

Thermodynamic data and measurements for biofuels

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Utilization of Biomass



Ethanol Production

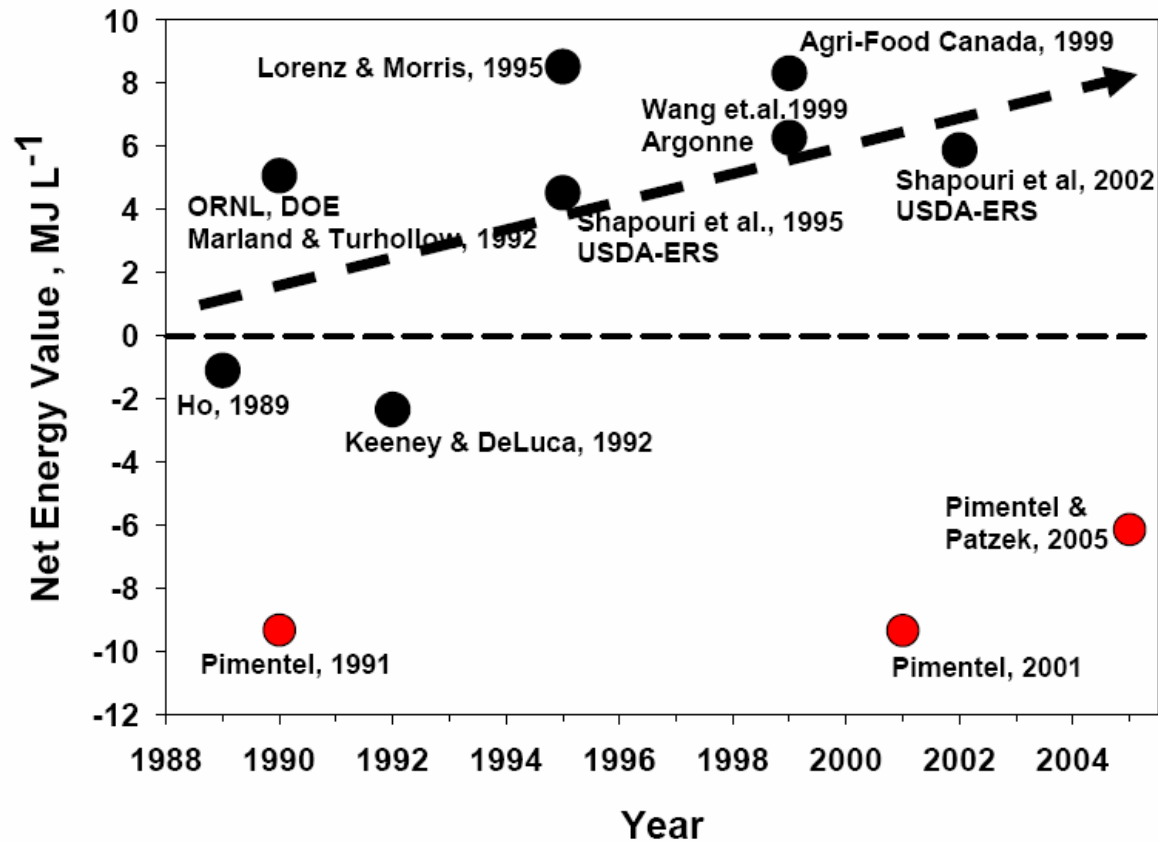
Biomass Basics (U.S. Department of Energy)

Cellulose and hemicellulose, two of the three main components of the great bulk of biomass resources, are [polymers of sugars and can be broken down to those component sugars for fermentation or other processing to ethanol and other valuable fuels and chemicals.](#)

Biomass includes all plant and plant-derived material — essentially all energy originally captured by photosynthesis. This means that [biomass is a fully renewable resource](#) and that its use for biomass-derived fuels, power, chemicals, materials, or other products essentially generates no net greenhouse gas. (You must consider any fossil-fuel used to grow, collect, and convert the biomass in a full life-cycle analysis, but the [carbon dioxide released when biomass is burned is balanced by the carbon dioxide captured when the biomass is grown](#)). Its production and use will also generally be domestic, so it has substantial environmental, economic, and security benefits.

[Biomass is already making key contributions today. It has surpassed hydro-electric power as the largest domestic source of renewable energy.](#) Biomass currently supplies over 3% of the U.S. total energy consumption — mostly through industrial heat and steam production by the pulp and paper industry and electrical generation with forest industry residues and municipal solid waste (MSW). Of growing importance are biomass-derived ethanol and biodiesel which provide the only renewable alternative liquid fuel for transportation, a sector that strongly relies on imported oil.

