NASA TECHNICAL NOTE

NASA TN D-2286

CRYOGENIC SOLUTIONS AND SOLUBILITIES IN LIQUID FLUORINE

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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SUMMARY

The solubilities of several substances in liquid fluorine have been determined between 68° and 83° K by vapor-pressure measurements. These experimental data, as well as a summary of literature data on solutions of solids in cryogenic liquids, are presented and compared with solubilities calculated by assuming regular solutions. Experimental and calculated values for the solubilities of carbon tetrafluoride, perfluorethane, and perchloryl fluoride in liquid fluorine show close agreement, while the solubilities of krypton and xenon in fluorine show considerable deviation from calculated values. Little of the literature data agrees with the calculated solubilities. Deviations from calculated values are discussed.

INTRODUCTION

Only a limited amount of past work has been concerned with the prediction of the solubilities of solids in cryogenic liquids. Information on solutions in liquid fluorine is essentially nonexistent, and in the case of carbon tetrafluoride the solubility data that are available (ref. 1) appear to be in considerable error. This lack of information, together with the importance of cryogenic liquids in space applications and the possible use of fluorine as a rocket propellant, prompted the present investigation. It was the intent of this investigation to determine the solubilities of several substances in liquid fluorine and to consider the possibility of predicting solubilities in cryogenic liquids in general.

Solubilities of the following substances in liquid fluorine were determined: carbon tetrafluoride (CF_4), perfluorethane (C_2F_6), krypton (Kr), xenon (Xe), perchloryl fluoride (ClO_3F), nitryl fluoride (NO_2F), silicon tetrafluoride (SiF_4), boron trifluoride (BF_3), tetrafluoroethylene polymer, cobalt trifluoride (CoF_3), and aluminum trifluoride (AlF_3). These substances were chosen for their physical and chemical properties. In addition, the liquid-liquid systems nitrogen-fluorine (N_2-F_2) and nitrogen trifluoride - fluorine (NF_3-F_2) were investigated. All solutions were studied in the temperature range 68° to 83° K by vapor-pressure measurements.

Experimental solubilities obtained in this study, as well as literature data on solutions of solids in cryogenic liquids, are compared with solubilities calculated by assuming regular solutions (refs. 2 and 3). Deviations from the calculated values are discussed.

SYMBOLS

b	van der Waal's constant
ΔC_p	change in heat capacity
E	energy of vaporization
ΔH	heat
N	number of moles
P	pressure
p	vapor pressure of liquid
Δp	vapor-pressure lowering
R	gas constant
T	temperature
V	molar volume
x	solubility
δ	solubility parameter
φ	volume fraction

Subscripts:

B	boiling
c	critical
f	melting or fusion
i	ideal
j	component, solvent or solute
t	transition
v	vaporization

2

1   solvent

2   solute

EXPERIMENTAL PROCEDURE

All solute materials were obtained commercially except NO_2F, which was prepared by reacting fluorine with nitrogen dioxide (ref. 4). The gaseous solutes with purities less than 99.9 percent were further purified by bulb-to-bulb distillation, while the solid solutes were used as obtained. Purity of these gases was checked by means of mass spectrometer and infrared analyses. Fluorine of 98.0-percent purity was obtained from a low-pressure cylinder and was further purified by bulb-to-bulb distillation at pressures not exceeding 1/2 atmosphere. Analysis of the fluorine was by reaction with cold mercury (ref. 5) and by use of infrared spectra. Vapor-pressure measurements of the purified fluorine (at least 99.9-percent purity) agreed with previously reported data (ref. 6).

The gases were all handled in a glass vacuum system that had been conditioned with fluorine at 1-atmosphere pressure for at least 20 hours. A chlorofluorocarbon grease was used on all stopcocks. A soda lime scrubber was used for disposal of the fluorine.

Helium
Stirrer
Electromagnet

Sample bulbs
Resistance thermometer
Cooling coil
Heater

[CD-7702]

(a) Cryostat.

