) Diplutonium(IV) trioxo(*o*-hydroxybenzoate); $Pu_2O_3(C_7H_5O_3)$; [ ]
(2) Ammonium *o*-hydroxybenzoate; $C_7H_9NO_3$; [ ]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

O. E. Zvyagintsev and B. N. Sudarikov, Zh. Neorg. Khim. **3**, 975–85 (1958); Russ. J. Inorg. Chem. **3**, 217–33 (1958).

Variables:

T/K: 298 and 333
m_2 /mol kg^{-1}: 0.02–4.3
pH: 1.2–10.2

Prepared by:

J. Hála

Experimental Data

Solubility at 25 and 60 °C of $Pu_2O_3(C_7H_5O_3)$ in ammonium salicylate solutions[a]

Temperature (°C)	$C_7H_5O_3^-$ (g kg^{-1} solution)[b]	$C_7H_9NO_3$ (m_2 /mol kg^{-1})[c]	pH	Pu^{4+} (mg kg^{-1} solution)	$Pu_2O_3(C_7H_5O_3)$ (10^6 m_1 /mol kg^{-1})[c]
25	5	0.0324	1.2	2.5	10.5
	5	0.0324	1.7	1.5	6.31
	5	0.0324	2.7	0.5	2.10
	5	0.0324	5.5	0.3	1.26
	5	0.0324	6.2	0.3	1.26
	5	0.0324	7.4	0.2	0.84
	5	0.0324	9.2	0.1	0.42
	5	0.0324	10.2	0.1	0.42
	0	0	7	0.3	1.25
	3	0.0194	7	0.4	1.68
	5	0.0324	7	0.2	0.841
	50	0.339	7	1.4	6.16
	75	0.526	7	2.9	13.1
	100	0.716	6	0.5	2.32
	100	0.716	7	3.0	13.9
	100	0.716	8.9	1.5	6.97
	100	0.716	9.7	2.8	13.0
	200	1.61	4.2	1.5	7.84
	200	1.61	7	3.4	17.8
	200	1.61	7.4	3.4	17.8
	300	2.76	7	4.9	29.3
	300	2.76	7.3	4.9	29.3
	300	2.76	9.2	6.5	38.8
	400	4.30	6.9	6.8	47.4
	400	4.30	7	4.9	34.2
	400	4.30	9.8	9.0	62.7
60	0	0	[d]	6.4	26.7
	100	0.716	[d]	50.0	232
	170	1.32	[d]	68.0	343
	250	2.15	[d]	87.0	485
	400	4.30	[d]	239.0	1670

[a] The composition of the equilibrium solid phase was not reported.
[b] Concentration of the salicylate ion; given by authors as approximate values.
[c] Calculated by compiler. For plutonium, $A_r(Pu)=239.053$ was used.
[d] Not reported.

7.11. Plutonium(IV) 8-Hydroxyquinolinates

Components:

(1) Plutonium(IV) tetrakis(halogeno-8-hydroxy-quinolinates)
(2) Ammonium perchlorate; NH_4ClO_4;[7790-98-9]
(3) Sodium acetate; $C_2H_3O_2Na$; [127-09-3]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

C. Keller and S. H. Eberle, Radiochim. Acta **4**, 141–5 (1965).

Variables:

T/K: 298
c_2 /mol dm^{-3}: 0.09; 0.1
c_3 /mol dm^{-3}: 0; 0.01

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of plutonium(IV) tetrakis(8-hydroxy-quinolinates) in NH_4ClO_4 /$C_2H_3O_2Na$ solutions[a]

Complexing ligand	Pu(IV) complex (formula)	NH_4ClO_4 (c_2 /mol dm^{-3})	$C_2H_3O_2Na$ (c_3 /mol dm^{-3})	Pu(IV) complex (10^6 c_1 /mol dm^{-3})
8-hydroxyquinoline, C_9H_7NO	$Pu(C_9H_6NO)_4$;	0.1	0	2.0
	[ ] (I)	0.09	0.01	1.5
5-chloro-8-hydroxyquinoline,	$Pu(C_9H_5ClNO)_4$;	0.1	0	0.69
C_9H_6ClNO	[ ] (II)	0.09	0.01	3.9
5,7-dichloro-8-hydroxyquinoline,	$Pu(C_9H_4Cl_2NO)_4$;	0.1	0	0.59
$C_9H_5Cl_2NO$	[ ] (III)	0.09	0.01	5.3
5,7-dibromo-8-hydroxyquinoline,	$Pu(C_9H_4Br_2NO)_4$;	0.1	0	0.21
$C_9H_5Cl_2NO$	[ ] (IV)	0.09	0.01	1.6
5-chloro-7-iodo-8-hydroxyquinoline,	$Pu(C_9H_4ClINO)_4$;	0.1	0	0.82
$C_9H_5Cl_2NO$	[ ] (V)	0.09	0.01	0.92

[a] The composition of the equilibrium solid phase was not reported. Saturated solutions showed pH of 6.

Additional information:

For the $Pu(C_9H_6NO)_4$ chelate (I) the solubility was also measured as a function of pH in the two solutions shown above. The results were reported in graphical form.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method was used. Excess $Pu_2O_3(C_7H_5O_3)\cdot xH_2O$ was equilibrated by stirring with solutions of the desired concentration for 1–2 h. Plutonium concentration in the saturated solutions was determined by an unspecified radiometric method. Chemicals used to adjust pH not reported.

Source and Purity of Materials:

$Pu_2O_3(C_7H_5O_3)\cdot xH_2O$ was prepared as amorphous gray–yellow to brown solid by boiling solutions of $PuO(C_7H_5O_3)_2$ in ammoniacal solutions of ammonium salicylate or in alkaline solutions of sodium salicylate. The Pu(IV):salicylate ratio in the product was within 2:0.92–2:1.09. Source and purity of plutonium and other chemicals not specified.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method was used. Thermostating of the solutions and equilibration time not reported. Plutonium concentration in the saturated solutions was determined by an unspecified radiometric method.

Source and Purity of Materials:

Plutonium (99.8% purity) was dissolved in acid and the ^{241}Am accumulated by β decay of ^{241}Pu was removed by precipitation of plutonium as peroxide. The absence of ^{241}Am was checked by paper chromatography according to Ref. 1. The Pu solution was fumed with $H_2SO_4+HNO_3$ mixture to obtain Pu(IV). The chelate (I) was prepared by adding dropwise 0.05 mmol Pu(IV) in 10 mL 1 mol dm^{-3} H_2SO_4 to a solution of 0.25 mmol 8-hydroxyquinoline in 50 mL 0.1 mol dm^{-3} $C_2H_3O_2Na$ solution under vigorous stirring. The pH was continuously adjusted during precipitation to 4.5–4.9 with NH_3 solution. The mixture was heated to 50–60 °C, slowly cooled to room temperature, filtered, the precipitate was washed with warm water, and dried over P_2O_5. The chelates (II)–(V) were prepared by adding dropwise 0.05 mmol Pu(IV) in 10 mL 1 mol dm^{-3} H_2SO_4 to 50 mL 0.1 mol dm^{-3} $C_2H_3O_2Na$ in 40%–60% dioxane. The solutions contained 2%–5% excess of the chelating agent over the stoichiometric amount. The pH was continuously adjusted during precipitation to 4.5–4.9 with NH_3 solution. The mixture was then diluted with water to a dioxane content of 30%, the precipitate was sucked dry, washed with 30% dioxane at 60 °C, and dried at 110 °C. Analysis of the chelates, found/calculated for Pu(ligand)$_4$ (mass %): (I) Pu 29.2/29.30, ligand 71.2/70.70; (II) Pu 25.2/25.06, ligand 78.0/74.94; (III) 22.4/21.91, ligand 79.7/78.09; (IV) Pu 16.6/16.51, ligand 83/83.49; (V) Pu 16.0/16.40, ligand 82/83.60.

Estimated Error:

Temperature: precision not reported.

Solubility: insufficient data given to allow for error estimate.

References:

[1]C. Keller, J. Chromatrography **7**, 535 (1962).

7.12. Plutonium(IV) N-Hydroxy-N-Nitrosobenzeneaminate

Components:

(1) Plutonium(IV) tetrakis(N-hydroxy-N-nitroso-benzeneaminate); $C_{24}H_{20}N_8O_8Pu$ or $Pu(C_6H_5N_2O_2)_4$; [ ]
(2) N-hydroxy-N-nitrosobenzeneamine (cupferron); $C_6H_6N_2O_2$; [148-97-0]
(3) Sulfuric acid; H_2SO_4; [7664-93-9]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

I. V. Moiseev, N. N. Borodina, and V. T. Tsvetkova, Zh. Neorg. Khim. **6**, 543–8; (1961) Russ. J. Inorg. Chem. **6**, 277–9 (1961).

Variables:

T/K: 294
c_2 /mol dm^{-3}: 0.00189–0.0152
c_3 /mol dm^{-3}: 0.25–1.5

Prepared by:

J. D. Navratil

Experimental Data

Solubility at 21 °C of Pu(IV) tetrakis (cupferrate), $Pu(C_6H_5N_2O_2)_4$, in H_2SO_4 solutions[a]

H_2SO_4 (c_3 /mol dm^{-3})[b]	[H^+][c] (mol dm^{-3})	Cupferron[d] (10^3 c_2 /mol dm^{-3})	$Pu(C_6H_5N_2O_2)_4$[e] (10^6 c_1 /mol dm^{-3})
0.25	0.278	1.89 3.47	7.9(0.79)[f] 2.07 (0.153)[f]
0.50	0.538	3.48 5.07	4.93 (0.416)[f] 2.53 (0.116)[f]
1.0	1.055	10.1	1.76 (0.386)
1.5	1.568	15.2	1.38 (0.0566)

[a] The nature of the equilibrium solid phases was not investigated.

[b] Initial concentration of sulfuric acid.

[c] Hydrogen ion concentration at equilibrium. It was obtained from the initial concentration of sulfuric acid, and the apparent dissociation constants of the acid taken from Ref. 1.

[d] Equilibrium concentration of cupferron. It was calculated from the initial concentrations of Pu(IV) and cupferron, the final volume of the solution, and the Pu(IV) concentration in the saturated solution.

[e] Average values and standard deviations (in parentheses) calculated by the compiler from three parallel experiments.

[f] This pair of measurements differed in the initial cupferron concentration.

Additional information:

The equilibrium constant for the precipitation of Pu(IV) by cupferron (HR), $K=[H^+]^4[\mathrm{Pu(IV)}]^{-1}[HR]^{-4}$ was calculated to be 6.6×10^{-13} mol^{-1} dm^3. From this constant the solubility product of Pu(IV) cupferrate, was obtained as $K_{sp}=K_a^4K^{-1}=[\mathrm{Pu(IV)}][R^-]^4=1.2\times10^{-31}$ mol^5 dm^{-15} using the dissociation constant of cupferron, $K_a=5.3\times10^{-4}$.[2]

Auxiliary Information

Method/Apparatus/Procedure:

The solubility of Pu(IV) cupferrate was determined according to Ref. 3. About 10 mL Pu(IV) in 0.5 mol dm^{-3} H_2SO_4 and the calculated quantities of water, acid, and the cupferron solution were stirred for about 3 min in a 50 mL beaker. Then the precipitate was filtered off using a No. 4 glass filter crucible. The first 15 mL of filtrate were rejected, and the Pu(IV) content in the remaining solution was determined radiometrically.