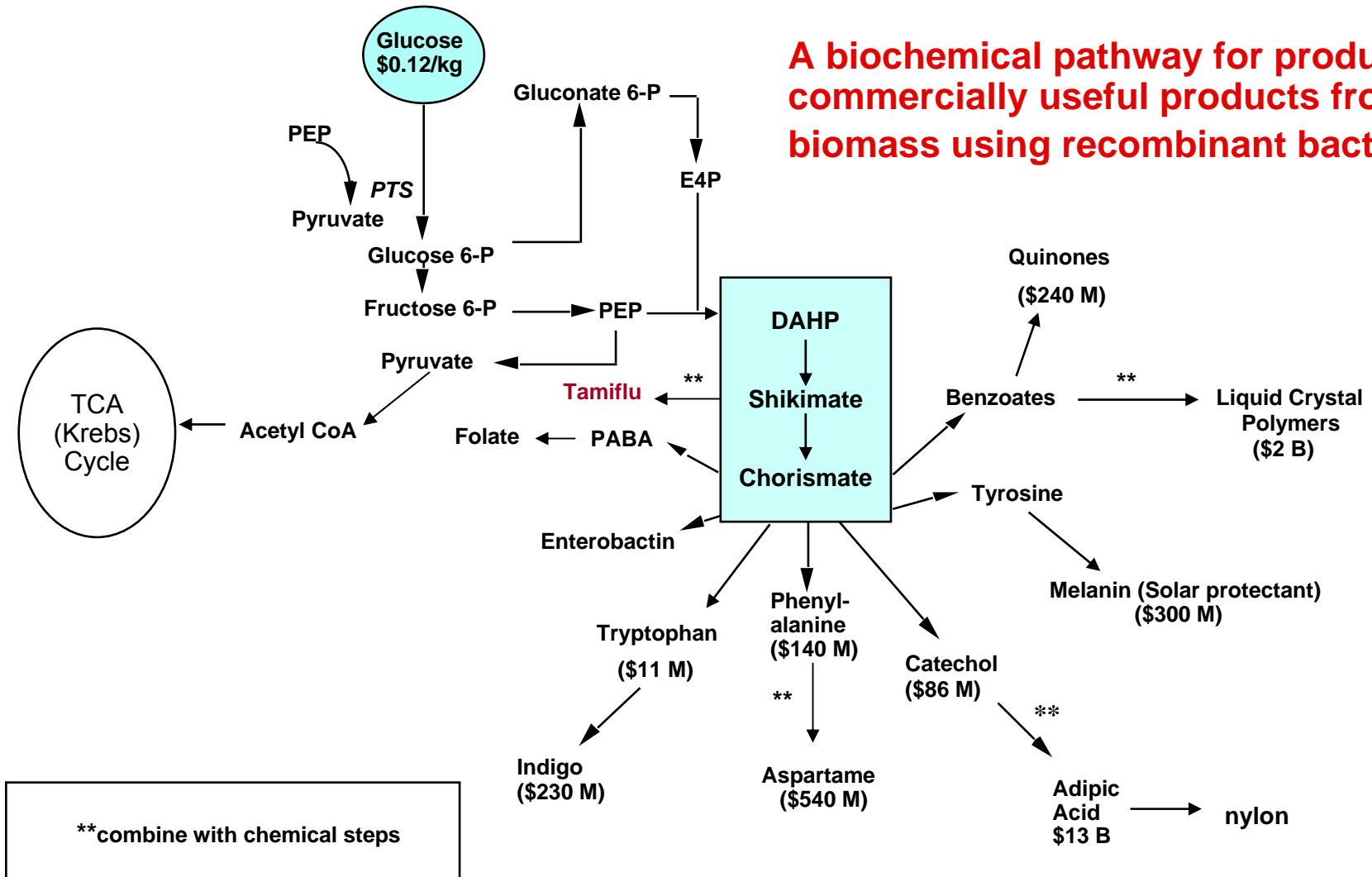
Published Corn-Ethanol Energy Balances, 1989-2005



From: K.G. Cassman, Renewable Biofuels Forum, Washington, D.C. (2005)

Biofuels are one part of Biomanufacturing

A biochemical pathway for producing commercially useful products from biomass using recombinant bacteria