Mercury manometer

Differential manometers

[CD-7703]

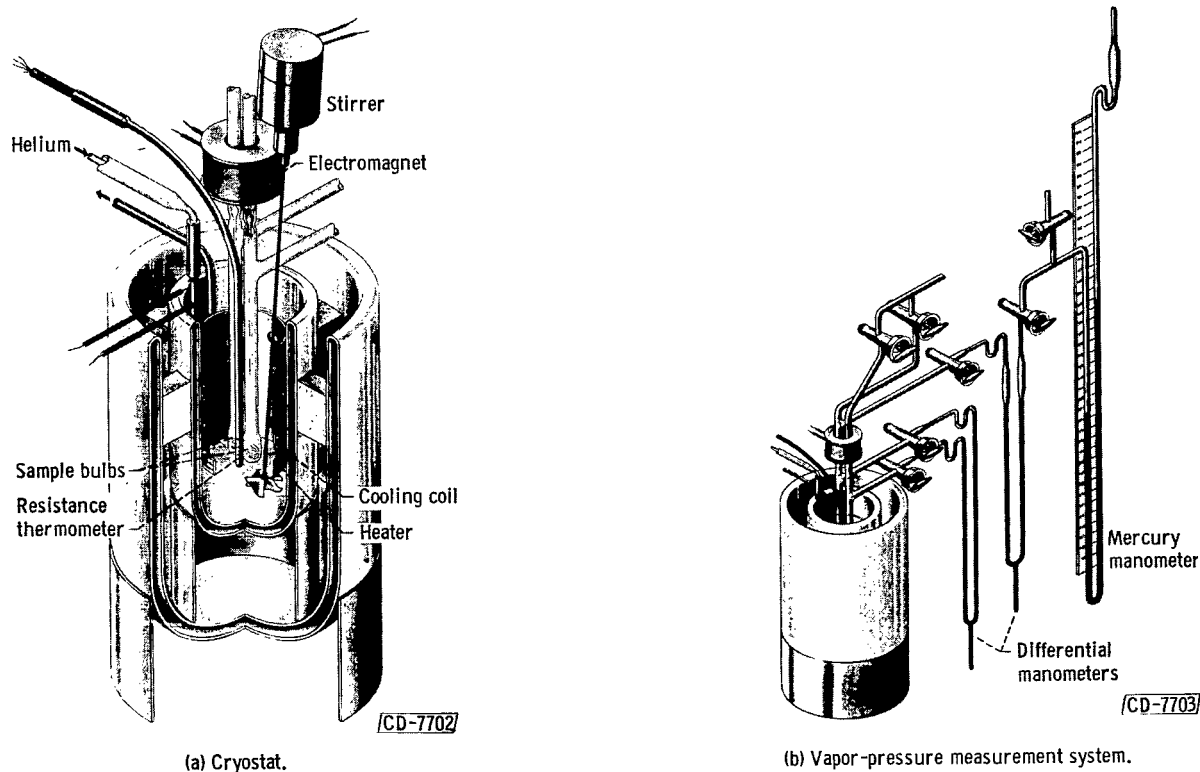(b) Vapor-pressure measurement system.

Figure I. - Experimental apparatus.

The cryostat and the vapor-pressure measurement system are shown in figure 1. The cryostat consisted of two concentric glass Dewars, each containing liquid nitrogen. The liquid nitrogen in the inner Dewar was cooled constantly by cold helium gas flowing through the copper cooling coil and was maintained at a constant temperature by means of the heating unit. The helium gas was cooled below 80° K by being passed through liquid helium. The temperature in the inner Dewar was controlled to ±0.03° K and was measured by means of a platinum resistance thermometer. The liquid nitrogen in the inner Dewar was stirred by an electric stirrer.

Two sample bulbs, one for pure fluorine and one for the fluorine solutions, were immersed in the inner Dewar. The bulbs were both connected to a differential manometer containing chlorofluorocarbon oil. One bulb was connected to another differential manometer, which was in turn connected to a mercury manometer used for absolute-pressure measurements. All pressure readings were taken with the aid of a cathetometer. Samples in the bulbs were stirred by glass stirring rods having tops in which pieces of steel were enclosed. The stirring rods were intermittently actuated by an electromagnet. Volumes of the sample bulbs and the manometers were calibrated for various pressure differentials.

