

Thermodynamics of the Hydrolysis of Adenosine Triphosphate as a Function of Temperature, pH, pMg, and Ionic Strength

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The hydrolysis of adenosine triphosphate plays such an important role in energy metabolism that the thermodynamic properties of the species involved have been determined, including the standard Gibbs energies and enthalpies of formation of its magnesium complex ions. When the pH and pMg are specified in addition to temperature, pressure, and ionic strength, the criterion for spontaneous change and equilibrium is provided by the transformed Gibbs energy G' that is defined by a Legendre transform. The use of a Legendre transform makes it possible to express all the thermodynamic properties of a reactant by use of a single function of temperature, pH, pMg and ionic strength. The expression for the standard transformed Gibbs energy of formation of a reactant like ATP (a sum of species) is a function of temperature, pressure, pH, pMg, and ionic strength. Nine Maxwell relations are used to calculate various thermodynamic properties and relations between them. It is of particular interest to see that the derivatives of the standard transformed enthalpy and entropy with respect to pH and pMg are determined by the temperature derivatives of the average numbers of hydrogen ions and magnesium ions bound. Ten transformed thermodynamic properties for $\text{ATP} + \text{H}_2\text{O} = \text{ADP} + \text{P}_i$ are calculated as functions of temperature, pH, pMg, and ionic strength.

1. Introduction

When pH and pMg are specified in addition to temperature, pressure, and ionic strength, the criterion for spontaneous change and equilibrium is provided by the transformed Gibbs energy G' that is defined by the Legendre transform^{1–3}

$$G' = G - n_{\text{c}}(\text{H})\mu(\text{H}^+) - n_{\text{c}}(\text{Mg})\mu(\text{Mg}^{2+}) \quad (1)$$

where $n_{\text{c}}(\text{H})$ is the amount of the hydrogen component and $n_{\text{c}}(\text{Mg})$ is the amount of the magnesium component in the system. The specified chemical potentials $\mu(\text{H}^+)$ and $\mu(\text{Mg}^{2+})$ correspond with the pH and pMg at the specified temperature and ionic strength. When one reactant like ATP (a sum of species) is present in dilute aqueous solution, the fundamental equation for the transformed Gibbs energy at specified pH and pMg is given by

$$dG' = -S' dT + V dP + \Delta_{\text{f}}G' dn' + RT \ln(10) n_{\text{c}}(\text{H}) dp\text{H} + RT \ln(10) n_{\text{c}}(\text{Mg}) dp\text{Mg} \quad (2)$$

where n' is the amount of the reactant and $\Delta_{\text{f}}G'$ is its transformed Gibbs energy of formation. The thermodynamic properties are functions of temperature, $\text{pH} = -\log[\text{H}^+]$, $\text{pMg} = -\log[\text{Mg}^{2+}]$, and ionic strength. The transformed entropy S' and the transformed enthalpy H' of the system are given by

$$S' = S - n_{\text{c}}(\text{H})\bar{S}(\text{H}^+) - n_{\text{c}}(\text{Mg})\bar{S}(\text{Mg}^{2+}) \quad (3)$$

$$H' = H - n_{\text{c}}(\text{H})\bar{H}(\text{H}^+) - n_{\text{c}}(\text{Mg})\bar{H}(\text{Mg}^{2+}) \quad (4)$$

where the overbars indicate molar properties. When the system contains a single reactant (sum of species) and the $V dP$ term is ignored, eq 2 yields six Maxwell relations. Replacing S' in eq 2 with $H'/T - G'/T$ yields three more Maxwell relations

involving the transformed enthalpy, so that there is a total of nine Maxwell relations, which are given later. Notice that performing Legendre transforms leads to new types of Maxwell relations. Some new types of Maxwell relations have been discussed recently.^{4–6} This paper is closely related to ref 4, but specifying pMg increases the number of Maxwell relations.

When a system involves a single biochemical reaction like $\text{ATP} + \text{H}_2\text{O} = \text{ADP} + \text{P}_i$, the $\Delta_{\text{f}}G' dn'$ term in eq 2 is replaced with $\Delta_{\text{r}}G' d\xi'$, where ξ' is the extent of the biochemical reaction.

$$dG' = -S' dT + V dP + \Delta_{\text{r}}G' d\xi' + RT \ln(10) n_{\text{c}}(\text{H}) dp\text{H} + RT \ln(10) n_{\text{c}}(\text{Mg}) dp\text{Mg} \quad (5)$$

This leads to nine Maxwell relations that are like those of eq 2 except that subscript f is replaced with subscript r, the average number of hydrogen ions bound \bar{N}_{H} is replaced by the change in the binding of hydrogen ions $\Delta_{\text{r}}N_{\text{H}}$, and the average number of magnesium ions bound \bar{N}_{Mg} is replaced by the change in the binding of magnesium ions $\Delta_{\text{r}}N_{\text{Mg}}$.

