8460 *J. Phys. Chem. A* **1998,** *102,* 8460−8466

Calculation of Standard Transformed Entropies of Formation of Biochemical Reactants and Group Contributions at Specified pH

Robert A. Alberty

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received: February 4, 1998; In Final Form: March 26, 1998

When the pH is specified, the criterion for spontaneous change and equilibrium is stated in terms of the transformed Gibbs energy G' that is defined by a Legendre transform introducing pH as an intensive variable. The change in the standard transformed Gibbs energy of reaction $\Delta_r G'^\circ$ gives the apparent equilibrium constant K', and the standard transformed enthalpy $\Delta_r H'^\circ$ gives the temperature coefficient of K'. The corresponding standard transformed entropy of reaction $\Delta_r S'^\circ$ is less often discussed but is often easier to interpret in terms of structure. The standard transformed entropies of formation of 44 biochemical reactants are calculated at 298.15 K, 1 bar, pH 7, and ionic strengths of 0, 0.10, and 0.25 M from values of the standard Gibbs energies of formation $\Delta_f G^\circ$ and standard enthalpies of formation $\Delta_f H^\circ$ of the species involved. These values are used to calculate $\Delta_r S'^\circ$ for 19 biochemical reactions to illustrate the role that entropy plays in these reactions. $\Delta_f S'^\circ$ values for biochemical reactants at a specified pH can also be calculated from standard molar entropies of the species involved in a reactant. The standard transformed formation properties of biochemical reactants can be estimated by adding up group contributions. The contributions of 15 groups to $\Delta_f G'^\circ$ and $\Delta_f H'^\circ$ at pH 7 and three ionic strengths are calculated and used to estimate $\Delta_f G'^\circ$ and $\Delta_f H'^o$ for seven reactants. This shows that standard transformed formation properties can be estimated for biochemical reactants for which there are no equilibrium or calorimetric data.

Introduction

It is useful[1] to distinguish between chemical equations like

$$ATP^{4-} + H_2O = ADP^{3-} + HPO_4^{2-} + H^+ \quad (1)$$

for the hydrolysis of adenosine triphosphate with equilibrium constant K

$$K = \frac{[ADP^{3-}][HPO_4^{2-}][H^+]}{[ATP^{4-}]} \quad (2)$$

and biochemical equations at a specified pH like

$$ATP + H_2O = ADP + P_i \quad (3)$$

with apparent equilibrium constant K'

$$K' = \frac{[ADP][P_i]}{[ATP]} \quad (4)$$

where ATP, ADP, and P_i represent sums of species that are at equilibrium at the specified pH. (These equilibrium constants are considered to be dimensionless quantities, but the factors $c^\circ = 1$ mol L^{-1} have been omitted as a simplification.) The criterion for spontaneous change and equilibrium for a chemical reaction is $(\mathrm{d}G)_{T,P} \le 0$, but, when the pH is specified, the criterion for a biochemical reaction is $(\mathrm{d}G')_{T,P,\mathrm{pH}} \le 0$, where G' is the transformed Gibbs energy defined by the Legendre transform[2−4]

$$G' = G - n_c(\mathrm{H})\mu(\mathrm{H}^+) \quad (5)$$

The amount of the hydrogen component in the system, represented by $n_c(\mathrm{H})$, and the chemical potential of the hydrogen ion at the specified pH and ionic strength, represented by $\mu(\mathrm{H}^+)$, are the conjugate variables in the Legendre transform.[5,6] The Gibbs energy G is additive in the chemical potentials μ_i of species and the transformed Gibbs energy is additive in the transformed chemical potentials μ_i' of species: $G = \Sigma\, n_i\mu_i$ and $G' = \Sigma\, \mu_i' n_i$. The amount of the hydrogen component can be represented by $n_c(\mathrm{H}) = \Sigma N_\mathrm{H}(i) n_i$, where $N_\mathrm{H}(i)$ is the number of hydrogen atoms in species i. Substituting these relations in eq 5 yields the expression for the transformed chemical potential of species i:

$$\mu_i' = \mu_i - N_\mathrm{H}(i)\mu(\mathrm{H}^+) \quad (6)$$

It can be shown that when acid dissociations are at equilibrium, the transformed chemical potentials of the species making up a reactant (for example, ATP^{4-} $HATP^{3-}$, and H_2ATP^{2-}, for the reactant ATP in eqs 3 and 4) are equal.[2] Thus the fundamental equation for the transformed Gibbs energy for the system can be written in terms of amounts n_i' of reactants (sums of species):

$$\mathrm{d}G' = -S'\mathrm{d}T + V\mathrm{d}P + \sum_{i=1}^{N'} \mu_i' \mathrm{d}n_i' + 2.303 n_c(H) RT\, \mathrm{dpH} \quad (7)$$

where the number of reactants is represented by N'. The transformed entropy S' of the system is given by[3]

$$S' = S - n_c(\mathrm{H})\bar{S}(\mathrm{H}^+) \quad (8)$$

where $\bar{S}(\mathrm{H}^+)$ is the partial molar entropy of hydrogen ions at the specified pH and ionic strength. Defining the transformed

10.1021/jp981003p CCC: $15.00

enthalpy of the system by H′ = G′ − TS′ yields

$$H' = H - n_c(H)\bar{H}(\mathrm{H}^+) \tag{9}$$

where $\bar{H}(\mathrm{H}^+)$ is the partial molar enthalpy of hydrogen ions at the specified ionic strength.

In dealing with dilute solutions of biochemical reactants, it is convenient to assume that

$$\mu_i = \mu_i^\circ + RT\ln[i] \tag{10}$$

where the chemical potential of species *i* and the standard chemical potential of species *i* are at the specified ionic strength. Substituting eq 10 in eq 6 yields the dependence of the transformed chemical potential of species *i* on its concentration:

$$\mu_i' = \mu_i'^\circ + RT\ln[i] \tag{11}$$

where the standard transformed chemical potential of species *i* is given by

$$\mu_i'^\circ = \mu_i^\circ - N_\mathrm{H}(i)\mu(\mathrm{H}^+) \tag{12}$$

The standard transformed molar entropy of species *i* at a specified pH is given by

$$\bar{S}_i'^\circ = -\left(\frac{\partial \mu_i'^\circ}{\partial T}\right)_{P,\mathrm{pH}} = \bar{S}_i^\circ - N_\mathrm{H}(i)\bar{S}(\mathrm{H}^+) \tag{13}$$