Mixtures of known composition were prepared in one of the sample bulbs by adding a known amount of solute and then condensing a known amount of fluorine into the bulb. The number of moles of solutes that were gases at room temperature was determined in calibrated bulbs by assuming the solutes to be ideal gases at low pressures (less than 1 atm); the gaseous solutes were subsequently condensed or frozen into the sample bulb. The solid solutes were weighed before they were introduced into the sample bulb. Fluorine as a liquid was measured out to ±0.002 milliliter in a calibrated glass tube immersed in liquid nitrogen, and the number of moles was determined by applying the density data of Jarry and Miller (ref. 7). The fluorine was transferred into the sample bulb by lowering the temperature of the cryostat below that of the calibrated tube.

All the solutes appeared to be inert to fluorine under the conditions of this study. Prior to this investigation it was suspected that tetrafluoroethylene polymer might break down while being stirred with fluorine; however, no evidence of decomposition or reaction was found.

Three methods were used to obtain solubility data. Method 1 consisted in plotting vapor-pressure lowering Δp against composition at a constant temperature. The point at which Δp became constant determined the solubility of the solute. This method is illustrated in figure 2 for the vapor-pressure lowering of solutions of CF_4 and krypton in liquid fluorine at 77.5° K. The CF_4 solution was nearly ideal, while the krypton solution showed a deviation from ideality.
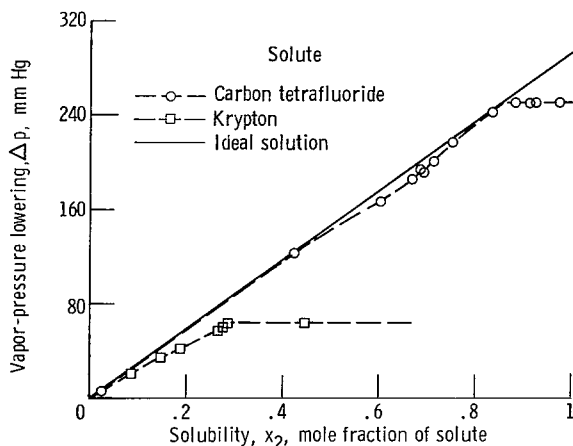

Figure 2. - Vapor-pressure lowering of solutions of carbon tetrafluoride and krypton in fluorine at 77.5° K.

In method 2 the vapor pressure of the solution was plotted against the temperature for known compositions. The intersection of a vapor-pressure curve of an unsaturated solution with that of the saturated solution determined the temperature of saturation for a particular concentration. This method is illustrated in figure 3 for solutions of CF_4 and krypton in fluorine. The minimum point in the saturated-solution curve for CF_4 indicates the solid-solid transition of CF_4 at 76.09° K (ref. 8).
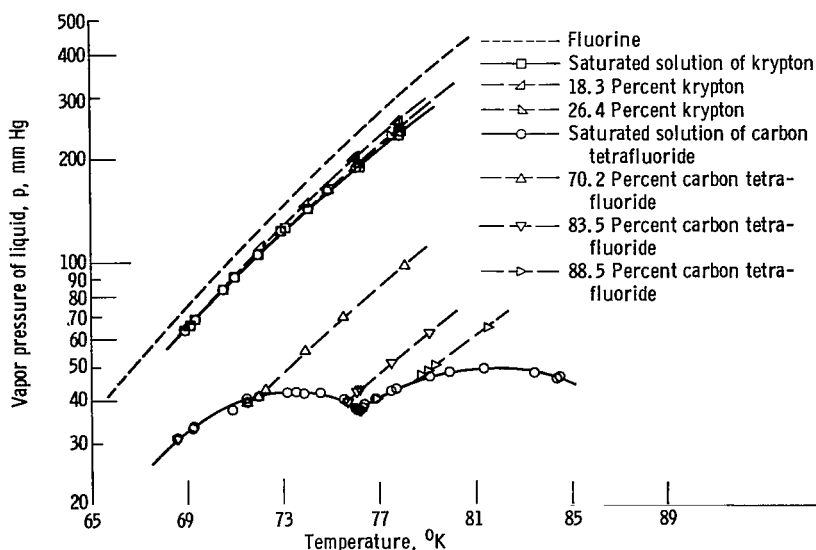

Figure 3. - Vapor pressures of solutions of carbon tetrafluoride and krypton in liquid fluorine.