2. Data on Species in the Hydrolysis of ATP

It is possible to calculate the effects of temperature, pH, pMg, and ionic strength on the transformed thermodynamic properties of ATP, ADP, and AMP because the equilibrium constants and standard enthalpies of reaction involved have been obtained by Goldberg and Tewari⁷ and Larson, Tewari, and Goldberg⁸ or evaluated from work of others. The values used by Alberty and Goldberg⁹ in 1992 have been updated by using the standard thermodynamic properties of adenosine determined by Boerio-Goates and co-workers.¹⁰ The properties for species that do not contain magnesium ions have been calculated by Alberty,⁴ and the properties of the species involving magnesium ions have been recalculated for this paper. The data on species used in the calculations presented here are given in Table 1.

TABLE 1: Thermodynamic Properties of Species in Dilute Aqueous Solutions at 298.15 K and Zero Ionic Strength

species	$\Delta_f G^\circ$ (kJ mol ⁻¹)	$\Delta_f H^\circ$ (kJ mol ⁻¹)	z_j	N_H	N_{Mg}
ATP					
ATP ⁴⁻	-2768.10	-3619.21	-4	12	0
HATP ³⁻	-2811.48	-3612.91	-3	13	0
H ₂ ATP ²⁻	-2838.18	-3627.91	-2	14	0
MgATP ²⁻	-3258.68	-4063.31	-2	12	1
MgHATP ⁻	-3287.50	-4063.01	-1	13	1
Mg ₂ ATP	-3729.33	-4519.51	0	12	2
ADP					
ADP ³⁻	-1906.13	-2626.54	-3	12	0
HADP ²⁻	-1947.10	-2620.94	-2	13	0
H ₂ ADP ⁻	-1971.98	-2638.54	-1	14	0
MgADP ⁻	-2387.97	-3074.54	-1	12	1
MgHADP	-2416.67	-3075.44	0	13	1
AMP					
AMP ²⁻	-1040.45	-1635.37	-2	12	0
HAMP ⁻	-1078.86	-1629.97	-1	13	0
H ₂ AMP	-1101.63	-1648.07	0	14	0
MgAMP	-1511.68	-2091.07	0	12	1
P _i					
HPO ₄ ²⁻	-1096.1	-1299.00	-2	1	0
H ₂ PO ₄ ⁻	-1137.30	-1302.60	-1	2	0
MgHPO ₄	-1566.87	-1753.80	0	1	1
Single Species					
H ₂ O	-237.19	-285.83	0	2	0
H ⁺	0	0	1	1	0
Mg ²⁺	-455.30	-467.00	2	0	1

The data in Table 1 are used in the form of matrices for ATP, ADP, AMP, P_i, and H₂O constructed in *Mathematica*.¹¹

3. Calculation of Standard Transformed Gibbs Energies of Formation of Reactants as Functions of Temperature, pH, pMg, and Ionic Strength

The calculation of the standard transformed Gibbs energy of formation of a reactant like ATP as a function of pH, pMg, and ionic strength was discussed earlier¹² for a constant temperature of 298.15 K. The first step in this calculation is to express the standard transformed Gibbs energies of formation $\Delta_f G_j'^\circ$ of the individual species of ATP, ADP, AMP, P_i, and H₂O as functions of pH and pMg using

$$\Delta_f G_j'^\circ = \Delta_f G_j^\circ - N_H(j)\{\Delta_f G^\circ(H^+) - RT \ln(10) \text{pH}\} - N_{Mg}(j)\{\Delta_f G^\circ(Mg^{2+}) - RT \ln(10) \text{pMg}\} \quad (6)$$