Source and Purity of Materials:

A solution of Pu(IV) was prepared by dissolving pure $Pu(OH)_4$, freshly precipitated in the cold, in 1:1 H_2SO_4. After dilution with water the concentration of H_2SO_4 was 0.5 mol dm^{-3}. The plutonium concentration in this solution was determined gravimetrically by precipitating $Pu(OH)_4$ with ammonia, and igniting to PuO_2 at 1000 °C. Cupferron solution was prepared by washing the reagent repeatedly with ethanol, dissolving it in water, and standardizing by titration with a standard Fe(III) solution in a stream of CO_2 using a platinum indicator electrode.

Estimated Error:

Temperature: ±0.02 K (authors).

Solubility: standard deviation calculated by the compiler.

References:

[1]T. F. Young and L. A. Blatz, Chem. Rev. **44**, 93 (1949).
[2]I. V. Pyatnitskii, Zh. Anal. Khim. **1**, 135 (1946).
[3]I. V. Pyatnitskii, Zh. Anal. Khim. **1**, 57 (1946).

8. The Solubility of Americium Compounds

8.1. Americium(III) Carbonate and Americium(III) Hydrogencarbonate

8.1.1. Evaluation of the Am(OH)CO_3 or $\text{Am}_2(\text{CO}_3)_3+\text{CO}_3^{2-}+\text{NaClO}_4+\text{H}_2\text{O}$ System

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Components:

(1) Americium hydroxocarbonate; Am(OH)CO_3; [101362-32-7]; or
Diamericium tris(carbonate); $\text{Am}_2(\text{CO}_3)_3$; [ ]
(2) Carbonate ion; CO_3^{2-}; [3812-32-6]
(3) Sodium perchlorate; NaClO_4; [7601-89-0]
(4) Water; H_2O; [7732-18-5]

Evaluator:

J. Hála, Department of Inorganic Chemistry, Masaryk University, 61137 Brno, Czech Republic, June 2000

Critical Evaluation:

The two americium carbonates, Am(OH)CO_3 and $\text{Am}_2(\text{CO}_3)_3$, are solid phases important from the point of view of potential leaching of americium from radioactive waste repositories. Their solubility in carbonate containing NaClO_4 solutions has been studied in Refs. 1–4. The hydroxocarbonate is the thermodynamically stable solid phase in solutions that are in contact with atmospheric partial pressure of $\text{CO}_2(<1\%)$,[3] and/or at low equilibrium carbonate ion concentration,[4] while at higher partial pressures of CO_2 it is the crystalline carbonate, $\text{Am}_2(\text{CO}_3)_3$.[1–3] These solid phases have also been studied in related systems not containing NaClO_4. Thus Felmy *et al.*[5] observed Am(OH)CO_3 as the solid phase in solutions containing <0.1 mol dm^{-3} Na_2CO_3, and at pH 5.5–13, and Shiloh *et al.*[6] observed $\text{Am}_2(\text{CO}_3)_3$ in equilibrium with solutions containing >0.12 mol dm^{-3} K_2CO_3.

The solubility data were obtained in measurements conducted as pH titrations[1–3] or by using the isothermal method,[4,5] with careful control of pH and other experimental parameters. The carbonate ion concentration in the saturated solutions was controled either by saturating the solutions with CO_2 gas at various pH,[1–3,5] or by using NaHCO_3[4,5] or Na_2CO_3.[5] Except for measurements in Refs. 1, 2 where equilibration time of 2–3 days was used, other authors equilibrated the systems for several weeks. The long equilibration time was needed because of the slow transition of initially amorphous solid to crystalline form.[5] This is possibly also the reason for rather wide scatter of experimental solubility data observed even after long equilibration.[1,5] Numerical solubility data have been reported by Silva[4] only, other authors reported their data in graphical form,[1,5] or reported solubility products only.[2,3] This situation does not make a detailed comparison possible. As with the carbonates of uranium, neptunium, and plutonium, the solubilities of both Am(OH)CO_3 and $\text{Am}_2(\text{CO}_3)_3$ pass through a minimum when plotted against equilibrium carbonate ion concentration.[1,2,5] The enhanced solubility at higher $[\text{CO}_3^{2-}]$ values has been ascribed to the formation of Am(III) carbonatocomplexes, i.e., $\text{Am(CO}_3)_2^-$,[1,5] $\text{Am(CO}_3)_3^{3-}$,[5] or $\text{Am(OH)(CO}_3)_3^{4-}$.[6] Likewise, no direct comparison of solubility product values is possible. For K_{sp} of $\text{Am}_2(\text{CO}_3)_3$, the results of the German group[1–3] are available only. The authors obtained the solubility product in several repeated measurements with very good reproducibility. The values, as $-\log K_{\text{sp}}$, for 0.1 mol dm^{-3} NaClO_4, are 29.89 ± 0.18 at 298.1 K and $p(\text{CO}_2)$ of 1%,[1] 29.57 ± 0.10 at 295.1 K and $p(\text{CO}_2)$ of 100%,[2] 29.32 ± 0.08 at 295.1 K and $p(\text{CO}_2)$ of 1%,[2] and 29.45 ± 0.18 at 298.1 K and $p(\text{CO}_2)$ of 1% or 100%.[3] The evaluator suggests these values as recommended ones. The solubility product of Am(OH)CO_3 has been reported to be $10^{-(18.70\pm0.12)}$ mol^3 dm^{-9} (298.1 K, $p(\text{CO}_2)$ 0.03%, 0.1 mol dm^{-3} NaClO_4),[3] and $10^{-22.5}$ mol^3 dm^{-9} at unspecified ionic strength and room temperature.[5] Silva[4] obtained the equilibrium contant, $K=[\text{Am}^{3+}][\text{CO}_3^{2-}][\text{H}^+]^{-2}=583\pm206$ (0.1 mol dm^{-3} NaClO_4) for the reaction $\text{Am(OH)CO}_{3(s)}+2\text{H}^+\leftrightarrows\text{Am}^{3+}+\text{HCO}_3^-+\text{H}_2\text{O}$. From this constant the evaluator calculated the solubility product as $K_{\text{sp}}=KK_{\text{w}}K_{\text{a2}}=10^{-(21.7\pm0.2)}$ mol^3 dm^{-9} (K_{w} is the ion product of water, K_{a2} is the second dissociation constant of carbonic acid). Although this value is close to that of Felmy,[5] the evaluator recommends the value of Runde and Kim[3] be used since it was obtained under well defined conditions.

References:

[1] G. Meinrath and J. I. Kim, Radiochim. Acta **52/53**, 29 (1991).

[2] G. Meinrath and J. I. Kim, Eur. J. Solid State Inorg. Chem. **28**, 383 (1991).

[3] W. Runde, G. Meinrath, and J. I. Kim, Radiochim. Acta **58/59**, 93 (1992).

[4] R. J. Silva, Mater. Res. Sol. Symp. Proc. **26**, 875 (1989).

[5] A. R. Felmy, D. Rai, and R. W. Fulton, Radiochim. Acta **50**, 193 (1990).

[6] M. Shiloh, M. Givon, and Y. Marcus, J. Inorg. Nucl. Chem. **30**, 1807 (1969).

Components:

(1) Diamericium tris(carbonate); $\text{Am}_2(\text{CO}_3)_3$; [ ]
(2) Potassium carbonate; K_2CO_3; [584-08-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

M. Shiloh, M. Givon, and Y. Marcus, J. Inorg. Nucl. Chem. **30**, 1807–14 (1969).

Variables:

T/K: 298
c_2 /mol dm^{-3}: 0.12–0.6

Prepared by:

J. Hála

Experimental Data

Solubility of $\text{Am}_2(\text{CO}_3)_3$ at 25 °C in K_2CO_3 solutions

The solubility of $\text{Am}_2(\text{CO}_3)_3$ at 25 °C as a function of K_2CO_3 concentration, in mol dm^{-3}, was reported to be given by the equation

$$S=K[\text{CO}_3^{2}]^2$$

with $K=1.8\times10^{-3}$ mol^{-1} dm^3. Experimental data were reported in graphical form. Also in graphical form was reported the solubility of $\text{Am}_2(\text{CO}_3)_3$ as a function of pH. The Am(III) species present in 0.12–0.6 mol dm^{-3} K_2CO_3 solutions was identified as $\text{Am(OH)(CO}_3)_3^{4-}$. The equilibrium solid phase was $\text{Am}_2(\text{CO}_3)_3$, [ ], in all solutions.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. 25 μL of the Am(III) stock solution (pH 3, dilute HClO_4) was introduced into 2.5 mL K_2CO_3 solution of the desired concentration in a centrifuge cone. After standing 24 h at room temperature with occasional shaking, the precipitate was centrifuged off, and americium in the saturated solution was determined by α counting. The equilibrium solid phases were analyzed for carbonate and americium, and the CO_3/Am ratio was found to be 1.60.

Source and Purity of Materials:

^{241}Am (U.S.A.E.C.) was dissolved in HClO_4 solution to form a stock solution of about 0.1 mol dm^{-3} Am(III). Portions of this solution were used to precipitate americium carbonate directly in the solubility experiments. K_2CO_3 was a reagent grade product.

Estimated Error:

Temperature: precision not reported.
Solubility: insufficient data given to allow for error estimate.

Components:

(1) Diamericium tris(carbonate); $Am_2(CO_3)_3$; [ ]
(2) Carbon dioxide; CO_2; [124-38-9]
(3) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

[1] G. Meinrath and J. I. Kim, Radiochim. Acta **52/53**, 29–34 (1991).
[2] G. Meinrath and J. I. Kim, Eur. J. Solid State Inorg. Chem. **28**, 383–8 (1991).

Variables:

T/K: 298; 295
p_2 (partial pressure of CO_2)/%: 1; 100
c_3 /mol dm^{-3}: 0.1; 0.3

Prepared by:

J. Hála

Experimental Data

In the original Ref. 1, the solubility of $Am_2(CO_3)_3$ as a function of pH and equilibrium concentration of CO_3^{2-} ion, at 25 °C and partial pressure of CO_2 of 1%, were reported in graphical form (see Fig. 23). The concentration of CO_3^{2-} ion was calculated from the measured pH, and a series of equilibria including partial pressure of CO_2, Henry constant, and dissociation constants of carbonic acid:

$$CO_{2(g)} \overset{K_H}{\leftrightarrows} CO_{2(aq)} \overset{K^*}{\leftrightarrows} H_2CO_3 \overset{K_{a1}}{\leftrightarrows} HCO_3^- \overset{K_{a2}}{\leftrightarrows} CO_3^{2-}$$

as $\log[CO_3^{2-}] = \log K + \log p(CO_2) + 2$ pH, with $\log K = \log(K_H\, K^* K_{a1} K_{a2}) = -17.78$. The course of the solubility curve was interpreted by the authors in terms of the formation of $Am(CO_3)_n^{3-2n}$ complexes in the solution. Using the equation $[Am]_{tot} = \{K_{sp}/[CO_3^{2-}]^3\}^{1/2}\Sigma\beta_n[CO_3^{2-}]^n$, where $[Am]_{tot}$ is the total concentration of Am(III) in the saturated solution, $K_{sp} = [Am^{3+}]^2[CO_3^{2-}]^3$, and $\beta_n = [Am(CO_3)_n^{3-2n}]/[Am^{3+}][CO_3^{2-}]^n$ (overall stability constants of the $Am(CO_3)_n^{3-2n}$ complexes), the following values were obtained: $\beta_1 = 10^{(5.97\pm0.15)}$ mol^{-1} dm^3, $\beta_2 = 10^{(9.58\pm0.24)}$ mol^{-2} dm^6, and $K_{sp} = 10^{-(29.89\pm0.18)}$ mol^5 dm^{-15}. These constants were reported to be valid for solutions with ionic strength of 0.1–0.3 mol dm^{-3} $NaClO_4$.