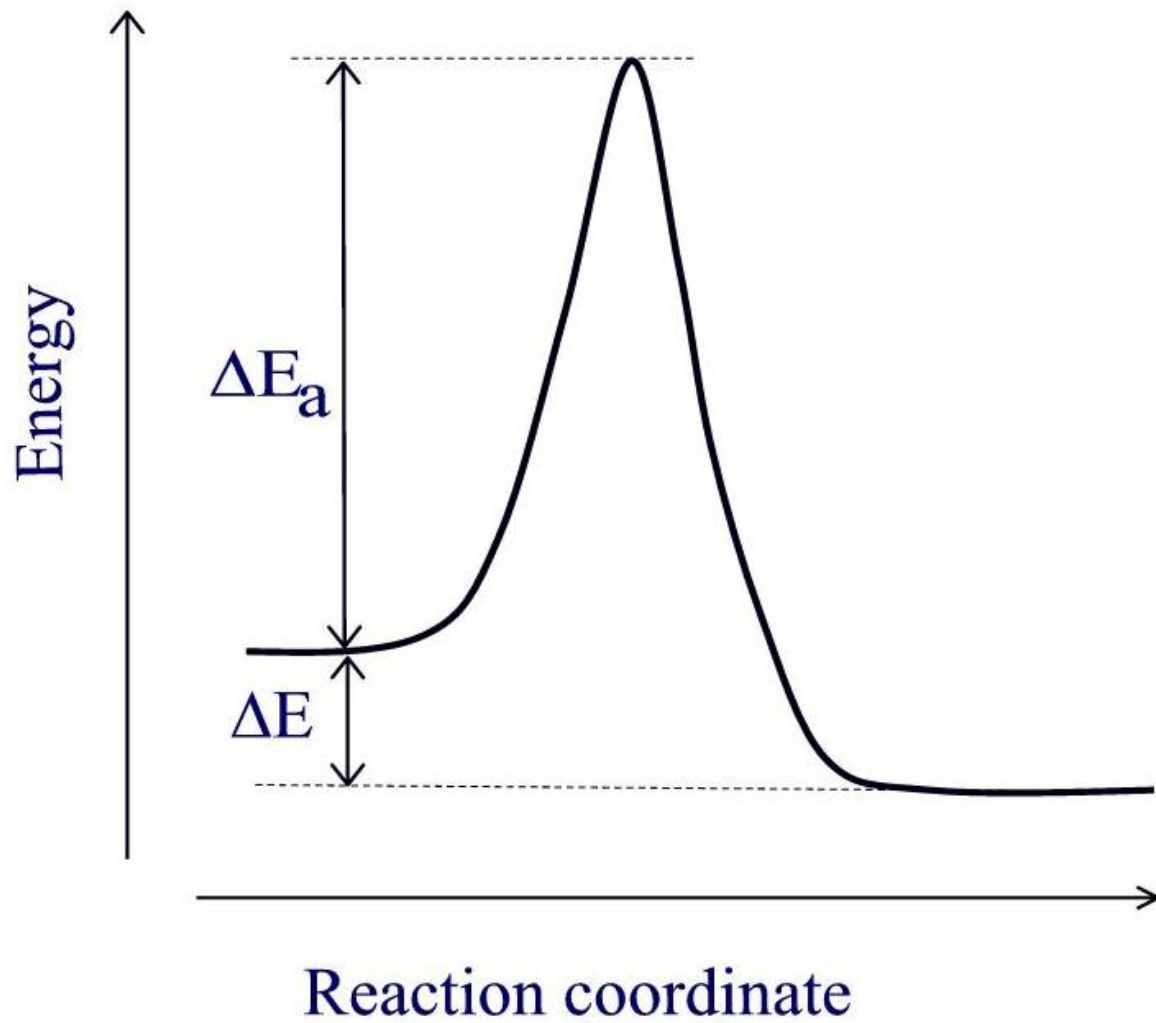


Essential Scientific Data

Structural and molecular biology

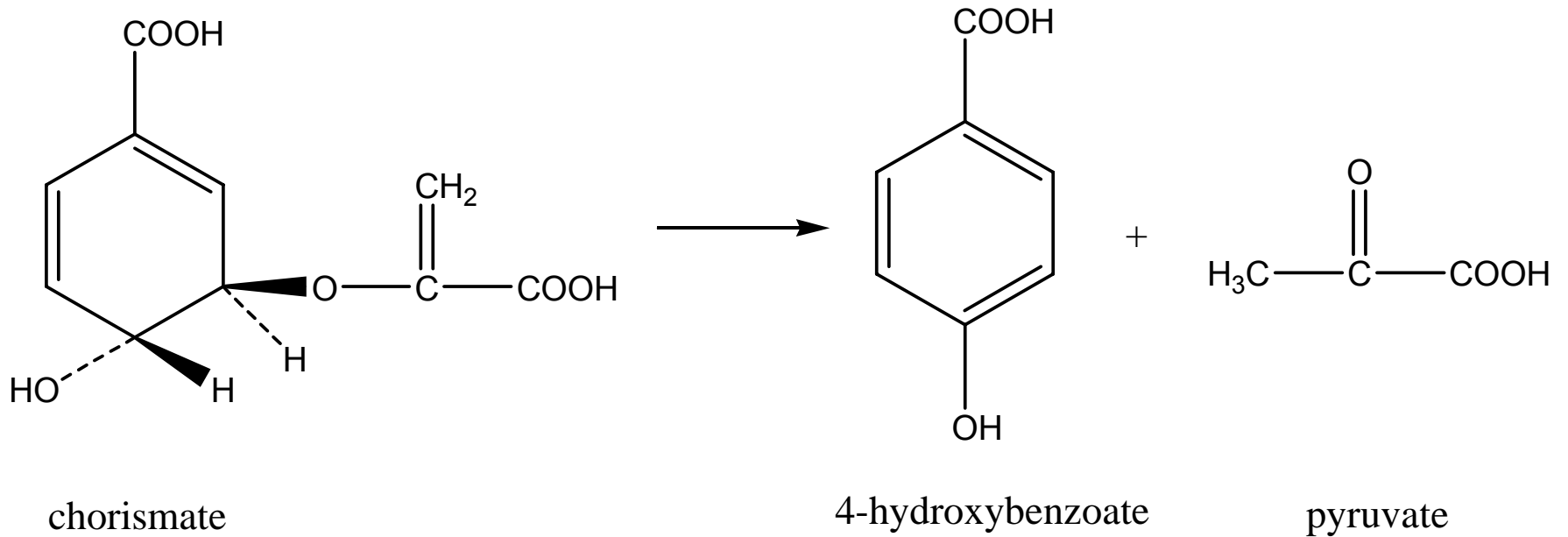
Thermodynamics – what happens

Kinetics – how fast it happens