The standard Gibbs energies of species j , H⁺, and Mg²⁺ are functions of ionic strength that are taken to be given by the extended Debye–Huckel equation^{7,12}

$$\Delta_f G_j^\circ(I) = \Delta_f G_j^\circ(I=0) - RT\alpha z_j^2 I^{1/2} / (1 + 1.6I^{1/2}) \quad (7)$$

where the coefficient α is in the limiting law written in terms of $\ln \gamma_j$. The coefficient $RT\alpha$ is given in kJ mol⁻¹ by^{4,13}

$$RT\alpha = 9.20483 \times 10^{-3}T - 1.28467 \times 10^{-5}T^2 + 4.95199 \times 10^{-8}T^3 \quad (8)$$

To obtain the standard transformed Gibbs energy of formation of species j as a function of temperature, pH, pMg, and ionic strength, eq 8 is substituted in eq 7, and eq 7 is used in eq 6 in three places. This still leaves the problem that $\Delta_f G_j^\circ$ and $\Delta_f G^\circ$

(Mg²⁺) in eq 6 are functions of temperature. By convention the standard Gibbs energy of formation of hydrogen ions is set equal to zero at each temperature. When $\Delta_f G^\circ$ (298.15 K) and $\Delta_f H^\circ$ (298.15 K) are known for a species, $\Delta_f G^\circ$ at other temperatures where $\Delta_f H^\circ$ is essentially unchanged can be calculated by using

$$\Delta_f G^\circ(T) = (T/298.15)\Delta_f G^\circ(298.15) + (1 - T/298.25)\Delta_f H^\circ(298.15) \quad (9)$$

This equation has to be substituted in eq 7 for $\Delta_f G_j^\circ$ and $\Delta_f G^\circ$ (Mg²⁺) before it is substituted in eq 6.

At specified pH and pMg, the various forms of a reactant have the same $\Delta_f G_j'$ at chemical equilibrium, and so the final step in the calculation of the standard transformed Gibbs energy of formation of a reactant like ATP is to use

$$\Delta_f G_i'^\circ = -RT \ln \left\{ \sum_{j=1}^{N_{iso}} \exp[-\Delta_f G_j'^\circ / RT] \right\} \quad (10)$$

where N_{iso} is the number of species in the pseudoisomer group. N_{iso} is 6 for ATP. With all these substitutions, the expression $\Delta_f G'^\circ$ for a reactant like ATP is very complicated and is not the kind of equation to derive or use by hand. Fortunately, it is convenient to make symbolic calculations such as this using *Mathematica*. The program calcdGmatMgT for doing this is given in the Appendix. This is the only program used in the calculations described in this paper. The input for the program is a matrix of species properties for a reactant in the form in which they are given in Table 1. Calculations of standard transformed Gibbs energies of formation over a range in temperature in the absence of magnesium ions can currently be carried out for about 70 biochemical reactants.^{14,15} As we will see in the next section, all the thermodynamic properties of a reactant can be calculated by taking partial derivatives of the expression for $\Delta_f G_i'^\circ$ as a function of temperature, pH, pMg, and ionic strength.

4. Maxwell Relations Obtained from the Fundamental Equation for a System Containing a Single Reactant

Ignoring the $V dP$ term, eq 2 has six Maxwell relations. The transformed enthalpy of formation $\Delta_f H'$ is not in this equation, but Maxwell equations involving it can be obtained by use of $S' = H'/T - G'/T$ or $\Delta_f S' = \Delta_f H'/T - \Delta_f G'/T$. It is convenient to write the nine Maxwell relations in terms of standard thermodynamic properties.

$$\Delta_f H'^\circ = -T^2 \left(\frac{\partial(\Delta_f G'^\circ / T)}{\partial T} \right)_{P, \text{pH}, \text{pMg}} \quad (11)$$

$$\Delta_f S'^\circ = - \left(\frac{\partial \Delta_f G'^\circ}{\partial T} \right)_{P, \text{pH}, \text{pMg}} \quad (12)$$

$$\bar{N}_H = \frac{1}{RT \ln(10)} \left(\frac{\partial \Delta_f G'^\circ}{\partial \text{pH}} \right)_{T, P, \text{pMg}} \quad (13)$$

$$\bar{N}_{Mg} = \frac{1}{RT \ln(10)} \left(\frac{\partial \Delta_f G'^\circ}{\partial \text{pMg}} \right)_{T, P, \text{pH}} \quad (14)$$

$$\left(\frac{\partial \bar{N}_H}{\partial \text{pMg}} \right)_{T, P, \text{pH}} = \left(\frac{\partial \bar{N}_{Mg}}{\partial \text{pH}} \right)_{T, P, \text{pMg}} \quad (15)$$