In the original reference,[2] the value of log K was refined to be $-(17.62\pm0.07)$, and the solubility product of $Am_2(CO_3)_3$ at 22 °C was obtained as $10^{-(29.32\pm0.08)}$ mol^5 ^{5}dm^{-15} at 100% and 1% partial pressure of CO_2, respectively, and ionic strength of 0.1 mol dm^{-3} $NaClO_4$. In both documents, the equilibrium solid phase was $Am_2(CO_3)_3$, [ ], over the whole pH range investigated.

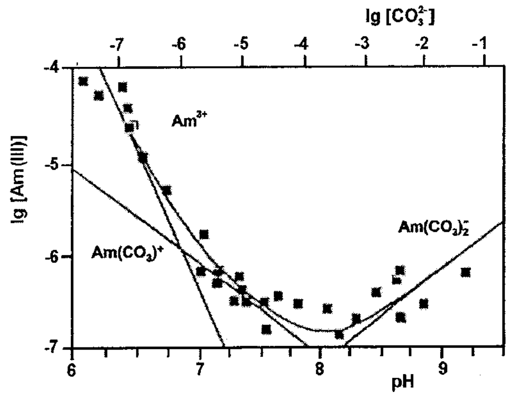

FIG. 23. Diamericium tris(carbonate)–sodium perchlorate–carbon dioxide–water system.

Auxiliary Information

Method/Apparatus/Procedure:

The solubility experiment, combined with pH titration, was conducted in a 100 mL thermostated vessel in the pH range from 6.0 to 9.2 under argon/1% CO_2 atmosphere. The desired carbonate concentration was attained by pH control. The Am^{3+} ion 0.1 mol dm^{-3} $HClO_4$ was introduced into the vessel ($[Am^{3+}]_{tot} = 5\times10^{-4}$ mol dm^{-3}) and precipitated by addition of 0.05 mol dm^{-3} Na_2CO_3. The solution with the precipitate was left to stand under Ar/CO_2 atmosphere for 2 weeks. Then the pH of the solution was gradually adjusted by additions of either 0.1 mol dm^{-3} $HClO_4$ or 0.05 mol dm^{-3} Na_2CO_3 for the pH range of 6–8 in the presence of 0.1 mol dm^{-3} $NaClO_4$, or by 0.3 mol dm^{-3} $HClO_4$ or 0.1 mol dm^{-3} Na_2CO_3 for the pH range of 8–9 in the presence of 0.3 mol dm^{-3} $NaClO_4$. Combination glass electrodes (ROSS-type, Orion) used for pH measurement were calibrated against standard buffer solutions adjusted to the desired ionic strength. Equilibrium at a given pH was established in 2–3 days. The americium concentration was measured after filtration of the saturated solution through 450 nm pore size filter by liquid scintillation counting (Beckman LS 6800). In a number of samples, the Am concentration was also determined by either UV spectroscopy (at $[Am^{3+}]_{tot} > 10^{-5}$ mol dm^{-3}) or by laser-induced photoacoustic spectroscopy (at $[Am^{3+}]_{tot} < 10^{-6}$ mol dm^{-3}). The equilibrium solid phases were investigated by means of Nd^{3+} as a model ion which is known to be very close in chemical behavior to Am^{3+}. The Nd^{3+} ion was precipitated under the same conditions as was Am^{3+} in the solubility experiment, and the precipitate was confirmed to be $Nd_2(CO_3)_3\cdot 8H_2O$ by x-ray diffraction and IR spectroscopy.

Source and Purity of Materials:

Isotopically pure ^{241}Am was used. The $Ar^+1\%CO_2$ gas mixture was a product of Linde. No other details were specified.

Estimated Error:

Temperature: precision ±1 K (authors).
pH: precision ±0.03 units (authors).
Solubility product: standard deviation see above.

Components:

(1) Diamericium tris(carbonate); $Am_2(CO_3)_3$; [ ]; or Americium hydroxocarbonate; $Am(OH)CO_3$; [101362-32-7]
(2) Carbon dioxide; CO_2; [124-38-9]
(3) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

W. Runde, G. Meinrath, and J. I. Kim, Radiochim. Acta **58/59**, 93–100 (1992).

Variables:

T/K: 298
p_2 (partial pressure of CO_2)/%: 0.03; 1; 100
c_3 /mol dm^{-3}: 0.1

Prepared by:

J. Hála

Experimental Data

The solubility of $Am_2(CO_3)_3$ and $Am(OH)CO_3$ in 0.1 mol dm^{-3} $NaClO_4$ solution was measured as a function of pH and equilibrium concentration of CO_3^{2-} ion, at 25 °C and partial pressures of CO_2 of 0.03%, 1%, and 100%. The experimental data were not reported. Using the same computational procedure as in the authors' previous work[1,2] the authors obtained the following solubility products: $K_{sp}=[Am^{3+}]^2[CO_3^{2-}]^3=10^{-(29.45\pm0.18)}$ mol^5 dm^{-15} at partial pressure of CO_2 of 1% or 100%, and $K_{sp}=[Am^{3+}][OH^-][CO_3^{2-}]=10^{-(18.70\pm0.12)}$ mol^3 dm^{-9} at partial pressure of CO_2 of 0.03%. Solid phases at equilibrium were identified as $Am_2(CO_3)_3$, [ ] at partial pressure of CO_2 of 1% or 100%, and $Am(OH)CO_3$, [101362-32-7], at partial pressure of CO_2 of 0.03%.

Auxiliary Information

Method/Apparatus/Procedure:

The solubility experiment, combined with pH titration, was conducted in a 100 mL thermostated vessel under different CO_2 partial pressures using argon/CO_2 gas mixtures. The Am^{3+} in acidic 0.1 mol dm^{-3} $NaClO_4$ solution was precipitated by the addition of 0.1 mol dm^{-3} NaOH. The solution with the precipitate was left to stand under the desired Ar/CO_2 atmosphere for more than 2 weeks. The gas with a given composition was continuously passed through the vessel to maintain a constant pressure of CO_2. Then the pH of the solution was gradually adjusted by additions of either 0.1 mol dm^{-3} $NaHCO_3$ or NaOH. After equilibrium had been attained, the pH was measured by a combination glass electrode (ROSS-type, Orion), which was calibrated with more than five standard buffer solutions. The equilibrium Am^{3+} concentration in the saturated solutions was determined by UV spectroscopy measuring the absorbance at 503.2 nm. The total americium concentration was determined by liquid scintillation counting. The equilibrium solid phases were characterized by thermographic analysis combined with DTA, by FTIR spectroscopy, and x-ray powder diffraction.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: precision ±0.2 K (authors).
pH: precision ±0.02 units (authors).
Solubility product: standard deviation, see above.

References:

[1] G. Meinrath and J. I. Kim, Radiochim. Acta **52/53**, 29 (1991).
[2] G. Meinrath and J. I. Kim, Eur. J. Solid State Inorg. Chem. **28**, 383 (1991).

Components:

(1) Americium hydroxocarbonate; $Am(OH)CO_3$; [101362-32-7]
(2) Sodium hydrogencarbonate; $NaHCO_3$; [144-55-8]
(3) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

R. J. Silva, Mater. Res. Soc. Symp. Proc. **26**, 875–81, (1984).
Americium and Curium Chemistry and Technology, edited by N. M. Edelstein *et al.*, (Reidel Dordrecht, 1985), pp. 225–238.
R. J. Silva and H. Nitsche, NUREG/CP-0052, Proceedings U.S. NRC, Nucl. Waste Geochem. '83, Reston, VA, 1983, pp. 70–93.

Variables:

T/K: 298
c_2 /mol dm^{-3}: 2×10^{-4}
c_3 /mol dm^{-3}: 0.1

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $Am(OH)CO_3$ in 2×10^{-4} mol dm^{-3} $NaHCO_3$/0.1 mol dm^{-3} $NaClO_4$ solutions[a]

Equilibration time (days)	pH	HCO_3^- (10^4 c_2 /mol dm^{-3})	$Am(OH)CO_3$ (10^6 c_1 /mol dm^{-3})	10^{-2} K[d]
1[b]	6.13	2.09	28.6±2.5	63.2±1.0
3	6.13	2.09	11.9±0.4	26.3±3.6
7	6.15	2.19	2.17±0.54	5.51±1.56
14	6.13	2.09	2.39±0.21	5.28±0.85
21	6.14	2.14	2.02±0.04	4.79±0.65
30	6.14	2.14	2.29±0.03[e]	5.43±0.73
			1.54±0.13[f]	3.65±0.58
			1.40±0.13[g]	3.32±0.07
1[c]	6.09	1.91	366±13	614±82
3	6.11	2.00	315±5	607±82
7	6.12	2.05	356±13	735±102
14	6.10	1.95	78.6±16.7	141±35
22	6.13	2.09	7.67±0.72	17.0±2.8
31	6.14	2.14	3.21±0.14	7.60±1.07
37	6.13	2.09	4.42±0.17	9.77±1.36
44	6.13	2.09	4.71±0.30	10.4±1.5
51	6.11	2.00	4.88±0.11[e]	9.40±1.33

[a] Equilibrium solid phase was $Am(OH)CO_3$, [101362-32-7], in all solutions.
[b] This and the following five measurements performed using procedure (a).
[c] This and the following seven measurements performed using procedure (b).
[d] Equilibrium constant for the reaction $Am(OH)CO_{3(s)}+2H^+\leftrightarrows Am^{3+}+HCO_3^-+H_2O$. It was calculated from the measured americium and HCO_3^- concentrations, and the calculated H^+ ion concentration, which was obtained from the measured pH value using the activity coefficient of 0.78. Based on literature data for the hydrolysis of Cm^{3+} ion, as a close analog of Am^{3+}, and the stability constant of the $Am(CO_3)^+$ complex, the concentration of the Am^{3+} ions was found to be equal to (95.9±1.3)% of the measured concentration of Am(III) in the solutions. The values of the constant K obtained in method (a) by the three different solid–liquid separation procedures after 30 day equilibration time, and in method (b) after 51 day equilibration time were averaged by the authors to obtain $K=583\pm206$. Using activity coefficients of 0.46, 0.76, and 0.78 for the Am^{3+}, HCO_3^-, and H^+ ions, respectively, the constant at zero ionic strength was obtained as $K^0=335\pm120$.
[e] Centrifugation only.
[f] Centrifugation and filtration through a 0.2 μm filter.
[g] Centrifugation and filtration through a 0.015 μm filter.