The standard transformed molar enthalpy of species i at a specified pH is given by the Gibbs−Helmholtz equation

$$\bar{H}_i'^\circ = -T^2\left(\frac{\partial(\mu_i'^\circ/T)}{\partial T}\right)_{P,\mathrm{pH}} = \bar{H}_i^\circ - N_\mathrm{H}(i)\bar{H}(\mathrm{H}^+) \tag{14}$$

In working with the fundamental equation of thermodynamics for *G*′, it is convenient to use $\mu_i'^\circ$, $\bar{S}_i'^\circ$, and $\bar{H}_i'^\circ$ for species, but in calculations on experimental data it is more convenient to use the standard transformed formation properties $\Delta_\mathrm{f}G'^\circ(i)$, $\Delta_\mathrm{f}S'^\circ(i)$, and $\Delta_\mathrm{f}H'^\circ(i)$. The remainder of this paper will use the standard formation properties $\Delta_\mathrm{f}G^\circ(i)$, $\Delta_\mathrm{f}S^\circ(i)$, and $\Delta_\mathrm{f}H^\circ(i)$ for species to calculate $\Delta_\mathrm{f}G'^\circ(i)$, $\Delta_\mathrm{f}S'^\circ(i)$, and $\Delta_\mathrm{f}H'^\circ(i)$ for biochemical reactants (sums of species) and standard transformed reaction properties $\Delta_\mathrm{r}G'^\circ(i)$, $\Delta_\mathrm{r}S'^\circ(i)$, and $\Delta_\mathrm{r}H'^\circ(i)$ for biochemical reactions at pH 7.

In discussing the thermodynamics of biochemical reactions, there has been a tendency to emphasize $\Delta_\mathrm{r}G'^\circ$ because it gives the apparent equilibrium constant *K*′ and $\Delta_\mathrm{r}H'^\circ$ because it gives the temperature coefficient of *K*′. But it is of interest to calculate $\Delta_\mathrm{r}S'^\circ$ because entropy changes in reactions are often easier to interpret than changes in Gibbs energies and enthalpies. For example, Pitzer[9] writes “The energies of substances are, however, much more dependent than entropies on the detailed electronic structure of the atoms, the type of bonding, etc.” Biochemical reactions are often discussed in terms of strengths of bonds, but, as shown by reactions discussed here, entropy changes are equally important and may determine whether a reaction goes to the right or left at a specified pH. This introduction has involved the molar entropies of species, but these are not known for very many species involved in biochemical reactions, and so the question is how entropy effects can be discussed without this information.

Calculation of Standard Transformed Entropies of Formation of Biochemical Reactants

The first step in the calculation of $\Delta_\mathrm{f}G'^\circ(i)$, $\Delta_\mathrm{f}S'^\circ(i)$, and $\Delta_\mathrm{f}H'^\circ(i)$ for a reactant is to calculate these properties for the various species of the reactant. Equations 12−14 for species are used in the form

$$\Delta_\mathrm{f}G'^\circ(i) = \Delta_\mathrm{f}G^\circ(i) - N_\mathrm{H}(i)\{\Delta_\mathrm{f}G^\circ(\mathrm{H}^+) + RT\ln[\mathrm{H}^+]\} \tag{15}$$

$$\Delta_\mathrm{f}S'^\circ(i) = \Delta_\mathrm{f}S^\circ(i) - N_\mathrm{H}(i)\{\Delta_\mathrm{f}S^\circ(\mathrm{H}^+) - R\ln[\mathrm{H}^+]\} \tag{16}$$

$$\Delta_\mathrm{f}H'^\circ(i) = \Delta_\mathrm{f}H^\circ(i) - N_\mathrm{H}(i)\Delta_\mathrm{f}H^\circ(\mathrm{H}^+) \tag{17}$$

The standard formation properties of an ionic species depends on the ionic strength, and in the absence of data on specified solutions, the extended Debye−Hoiickel theory at 298.15 K is used in the form:[8,9]

$$\Delta_\mathrm{f}G^\circ(I) = \Delta_\mathrm{f}G^\circ(I=0) - 2.91482z_i^2I^{1/2}/(1+BI^{1/2}) \tag{18}$$

$$\Delta_\mathrm{f}H^\circ(I) = \Delta_\mathrm{f}H^\circ(I=0) + 1.4775z_i^2I^{1/2}/(1+BI^{1/2}) \tag{19}$$

$$\Delta_\mathrm{f}S^\circ(I) = \Delta_\mathrm{f}S^\circ(I=0) + 14.7319z_i^2I^{1/2}/(1+BI^{1/2}) \tag{20}$$

where z_i is the charge number, $B = 1.6\ \mathrm{L}^{1/2}\ \mathrm{mol}^{-1/2}$, $\Delta_\mathrm{f}G^\circ$ and $\Delta_\mathrm{f}H^\circ$ are in kJ mol^{-1}, and $\Delta_\mathrm{f}S^\circ$ is in J K^{-1} mol^{-1}.

When a reactant consists of a single species, eqs 15−20 yield the desired standard transformed formation properties at the specified pH, but, when a reactant consists of several species at equilibrium at the specified pH, a further step is required. An example of such a reactant is ATP, which at pH 7 is a mixture of the species $\mathrm{ATP},^{4-}$ HATP^{3-}, and $\mathrm{H_2ATP}^{2-}$. The question to be answered is “What values of $\Delta_\mathrm{f}G'^\circ$, $\Delta_\mathrm{f}H'^\circ$, and $\Delta_\mathrm{f}S'^\circ$ apply to the reactant ATP at the specified pH?” This question was answered earlier[10,11] in investigating $\Delta_\mathrm{f}G^\circ$, $\Delta_\mathrm{f}H^\circ$, $\Delta_\mathrm{f}S^\circ$, and $\Delta_\mathrm{f}C_P^\circ$ for equilibrium mixtures of isomers of gas molecules at specified *T* and *P*. Since the Gibbs energies of isomers are equal at equilibrium, we can refer to the species of a reactant at a specified pH as forming a pseudoisomer group. The effective standard transformed Gibbs energy of formation of the pseudoisomer group, $\Delta_\mathrm{f}G'^\circ(\mathrm{iso})$, is given by[10,11]

$$\Delta_\mathrm{f}G'^\circ(\mathrm{iso}) = -RT\ln\Sigma\exp(-\Delta_\mathrm{f}G'^\circ(i)/RT) \tag{21}$$

which is a kind of partition function. This equation can also be written as

$$\Delta_\mathrm{f}G'^\circ(\mathrm{iso}) = \Sigma r_i\Delta_\mathrm{f}G'^\circ(i) + RT\Sigma r_i\ln r_i \tag{22}$$

where the equilibrium mole fraction r_i of species *i* is given by

$$r_i = \exp\{[\Delta_\mathrm{f}G'^\circ(\mathrm{iso}) - \Delta_\mathrm{f}G'^\circ(i)]/RT\} \tag{23}$$

which is a kind of Boltzmann equation. The standard transformed molar enthalpy of the pseudoisomer group is given by

$$\Delta_\mathrm{f}H'^\circ(\mathrm{iso}) = \Sigma r_i\Delta_\mathrm{f}H'^\circ(i) \tag{24}$$