In method 3 solubilities were calculated directly from Raoult's law by the use of vapor-pressure-lowering measurements. This method was used only where solubilities were small. Before Raoult's law was used to determine solubilities, tests were made to show the applicability of the law. Applicability was shown by determining the vapor-pressure depression for unsaturated solutions at known concentrations that were near those of the saturated solutions.

The major factor in the experimental error for methods 1 and 2 was the accuracy with which the mole fraction of solute could be determined (±0.5 percent at higher concentrations to ±1.3 percent at lower concentrations of solute), while for method 3 the major factor was the accuracy of the Δp measurements (±0.1 mm Hg).

RESULTS AND DISCUSSION

For an ideal system the solubility of a solid in a liquid at temperature T may be calculated from (refs. 2 and 3)

$$\ln \frac{1}{x_i} = \frac{\Delta H_f}{R} \frac{T_f - T}{TT_f} - \frac{\Delta C_{p,f}}{R} \left(\frac{T_f - T}{T} - \ln \frac{T_f}{T} \right)$$

$$+ \frac{\Delta H_t}{R} \frac{T_t - T}{TT_t} - \frac{\Delta C_{p,t}}{R} \left(\frac{T_t - T}{T} - \ln \frac{T_t}{T} \right) \quad (1)$$

The ΔC_p terms take into account the change in the heats of fusion and transition with temperature. The terms involving transition temperature T_t are used only for solutes with a solid-solid transition at a temperature greater

than T.

Since few systems behave ideally, equation (1) cannot be expected to give good predictions of solubilities. More realistic predictions of solubilities may be obtained if the regular solution concept is taken into consideration. Hildebrand (refs. 2 and 3) has presented for regular solutions an equation that takes into account the heat of mixing of solute and solvent:

$$\ln \frac{1}{x_2} = \ln \frac{1}{x_i} + \frac{V_2}{RT} (\delta_1 - \delta_2)^2 \varphi^2 \tag{2}$$

According to Hildebrand, the volume fraction φ may be expressed as

$$\varphi_1 = \frac{N_1 V_1}{N_1 V_1 + N_2 V_2}$$

Since

$$x_2 = \frac{N_2}{N_1 + N_2}$$

and

$$x_1 = 1 - x_2 = \frac{N_1}{N_1 + N_2}$$

then

$$\varphi_1 = \frac{(1 - x_2) V_1}{(1 - x_2) V_1 + x_2 V_2}$$

Thus, equation (2) becomes

$$\ln \frac{1}{x_2} = \ln \frac{1}{x_i} + \frac{V_2}{RT} (\delta_1 - \delta_2)^2 \left[\frac{(1 - x_2) V_1}{(1 - x_2) V_1 + x_2 V_2} \right]^2 \tag{3}$$

The solubility parameters δ_j are defined in references 2 and 3 as $\delta_j = (-E_j / V_j)^{1/2}$. For low pressures $-E$ may be replaced by the energy of vaporization ΔE, which may in turn be replaced by $\Delta H_V - RT$. Thus,

$$\delta_j = \left(\frac{\Delta H_{V,j} - RT}{V_j} \right)^{1/2} \tag{4}$$

Since $\Delta H_{V,j}$ is not often available at temperatures other than the boiling point $T_{B,j}$, the change in the heat of vaporization with temperature must be

taken into consideration. This may be done by use of the Clausius-Clapeyron equation

$$\delta_j = \left[\frac{\Delta H_{B,j}\left(\dfrac{T}{T_{B,j}}\right)^2 \dfrac{\left(\dfrac{d \ln p}{dT}\right)_T}{\left(\dfrac{d \ln p}{dT}\right)_{T_{B,j}}} - RT}{V_j} \right]^{1/2} \tag{5}$$

Values of solubility parameters for several substances were calculated from equation (5) and plotted against temperature (fig. 4). Thus, if regular solutions are assumed and δ values calculated from equation (5) are used, solubilities may be calculated from equation (3).