Components:	Original Measurements:
(1) Americium hydroxocarbonate; $Am(OH)CO_3$; [101362-32-7] In method (a): (2) Sodium hydrogencarbonate; $NaHCO_3$; [144-55-8] (3) Carbon dioxide; CO_2; [124-38-9]; (4) Water; H_2O; [7732-18-5] In method (b): (2) Sodium carbonate; Na_2CO_3; [497-19-8]; (3) Sodium hydroxide; NaOH; [1310-73-2] (4) Water; H_2O; [7732-18-5]	A. R. Felmy, D. Rai, and R. W. Fulton, Radiochim. Acta **50**, 193–204 (1990).

Variables:	Prepared by:
T/K: unspecified room temperature c_2 and c_3 /mol dm^{-3}: see the text below	J. Hála

Experimental Data

The solubility of $Am(OH)CO_3$ was measured in $NaHCO_3/CO_2$ and Na_2CO_3/NaOH solutions. The results, which showed a rather wide scatter, were reported in graphical form only. In method (a) (see below; $p_2 = 0.001$ atm, $NaHCO_3$ solutions), using $Am(OH)CO_3$ prepared by two different methods, the systems required 36 day equilibration to obtain steady state Am concentration in the solutions. The authors explained this by conversion of the initially amorphous solid to crystalline $Am(OH)CO_3$, [101362-32-7]. The same equilibrium solid phase was found also in method (b) with either 0.07 mol dm^{-3} Na_2CO_3+NaOH at pH 10.5–13, or with 0.003–0.1 mol dm^{-3} Na_2CO_3 at pH 8.5–11 after 61 days of equilibration. Thus $Am(OH)CO_3$ is the equilibrium solid phase in solutions containing <0.1 mol dm^{-3} Na_2CO_3, and at pH 5.5–13. The authors concluded that the solubility of $Am(OH)CO_3$ under the conditions used could best be explained by assuming Am^{3+} and $Am(CO_3)_n^{3-2n}$ species in the saturated solutions. At pH<7, the uncomplexed Am^{3+} ion is the dominant species. At pH 7–8.5, and at pH>8.5 the complexes $Am(CO_3)^+$ and $Am(CO_3)_2^-$ and $Am(CO_3)_2^-$ and $Am(CO_3)_3^{3-}$ predominate, respectively. No indication of solution complexes containing either OH^- or HCO_3^- ligands was observed. The following constants, at zero ionic strength, were obtained by applying the ion interaction theory to experimental data (β_n are overall stability constants): $Am(OH)CO_{3(s,cryst)} \leftrightarrows Am^{3+} + OH^- + CO_3^{2-}$, $K_{sp}^0 = 10^{-22.5}$ $Am^{3+} + CO_3^{2-} \leftrightarrows Am(CO_3)^+$, $\beta_1 = 10^{7.6}$ $Am^{3+} + 2CO_3^{2-} \leftrightarrows Am(CO_3)_2^-$, $\beta_2 = 10^{12.3}$ $Am^{3+} + 3CO_3^{2-} \leftrightarrows Am(CO_3)_3^{3-}$, $\beta_3 = 10^{15.2}$

Auxiliary Information

Method/Apparatus/Procedure:

The solubility of $Am(OH)CO_3$ was measured by isothermal method in two series of experiments. In the first method (a) the solutions were contacted with crystalline $Am(OH)CO_3$. 8 mg of $Am(OH)CO_3$ were placed in a polypropylene cell with 50 mL aqueous phase. Samples were taken after different time intervals, centrifuged, and ^{243}Am in the saturated solutions was determined by liquid scintillation counting. The counting was performed periodically for 3–4 weeks to allow secular equilibrium with ^{239}Np to be established. In the 30 days experiment, additional aliquots were taken and filtered through 0.2 and 0.015 μm filters after centrifugation. In the second method (b) the saturated solutions from the above procedure were made 0.1 mol dm^{-3} $HClO_4$ to dissolve the solid $Am(OH)CO_3$, the volume was made up to 50 mL with water, and $NaHCO_3$ or NaOH solutions to produce again the same composition as in method (a), and the remainder of the procedure was adopted as described for method (a). All measurements were conducted at fixed pH which was controlled with a potentiostat. The pH of the measurements was selected so as to be within a well buffered region, and at the same time within the pH interval necessary to avoid hydrolysis of Am(III) (occurs at pH>6.5), and dissolution of all $Am(OH)CO_3$ (occurs at pH<5.0). The concentration of HCO_3^- ion was fixed by contacting the solutions with an atmosphere of 0.792% CO_2+99.2% Ar. The solid phases were identified by x-ray diffraction patterns which were found to be nearly identical with those of $Nd(OH)CO_3$.[1]

Source and Purity of Materials:

$Am(OH)CO_3$ was prepared by hydrolysis of Am(III) trichloroacetate according to the procedure for lanthanides.[2]

Estimated Error: (authors)

Temperature: precision ±1 K.
pH: precision ±0.03 units.
Solubility: the error (see the table) is the deviation from the average of two aliquots taken at each sampling period.
HCO_3^- ion concentration: $\pm(0.17-0.19)\times 10^{-4}$ mol dm^{-3}.

References:

[1] H. Dexpert and P. Caro, Mat. Res. Bull. **9**, 1577 (1974).
[2] I. Salutsky and L. L. Quill, J. Am. Chem. Soc. **72**, 3306 (1950).

Auxiliary Information

Method/Apparatus/Procedure:

Two series of measurements were conducted. In one [method (a)], a fixed partial pressure of CO_2 o.d. 0.001 atm in ultrapure Ar gas was adjusted in a glove box. All HCO_3 solutions were initially equilibrated with the chamber gas for 2–3 days before these solutions were added to the precipitated material in centrifuge tubes. The tubes were kept slightly capped to allow exchange of CO_2 with the glove box atmosphere, and were shaken on an orbital shaker. In the second series of experiments [method (b)], the precipitated $Am(OH)CO_3$ obtained in method (a) was washed with de-ionized water, resuspended in either 0.003–0.1 mol dm^{-3} Na_2CO_3 (initial pH 10.6–11.3), or in 0.07 mol dm^{-3} Na_2CO_3 whose pH was adjusted with CO_2-free NaOH to reach pH 11.7–13, and shaken. Each of these two procedures were run with $Am(OH)CO_3$ prepared by procedures (A) and (B) (see below). Suspensions of $Am(OH)CO_3$ were equilibrated for prolonged periods of time, and samples from the saturated solutions were taken after intervals ranging from 2 to 78 days. The pH of the suspensions was measured with a combination glass electrode Orion/Ross, calibrated with pH buffers. The samples were centrifuged at 2000 g for 7–10 min, aliquots of the supernatant were filtered through Amicon type F-25 Centriflo membrane cones ($\sim$0.0018 μm pore size). Filtrates were acidified, and before Am analysis stored for $\sim$30 days to allow the ^{239}Np (produced from the $^{243}Am(OH)CO_3$ in the original suspensions) to decay to near secular equilibrium with ^{243}Am present in each vial. Samples were counted using high-purity Ge planar detectors. Total chemical analysis of the saturated solutions was performed by the inductively coupled plasma (ICP) method. Total inorganic carbon was determined by using a Coulometrics Inc. Model 5020 total carbon analyzer. Solid phases were characterized by x-ray diffraction.

Source and Purity of Materials:

$Am(OH)CO_3$ was prepared by two methods: (A) by precipitation by adding 0.1 mL ($\sim$ 4.5 mg Am) of ^{243}Am stock solution to 30 mL 0.01 mol dm^{-3} $NaHCO_3$ at pH 7 in a polypropylene centrifuge cone; the precipitate was washed twice with 20 mL 0.0004 mol dm^{-3} $NaHCO_3$ at pH 8; (B) by homogeneous precipitation of Am(III) trichloroacetate.[1] Solutions with $Am(OH)CO_3$ precipitate were heated for about 6 h at 50 °C, allowed to cool overnight, and then washed with 0.0004 mol dm^{-3} $NaHCO_3$ at pH 8.

References:

[1] R. G. Charles, J. Inorg. Nucl Chem. **27**, 1489 (1965).

8.2. Salts of Carbonatodioxoamericiate(V)(-1)

Components:

(1) Diamericium tris(carbonate); $Am_2(CO_3)_3$; [ ]; or
(2) Sodium carbonatodioxoamericiate(V); $Na(AmO_2)CO_3$; [ ]
(3) Carbonate ion; CO_3^{2-}; [3812-32-6]
(4) Sodium chloride; NaCl; [7647-14-5]
(5) Water; H_2O; [7732-18-5]

Original Measurements:

E. Giffaut and P. Vitorge, Mater. Res. Soc. Symp. Proc. **294**, 747–51 (1993).

Variables:

T/K: 294
p_2 /%: 100 (partial pressure)
c_3 /mol dm^{-3}: 0.1; 4

Prepared by:

J. Hála

Experimental Data

Solubility products of $Am_2(CO_3)_3$ and $Na(AmO_2)CO_3$ at 21 °C in NaCl solutions

NaCl (c_3 /mol dm^{-3})	$-\log K_{sp(1)}$ [a,c]	$-\log K_{sp(2)}$ [b,c]
0.1	34.2±0.3	—
4	30.4±0.4	10.5±0.3

[a] $K_{sp}=[Am^{3+}]^2[CO_3^{2-}]^3$.
[b] $K_{sp}=[Na^+][AmO_2^+][CO_3^{2-}]$.
[c] Concentrations in mol dm^{-3}.

Additional information:
In 4 mol dm^{-3} NaCl the Am solubility was found to be higher by 1–3 orders of magnitude than that in 0.1 mol dm^{-3} NaCl, and close to Np(V) solubility under similar conditions.[1,2] In the presence of metallic iron as a reducing agent, the Am solubility decreased within 1 week to that 0.1 mol dm^{-3} NaCl. This behavior was explained by the authors as being due to radiolytic oxidation of Am(III) to Am(V).[3] At pH<6.5, $NaAmO_2CO_3$ was the equilibrium solid phase at equilibrium CO_3^{2-} ion concentrations $>10^{-5}$ mol dm^{-3}. Solubility data were reported in graphical form only, and show that minimum Am(III) and Am(V) solubility occurs at approximately 10^{-5}–10^{-4} mol dm^{-3} carbonate ion concentration. Also reported were stability constants of of $Am(III)(CO_3)^{3-2n}$ ($n=1-3$) complexes in 0.1 and 4 mol dm^{-3} NaCl, and $AmO_2(CO_3)^{1-2n}$ ($n=1$ and 2) complexes in 4 mol dm^{-3} NaCl.