Today's Featured Movie

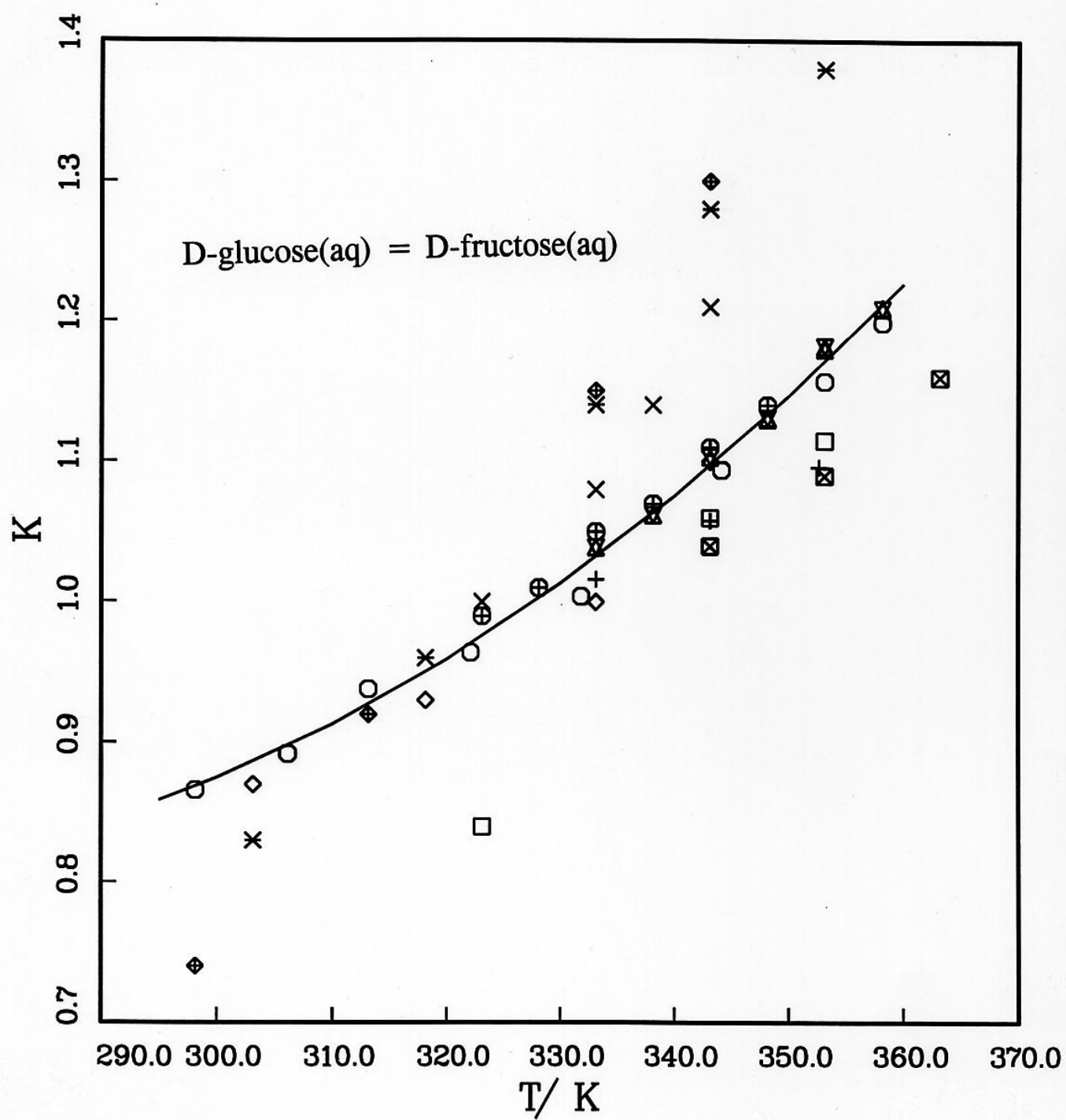
“The conversion of chorismate to 4-hydroxybenzoate + pyruvate”



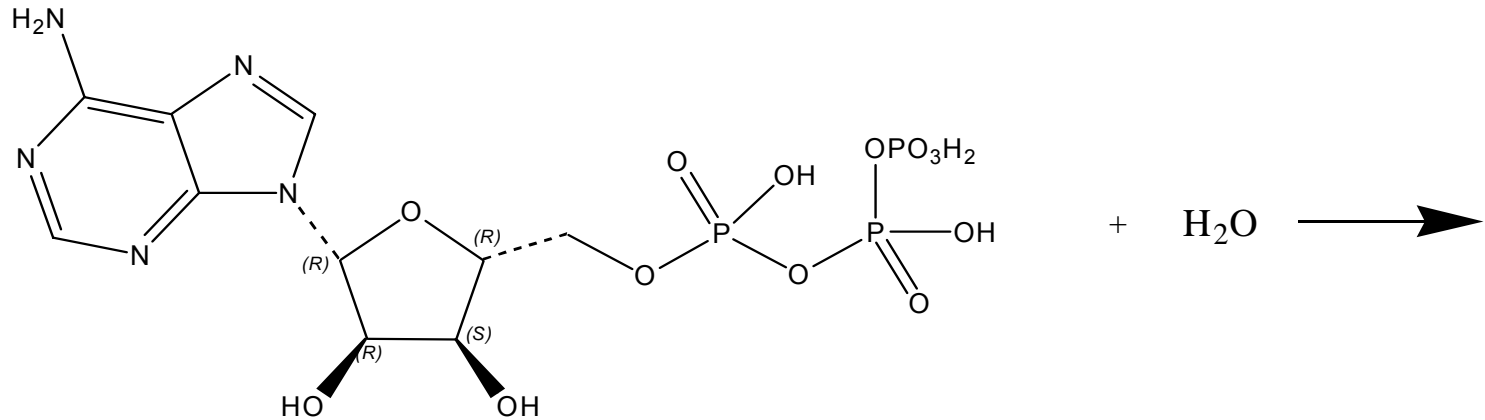
[Movie](#)