Figure 4. – Solubility parameters of several substances.

The experimental values of solubilities in liquid fluorine are presented in table I along with the ideal solubilities calculated from equation (1), the solubilities calculated from equation (3) by assuming regular solutions, and the estimated experimental error at 77.5° K. Also included for comparison are the differences in liquid molar volumes of the solute and the solvent, in calculated δ values at 77.5° K, and in van der Waal's constant b, which is used here as a measure of molecular size.

Solubilities of CF_4, C_2F_6, and ClO_3F generally agree with values calculated from equation (3), although disagreement is noted for krypton and xenon solutions. Experimental solubilities for these solutions are plotted against temperature in figure 5, as are the calculated results. The disagreement of krypton and xenon is unexpected and cannot be immediately explained. A comparison of the NO_2F solubility with calculated values is difficult because of the lack of a value for the heat of fusion. A heat of fusion of 700 calories per mole was estimated for NO_2F, however, from the relation of the heat of fusion to the melting point for several substances. With this value good agreement was obtained between calculated and experimental solubilities.

Figure 5. - Solubilities in liquid fluorine.

Powdered tetrafluoroethylene polymer, SiF_4, BF_3, CoF_3, and AlF_3 are all less soluble than can be determined by the experimental apparatus. These low solubilities agree with the calculations based on equation (3).

In the course of this investigation two liquid-liquid systems were studied. The NF_3-F_2 system is nearly ideal throughout the entire compo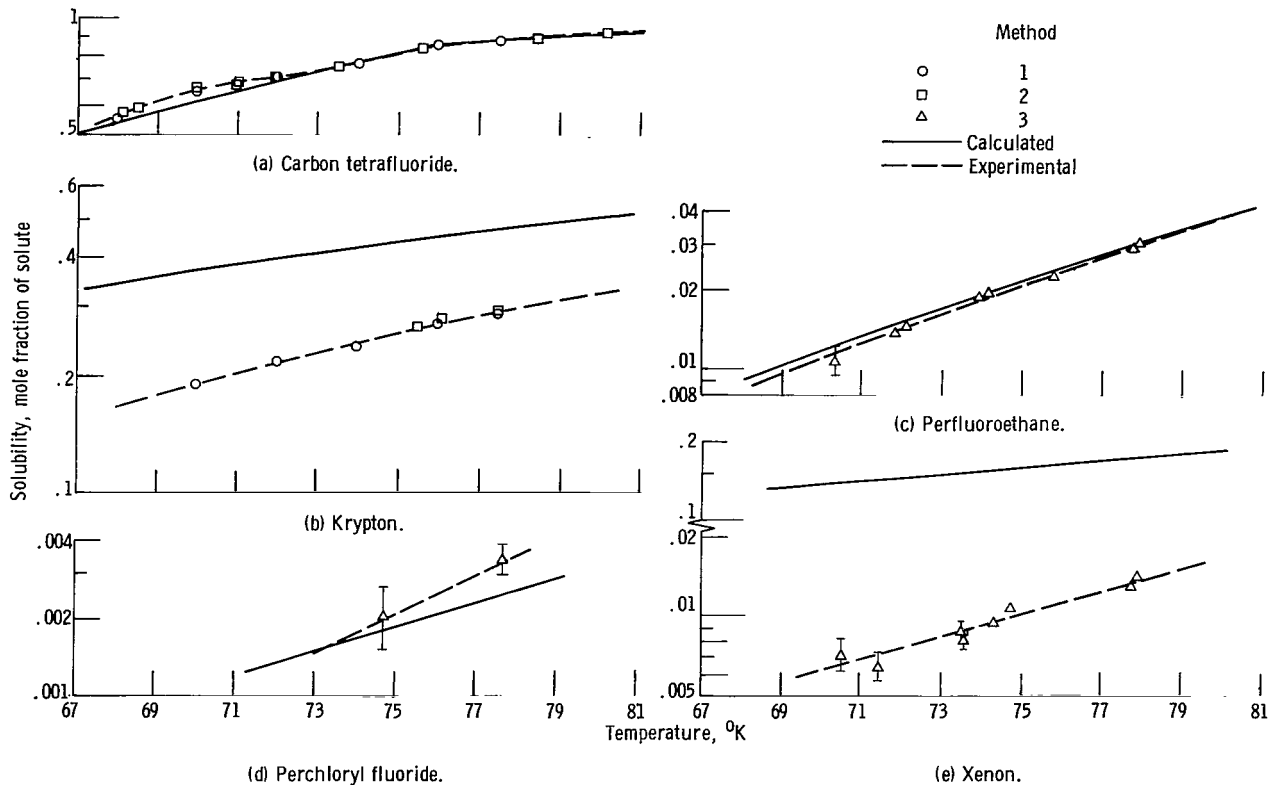sition range of 0 to 100 percent NF_3 as determined by vapor-pressure measurements between 68° and 78° K. The nitrogen-fluorine system is completely miscible at 77.5^O K. The results are as expected for these systems since the differences in δ values are small $(\delta_{F_2} - \delta_{N_2} = 1.82;\ \delta_{NF_3} - \delta_{F_2} = 1.72)$.