Auxiliary Information

Method/Apparatus/Procedure:

Solubility measurements were performed as pH titration procedure with $Am_2(CO_3)_3$ as the starting solid in carbonate buffer solutions. The suspension was stirred at the desired pH for 13 weeks. After equilibration, samples of the saturated solutions were filtered, the pH was measured with a combined glass electrode that was calibrated with $NaHCO_3$ /Na_2CO_3 /NaCl or HCl/NaCl solutions, and the Am solubility was determined by liquid scintillation counting.

Source and Purity of Materials:

$Am_2(CO_3)_3$ was prepared by equilibrating an americium solution in 0.5 mol dm^{-3} carbonate with bubbling CO_2 gas through the solution for a period of 3 weeks.

Estimated Error:

No information reported.

References:

[1] L. Maya, Inorg. Chem. **22**, 2093 (1983).
[2] I. Grenthe, P. Robouch, and P. Vitorge, J. Less-Common Metals **122**, 225 (1986).
[3] S. Magirius, W. T. Carnall and J. I. Kim, Radiochim. Acta **38**, 29 (1985).

Components:

(1) Rubidium carbonatodioxoameriiciate(V); $RbAmO_2CO_3$; [ ]
(2) Rubidium carbonate; Rb_2CO_3; [ ]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

J. P. Nigon, R. A. Pennemann, E. Staritzki, T. K. Keenan, and L. B. Asprey, J. Phys. Chem. **58**, 403–4 (1954).

Variables:

100 w_2 /mass %: 5.64; 6.73

Prepared by:

J. Hála

Experimental Data

Solubility of $RbAmO_2CO_3$ in Rb_2CO_3 solutions[a]

Rb_2CO_3 (100 w_2 /mass %)	Rb_2CO_3 (m_2 /mol kg^{-1})[b]	$(AmO_2)_2CO_3$ (100 w/mass %)	$RbAmO_2CO_3$ (100 w_1 /mass %)[b]	$RbAmO_2CO_3$ (m_1 /mol kg^{-1})[b]
5.64	0.259	0.0043	0.0059	0.000149
6.73	0.314	0.376	0.518	0.0133

[a] Composition of the equilibrium solid phase was reported to be $RbAmO_2CO_3$, [ ]. The authors stated, however, that a hydrate of the salt could not be ruled out. Temperature of the measurements was not specified.

[b] Calculated by compiler. For americium, $A_r = 243.06(^{243}Am)$ was used.

Auxiliary Information

Method/Apparatus/Procedure:

Very dilute solutions of Am(III) in 1 mol dm^{-3} Rb_2CO_3 were oxidized by ozone to Am(V). The resulting precipitate was centrifuged and then slurried in 0.1 mol dm^{-3} Rb_2CO_3. Weighed samples of the supernatant liquid were withdrawn for analysis. Americium was determined radiometrically, CO_2 was determined by evolution into $Ba(OH)_2$ solution according to Ref. 1 using a closed system with a peristaltic pump to circulate the gas and ensure complete absorption of CO_2. Composition of the solid phases was determined by Schreinemakers' method. Temperature and equilibration time was not reported.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Solubility: precision ±1% (authors).

References:

[1] W. C. Schroeder and E. P. Partridge, Ind. Eng. Chem., Anal. Ed. **4**, 262 (1935).

8.3. Americium(III) Formate

Components:

(1) Americium(III) tris(formate); $Am(CHO_2)_3$; [18274-71-0]
(2) Formic acid; CH_2O_2; [64-18-6]
(3) Perchloric acid; $HClO_4$; [7601-90-3]
(4) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(5) Water; H_2O; [7732-18-5]

Original Measurements:

A. V. Ananev and N. N. Krot, Radiokhimiya **26**, 755–8 (1984).

Variables:

T/K: 298
c_2 /mol dm^{-3}: 0.2
c_3 /mol dm^{-3}: 0–0.1
c_4 /mol dm^{-3}: 1.9–2.0

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $Am(CHO_2)_3$ in CH_2O_2 /$HClO_4$ /$NaClO_4$ solutions

Solubility at 25 °C of $Am(CHO_2)_3$ was measured in 0.2 mol dm^{-3} solutions of formic acid containing 0–0.1 mol dm^{-3} $HClO_4$, and $NaClO_4$ to maintain ionic strength of 2.0 mol dm^{-3}. The results were reported in graphical form. From the solubility data the solubility product of $Am(CHO_2)_3$ was calculated to be 1.05×10^{-9} mol^4 dm^{-12} at ionic strength of 2.0 mol dm^{-3}. The calculations were performed using the dissociation constant of formic of $K_a = 2.7\times10^{-4}$ mol dm^{-3} at ionic strength of 2.0 mol dm^{-3}, and taking into account the existence in the saturated solutions of the $Am(CHO_2)^{2+}$ and $Am(CHO_2)_2^+$ complexes. Their stability constants were also calculated. The equilibrium solid phase was $Am(CHO_2)_3$, [18274-71-0]. Also reported, in graphical form, was the solubility at 25 °C of $Am(CHO_2)_3$ in sodium formate-$NaClO_4$ solutions. The solubility of $Am(CHO_2)_3$ in water was reported to be $c_1 = 7.32\times10^{-3}$ mol dm^{-3}. It was not stated explicitly if the latter value was obtained by calculation or experimentally.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess $Am(CHO_2)_3$ was equilibrated with solutions of the desired concentration for 10 h in thermostated flasks. Before measurements, the solutions were freed from air by passing through them a stream of argon gas. In the filtered saturated solutions, pH was determined potentiometrically, and the concentration of Am(III) spectrophotometrically in ~0.6 mol dm^{-3} $HClO_4$ at 503 nm. The pH meter used was callibrated against 2.0 mol dm^{-3}$NaClO_4$. Solid phases were identified by x-ray diffraction.

Source and Purity of Materials:

$^{243}Am(CHO_2)_3$ was prepared from freshly precipitated $Am(OH)_3$ and concentrated formic acid according to Refs. 1, 2. The solid product was centrifuged, washed with 10 mol dm^{-3} formic acid and 50% ethanol, and kept over KOH. All other chemicals were reagent grade products. Doubly distilled water was used.

Estimated Error:

Temperature precision ±0.5 K (authors)
Solubility: error not reported.

References:

[1] L. R. Crisler, J. Inorg. Nucl. Chem. **34**, 3263 (1972).
[2] F. Weigel and N. terMeer, Inorg. Nucl. Chem. Lett. **3**, 403 (1967).

8.4. Americium(III) Oxalate

Components:

(1) Diamericium(III) tris(oxalate); $Am_2(C_2O_4)_3$; [65113-20-4]
(2) Perchloric acid; $HClO_4$; [7601-90-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. Lebedev, S. V. Pirozhkov, V. M. Razbitnoi, and G. N. Yakovlev, Radiokhimiya **2**, 351–6 (1960).

Variables:

T/K: 298
c_2 /mol dm^{-3}: 0.05–0.286

Prepared by:

J. D. Navratil and J. Hála

Experimental Data

Solubility at 25 °C of $Am_2(C_2O_4)_3$ in $HClO_4$ solutions[a]

$HClO_4$ (c_2 /mol dm^{-3})	Am (10^4 mol dm^{-3})	$Am_2(C_2O_4)_3$ (10^4 c_1 /mol dm^{-3})[b]	K_{sp}[c] (10^{31} mol^5 dm^{-15})
0.050	0.557	0.279	[d]
0.100	1.16	0.580	[d]
0.192	4.40	2.20	2.28
0.286	7.69	3.85	2.31

[a] The nature of the equilibrium solid phases was not investigated. Based on the authors' chemical analysis of americium oxalate precipitate obtained in 0.5 mol dm^{-3} HNO_3, the solid phase could be taken to be $Am_2(C_2O_4)_3\cdot 9H_2O$, [ ], or, according to Ref. 5, $Am_2(C_2O_4)_3\cdot 7H_2O$.
[b] Calculated by compiler.
[c] Calculated by authors as $K_{sp}=\gamma_3^2 a_{ox}^3[Am^{3+}]^2$, where γ_3 is the activity coefficient of the Am^{3+} ion and a_{ox} is the activity of the $C_2O_4^{2-}$ ion calculated as $a_{ox}=K_{a1}K_{a2}c_{ox}/\{a_H^2+K_{a1}a_H/\gamma_1+K_{a1}K_{a2}/\gamma_2\}$.[1] Here c_{ox} is the total concentration of oxalate in solution (obtained as $c_{ox}=3/2[Am^{3+}]$), a_H is the activity of H^+ ion, K_{a1} and K_{a2} are the dissociation constants of oxalic acid, $K_{a1}=5.36\times 10^{-2}$ mol dm^{-3},[2] and $K_{a2}=5.42\times 10^{-5}$ mol dm^{-3},[3] both at 25 °C, and γ_1 and γ_2 are the activity coefficients of the $HC_2O_4^-$ and $C_2O_4^{2-}$ ions, respectively. Numerical values of the activity coefficients of ions in oxalate solutions were taken from Ref. 4.
[d] Not reported.

Additional information:
The authors also reported on their unsuccessful attempts to determine the solubility of $Am_2(C_2O_4)_3$ in water. In repeated measurements, the solubility fluctuated between 10^{-5} and 10^{-4} mol dm^{-3}, Am(III) and the authors ascribed this to the hydrolysis of Am^{3+} ion.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess $Am_2(C_2O_4)_3\cdot 9H_2O$ was periodically stirred with $HClO_4$ solutions in thermostated test tubes for 3–5 h, the time required to reach equilibrium. The concentration of americium in the saturated solutions was determined radiometrically. Details of the method were not specified.

Source and Purity of Materials:

Am(III) oxalate was prepared by action of a saturated solution of oxalic acid or sodium oxalate on a 0.5 mol dm^{-3} HNO_3 solution containing 10–15 g dm^{-3} of ^{241}Am. The precipitate was analyzed gravimetrically by ignition to AmO_2. Precipitates obtained at 20–90 °C had the composition of $Am_2(C_2O_4)_3\cdot 9H_2O$. Source and purity of ^{241}Am and other chemicals used not specified.

Estimated Error:

Temperature: ± 0.1 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] C. E. Crouthamel and D. S. Martin, J. Am. Chem. Soc. **72**, 1382 (1950).
[2] L. S. Darken, J. Am. Chem. Soc. **63**, 1007 (1941).
[3] G. D. Pinching and R. G. Bates, J. Res. Nat. Bur. Std. **40**, 405 (1948).
[4] C. E. Crouthamel and D. S. Martin, J. Am. Chem. Soc. **73**, 569 (1951).
[5] T. L. Markin, J. Inorg. Nucl. Chem. **7**, 290 (1958).

Components:

(1) Diamericium(III) tris(oxalate); $Am_2(C_2O_4)_3$; [65113-20-4]
(2) Potassium oxalate; $C_2O_4K_2$; [583-52-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. Lebedev, S. V. Pirozhkov, V. M. Razbitnoi, and G. N. Yakovlev, Radiokhimiya **2**, 351–6 (1960).