The standard transformed entropy of formation of the pseudoisomer group is given by

$$\Delta_\mathrm{f}S'^\circ(\mathrm{iso}) = \Sigma r_i\Delta_\mathrm{f}S'^\circ(i) - R\Sigma r_i\ln r_i \tag{25}$$

The second term is an additional contribution of entropy to the standard transformed Gibbs energy of reaction that is only effective at specified pH. The remainder of the paper is concerned with the standard transformed properties of reactants (pseudoisomer groups), and so they will be referred as simply $\Delta_\mathrm{f}G'^\circ$, $\Delta_\mathrm{f}H'^\circ$, and $\Delta_\mathrm{f}S'^\circ$.

TABLE 1: Standard Transformed Entropies of Formation and Standard Transformed Enthalpies of Formation Divided by Temperature for Reactants in Biochemical Reactions at 298.15 K, 1 bar, pH 7, and Three Ionic Strengths[a]

	$\Delta_f S'^\circ$/J K^{-1} mol^{-1}, at I/M			($\Delta_f H'^\circ/T$)/J K^{-1} mol^{-1}, at I/M		
reactant	0	0.10	0.15	0	0.10	0.25
ATP	−3001.59	−3011.11	−3010.90	−10038.30	−10046.30	−10047.30
ADP	−2574.31	−2596.84	−2602.04	−6714.38	−6725.54	−6727.90
AMP	−2162.28	−2193.08	−2202.19	−3394.89	−3407.21	−3410.62
adenosine	−1742.2	−1782.41	−1795.40	−0.02	−13.55	−17.91
P_i	−813.96	−807.46	−804.63	−4364.39	−4359.93	−4358.17
glucose 6-phos	−3189.88	−3213.80	−3221.13	−7633.96	−7642.33	−7644.82
glucose	−2769.63	−2806.75	−2818.74	−4233.41	−4245.89	−4249.92
H_2O	−431.17	−437.35	−439.35	−958.68	−960.76	−961.43
NAD_{ox}	−3484.37	−3561.70	−3586.67	0	−26.02	−34.41
NAD_{red}	−3801.48	−3872.63	−3895.60	−107.13	−131.06	−138.79
$NADP_{ox}$	−3350.35	−3399.85	−3415.83	0	−16.65	−22.02
$NADP_{red}$	−3669.41	−3700.34	−3710.33	−97.87	−108.28	−111.64
acetaldehyde	−782.01	−794.38	−798.38	−712.16	−716.32	−717.66
acetate	−793.46	−799.64	−801.64	−1630.09	−1632.17	−1632.84
alanine	−1554.57	−1576.22	−1583.21	−1860.81	−1868.09	−1870.44
ammonia	−714.49	−723.77	−726.77	−444.44	−447.56	−448.57
ethanol	−1161.82	−1180.38	−1186.38	−966.96	−973.21	−975.22
pyruvate	−817.77	−823.96	−825.96	−1999.73	−2001.81	−2002.48
formate	−384.06	−384.06	−384.06	−1427.30	−1427.30	−1427.30
sucrose	−5078.68	−5146.74	−5168.71	−7378.40	−7401.29	−7408.68
$TotCO_2$	−490.00	−489.19	−488.93	−2325.76	−2324.33	−2323.92
2-propanol	−1560.47	−1585.22	−1593.21	−1109.61	−1117.93	−1120.62
acetone	−1012.06	−1030.62	−1036.61	−743.62	−749.86	−751.88
glycerol	−1672.73	−1697.48	−1705.47	−2269.17	−2277.49	−2280.18
lactose	−5181.27	−5249.33	−5271.30	−7489.80	−7512.69	−7520.09
maltose	−5173.27	−5241.33	−5263.30	−7506.50	−7529.39	−7536.79
succinate	−1268.03	−1268.03	−1268.03	−3047.73	−3047.73	−3047.73
fumarate	−856.72	−850.53	−848.54	−2607.37	−2605.29	−2604.62
lactate	−1239.96	−1252.33	−1256.33	−2302.99	−2307.15	−2308.50
glycine	−1150.01	−1165.47	−1170.47	−1754.15	−1759.35	−1761.03
urea	−921.27	−933.64	−937.64	−1065.40	−1069.56	−1070.91
ribulose	−2303.01	−2333.95	−2343.93	−3431.23	−3441.63	−3444.99
fructose	−2761.51	−2798.64	−2810.62	−4223.98	−4236.47	−4240.50
ribose	−2330.28	−2361.21	−2371.20	−3468.05	−3478.46	−3481.82
ribose 5-phos	−2729.57	−2754.20	−2760.96	−6834.72	−6847.17	−6850.26
aspartate	−1634.29	−1649.76	−1654.75	−3164.21	−3169.41	−3171.09
glutamate	−2019.35	−2041.01	−2048.00	−3286.58	−3293.86	−3296.21
glutamine	−2269.14	−2300.07	−2310.06	−2699.99	−2710.39	−2713.75
citrate	−1852.49	−1840.19	−1836.09	−5083.94	−5078.47	−5076.85
CO_2(g)	2.85	2.85	2.85	−1319.84	−1319.84	−1319.84
O_2(g)	0	0	0	0	0	0
O_2(aq)	−94.25	−94.25	−94.25	−39.24	−39.24	−39.24
H_2(g)	−268.03	−274.21	−276.21	0	−2.08	−2.75
H_2(aq)	−341.15	−347.33	−349.33	−14.09	−16.17	−16.84

[a] This table is based on the conventions that $\Delta_f G^\circ = \Delta_f H^\circ = 0$ for H^+, adenosine, NAD^-, and $NADP^{3-}$ at zero ionic strength.