Thermodynamics answers several questions

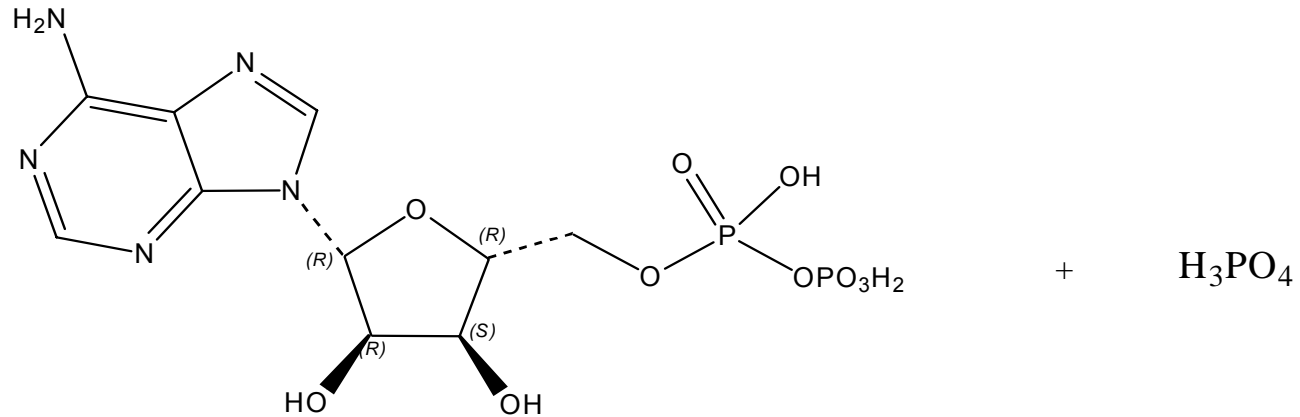
- Direction and extent of reaction.
- Effects of temperature, pressure, pH, ionic strength, and metal ion concentrations on the position of equilibrium.
- Enthalpy change for a reaction.
- Change in binding of ligand X for a reaction.
- Maximum amount of non- PV work that can be obtained from a reaction or series of reactions.
- Serves as a basis for discussion of the kinetics – Haldane relationships.
- Thermodynamic networks can be established to calculate the properties of many (unstudied) substances and reactions.
- Results can be correlated with molecular structure - serves as a basis for estimation methods.
- Magnitude of departure from equilibrium can be calculated.



The Hydrolysis Reaction of ATP



adenosine 5'-triphosphate (ATP)



adenosine 5'-diphosphate (ADP)