Variables:

T/K: 298
c_2 /mol dm^{-3}: 0.1–1.45

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $Am_2(C_2O_4)_3$ in $C_2O_4K_2$ solutions at constant ionic strength of 4.35 mol dm^{-3} [a]

$C_2O_4K_2$ (c_2 /mol dm^{-3})	Am (10^4 mol dm^{-3})	$Am_2(C_2O_4)_3$ (10^4 c_1 /mol dm^{-3})[b]
0.100	1.42	0.71
0.200	4.64	2.32
0.351	9.32	4.66
0.600	32.8	16.4
1.00	70.5	35.3
1.45	8.86	44.3

[a] The nature of the equilibrium solid phases was not investigated. The salt used to maintain constant ionic strength was not specified.
[b] Calculated by compiler.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess $Am_2(C_2O_4)_3\cdot 9H_2O$ was periodically stirred with $C_2O_4K_2$ solutions in thermostated test tubes for 3–5 h, the time required to reach equilibrium. The concentration of americium in the saturated solutions was determined radiometrically, the total oxalate concentration was determined by titration with standard $KMnO_4$ solution.

Source and Purity of Materials:

Am(III) oxalate was prepared by action of a saturated solution of oxalic acid or sodium oxalate on a 0.5 mol dm^{-3} HNO_3 solution containing 10–15 g dm^{-3} of ^{241}Am. The precipitate was analyzed gravimetrically by ignition to AmO_2. Precipitates obtained at 20–90 °C had the composition of $Am_2(C_2O_4)_3\cdot 9H_2O$. Source and purity of ^{241}Am and other chemicals used not specified.

Estimated Error:

Temperature: ± 0.1 K (authors).
Solubility: insufficient data given to allow for error estimate.

Components:

(1) Diamericium(III) tris(oxalate); $Am_2(C_2O_4)_3$; [65113-20-4]
(2) Potassium oxalate; $C_2O_4K_2$; [583-52-8]
(3) Perchloric acid; $HClO_4$; [7601-90-3]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

A. Lebedev, S. V. Pirozhkov, V. M. Razbitnoi and G. N. Yakovlev, Radiokhimiya **2**, 351–6 (1960).

Variables:

T/K: 298
c_2 /mol dm^{-3}: 0.05–0.238
activity of H$^+$ ion/mol dm^{-3}: 0.000 22–0.359

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $Am_2(C_2O_4)_3$ in $C_2O_4K_2-HClO_4$ solutions[a]

$C_2O_4^{2-}$ (mol dm^{-3})	H^{+b} (mol dm^{-3})	$-\log a(C_2\ O_4^{2-})^c$ (mol dm^{-3})	Am(III)^d (10^5 mol dm^{-3})
0.238	—	1.301	24.6
0.214	—	1.347	21.8
0.130	—	1.495	8.04
0.0919	—	1.602	3.99
0.0554	—	1.745	2.57
0.140	0.000 224	1.818	3.79
0.115	0.000 316	1.983	3.15
0.100	0.000 447	2.221	1.30
0.090	0.000 852	2.417	1.41
0.080	0.001 55	2.695	0.892
0.120	0.003 16	2.857	0.544
0.100	0.005 13	3.143	0.523
0.100	0.009 14	3.411	0.341
0.100	0.0123	3.558	0.400
0.100	0.0199	3.801	0.456
0.100	0.0289	4.004	0.483
0.100	0.0489	4.313	0.407
0.100	0.0562	4.304	0.290
0.100	0.0832	4.652	0.393
0.100	0.115	4.873	0.425
0.100	0.138	5.004	0.537
0.100	0.196	5.257	0.693
0.100	0.285	5.547	0.839
0.100	0.382	5.780	1.44
0.050	0.359	6.031	1.76
0.000 66	0.155	7.261	44.0

[a] The nature of the equilibrium solid phases was not investigated. Based on the authors' analysis of Am(III) oxalate obtained in 0.5 mol dm^{-3} HNO_3 solutions the compiler assumes the solid phase was $Am_2(C_2O_4)_3\cdot 9H_2O$, [ ].

[b] Activity of the H$^+$ ion.

[c] Activity of the $C_2O_4^{2-}$ ion calculated as $a_{ox}=K_{a1}K_{a2}c_{ox}/\{a_H^2+K_{a1}a_H/\gamma_1+K_{a1}K_{a2}/\gamma_2\}$.[1] Here c_{ox} is the total concentration of oxalate in solution, a_H is the activity of H$^+$ ion, K_{a1} and K_{a2} are the dissociation constants of oxalic acid, $K_{a1}=5.36\times 10^{-2}$ mol dm^{-3},[2] and $K_{a2}=5.42\times 10^{-5}$ mol dm^{-3},[3] both at 25 °C, and γ_1 and γ_2 are the activity coefficients of the $HC_2O_4^{2-}$ ions, respectively, taken from Crouthamel and Martin.[4]

[d] Concentration of Am(III) in the saturated solutions.

Additional information:

From the dependence of the solubility of Am(III) oxalate on the oxalate ion activity the consecutive instability constants, at zero ionic strength, of the $Am(C_2O_4)^+$, $Am(C_2O_4)_2^-$, and $Am(C_2O_4)_3^{3-}$ complexes were obtained as $K_1=(5.0\pm 0.3)\times 10^{-8}$, $K_2=(6.9\pm 0.7)\times 10^{-5}$, and $K_3=(1.6\pm 0.2)\times 10^{-1}$, all in dm^3 mol^{-1}, respectively.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess $Am_2(C_2O_4)_3\cdot 9H_2O$ was periodically stirred with solutions of the desired composition in thermostated test tubes for 3–5 h, the time required to reach equilibrium. The concentration of americium in the saturated solutions was determined radiometrically, the total oxalate concentration was determined by titration with standard $KMnO_4$ solution. The pH of the saturated solutions was determined with a quinhydrone electrode.

Source and Purity of Materials:

Am(III) oxalate was prepared by action of a saturated solution of oxalic acid or sodium oxalate on a 0.5 mol dm^{-3} HNO_3 solution containing 10–15 g dm^{-3} of ^{241}Am. The precipitate was analyzed gravimetrically by ignition to AmO_2. Precipitates obtained at 20–90 °C had the composition of $Am_2(C_2O_4)_3\cdot 9H_2O$. Source and purity of ^{241}Am and other chemicals used not specified.

Estimated Error:

Temperature: ±0.1 K (authors).
Solubility: insufficient data given to allow for error estimate.

References:

[1] C. E. Crouthamel and D. S. Martin, J. Am. Chem. Soc. **72**, 1382 (1950).
[2] L. S. Darken, J. Am. Chem. Soc. **63**, 1007 (1941).
[3] G. D. Pinching and R. G. Bates, J. Res. Nat. Bur. Std. **40**, 405 (1948).
[4] C. E. Crouthamel and D. S. Martin, J. Am. Chem. Soc. **73**, 569 (1951).

Components:

(1) Diamericium(III) tris(oxalate); $Am_2(C_2O_4)_3$; [65113-20-4]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Nitric acid; HNO_3; [7697-37-2]
(4) Water; H_2O; [7732-18-5]

Evaluator:

J. Hála, Department of Inorganic Chemistry, Masaryk University, 611 37 Brno, Czech Republic, May 2000

Critical Evaluation:

The solubility of $Am_2(C_2O_4)_3$ in oxalic acid/HNO_3 solutions has been studied in two references. Zakolupin and Korablin[1] reported numerical data for the solubility of $Am_2(C_2O_4)_3$ as a function of oxalic acid concentration at various concentrations of HNO_3 and temperatures while Burney and Porter[2] reported their data at one temperature (296.1 K) in graphical form only (see the respective compilations). Because of this, a precise comparison between the two sets of data is not possible. However, an approximate read-out of the solubility data for 0.05 and 0.1 mol dm^{-3} HNO_3 from the graph in Burney and Porter[2] reveals that these data fall reasonably well between those in Ref. 1 obtained at 287.1 and 303.1 K. For this reason the data of Zakolupin and Korablin[1] can be recommended as tentative values for $Am_2(C_2O_4)_3$ solubility in oxalic acid/HNO_3 solutions.

References:

[1] S. A. Zakolupin and E. V. Korablin, Radiokhimiya **19**, 698 (1977).
[2] G. A. Burney and J. A. Porter, Inorg. Nucl. Chem. Lett **3**, 79 (1967).

Components:

(1) Diamericium(III) tris(oxalate); $Am_2(C_2O_4)_3$; [13278-81-4]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Nitric acid; HNO_3; [7697-37-2]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

S. A. Zakolupin and E. V. Korablin, Radiokhimiya, **19**, 698–701 (1977).

Variables:

T/K: 287–333
c_2 /mol dm^{-3}; 0.01–0.4
c_3 /mol dm^{-3}: 0–1.0

Prepared by:

J. D. Navratil and J. Hála

Experimental Data

Solubility of $Am_2(C_2O_4)_3$ in $C_2H_2O_4$–HNO_3 solutions as a function of temperature[a]

Temperature (°C)	$C_2H_2O_4$ (c_2 /mol dm^{-3})	HNO_3 (c_3 /mol dm^{-3})					
		0	0.1	0.3	0.5	0.7	1.0
Solubility of $Am_2(C_2O_4)_3$ reported as mg Am(III)/dm^3:							
14	0	36.4	137	283	592	718	992
	0.01	0.19	0.66	5.6	29	83	232
	0.05	0.16	0.5	1.13	3.48	10.5	26.4
	0.1	0.16	0.38	0.7	1.7	4.2	13.5
	0.2	0.21	0.4	0.58	1.36	2.6	6.1
	0.3	0.30	0.38	0.68	1.3	2.0	4.1
	0.4	0.40	0.44	0.78	1.26	1.84	3.54
30	0.01	9.1	17.6	73.5	201.6	414	1077
	0.05	5.2	12.6	26.1	58.4	113.6	225
	0.1	3.7	6.4	10.4	16.4	37.8	57.6
	0.2	2.6	3.3	4.3	6.1	11.8	19.6
	0.3	2.1	3.2	3.7	5.4	9.2	14.2
	0.4	3.0	3.3	4.0	5.9	9.5	12.6
45	0.01	19.2	45.3	280	537	1195	1840
	0.05	12.0	25.9	46.1	99.2	323	702
	0.1	5.0	8.9	16.2	38.3	115.6	232
	0.2	2.0	3.42	8.1	18	39.6	87.3
	0.3	2.3	3.65	8.73	18.45	33.3	75.5
	0.4	5.5	6.9	14.13	235	34.5	69.5
60	0.01	78	164	480	1248	2752	—
	0.05	25	55	76.8	149.6	672	—
Solubility of $Am_2(C_2O_4)_3$ as c_1 /mol dm^{-3} (compilers):							
14	0	7.55×10^{-5}	2.84×10^{-4}	5.87×10^{-4}	1.23×10^{-3}	1.49×10^{-3}	2.06×10^{-3}
	0.01	3.94×10^{-7}	1.37×10^{-6}	1.16×10^{-5}	6.02×10^{-5}	1.72×10^{-4}	4.81×10^{-4}
	0.05	3.32×10^{-7}	1.04×10^{-6}	2.34×10^{-6}	7.22×10^{-6}	2.18×10^{-5}	5.48×10^{-5}
	0.1	3.32×10^{-7}	7.88×10^{-7}	1.45×10^{-6}	3.53×10^{-6}	8.71×10^{-6}	2.80×10^{-5}
	0.2	4.36×10^{-7}	8.30×10^{-7}	1.20×10^{-6}	2.82×10^{-6}	5.39×10^{-6}	1.26×10^{-5}
	0.3	6.22×10^{-7}	7.88×10^{-7}	1.41×10^{-6}	2.70×10^{-6}	4.15×10^{-6}	8.51×10^{-6}
	0.4	8.30×10^{-7}	9.13×10^{-7}	1.62×10^{-6}	2.61×10^{-6}	3.82×10^{-6}	7.34×10^{-6}
30	0.01	1.89×10^{-5}	3.65×10^{-5}	1.52×10^{-4}	4.81×10^{-4}	8.59×10^{-4}	2.23×10^{-3}
	0.05	1.08×10^{-5}	2.61×10^{-5}	5.41×10^{-5}	1.21×10^{-4}	2.36×10^{-4}	4.67×10^{-4}
	0.1	7.68×10^{-6}	1.33×10^{-5}	2.16×10^{-5}	3.40×10^{-5}	2.84×10^{-5}	1.20×10^{-4}
	0.2	5.39×10^{-6}	6.85×10^{-6}	8.92×10^{-6}	1.26×10^{-5}	2.45×10^{-5}	4.07×10^{-5}
	0.3	4.36×10^{-6}	6.64×10^{-6}	7.68×10^{-6}	1.12×10^{-5}	1.91×10^{-5}	2.95×10^{-5}
	0.4	6.22×10^{-6}	6.85×10^{-6}	8.30×10^{-6}	1.22×10^{-5}	1.97×10^{-5}	2.61×10^{-5}
45	0.01	3.98×10^{-5}	9.40×10^{-5}	5.81×10^{-4}	1.11×10^{-3}	2.48×10^{-3}	3.82×10^{-3}