Literature data on cryogenic solutions of solids in liquids are summarized in table II and are compared with values calculated from equation (3). The differences in δ values and in molar volumes at 80° K, as well as the difference in van der Waal's constant b, are presented for comparison. Melting-point data, where available, and freezing-point (solubility) data are given for cases in which solid solutions are formed. When more than one reference gives data, what is considered the best value is presented.

The solubility of CF_4 in fluorine reported in reference 1 appears to be quite low (4.5 mole percent at 77.8^O K), and is in disagreement with the value found in this study (86.7 mole percent at 77.5^O K). The reported solubility was determined by observing the concentration at which a solid phase first appeared. It is suggested that perhaps some impurities were present in the re-

8

ported system and were mistaken for solid CF_4.

Some of the literature data agree with the calculated values, but many of the reported solubilities are considerably less than expected from equation (3). Particularly outstanding are the low solubilities of the hydrocarbons in liquid oxygen. In general, the more unsaturated the hydrocarbon, the larger the percentage deviation of the experimental data from the calculated values. In cases where solid solutions are formed, the solidus curve is in closer agreement with calculated values than the liquidus or solubility curve. Melting-point (solidus) data, however, generally are less than calculated values for low concentrations of solute, and the data approach the calculated values at higher concentrations.

It is well known that solid solutions tend to be formed by substances whose molecules are similar in size and shape. If b as calculated from $b = RT_c/8P_c$ is taken as a measure of molecular size, then the smaller the differences in b, the more likely the formation of a solid solution. This is indeed the case, as indicated in table II for known solid solutions. In these cases, solubilities are less than values calculated from equation (3). Thus, the small difference in b for the krypton-fluorine system suggests that the low solubility of krypton might be at least partially due to the formation of a solid solution.

No other correlations were found between the deviations of experimental and reported solubilities from the calculated values and the molecular or the physical properties of the solution components. Equation (3) can at best be expected to give a general approximation for cryogenic solubilities even though in some cases calculated and experimental values are in good agreement.