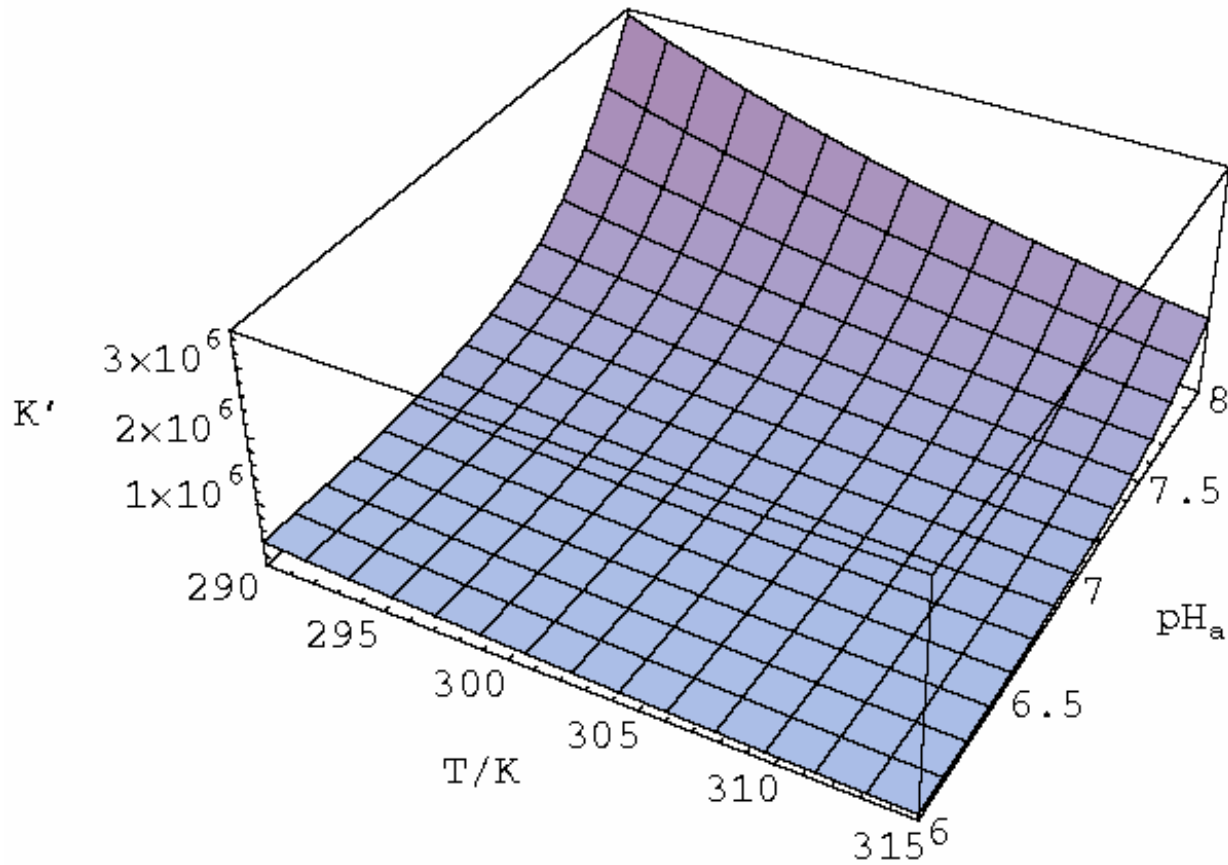
Thermodynamic Background

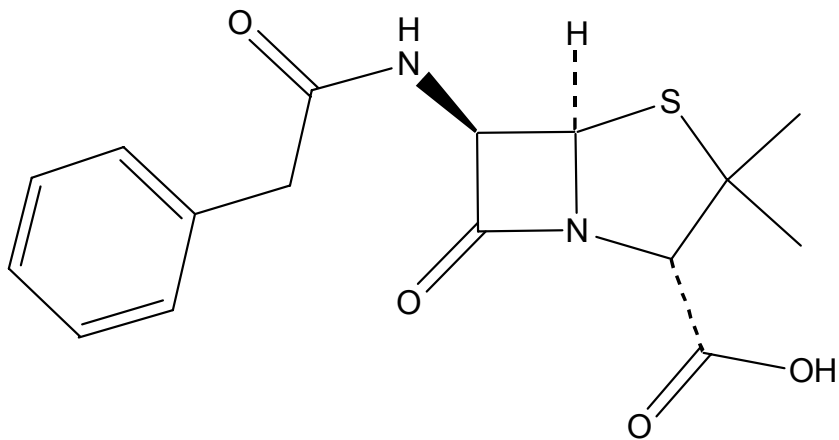
- ATP is a mixture of several ions: ATP^{4-} , HATP^{3-} , $\text{H}_2\text{ATP}^{2-}$, MgATP^{2-} , MgHATP^- , and Mg_2ATP . Similar situations exist for ADP and phosphate. Thus, one is dealing with a mixture of related species:

$$K' = [\text{total ADP}][\text{total phosphate}]/[\text{total ATP}]$$

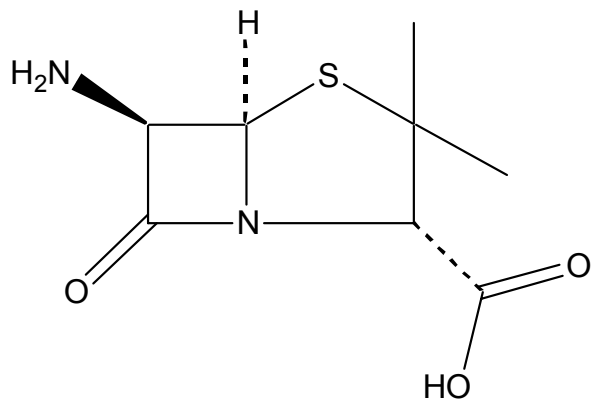
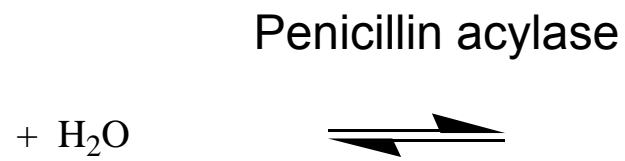
- K' is called an *apparent* equilibrium constant. It is a function of temperature, pH, pMg, and ionic strength. There is also an apparent (or, more formally, a standard transformed) enthalpy of reaction $\Delta_r H'^\circ$. This quantity is also a function of these several variables.
- The thermodynamics of biochemical reactions can be described by an equilibrium model that contains the thermodynamic data (K , $\Delta_r H^\circ$, and $\Delta_r C_p^\circ$) for the individual ionic reactions.

Thermodynamic Surface for the Hydrolysis of Adenosine 5'-triphosphate (ATP)