	0.05	2.49×10^{-5}	5.37×10^{-5}	9.56×10^{-5}	2.06×10^{-4}	6.70×10^{-4}	1.46×10^{-3}
	0.1	1.04×10^{-5}	1.85×10^{-5}	3.36×10^{-5}	7.95×10^{-5}	2.40×10^{-4}	4.81×10^{-4}
	0.2	4.15×10^{-6}	7.10×10^{-6}	1.68×10^{-5}	3.73×10^{-5}	8.22×10^{-5}	1.81×10^{-4}
	0.3	4.77×10^{-6}	7.57×10^{-6}	1.81×10^{-5}	3.83×10^{-5}	6.91×10^{-5}	1.57×10^{-4}
	0.4	1.44×10^{-5}	1.43×10^{-5}	2.93×10^{-5}	4.88×10^{-5}	7.16×10^{-5}	1.44×10^{-4}
60	0.01	1.62×10^{-4}	3.40×10^{-4}	9.96×10^{-4}	2.60×10^{-3}	5.71×10^{-3}	—
	0.05	5.19×10^{-5}	1.14×10^{-4}	1.59×10^{-4}	3.10×10^{-4}	1.39×10^{-3}	—

HNO_3 (c_3 /mol dm^{-3})	$C_2H_2O_4$ (c_2 /mol dm^{-3})	Am[b] (mol dm^{-3})	Ionic strength (mol dm^{-3})	a_{ox}[c] (mol dm^{-3})	a_{H^+}[d] (mol dm^{-3})	γ_3[e]	K^0_{sp} (mol^5 dm^{-15})
Solubility product of $Am_2(C_2O_4)_3$ at 14 °C calculated by the authors:							
0	0.05	6.7×10^{-7}	0.15	8.84×10^{-6}	0.10	0.099	3.0×10^{-30}
0.1	0.00085	5.7×10^{-4}	0.104	1.52×10^{-7}	0.10	0.123	1.76×10^{-29}
0.1	0.01	2.74×10^{-6}	0.13	1.32×10^{-6}	0.12	0.107	2.0×10^{-31}
0.1	0.05	2.07×10^{-6}	0.25	2.75×10^{-6}	0.20	0.07	4.3×10^{-31}
0.1	0.10	1.57×10^{-6}	0.4	2.66×10^{-6}	0.3	0.053	1.36×10^{-31}
0.3	0.00175	1.17×10^{-3}	0.30	4.7×10^{-8}	0.3	0.061	5.35×10^{-31}

[a] The nature of the equilibrium solid phases was not investigated. Based on the authors' analysis of Am(III) oxalate obtained in 0.5 mol dm^{-3} HNO_3 at ≤30 °C the compiler assumes the solid phase was $Am_2(C_2O_4)_3\cdot 9H_2O$, [ ]. Markin[1] reported the existence of $Am_2(C_2O_4)_3\cdot 7H_2O$.

[b] Concentration of Am(III) in the saturated solutions.

[c] Activity of the $C_2O_4^{2-}$ ion calculated according to Ref. 2 as $a_{ox}=K_{a1}K_{a2}c_{ox}/\{a_H^2+K_{a1}a_H/\gamma_1+K_{a1}K_{a2}/\gamma_2\}$. Here c_{ox} is the total concentration of oxalate in solution, a_H is the activity of H^+ ion, K_{a1} and K_{a2} are the dissociation constants of oxalic acid, $K_{a1}=5.37\times10^{-2}$ mol dm^{-3} and $K_{a2}=5.6\times10^{-5}$ mol dm^{-3}, both at 14 °C, and γ_1 and γ_2 are the activity coefficients of the $HC_2O_4^{2-}$ and $C_2O_4^{2-}$ ions, respectively, taken from Refs. 3,4.

[d] Activity of H^+ ions.

[e] Activity of the Am^{3+} ion. Source not reported.

[f] Obtained as $K^o_{sp}=\gamma_3^2[Am^{3+}]^2a^3_{ox}$. The authors explained the scatter of K^o_{sp} values as being due to variations in ionic strength.

Additional information:

At HNO_3 concentrations of 0.1 and 0.3 mol dm^{-3}, the solubility of Am(III) oxalate as a function of oxalic acid concentration showed a minimum. With reference to Ref. 2, the authors ascribed this to the formation of Am(III) oxalatocomplexes, the predominating species being Am^{3+} at low oxalate concentrations, $Am(C_2O_4)^+$ and $Am(C_2O_4)_2^-$ in the range of the minimum, and $Am(C_2O_4)_3^{3-}$ at high oxalate concentrations.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. The work was conducted with the ^{241}Am isotope. Excess of freshly precipitated Am(III) oxalate was equilibrated with solutions of required composition with blade mixer in a thermostat for 1 h. Experiments established 30 min as the equilibrium time. After 20 min standing, a sample of the saturated solution was collected, centrifuged, and americium concentration was determined by γ counting. Details of γ counting and pH determination not specified.

Source and Purity of Materials:

Nothing specified.

Estimated Error:

Temperature: ±1 K (authors)

Solubility: insufficient data given to allow for error estimate.

References:

[1] T. J. Markin, J. Inorg. Nucl. Chem. **7**, 290 (1958).

[2] I. A. Lebedev, S. V. Pirozhkov, V. M. Razbitnoi, and G. N. Yakovlev, Radiokhimiya **2**, 351 (1960).

[3] C. E. Crouthamel and D. S. Martin, J. Am. Chem. Soc. **72**, 1382 (1950).

[4] C. E. Crouthamel and D. S. Martin, J. Am. Chem. Soc. **73**, 569 (1951).

Components:

(1) Diamericium(III) tris(oxalate); $Am_2(C_2O_4)_3$; [65113-20-4]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Nitric acid; HNO_3; [7697-37-2]
(4) Water; H_2O; [7732-18-5]

Original Measurements:

G. A. Burney and J. A. Porter, Inorg. Nucl. Chem. Lett. **3**, 79–85 (1967).

Variables:

T/K: 296
c_2 /mol dm^{-3}: 0.02–0.5
c_3 /mol dm^{-3}: 0.1–4.0

Prepared by:

J. Hála

Experimental Data

Solubility at 23 °C of $Am_2(C_2O_4)_3$ in HNO_3–$C_2H_2O_4$ solutions

The solubility of $Am_2(C_2O_4)_3$ at 23 °C in HNO_3–$C_2H_2O_4$ solutions were presented in graphical form (see Fig. 24). The nature of the equilibrium solid phases was not investigated. Based on the work of Markin[1] the authors assumed the equilibrium solid phase be the heptahydrate, $Am_2(C_2O_4)_3\cdot 7H_2O$, [ ].

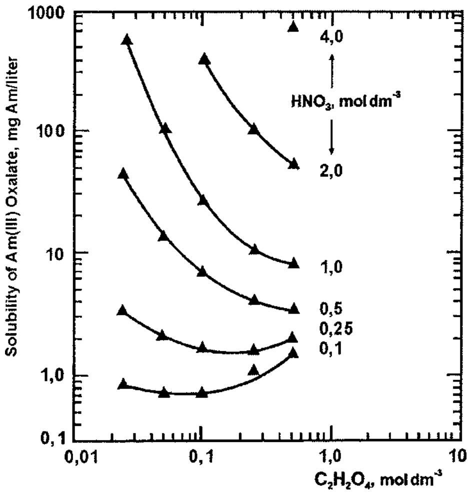

FIG. 24. Diamericium (III)–tris(oxalate)–oxalic acid–nitric acid–water system.