Recently, standard transformed Gibbs energies of formation and standard transformed enthalpies of formation of biochemical reactant have been calculated[12] at 298.15 K, 1 bar, pH 7, and ionic strengths of 0, 0.10, and 0.25 M from $\Delta_f G^\circ$ and $\Delta_f H^\circ$ values for species of 53 biochemical reactants. The input data have come from a number of sources.[4,13−19] The calculated $\Delta_f G'^\circ$ values were tested by calculating apparent equilibrium constants K' for biochemical reactions for which K' values have been reported in the literature. Since both $\Delta_f G'^\circ$ and $\Delta_f H'^\circ$ are available for 44 of these biochemical reactants, the corresponding $\Delta_f S'^\circ$ values can be calculated by using

$$\Delta_f S_i'^\circ = (\Delta_f H_i'^\circ - \Delta_f G_i'^\circ)/T \tag{26}$$

The standard transformed entropies of formation of biochemical reactants calculated in this way are given in Table 1 at 298.15 K, 1 bar, pH 7, and three values of the ionic strength.

Since it is not possible to connect the thermodynamic properties of adenosine, NAD^- (oxidized nicotinamide adenine dinucleotide), and $NADP^{3-}$ with the elements, these species have been assigned $\Delta_f G^\circ = \Delta_f H^\circ = 0$, in the same way that $\Delta_f G^\circ(H^+) = \Delta_f H^\circ(H^+) = 0$ in chemical thermodynamic tables. Note that the standard transformed formation properties of formate and succinate in Table 1 are independent of ionic strength because $z_i^2 = N_H(i)$. The standard transformed formation properties of CO_2(g), O_2(g), and O_2(aq) are independent of pH and ionic strength because they are nonelectrolytes and do not contain hydrogen atoms. The first three columns in this table were calculated by using eq 26, but they could have been calculated from the standard molar entropies of species of these reactants, as described in a later section.

Table 1 makes it possible to calculate $\Delta_r S'^\circ$ for a large number of biochemical reactions, but we will concentrate here on reactions for which K' values have been determined. Table 1 also contains $\Delta_f H'^\circ/T$, which is the entropy change in the surroundings due to the heat of reaction when the reactant is formed from its elements. Comparison of the first three columns with the second set of three columns makes it possible to see whether the standard transformed Gibbs energy of formation $\Delta_f G'^\circ$ is determined primarily by entropy contributions or enthalpy contributions.

Calculation of Standard Transformed Entropies of Reaction of Biochemical Reactions

Values of $\Delta_r S'^\circ$ and $\Delta_r H'^\circ/T$ are given in Table 2 for the following enzyme-catalyzed reactions and a net reaction catalyzed by a series of enzymes. These are reactions for which apparent equilibrium constants have been measured.[12] These reactions have been written in the direction they go spontaneously at 298.25 K, 1 bar, pH 7, and ionic strengths of 0, 0.10, and 0.25 M. EC numbers[20] are given where applicable.

1.12.1.2a $\text{NAD}_{ox} + H_2(g) = \text{NAD}_{red}$

1.12.1.2b $\text{NAD}_{ox} + H_2(aq) = \text{NAD}_{red}$

1.1.1.1a acetaldehyde + NAD_{red} = ethanol + NAD_{ox}

1.1.1.1b acetone + NAD_{red} = 2-propanol + NAD_{ox}

1.2.1.3 acetaldehyde + NAD_{ox} + H_2O = acetate + NAD_{red}

1.4.1.1 pyruvate + NAD_{red} + ammonia = L-alanine + NAD_{ox} + H_2O

1.2.1.2a formate + NAD_{ox} = $CO_2(g)$ + NAD_{red}

1.2.1.2b formate + NAD_{ox} + H_2O = TotCO_2 + NAD_{red}

1.1.1.27 pyruvate + NAD_{red} = (S)-lactate + NAD_{ox}

3.2.1.3 maltose + H_2O = 2 D-glucose

5.3.1.5 D-fructose = D-glucose

6.3.1.2 L-glutamate + ammonia + ATP = L-glutamine + P_i + ADP

3.6.1.32 ATP + H_2O = ADP + P_i

3.1.3.1a ADP + H_2O = AMP + P_i

3.1.3.1b AMP + H_2O = adenosine + P_i

2.7.4.3 ATP + AMP = 2ADP

3.1.3.1d D-glucose 6-phosphate + H_2O = D-glucose + P_i

2.7.1.1 ATP + D-glucose = ADP + D-glucose 6-phosphate

glycolysis D-glucose + $2P_i$ + 2ADP + 2NAD_{ox} = 2(pyruvate) + 2ATP + 2NAD_{red} + $2H_2O$

Table 2 also gives the values of $\Delta_r H'^\circ/T$, which are the entropy changes in the heat reservoir when the reaction occurs. The standard transformed reaction properties all depend on the ionic strength, except for the reactions of nonelectrolytes (3.2.1.3 and 5.3.1.5). Some of these ionic strength effects are quite large.

The standard transformed Gibbs energies of rection and apparent equilibrium constants are given in Table 3 to show the net effects of the entropy and enthalpy changes.

TABLE 2: Standard Transformed Entropies of Reaction and Standard Transformed Enthalpies of Reaction Divided by Temperature for 19 Biochemical Reactions at 298.15 K, 1 bar, pH 7, and Three Ionic Strengths[a]

	$\Delta_r S'^\circ$/J K^{-1} mol^{-1}, at I/M			($\Delta_r H'^\circ/T$)/J K^{-1} mol^{-1}, at I/M		
reaction	0	0.10	0.25	0	0.10	0.25
1.12.1.2a	−49.08	−36.71	−32.71	−107.13	−102.97	−101.62
1.12.1.2b	24.04	36.41	40.40	−93.04	−88.88	−87.53
1.1.1.1a	−62.71	−75.08	−79.08	−147.68	−151.84	−153.18
1.1.1.1b	−231.30	−243.68	−247.67	−258.86	−263.02	−264.37
1.2.1.3	102.61	121.17	127.16	−66.38	−60.13	−58.12
1.4.1.1	−136.36	−154.92	−160.92	−268.19	−274.43	−276.45
1.2.1.2a	69.80	75.98	77.98	0.34	2.42	3.09
1.2.1.2b	8.12	21.30	25.55	−46.91	−41.31	−39.56
1.1.1.27	−105.08	−117.45	−121.45	−196.13	−200.29	−201.64
3.2.1.3	65.18	65.18	65.18	−1.63	−1.63	−1.63
5.3.1.5	−8.12	−8.12	−8.12	−9.42	−9.42	−9.42
6.3.1.2	78.03	71.52	68.94	−9.41	−8.10	−7.78
3.6.1.32	44.49	44.17	43.59	−81.76	−78.36	−77.38
3.1.3.1a	29.24	33.65	34.58	−86.22	−80.84	−79.46
3.1.3.1b	37.29	40.56	41.52	−10.84	−5.51	−4.03
2.7.4.3	15.25	10.52	9.01	4.46	2.48	2.08
3.1.3.1d	37.46	36.94	37.11	−5.16	−2.73	−1.85
2.7.1.1	7.03	7.23	6.48	−76.60	−75.64	−75.53
glycolysis	410.89	448.66	461.79	183.20	188.90	190.97

[a] Note that all of these reactions have been written so that they are spontaneous to the right.