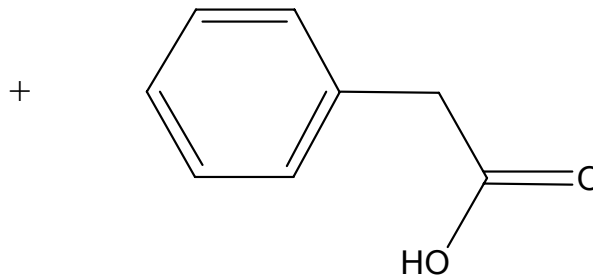




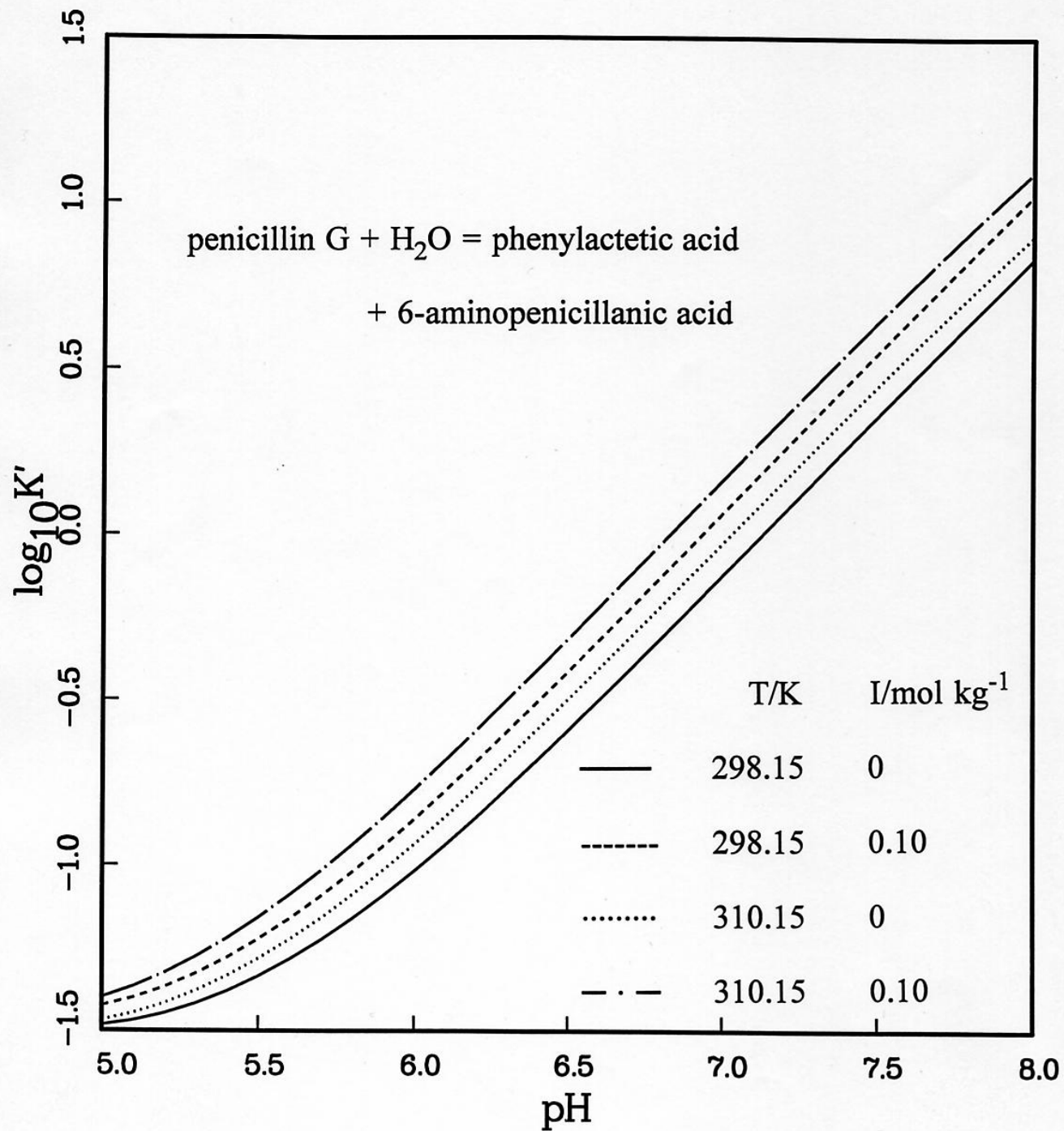
Penicillin G



6-aminopenicillanic acid



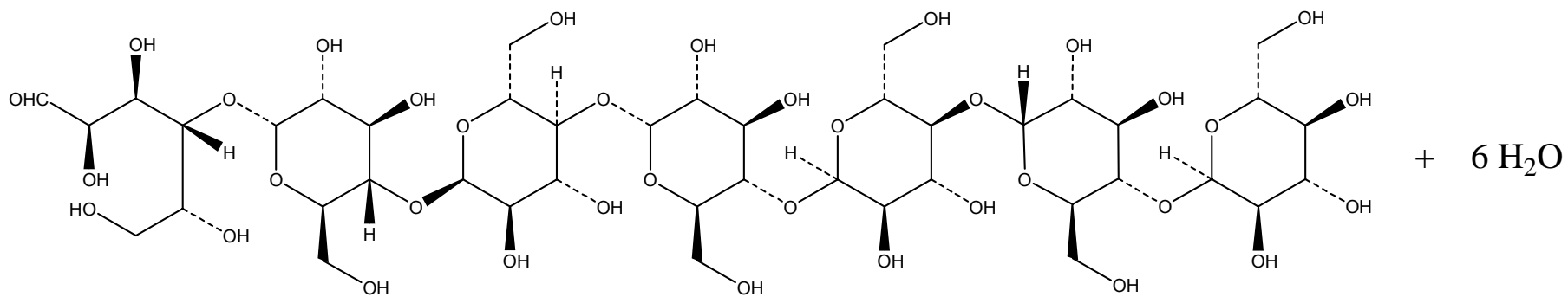
phenylacetic acid



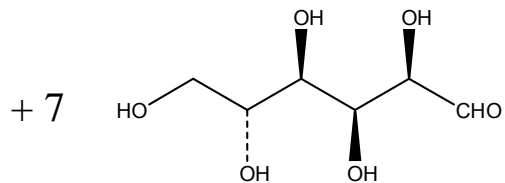
Thermodynamic quantities for the hydrolysis of disaccharides



Disaccharide	K	$\frac{\Delta_r G^\circ}{\text{kJ mol}^{-1}}$	$\frac{\Delta_r H^\circ}{\text{kJ mol}^{-1}}$	$\frac{\Delta_r S^\circ}{\text{J K}^{-1} \text{mol}^{-1}}$
cellobiose	>155	<-12.5	-2.43	>34
gentibiose	17.6	-7.1	2.58	33
isomaltose	17.3	-7.1	5.86	43
lactose	35	-8.8	0.44	31
lactulose	128	-12.0	2.21	48
maltose	>513	-15.5	-4.55	>37
α -D-melibiose	123	-11.9	-0.88	37
palatinose			-4.44	
sucrose	$4.44 \cdot 10^4$	-24.5	-15.00	32
D-trehalose	119	-11.9	-4.73	56
D-turanose			-2.68	



maltoheptaose



D-glucose

Enthalpies of hydrolysis of oligosaccharides



Oligosaccharide	$\frac{\Delta_r H^\ominus}{\text{kJ mol}^{-1}}$	$\frac{\Delta_r H^\ominus}{\text{kJ linkage}^{-1}}$
maltose	4.55	4.55
maltotriose	9.03	4.52
maltotetraose	13.79	4.60
maltopentaose	18.12	4.53
maltohexaose	22.40	4.48
maltoheptaose	26.81	4.47