Components:

(1) Diamericium(III) tris(oxalate); $Am_2(C_2O_4)_3$; [65113-20-4]
(2) Oxalic acid; $C_2H_2O_4$; [144-62-7]
(3) Potassium oxalate; $C_2O_4K_2$; [583-52-8]
(4) Nitric acid; HNO_3; [7697-37-2]
(5) Water; H_2O; [7732-18-5]

Original Measurements:

E. M. Pazukhin, A. S, Krivokhatskii, and S. M. Kochergin, Radiokhimiya **29**, 11–16 (1987).

Variables:

T/K: 298
equilibrium concentration of the $C_2O_4^{2-}$ ion/mol dm^{-3}: 1.7 $\times 10^{-6}$–0.3

Prepared by:

J. Hála

Experimental Data

Solubility at 25 °C of $Am_2(C_2O_4)_3$ in $C_2H_2O_4$–$C_2O_4K_2$ or $C_2H_2O_4$–HNO_3 solutions[a]

Total oxalate (mol dm^{-3})	Ionic strength[e] (mol dm^{-3})	$\gamma_{\pm}$[e]	a_{H+}	$[H^+]$ (mol dm^{-3})	$[C_2O_4^{2-}]$[f] (10^2 mol dm^{-3})	$-\log C_{Am}$ (mol dm^{-3})
1.50[b]					150	2.80
1.00[b]					100	3.07
0.60[b]					60	3.37
0.30[c]	0.90	1.04	5.62×10^{-9}	5.41×10^{-9}	30	3.84
0.15[c]	0.45	0.87	5.62×10^{-9}	6.49×10^{-9}	15	4.44
0.10[b]					10	4.57
0.070[c]	0.21	0.82	6.31×10^{-9}	7.72×10^{-9}	7	4.80
0.030[c]	0.09	0.83	6.17×10^{-9}	7.48×10^{-9}	3	5.36
0.020[c]	0.06	0.84	3.16×10^{-9}	3.77×10^{-9}	2	5.47
0.010[c]	0.03	0.87	4.47×10^{-9}	5.16×10^{-9}	1	5.67
0.008[c]	0.02	0.88	8.91×10^{-9}	1.01×10^{-8}	0.80	5.81
0.005[c]	0.02	0.88	5.50×10^{-9}	6.24×10^{-9}	0.50	5.88
0.30[d]	0.27	0.82	7.76×10^{-3}	9.42×10^{-3}	0.84	5.81
0.030[d]	0.04	0.85	1.78×10^{-4}	2.08×10^{-4}	1.42	5.84
0.010[d]	0.01	0.91	3.98×10^{-3}	4.36×10^{-3}	3.90×10^{-2}	5.89
0.010[d]	0.01	0.91	1.07×10^{-2}	1.18×10^{-2}	1.40×10^{-2}	5.90
0.010[d]	0.01	0.91	1.82×10^{-2}	2.00×10^{-2}	7.60×10^{-3}	5.88
0.010[d]	0.006	0.92	3.80×10^{-2}	4.14×10^{-2}	2.80×10^{-3}	5.73
0.005[d]	0.003	0.94	3.80×10^{-2}	4.03×10^{-2}	1.60×10^{-3}	5.25
0.005[d]	0.002	0.95	5.50×10^{-2}	5.77×10^{-2}	9.90×10^{-4}	4.73
0.005[d]	0.002	0.95	1.07×10^{-1}	1.12×10^{-1}	3.70×10^{-4}	4.29
0.005[d]	0.0001	0.97	1.78×10^{-1}	1.84×10^{-1}	1.70×10^{-4}	3.72

[a] Equilibrium solid phases were not investigated.
[b] Concentration adjusted by means of $C_2O_4K_2$.
[c] Concentration adjusted by means of $C_2O_4H_2$ neutralized by CO_2-free NH_3 gas.
[d] Concentration adjusted by means of $C_2O_4H_2$ and HNO_3.
[e] See Additional Information.
[f] Obtained as second approximation.

Additional information:
As the first approximation, equilibrium concentrations of $C_2O_4^{2-}$ and $HC_2O_4^-$ ions were calculated using the dissociation constants of oxalic acid taken from Lurye,[1] and the measured pH value. From the concentrations so obtained, ionic strength was calculated and used to calculate activity coefficients and concentration of the H^+ ion. From these values, and using dissociation constants of oxalic acid of $K_{a1}=1.05\times10^{-1}$ and $K_{a2}=1.88\times10^{-4}$ for ionic strength of 0.1 mol dm^{-3}, the equilibrium concentration of the $C_2O_4^{2-}$ ion was then obtained as the second approximation.

With increasing oxalate ion concentration, the solubility of Am(III) oxalate first decreased, then passed through a minimum, and increased at higher oxalate concentrations because of the formation of oxalato complexes of Am(III). Overall stability constants of the $Am(C_2O_4)_n^{3-2n}$ complexes, $\beta_n=[Am(C_2O_4)_n^{3-2n}]\times[Am^{3+}]^{-1}[C_2O_4^{2-}]^{-n}$, were obtained graphically for zero ionic strength as $\beta_1 = 4.8\times10^6$ mol^{-1} dm^3, $\beta_2=8.7\times10^9$ mol^{-2} dm^6, and $\beta_3=4.15\times10^{11}$ mol^{-3} dm^9. The fit with experimental data was further improved when also the complex $Am(HC_2O_4)^{2+}$, $\beta_{1h}=4.37\times10^4$ mol^{-1} dm^3 was considered.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. An aliquot of Am(III) stock solution, enough to ensure excess of $Am_2(C_2O_4)_3\cdot7H_2O$ at equilibrium, was added to solutions of the desired composition, in a polyethylene bottle. The bottle was mechanically shaken until equilibrium was achieved, which took less than 16 h. Then aliquots of the solutions were withdrawn, filtered, and concentration of americium determined by α spectrometry. The concentrations of acid and oxalate were determined by titration with standard NaOH and $KMnO_4$ solutions, respectively. Depletion of oxalate or H^+ ions by radiolysis did not occur for ^{243}Am. After the first 4–12 h in some 3 day equilibrations, there were no detectable variations in solution composition or changes in solubility.

Source and Purity of Materials:

Stock solution of Am(III) nitrate was prepared by prior separation from neutron irradiated ^{239}Pu, lanthanides, and curium with tributylphosphate/tertiary amine extraction, and K_2CO_3 precipitation. The $K_3Am(CO_3)_2$ was dissolved, Am(III) reprecipitated as oxalate, calcined, dissolved in HCl, purified by anion exchange, and precipitated with NH_3 solution. The americium hydroxide was dissolved in HNO_3. The americium was pure ^{243}Am containing <2000 ppm curium and <1000 ppm of other cationic impurities. The americium was shown to be trivalent by spectrophotometric analysis. All other chemicals were reagent grade products.

Estimated Error:

Temperature: precision not reported.

References:

[1] T. L. Markin, J. Inorg. Nucl. Chem. **7**, 290 (1958).

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. Excess Am(III) oxalate was equilibrated for 6–10 h with solutions of oxalic acid and potassium oxalate containing various concentrations of oxalate ions. Samples were taken periodically from each solution to check if equilibrium had been attained. In the saturated solutions pH was measured, and Am(III) was determined by an unspecified radiometric method.

Source and Purity of Materials:

$Am_2(C_2O_4)_3 \cdot 7H_2O$ was prepared in the following way. A solution of $^{241}AmO_2$ in 7 mol dm^{-3} HNO_3 was precipitated with ~12 mol dm^{-3} NH_3 solution, and the $Am(OH)_3$ was dissolved in 4 mol dm^{-3} K_2CO_3. The solution was filtered and the carbonato complex decomposed with 4 mol dm^{-3} HNO_3. The CO_2 was removed from the resulting solution by heating at 95 °C for 1.5 h. The nitrate solution of Am(III) was purified by extraction with di-(2-ethylhexyl)phosphoric acid, and after stripping into HNO_3 solution, it was poured into a solution of oxalic acid neutralized with ammonia to pH 2. The Am(III) oxalate was washed several times with 0.1 mol dm^{-3} $C_2H_2O_4$/0.1 mol dm^{-3} HNO_3 solution, and kept under distilled water. Twice recrystallized oxalic acid and potassium oxalate were used.[2]

Estimated Error:

Temperature: ±0.02 K (authors).

Solubility: insufficient data given to allow for error estimate.

References:

[1] Yu. Yu. Lurye, *Handbook of Analytical Chemistry* (in Russian) (Khimiya, Moscow, 1971), p. 95.

[2] A. V. Stepanov and E. M. Pazukhin, Zh. Neorg. Khim. **15**, 1483 (1970).

9. The Solubility of Curium Compounds

9.1. Curium(III) Oxalate

Components:	Original Measurements:
(1) Dicurium(III) tris(oxalate); $Cm_2(C_2O_4)_3$; [ ] (2) Oxalic acid; $C_2H_2O_4$; [144-62-7] (3) Nitric acid; HNO_3; [7697-37-2] (4) Water; H_2O; [7732-18-5]	G. A. Burney and J. A. Porter, Inorg. Nucl. Chem. Lett. **3**, 79–85 (1967).

Variables:	Prepared by:
T/K: 296 c_2 /mol dm^{-3}: 0.025–0.5 c_3 /mol dm^{-3}: 0.1–4.0	J. Hála

Experimental Data

Solubility at 23 °C of $Cm_2(C_2O_4)_3$ in HNO_3–$C_2H_2O_4$ solutions

The solubility of $Cm_2(C_2O_4)_3$ at 23 °C in HNO_3–$C_2H_2O_4$ solutions was presented in graphical form (see Fig. 25). The nature of the equilibrium solid phases was not investigated. Radiolytic decomposition of oxalate by α radiation from ^{244}Cm affected the accuracy of solubility determination. The rate of radiolytic depletion of oxalate was relatively rapid at solubilities >500 mg ^{244}Cm/dm^3 and at <0.5 mol dm^{-3} oxalate concentration. The data obtained in these regions were considered by the authors as approximate.

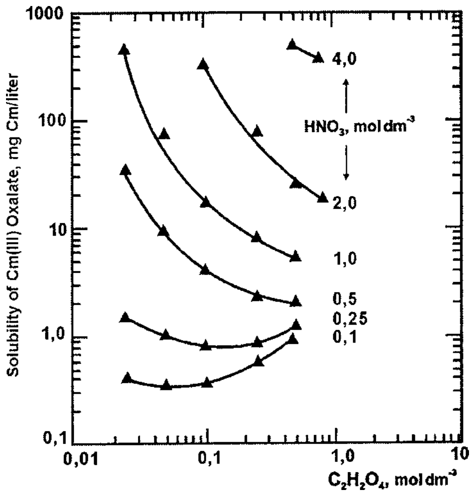

FIG. 25. Dicurium (III)–tris(oxalate)–oxalic acid–nitric acid–water system.

Auxiliary Information

Method/Apparatus/Procedure:

Isothermal method used. An aliquot of Cm(III) stock solution, enough to ensure excess of solid Cm(III) oxalate at equilibrium, was added to solutions of the desired composition, in a polyethylene bottle. The bottle was mechanically shaken until equilibrium was achieved, which took less than 16 h. Then aliquots of the solutions were withdrawn, filtered, and concentration of curium was determined by α spectrometry. The concentrations of acid and oxalate were determined by titration with standard NaOH and $KMnO_4$ solutions, respectively.

Source and Purity of Materials:

Curium was separated from neutron irradiated ^{239}Pu in the following way. Plutonium was extracted by tributylphosphate, then curium and americium were separated from fission product lanthanides with amine extraction. Americium was separated from curium by precipitation of $K_3Am(CO_3)_2$, and curium was finally precipitated as oxalate and calcined to the oxide. The latter was dissolved in HCl, curium was purified by anion exchange, precipitated with NH_3 solution, and dissolved in HCl. Purified curium was approximately 95% ^{244}Cm, and contained <2000 ppm americium, as determined by γ spectroscopy. All other chemicals were reagent grade products.

Estimated Error:

Temperature: precision not reported.

Solubility: $\sim 3\%$ for solubility <10 mg $^{244}Cm/dm^3$; $\sim 5\%$ for solubility, ~ 50 mg $^{244}Cm/dm^3$ and <0.1 mol dm^{-3} oxalate, due to radiolysis effects (authors).

10. System Index

Page numbers preceded by E refer to evaluation texts whereas those not preceded by E refer to compiled tables. The symbol (aq) stands for water as an additional component in the respective system.

11. Registry Number Index

Page numbers preceded by E refer to evaluation texts whereas those not preceded by E refer to compiled tables.

12. Author Index

Page numbers preceded by E refer to evaluation texts whereas those not preceded by E refer to compiled tables.