$$\left(\frac{\partial \Delta_r S'^{\circ}}{\partial pH}\right)_{T,P,pMg} = -R \ln(10) \left(\frac{\partial(T\bar{N}_H)}{\partial T}\right)_{P,pH,pMg} \quad (16)$$

$$\left(\frac{\partial \Delta_r S'^{\circ}}{\partial pMg}\right)_{T,P,pH} = -R \ln(10) \left(\frac{\partial(T\bar{N}_{Mg})}{\partial T}\right)_{P,pH,pMg} \quad (17)$$

$$\left(\frac{\partial \Delta_r H'^{\circ}}{\partial pH}\right)_{T,P,pMg} = -RT^2 \ln(10) \left(\frac{\partial \bar{N}_H}{\partial T}\right)_{P,pH,pMg} \quad (18)$$

$$\left(\frac{\partial \Delta_r H'^{\circ}}{\partial pMg}\right)_{T,P,pH} = -RT^2 \ln(10) \left(\frac{\partial \bar{N}_{Mg}}{\partial T}\right)_{P,pH,pMg} \quad (19)$$

More partial derivatives of $\Delta_r G_i'^{\circ}$ can be taken. For example, the standard transformed heat capacity $\Delta_r C_{p_i}'^{\circ}$ can be calculated by using $-T(\partial^2 \Delta_r G_i'^{\circ} / \partial T^2)$. We will see later that the standard transformed enthalpy of formation of a reactant depends on temperature even though the standard enthalpies of species making it up are assumed to be independent of temperature. There are two reasons for this: (1) $RT\alpha$ depends on temperature and (2) the equilibrium composition of a pseudoisomer group depends on temperature. Di Cera, Gill, and Wyman¹⁶ have defined the binding capacity and applied it to the binding of molecular oxygen by hemoglobin because the binding capacity is a measure of cooperativity. The binding capacity is equivalent to $\partial \bar{N}_H / \partial pH$ or $\partial \bar{N}_{Mg} / \partial pMg$.

Plots of 10 transformed thermodynamic properties of ATP at 298.15 K and 0.25 M ionic strength are given in Figure 1. The plots are all calculated using the function that gives $\Delta_r G'^{\circ}$ as a function of temperature, pH, pMg, and ionic strength. This function looks rather monotonic in the first plot because the term in $\bar{N}_H pH$ dominates, because \bar{N}_H is 12–14 for the various species. This is based on the convention⁹ that in small species all the hydrogen atoms are counted. Actually this surface contains a lot of information, as shown by its partial derivatives. As a test of this surface, we know that at high pH and high pMg, there is a single species, ATP^{4-} . At low pH and high pMg, there is a single species H_2ATP^{2-} . At high pH and low pMg, there is a single species, Mg_2ATP . The first and second plots at these limits yield the values of $\Delta_r G^{\circ}$ and $\Delta_r H^{\circ}$ of these species as expected. The first three plots satisfy the requirement that $\Delta_r G'^{\circ} = \Delta_r H'^{\circ} - T\Delta_r S'^{\circ}$. Notice that \bar{N}_H and \bar{N}_{Mg} approach the correct limits at high and low pH and pMg values. The reciprocal relation given in eq 15 is obeyed.

5. Calculation of Standard Transformed Gibbs Energies of Reaction as a Function of Temperature, pH, pMg, and Ionic Strength

When the $\Delta_r G_i'^{\circ}$ for all the reactants in a biochemical reaction can be expressed as functions of temperature, pH, pMg, and ionic strength, the $\Delta_r G'^{\circ} = -RT \ln K'$ for the biochemical reaction can be calculated by use of

$$\Delta_r G'^{\circ} = \sum \nu_i' \Delta_r G_i'^{\circ} \quad (20)$$

where ν_i' is the stoichiometric number for reactant i . Thus $\Delta_r G'^{\circ}$ is a sum of complicated functions. Equations 11–19 can be applied to a biochemical reaction by simply changing the subscripts f to r for reaction, replacing \bar{N}_H with $\Delta_r \bar{N}_H$, and replacing \bar{N}_{Mg} with $\Delta_r \bar{N}_{Mg}$. The thermodynamic properties of the reaction $ATP + H_2O = ADP + P_i$ at 298.15 K and 0.25 M ionic strength are shown in three-dimensional plots in Figure 2.