In the 19 reactions in Table 2, the $\Delta_r H'^\circ$ and the $\Delta_r S'^\circ$ are both favorable for 10 reactions. In three of the reactions, $\Delta_r H'^\circ$ opposes reaction, but the reaction goes to the right because of a favorable $\Delta_r S'^\circ$ change. Reaction 1.2.1.2a goes to the right because of the favorable $\Delta_r S'^\circ$ change due to the production of $CO_2(g)$. The opposing effects are nearly balanced in reaction 2.7.4.3. The fact that glycolysis goes to the right, although $\Delta_r H'^\circ$ is unfavorable, is quite striking; in other words, glycolysis goes on because of the driving force of entropy, rather than the driving force of enthalpy.

In six of the cases in Table 2, $\Delta_r S'^\circ$ opposes reaction, but the reactions go to the right because of favorable $\Delta_r H'^\circ$ changes. It is of interest to note the very different entropy contributions in reactions 1.12.1.2a and b. Although both reactions go to the right, the first has a much smaller apparent equilibrium constant because of the large entropy of gaseous hydrogen. This difference is in striking contrast to the difference in apparent equilibrium constants between reactions 1.2.1.2a and b, where 1.2.1.2a also involves the formation of a gas. There the effect of the large entropy of gaseous carbon dioxide is counterbalanced by the fact that reaction 1.2.1.2b involves H_2O as a reactant and TotCO_2 is a mixture of $H_2CO_3(aq)$, $CO_2(aq)$, $HCO_3^-(aq)$, and $CO_3^{2-}(aq)$. In the hydrolysis of maltose (3.2.1.3) the effects of the entropy changes are much larger than those of the enthalpy changes.

Calculation of Standard Transformed Entropies of Formation of Biochemical Reactants from Standard Molar Entropies

If the standard molar entropies $\bar{S}^\circ(i)$ of all of the species of a reactant are known, the standard transformed entropy of formation $\Delta_f S'^\circ$ can be calculated for the reactant at a specified pH and ionic strength. This is useful because if $\Delta_r H'^\circ$ has been measured calorimetrically, $\Delta_r G'^\circ$ and K' can then be calculated for a biochemical reaction. When the apparent equilibrium constant is very large, this provides a method for determining its value. For example, Kast et al.[21] estimated the standard molar entropy of reaction for the isomerization of chorismate^{2-}(aq) to prephenate^{2-}(aq) and used it in conjunction with

TABLE 3: Standard Transformed Gibbs Energies of Reaction and Apparent Equilibrium Constants for 19 Biochemical Reactions at 298.15 K, 1 bar, pH 7, and Three Ionic Strengths

	$\Delta_rG'^\circ$/J K^{-1} mol^{-1}, at I/M			K'; at I/M		
reaction	0	0.10	0.25	0	0.10	0.25
1.12.1.2a	−17.31	−19.75	−20.55	1.08×10^3	2.89×10^3	3.97×10^3
1.12.1.2b	−34.90	−37.35	−38.15	1.30×10^6	3.50×10^6	4.82×10^6
1.1.1.1a	−25.33	−22.89	−22.10	3.74×10^4	1.02×10^4	0.74×10^4
1.1.1.1b	−8.22	−5.77	−4.98	27.5	10.2	7.5
1.2.1.3	−50.38	−54.06	−55.24	0.67×10^9	2.95×10^9	4.76×10^9
1.4.1.1	−39.30	−35.63	−34.45	7.7×10^6	1.75×10^6	1.09×10^6
1.2.1.2a	−20.71	−21.93	−22.33	4.25×10^3	7.0×10^3	8.1×10^3
1.2.1.2b	−16.41	−18.67	−19.41	0.75×10^3	1.86×10^3	2.52×10^3
1.1.1.27	−27.15	−24.70	−23.91	5.7×10^4	2.12×10^4	1.54×10^4
3.2.1.3	−19.92	−19.92	−19.92	3.09×10^3	3.09×10^3	3.09×10^3
5.3.1.5	−0.39	−0.39	−0.39	1.17	1.17	1.17
6.3.1.2	−26.07	−23.74	−22.88	3.69×10^4	1.44×10^4	1.02×10^4
3.6.1.32	−37.64	−36.53	−36.07	3.93×10^6	2.51×10^6	2.08×10^6
3.1.3.1a	−34.43	−34.14	−34.00	10.7×10^5	9.6×10^5	9.1×10^5
3.1.3.1b	−14.35	−13.74	−13.58	3.27×10^2	2.55×10^2	2.39×10^2
2.7.4.3	−3.22	−2.40	−2.07	3.66	2.63	2.30
3.1.3.1d	−12.71	−11.83	−11.62	1.68×10^2	1.18×10^2	1.08×10^2
2.7.1.1	−24.93	−24.71	−24.451	2.33×10^4	2.13×10^4	1.92×10^4
glycolysis	−67.88	−77.44	−80.75	7.81×10^{11}	3.70×10^{13}	1.40×10^{14}

the measured enthalpy of reaction to obtain the standard Gibbs energy of reaction of -56 kJ mol^{-1} at 298.15 K, which leads to an equilibrium constant too large to be measured directly.