Lewis Research Center
    National Aeronautics and Space Administration
        Cleveland, Ohio, January 30, 1964

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11

12

TABLE I. - EXPERIMENTAL SOLUBILITIES OF SUBSTANCES IN LIQUID FLUORINE

Solute	Temperature, T, °K															Estimated experimental error (a)	Difference in solubility parameter, $\delta_2 - \delta_1$, $(cal/cc)^{1/2}$ (a)	Difference in molar volume, ΔV ml/mole (a)	Difference in van der Waal's constant, Δb, ml/mole	Method
	70.0			72.0			74.0			76.0			77.5							
	Exp.	Eq. (1)	Eq. (3)	Exp.	Eq. (1)	Eq. (3)	Exp.	Eq. (1)	Eq. (3)	Exp.	Eq. (1)	Eq. (3)	Exp.	Eq. (1)	Eq. (3)					
	Solubility, x_2, Mole fraction of solute																			
Carbon tetrafluoride	0.652	0.622	0.616	0.705	0.697	0.692	0.763	0.775	0.772	0.850	0.857	0.855	0.867	0.875	0.874	±0.005	0.77	15.8	36.4	1,2
Perfluoro-ethane	---	---	---	.0142	.0165	.0154	.0186	.0212	.0197	.0240	.0270	.0249	.0287	.0321	.0295	±.0010	.67	45.2	59.6	3
Krypton	.188	.372	.369	.216	.397	.392	.240	.422	.417	.269	.447	.442	.286	.466	.461	±.003	.47	6.4	12.6	1,2
Xenon	.0061	.176	.139	.0075	.189	.149	.0091	.203	.159	.0111	.217	.170	.0128	.227	.178	±.0006	1.69	13.4	24.2	3
Perchloryl fluoride	---	---	---	---	---	---	.0017	.0860	.0017	.0024	.1002	.0021	.0033	.1118	.0024	±.0005	3.67	26.3	44.4	
Nitryl fluoride[b]	---	---	---	---	---	---	---	---	---	.0011	.259	.0012	.0012	.284	.0014		4.80	6.9	---	
Silicon tetrafluoride	---	---	---	---	---	---	---	---	---	---	---	---	<.0005	.0002	.0001		1.77	26.7	53.4	
Boron trifluoride	---	---	---	---	---	---	---	---	---	---	---	---		.036	.0004		4.68	11.7	27.5	
TFEP[c]	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---		---	---	---	
Cobalt trifluoride	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---		---	---	---	
Aluminum trifluoride	---	---	---	---	---	---	---	---	---	---	---	---		---	---		---	---	---	

[a] At 77.5° K.
[b] Estimated heat of fusion of 700 cal/mole used in calculations.
[c] Powdered tetrafluorethylene polymer.