The surface for $\Delta_r G'^{\circ}$ has a very complicated shape, as indicated by the partial derivatives in the other nine plots. The hydrolysis of ATP goes pretty far to the right primarily because

of the standard transformed enthalpy of reaction, but the standard transformed entropy of reaction makes an increasing contribution to the apparent equilibrium constant K' as the pH is increased and more H^+ is produced. The relation $\Delta_r G'^{\circ} = \Delta_r H'^{\circ} - T\Delta_r S'^{\circ}$ is obeyed; this provides the first check on the validity of the calculations. The plots of $\Delta_r \bar{N}_H$, and $\Delta_r \bar{N}_{Mg}$ are related by the reciprocal relation, which is shown in the sixth plot. This provides a second check on the validity of the calculations. The last four plots can each be calculated in two different ways; this provides four more checks. Plots 7 and 8 show that the dependencies of $\Delta_r S'^{\circ}$ on pH and pMg depend on the temperature dependencies of $\Delta_r \bar{N}_H$, and $\Delta_r \bar{N}_{Mg}$. Plots 9 and 10 show that the dependencies of $\Delta_r H'^{\circ}$ on pH and pMg depend on the temperature dependencies of $\Delta_r \bar{N}_H$, and $\Delta_r \bar{N}_{Mg}$. The corresponding plots for the reaction $ATP + 2H_2O = AMP + 2P_i$ are provided in the Supporting Information.

The three-dimensional plots show how the 10 transformed reaction properties depend on pH and pMg, but they do not show the effect of temperature. This is shown in Table 2.

6. Discussion

Because all the equilibrium constants and standard enthalpies of formation are known for species of ATP, ADP, AMP, P_i , and H_2O , the standard transformed Gibbs energies of formation for these reactants can be calculated as functions of temperature, pH, pMg, and ionic strength in the ranges 273.15–313.15 K, pH 5–9, pMg 2–6, and ionic strengths 0–0.35 M. The functions representing $\Delta_r G'^{\circ}$ for these reactants in dilute solutions can be used to calculate all the thermodynamic properties for the reactions $ATP + H_2O = ADP + P_i$ and $ATP + 2H_2O = AMP + 2P_i$ simply by taking partial derivatives. The functions for $\Delta_r G'^{\circ}$ for these reactions are quite complicated and the functions for the partial derivatives are more complicated, but *Mathematica* makes it convenient to derive these functions and to make plots and tables. Ten transformed properties of ATP are given in three-dimensional plots, and 10 transformed thermodynamic properties of $ATP + H_2O = ADP + P_i$ are given in three-dimensional plots and a table in the Supporting Information.

The use of a Legendre transformed Gibbs energy of formation of a reactant like ATP makes it possible to express all the thermodynamic properties of the reactant by use of a single function of temperature, pH, pMg, and ionic strength. This function is derived using a *Mathematica* program calcdGmat-MgT. This is the only program used to calculate the various thermodynamic properties in this paper. The function $\Delta_r G_i'^{\circ}$ can be used to make many types of plots and tables for reactants. This raises the question as to whether the function $\Delta_r G'^{\circ}$ for a reactant can be obtained more directly from experimental studies of the effects of temperature, pH, pMg, and ionic strength on the apparent equilibrium constant K' .

This article has emphasized the importance of Maxwell relations in calculating and interpreting the thermodynamic properties of biochemical reactants and reactions. As the number of constraints is increased, the number of Maxwell equations increases rapidly. In the cases discussed, there are nine Maxwell relations. Four of them show how to calculate thermodynamic properties from the standard transformed Gibbs energy that can be determined in the laboratory, and five of them describe the relations between these experimentally determinable properties. There is a limit to the number of Legendre transforms that can be made for a reaction system because one component has to remain, but making the maximum number of Legendre transforms has the advantage of producing the standard transformed