The first step in the calculation of the standard transformed entropy of formation of a biochemical reactant (pseudoisomer group) from the standard molar entropies of the species is to adjust each of the $\bar{S}^o(i)$ values to the desired ionic strength using eq 20. The second step is to use these values to calculate the corresponding standard entropies of formation of the species. As an example, consider the formation reaction for the aqueous ion $H_2PO_4^-$:

$$H_2(g) + P(s) + 2O_2(g) + e^- = H_2PO_4^- \tag{27}$$

Since the formal electron e^- is not assigned standard thermodynamic properties, the reaction

$${}^1/_2H_2(g) = H^+ + e^- \tag{28}$$

is added to reaction 27 to obtain

$${}^3/_2H_2(g) + P(s) + 2O_2(g) = H^+ + H_2PO_4^- \tag{29}$$

Since $\bar{S}^\circ(H^+) = 0$ by convention, Δ_fS° $(H_2PO_4^-)$ can be calculated from $\bar{S}^\circ(H_2PO_4^-)$. This calculation is described in the Introduction to the *NBS Tables of Chemical Thermodynamics*,[14] which gives the relation

$$\Delta_fS^\circ(i) = \bar{S}^\circ(i) - \Sigma\bar{S}^\circ(\text{elem}) + (n/2)\bar{S}^\circ(H_2,g) \tag{30}$$

where n is defined by

$$X + (n/2)H_2(g) = X^{n-}(\text{ao}) + nH^+(\text{ao}) \tag{31}$$

The descriptor ao designates the thermodynamic properties of undissociated molecules in water. The third step is to adjust $\Delta_fS^\circ(i)$ for each species making up a reactant to the desired pH using eq 13 in the form

$$\Delta_fS'^\circ(i) = \Delta_fS^\circ(i) - N_H(i)\{\Delta_fS^\circ(H^+) - R\ln[H^+]\} \tag{32}$$

The last step step is to use eq 25 to calculate $\Delta_fS'^\circ$ for the reactant. These steps can be used to calculate columns 2 to 4 in Table 1 for the reactants for which the $\bar{S}^\circ(i)$ values are known, but $\bar{S}^\circ(i)$ values are not known for species of adenosine phosphates and nicotinamide adenine dinucleotides.

When the convention $\Delta_fG^\circ = \Delta_fH^\circ = 0$ for a species is used, the $\Delta_fG'^\circ$ and $\Delta_fH'^\circ$ values for that species and for others derived from it cannot be used to calculate $\bar{S}^\circ$ for any of these species. But $\Delta_fS'^\circ$ values calculated from $\Delta_fG'^\circ$ and $\Delta_fH'^\circ$ can be used to calculate $\Delta_rS'^\circ$. The fact that third law entropies cannot be calculated for species where calculations of $\Delta_fS'^\circ$ are based on this convention can be demonstrated with HPO_4^{2-} and $H_2PO_4^-$ by assigning $\Delta_fG^\circ(HPO_4^{2-}) = \Delta_fH^\circ(HPO_4^{2-}) = 0$, recalculating Δ_fG° and Δ_fH° for $H_2PO_4^-$, and using these values to calculate $\Delta_fS^\circ(H_2PO_4^-)$. The value of $\Delta_fS^\circ(H_2PO_4^-)$ and $\Delta_fS^\circ(HPO_4^{2-}) = 0$ can be used to calculate Δ_rS° for a reaction but cannot be used to calculate $\bar{S}^\circ(HPO_4^{2-})$ and $\bar{S}^\circ(H_2PO_4^-)$.

Calculation of Standard Transformed Formation Properties of Groups

Benson and co-workers[22−25] have shown that the standard formation properties and molar entropies and heat capacities of organic gases can be represented to a significant degree of accuracy in terms of group values that apply generally. The Benson method is based on a second-order approximation to additivity that treats a molecular property as being composed of contributions of groups of atoms. The group designation identifies the polyvalent atom and then its ligands. For example, $C(H)_2(C)_2$ represents a methylene group in which the carbon atom is singly bonded to two carbon atoms. H_2O and CH_4 are treated as irreducible entities. The values for standard enthalpies of formation can be estimated to ±2 kJ mol^{-1} for smaller molecules and ±12 kJ mol^{-1} for highly substituted molecules. The values of molar entropies can be estimated to ±1 J K^{-1} mol^{-1} for smaller molecules and to ±6 J K^{-1} mol^{-1} for heavily substituted molecules. The success of this method with gases raises the question as to whether the data in Table 1 can be represented with sufficient accuracy by a table with fewer lines of values and whether this shortened table can be used to estimate standard formation properties for biochemical reactants for which there are no experimental data.

There are several differences between the use of group values for gases and for solutes, which may be ions, at specified pH and ionic strength. First, there are a lot less data for reactants in enzyme-catalyzed reactions than in gas reactions. Second, some new types of groups are needed; for example, it is

TABLE 4: Group Contributions to $\Delta_f G'^\circ$ and $\Delta_f H'^\circ$ at 298.15 K, 1 bar, pH 7, and Three Ionic Strengths[a]

		$\Delta_f G'^\circ$/kJ mol^{-1}, at I/M			$\Delta_f H'^\circ$/kJ mol^{-1}, at I/M		
group	Benson symbol	0	0.10	0.25	0	0.10	0.25
carboxyl		−350.41	−351.02	−351.21	−420.91	−420.60	−420.50
methyl	$C(H)_3(C)$	100.97	102.80	103.40	−65.10	−66.03	−66.33
aldehyde	C(O)(H)(C)	−80.14	−79.53	−79.33	−147.23	−147.54	−147.64
-CH_2OH		−42.87	−41.03	−40.43	−223.20	−224.13	−224.43
keto	$CO(C)_2$	−121.90	−120.88	−121.89	−91.51	−91.51	−91.51
methylene	$C(H)_2(C)_2$	85.10	85.71	85.90	−33.43	−33.74	−33.84
-CHOH		−67.50	−66.27	−65.88	−200.63	−201.25	−201.45
-$CH_2NH_3^+$		170.28	173.94	175.13	−102.09	−103.95	−104.55
-$CHNH_3^+$		158.13	161.20	162.18	−68.79	−70.34	−70.84
amide		−106.38	−103.94	−103.13	−248.44	−249.68	−250.09
$HOC(C)_3$		−82.44	−83.86	−84.40	−186.19	−184.87	−184.48
primP		−886.93	−889.38	−890.25	−1012.18	−1011.82	−1011.54
secP		−866.86	−868.98	−869.83	−989.70	−989.36	−989.04
tertP		−863.64	−866.58	−867.77	−991.04	−990.10	−989.67
adenosine		519.43	527.39	529.96	−0.01	−4.04	−5.34

[a] This table is based on the conventions that $\Delta_f G^\circ = \Delta_f H^\circ = 0$ for adenosine, NAD^-, and $NADP^{3-}$ at zero ionic strength.