TABLE II. - SOLUBILITIES

Solute	Solvent	Temperature, T, °K									
		70.0		75.0		77.8		80.0		85.0	
		Ref.	Eq. (3)	Ref.	Eq. (3)	Ref.	Eq. (3)	Ref.	Eq. (3)	Ref.	Eq. (3)
		Solubility, x_2, mole fraction of solute									
Methane	Oxygen	0.567	0.728	0.685	0.792	------	-------	--------	--------	--------	--------
Acetylene[b]		.00000092	.0000014	.0000014	.000034	------	-------	0.0000023	0.000103	0.0000035	0.000245
Ethylene[b]		.00077	.072	.0018	.114	------	-------	.0038	.178	.0075	.276
Ethane		----------	---------	--------	--------	------	--------	.026	.598	.054	.793
Propylene[b]		.0032	.165	.0077	.341	------	-------	.024	.603	.175 (.010)	.860
Krypton		----------	---------	.22	.430	------	-------	.31	.493	--------	--------
Xenon		----------	---------	--------	--------	------	-------	.115	.192	.170	.219
Carbon dioxide[b]		.000002	<.0000001	.0000025	.0000004	------	-------	.0000031	.0000012	.0000036	.0000031
Nitrous oxide	↓	----------	---------	.000015	.0000001	------	-------	.000036	.0000011	.000074	.0000054
Acetylene[b]	Nitrogen	----------	---------	.0000012	<.0000001	------	-------	.0000018	.0000002	.0000028	.0000009
Ethylene		.00064	.0032	.0014	.0050	------	--------	.0032	.0075	.0060	.0107
Ethane	↓	-------	------	.0057	.0287	------	--------	.0103	.0384	-----	-----
Propylene[b]		.0027	.0014	.0071	.0019	------	--------	.023	.0027	-----	-----
Carbon dioxide[b]	↓	.0000025	<.000001	.000003	<.000001	------	--------	.0000036	<.000001	.0000045	<.000001
Xenon	Argon	--------	--------	-------	--------	------	-------	--------	--------	.044	.178
Methane[c]	Argon liquidus	---------	--------	-------	--------	------	-------	.66	.857	.81	.923
	solidus	---------	--------	-------	--------	------	-------	.84	-----	.92	----
Krypton[c]	Argon liquidus	---------	--------	-------	---------	------	--------	---	----	.10	.545
	solidus	---------	--------	-------	---------	------	--------	---	----	.33	----
Krypton[c]	Methane liquidus	---------	--------	-------	---------	------	--------	---	----	---	----
	solidus	---------	--------	-------	---------	------	--------	---	----	---	----
Methane[c]	Nitrogen liquidus	.42	.712	.56	.779	------	---------	.71	.849	.86	.920
	solidus	.67	----	.76	----	------	---------	.84	----	.92	----
Argon[c]	Nitrogen liquidus	.56	.703	.70	.812	------	---------	.86	.920	---	----
	solidus	.85	----	.92	----	------	---------	.97	----	---	----
Argon[c]	Oxygen liquidus	.43	.726	.61	.824	------	---------	.82	.923	---	----
	solidus	.65	----	.79	----	------	---------	.92	----	---	----
Chlorine	Fluorine	---	----	---	----	0.0056	0.00053	---	----	---	----
Carbon tetra-fluoride	Fluorine	---	----	---	----	.045	.813	---	----	---	-----
Sulfur hexa-fluoride	Fluorine	---	----	---	----	<.001	<.001	---	-----	---	----
Hydrogen fluoride	Fluorine	---	----	---	----	<.005	<.000001	---	----	---	----

[a] At 80° K.
[b] Change in heat capacity terms not used in equation (3).
[c] Solid solutions are known to form.

90.0		95.0		100.0		Differences in solubility parameter, $\delta_2 - \delta_1$, $(cal/cc)^{1/2}$ (a)	Difference in molar volume, ΔV, ml/mole (a)	Difference in van der Waal's constant, Δb, ml/mole	Data from ref. -	Other data in ref. -
Ref.	Eq. (3)	Ref.	Eq. (3)	Ref.	Eq. (3)					
---------	--------	--------	--------	----	-------	0.33	8.9	10.9	9	
0.0000055	0.00048	0.0000086	0.000807	----	-------	5.44	5.2	19.2	10	
.0141	.427	---------	--------	----	-------	1.96	4.4	26.1	11	12
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.0000043	.0000068	.0000049	.0000133	----	-------	5.74	.2	11.0	10	
.000142	.000019	.00026	--------	----	-------	7.32	2.3	12.4	14	
.000009	.0000089	.000021	--------	----	-------	7.30	13.5	12.5	10	
.0109	.0151	--------	--------	----	-------	3.82	3.9	19.4	11	
-----	-----	--------	--------	----	-------	3.45	1.8	26.5	12	
-----	-----	--------	--------	----	-------	4.05	8.4	43.6	11	
.0000053	<.000001	.0000064	<.000001	----	-------	7.60	8.4	4.3	10	
--------	--------	--------	--------	----	-------	2.14	8.1	18.9	15	
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.40	.616	.52	.690	0.61	0.764	1.02	3.2	7.3	17	16
.60	----	.68	----	.76	------					
---	----	.20	.692	.36	.766	.83	5.0	3.3	17	23
---	----	.29	----	.50	----					
.99	.990	---	----	---	----	1.53	.6	4.2	13	3,22
.99	----	---	----	---	----	----				
---	----	---	----	---	----	1.36	7.6	6.4	22	13
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---	----	---	----	---	----	.46	.7	.3	22	17,13,20
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---	----	---	----	---	----	3.46	16.4	29.5	21	
---	----	---	----	---	----	.77	15.8	36.4	1	
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