ENZYME NOMENCLATURE

1992



RECOMMENDATIONS OF THE NOMENCLATURE COMMITTEE
OF THE INTERNATIONAL UNION OF BIOCHEMISTRY
AND MOLECULAR BIOLOGY ON THE NOMENCLATURE
AND CLASSIFICATION OF ENZYMES

This edition is a revision of the Recommendations (1984) of the Nomenclature Committee of IUB, and has been approved for publication by the Executive Committee of the International Union of Biochemistry and Molecular Biology

Prepared for NC-IUBMB by Edwin C. Webb



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Thermodynamics of Enzyme-Catalyzed Reactions

Oxidoreductases

Lyases

Transferases

Hydrolases

Isomerases

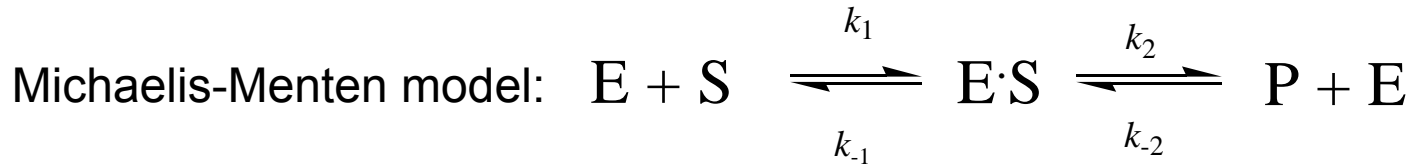
Ligases

This series of reviews covers the scientific literature on the thermodynamics of enzyme-catalyzed reactions. The articles have been published in the *Journal of Physical and Chemical Reference Data*.

This database is also available on the Web:

http://xpdb.nist.gov/enzyme_thermodynamics/

Kinetic Modeling



$$(d[\text{P}]/dt)_{t=0} = V_{\max}[\text{S}]/(K_M + [\text{S}])$$

where $K_M = (k_{-1} + k_2)/k_1$ and $V_{\max} = k_2[\text{E}]_T$

$$k_{\text{cat}} = V_{\max}/[\text{E}]_T$$

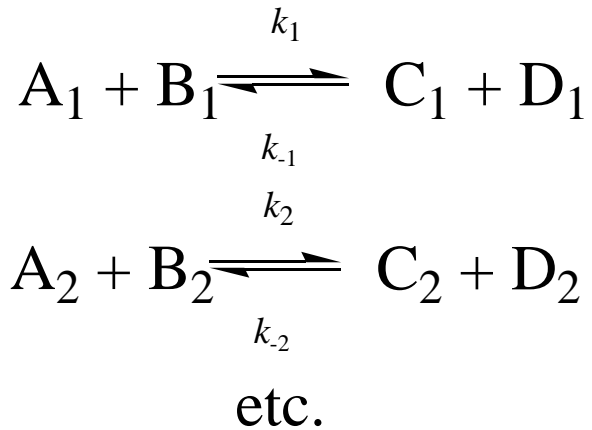
Also, have the Haldane relation:

$$K = [\text{P}]_{\text{eq}}/[\text{S}]_{\text{eq}} = k_1 k_2 / (k_{-1} k_{-2})$$

Thermodynamic and kinetic quantities are closely related

Kinetic Modeling - continued

A more general model would involve *all* of the species:



$$d[A_1]/dt = -k_1[A_1][B_1] + k_{-1}[C_1][D_1]$$

$$d[A_2]/dt = -k_2[A_2][B_2] + k_{-2}[C_2][D_2]$$

etc.

This system of differential equations can be solved using standard numerical methods.

Quantum Chemical Calculations: the Claisen Rearrangement of Chorismate to Prephenate

Solve: $H\psi = E\psi$. The effects of water solvation and solvent polarization were accounted for by using a Self-Consistent Isodensity Polarized Continuum Model. Calculations were done by Olaf Wiest (Notre Dame) and Ken Houk (UCLA).

Calculations yield: Energies, Entropies, Frequencies, Bond distances & angles

Comparison of results:

$$\Delta_{\text{r}}H^{\circ}(\text{calculated}) = -48.1 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{r}}H^{\circ}(\text{experimental}) = -(55.4 \pm 2.3) \text{ kJ mol}^{-1}$$

$$\Delta_{\text{r}}S^{\circ}(\text{calculated}) = 3 \text{ J K}^{-1} \text{ mol}^{-1}; \Delta_{\text{r}}S^{\circ}(\text{Benson estimation method}) = 0$$

Possible NIST Tasks

- Understanding, and perhaps modifying, the catalysts used to manufacture biofuels. Tools include molecular and structural biology, NMR, X-ray crystallography.
- Analytical chemistry. Development of methods and SRMs for the measurement of the hydrolysis products of cellulases acting on lignocellulosic materials.
- Thermodynamic and kinetic reference data both for pertinent processes, substances, and for metabolic engineering.
- Understanding the elementary steps (mechanisms) associated with the action of cellulases on lignocellulosic materials (microcrystalline cellulose would be a useful model system to start work on). At present, the mechanism(s) are not well understood. Solubilization may be (??) the rate determining step. Need to understand the mechanisms in order to enable the process engineering.
- Use of calorimetry to follow the kinetics (both short and long-term) of the action of cellulases.
- Calorimetric standards (combustion calorimetry) for the sale of biofuels based on energy content per kg instead of volume.

Additional ideas for pertinent research can be found at the DOE web-site:

Genomics: GTL
Systems Biology for Energy and Environment

<http://genomicsgtl.energy.gov/biofuels/b2bworkshop.shtml>

End of presentation