TABLE 5: Estimated Values of Standard Transformed Gibbs Energies of Formation and Standard Transformed Enthalpies of Formation of Biochemical Reactants Using Group Values from Table 4[a]

		$\Delta_f G'^\circ$/kJ mol^{-1}, at I/M			$\Delta_f H'^\circ$/kJ mol^{-1}, I/M		
reactant		0	0.10	0.25	0	0.10	0.25
aspartate	est	−457.59	−455.13	−454.34	−944.04	−945.28	−945.68
	actual	−456.15	−453.09	−452.10	−943.41	−944.96	−945.46
glutamate	est	−372.49	−369.42	−368.44	−977.47	−979.02	−979.52
	actual	−377.82	−373.54	−372.16	−979.89	−982.07	−982.77
(*S*)-malate	est	−683.22	−682.60	−682.4	−1075.88	−1076.19	−1076.29
	actual	−682.83	−682.83	−682.83			
glucose 6-phos	est	−1323.35	−1318.46	−1316.96	−2274.37	−2277.73	−2278.65
	actual	−1325.00	−1320.37	−1318.92	−2276.06	−2278.56	−2279.30
glucose 1-phos	est	−1323.35	−1318.46	−1316.96	−2274.37	−2277.73	−2278.65
	actual	−1318.03	−1313.34	−1311.89			
ribose 5-phos	est	−1226.16	−1222.49	−1221.38	−2046.18	−2048.92	−2049.64
	actual	−1223.95	−1220.32	−1219.22	−2037.77	−2041.48	−2042.40
fructose 6-phos	est	−1322.96	−1318.07	−1316.57	−2271.56	−2274.92	−2275.85
	actual	−1321.71	−1317.16	−1315.74			

[a] This table is based on the conventions that $\Delta_f G^\circ = \Delta_f H^\circ = 0$ for adenosine, NAD^-, and $NADP^{3-}$ at zero ionic strength.

convenient to use a carboxyl group bonded to carbon as a group. Formate is treated as an irreducible entity. It is also convenient to use some larger groups, like the adenosine group. Third, since electrostatic effects can be of longer range, it is necessary to treat ATP as involving four groups, adenosine, primary phosphate, secondary phosphate, and tertiary phosphate, as indicated by the following equation:

$$\Delta_f G'^\circ(\mathrm{ATP}) = \Delta_f G'^\circ(\mathrm{adengp}) + \Delta_f G'^\circ(\mathrm{primPgp}) + \Delta_f G'^\circ(\mathrm{secPgp}) + \Delta_f G'^\circ(\mathrm{tertPgp}) \quad (33)$$

where gp indicates a group value. The simultaneous equations for adenosine, AMP, ADP, and ATP can be solved for the four group values to obtain $\Delta_f G'^\circ(\mathrm{adengp}) = 529.93$ kJ mol^{-1}, $\Delta_f G'^\circ(\mathrm{primPgp}) = -890.25$ kJ mol^{-1}, $\Delta_f G'^\circ(\mathrm{secPgp}) = -869.83$ kJ mol^{-1}, and $\Delta_f G'^\circ(\mathrm{tertPgp}) = -867.77$ kJ mol^{-1} at 0.25 M ionic strength. These values exactly reproduce the values for ATP, ADP, AMP, and adenosine in Table 1.

To test the use of group values for the 44 biochemical reactants in Table 1, 15 groups were identified and 15 reactants, each of which introduced one of these groups, were used to set up 15 simultaneous equations. The reactants used were acetate, acetaldehyde, ethanol, acetone, succinate, lactate, 2-propanol, glycine, alanine, glutamine, citrate, AMP, ADP, ATP, and adenosine. The simultaneous equations were solved using LinearSolve in *Mathematica*,[26] and the group contributions to $\Delta_f G'^\circ$ and $\Delta_f H'^\circ$ at pH 7 and three ionic strengths are given in Table 4.

Some of the 15 groups are the same as Benson groups, and for them Benson symbols are also given. The CH_2OH of ethanol is represented by two Benson groups, but it is treated as a single group here because there are not enough data to calculate values for two groups. There is a similar situation for the groups −CHOH, $-CH_2NH_3^+$, and $-CHNH_3^+$. The $HO-C(C)_3$ group is the group in citric acid. These group values all depend on the ionic strength, and some of the effects of ionic strength are rather large. Table 4 can be used to calculate $\Delta_f S'^\circ$ for the groups by using $\Delta_f S'^\circ = (\Delta_f H'^\circ - \Delta_f G'^\circ)/T$. The group values will be different at a different pH and different temperature.

Table 5 gives estimated values of $\Delta_f G'^\circ$ and $\Delta_f H'^\circ$ for seven biochemical reactants calculated using the group values in Table 4; these formation properties at pH 7 were obtained by multiplying a 7 × 15 matrix of numbers of groups times the matrix of group contributions (see Supporting Information). These estimated values are compared with the actual values previously calculated from $\Delta_f G^\circ$ and $\Delta_f H^\circ$ values of the species involved.[12] The standard transformed enthalpies of formation of (*S*)-malate, glucose 1-phosphate, and fructose 6-phosphate are not known, and so here are predictions. The estimated ionic strength effects are in good agreement with the actual values. The standard deviation for the $\Delta_f G'^\circ$ values is 2.9 kJ mol^{-1}, and the standard deviation for the $\Delta_f H'^\circ$ values is 4.2 kJ mol^{-1}. To estimate the values for glucose 6-phosphate, glucose 1-phosphate, ribose 5-phosphate, and fructose 6-phosphate, the

$\Delta_f G'^\circ$ and $\Delta_f H'^\circ$ values for glucose, ribose, and fructose are used as group values. More calculations are needed, but it appears that the group additivity method will be very useful in estimating apparent equilibrium constants and heats of reaction for biochemical reactions for which these data are not available.

Discussion

The study of thermodynamic properties of solutes in water by use of enzyme-catalyzed reactions has several advantages over classical methods because of the specificity of enzyme catalysts. When bomb calorimeter experiments are made on substances containing elements other than C, H, and O, very complicated mixtures of oxidized compounds are frequently obtained. When chemical equilibria are studied without specific catalysts, complicated equilibrium mixtures may also be obtained. Many enzymes are absolutely specific, even with respect to stereochemistry, a fact that has to be taken into account in comparing thermodynamic properties determined in the chemical and enzymatic experiments.

Standard transformed entropies of formation at pH 7 and three ionic strengths are calculated for 44 biochemical reactants. These values are used to calculate the standard transformed entropies of reaction for 18 enzyme-catalyzed reactions and for glycolysis. These examples show that the transformed entropies of formation are as important as the transformed enthalpies of formation in determining the apparent equilibrium constants of the biochemical reactions. The calculation of $\Delta_f S'^\circ$ for biochemical reactants from standard partial molar entropies is discussed, but when the convention $\Delta_f G^\circ = \Delta_f H^\circ = 0$ has been used for a species, this convention affects the properties calculated for other species and $\bar{S}^o$ cannot be calculated for any of these species from the experimental value of $\Delta_f S'^\circ$. When this convention is involved, $\Delta_f S'^\circ$ can be calculated from $\Delta_f G'^\circ$ and $\Delta_f H'^\circ$ for a reactant and $\Delta_r S'^\circ$ can be calculated, even though $\bar{S}^\circ$ values for the species cannot be calculated from these data.

Since apparent equilibrium constants and heats of reaction are not known for so many biochemical reactions, the Benson group additivity method has been tested by calculating the contributions of 15 groups and using these contributions to estimate $\Delta_f G'^\circ$ and $\Delta_f H'^\circ$ for seven other reactants. The estimates are good enough to show that the group additivity method will be very useful for estimating these standard transformed properties for other biochemical reactants. The calculation of further group contributions will be needed for this purpose. The estimation of standard molar entropies and standard transformed entropies of formation is especially important for reactants in reactions with large apparent equilibrium constants. An indication of the size of the problem of estimating standard transformed thermodynamic properties of biochemical reactants is that equilibrium data are available on about 400 biochemical reactions[27−31] out of the 3500 known reactions that have been assigned EC numbers.[20] These 400 reactions involve about 800 reactants. In principle, $\Delta_f G'^\circ$ values can be calculated for these 800 reactants, but this leaves about 6000 biochemical reactants for which there are no equilibrium data.

Acknowledgment. I am indebted to Robert N. Goldberg for many helpful discussions. This research was supported by NIH-1-R01-GM48358-01A1.

Supporting Information Available: A *Mathematica* notebook for calculating the group contributions of 15 groups, which are used to estimate standard transformed formation properties of seven reactants at three ionic strengths, and all of the calculations involved in producing Tables 4 and 5; these programs can be used to calculate additional group values and to estimate the standard transformed properties of reactants for which there are no equilibrium data (9 pages). See any current masthead page for ordering and Internet access information.

References and Notes

(1) Alberty, R. A.; Cornish-Bowden, A.; Gibson, Q. H.; Goldberg, R. N.; Hammes, G. G.; Jencks, W.; Tipton, K. F.; Veech, R.; Westerhoff, H. V.; Webb, E. C. *Pure Appl. Chem*. **1994**, *66*, 1641. (Also published in: *Eur. J. Biochem*. **1996**, *240*, 1−14.)

(2) Alberty, R. A. *Biophys. Chem*. **1992**, *42*, 117.

(3) Alberty, R. A. *Biophys. Chem*. **1992**, *43*, 239.

(4) Alberty, R. A.; Goldberg, R. N. *Biochemistry* **1992**, *31*, 10 610−10 615.

(5) Alberty, R. A. *J. Phys. Chem.* **1992**, *96*, 9614−9621.

(6) Alberty, R. A. *Chem. Rev*. **1994**, *94*, 1457.

(7) Pitzer, K. S. *Thermodynamics*; McGraw-Hill: New York, 1995.

(8) Clarke, E. C. W.; Glew, D. N. *Trans. Faraday Soc.* **1966**, *62*, 539.

(9) Goldberg, R. N.; Tewari, Y. *Biophys. Chem*. **1991**, *40*, 241.

(10) Smith, W. R.; Missen, R. W. *Chemical Reaction Equilibrium Analysis: Theory and Algorithm*; Wiley-Interscience: New York, 1982.

(11) Alberty, R. A. *Ind. Eng. Chem. Fundam*. **1983**, *22*, 318.

(12) Alberty, R. A. *Arch. Biochem. Biophys*., in press.

(13) *Biochemical Microcalorimetry*; Brown, H. D., Ed.; Academic Press: New York, 1969.

(14) Wagman, D. D., Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. The NBS Tables of Chemical Thermodynamic Properties. *J. Phys. Chem. Ref. Data* **1982**, *11*, (Supplement No. 2).

(15) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*, Hemisphere Publishing Corp.: New York, 1989.

(16) Goldberg, R. N.; Tewari, Y. B. *J. Phys. Chem. Ref. Data* **1989**, *18*, 809−880.

(17) Alberty, R. A. *Arch. Biochem. Biophys*. **1993**, *307*, 8−14.

(18) Alberty, R. A. *J. Phys. Chem*. **1995**, *99*, 11 028−11 034.

(19) Alberty, R. A. *Arch. Biochem. Biophys*. **1997**, *348*, 116−124..

(20) Webb, E. C. *Enzyme Nomenclature*; Academic Press: San Diego, 1992.

(21) Kast, P.; Tewari, Y. B.; Weist, O.; Hilvert, D.; Houk, K. N.; Goldberg, R. N. *J. Phys. Chem. B* **1997**, *101*, 10 976−10 982.

(22) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976.

(23) Benson, S. W.; Buss, J. H. *J. Phys. Chem*. **1958**, *29*, 546.

(24) Benson, S. W.; et al. *Chem. Rev*. **1969**, *69*, 279.

(25) Eigenmann, H. K.; Golden, D. M.; Benson. S. W. *J. Phys. Chem*. **1973**, *77*, 1687.

(26) Wolfram, S. *Mathematica*, 3rd ed.; Cambridge University Press: Cambridge, 1996.

(27) Goldberg, R. N.; Tewari, Y. B.; Bell, D.; Fazio, K.; Anderson, E. J. *Phys. Chem. Ref. Data* **1993**, *22*, 515−582.

(28) Goldberg, R. N.; Tewari, Y. B. *J. Phys. Chem. Ref. Data* **1994**, *23*, 547−617.

(29) Goldberg, R. N.; Tewari, Y. B. *J. Phys. Chem. Ref. Data* **1994**, *23*, 1035−1103.

(30) Goldberg, R. N.; Tewari, Y. B. *J. Phys. Chem. Ref. Data* **1995**, *24*, 1669−1698.

(31) Goldberg, R. N.; Tewari, Y. B. *J. Phys. Chem. Ref. Data* **1995**, *24*, 1765−1801.