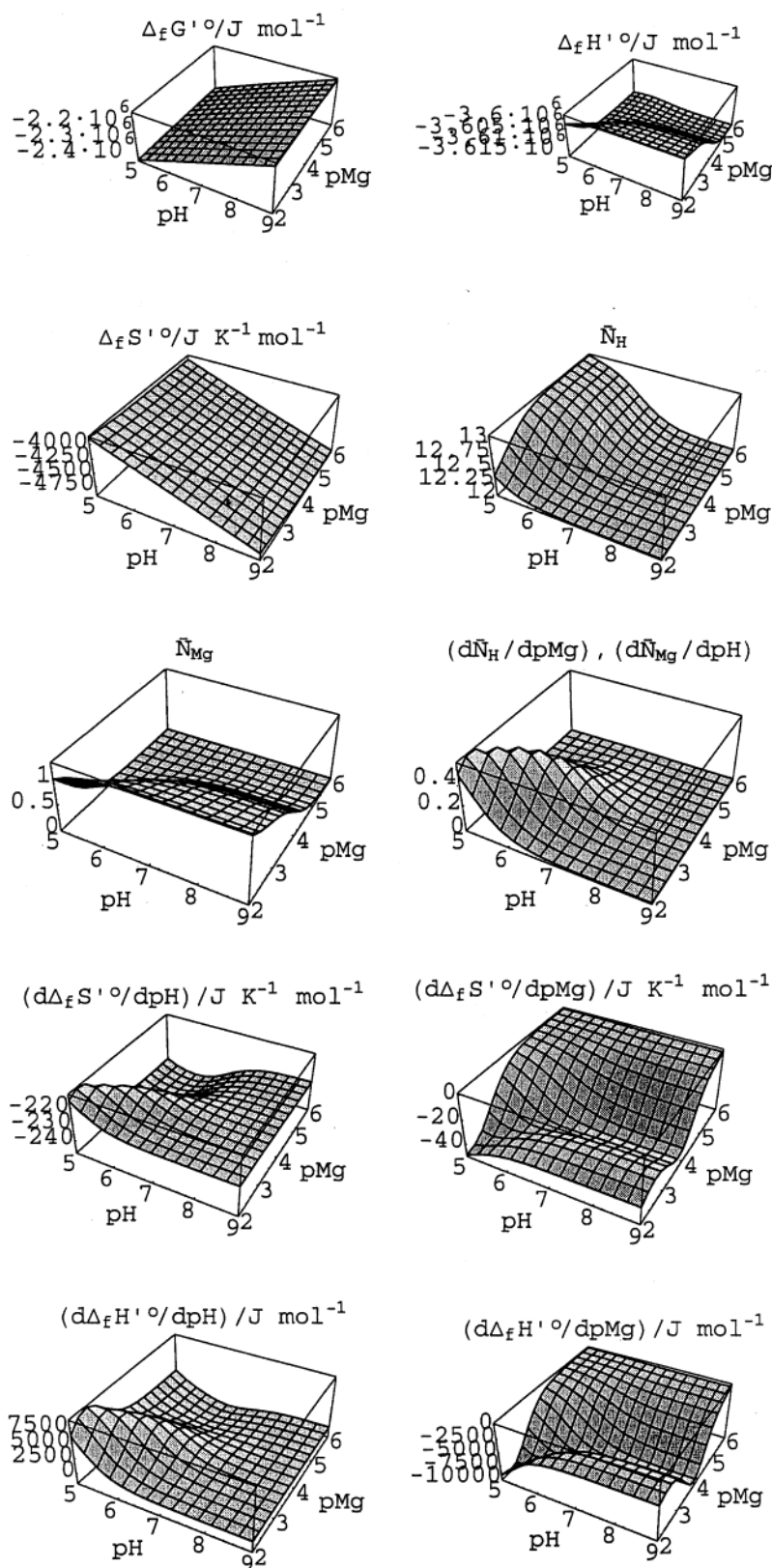


Figure 1. Plots of transformed thermodynamic properties of ATP at 298.15 K and ionic strength 0.25 M. The last five plots can be obtained in a second way as indicated by the Maxwell relations. Thus we can consider the dependencies of $\Delta_f S'^{\circ}$ and $\Delta_f H'^{\circ}$ on pH and pMg to be determined by the temperature dependencies of \bar{N}_H and \bar{N}_{Mg} .

Gibbs energy for a system that yields all the other thermodynamic properties by taking partial derivatives.

When the functions for $\Delta_f G_i'^{\circ}$ for all the reactants in a biochemical reaction are known except one, the calculation of

$\Delta_f G^{\circ}$ and $\Delta_f H^{\circ}$ for the species in this remaining reactant from its $\Delta_f G_i'^{\circ}$ can be viewed as the use of an inverse Legendre transform. Callen¹⁷ introduced this term and pointed out that the sign of the products of the conjugate variables is reversed

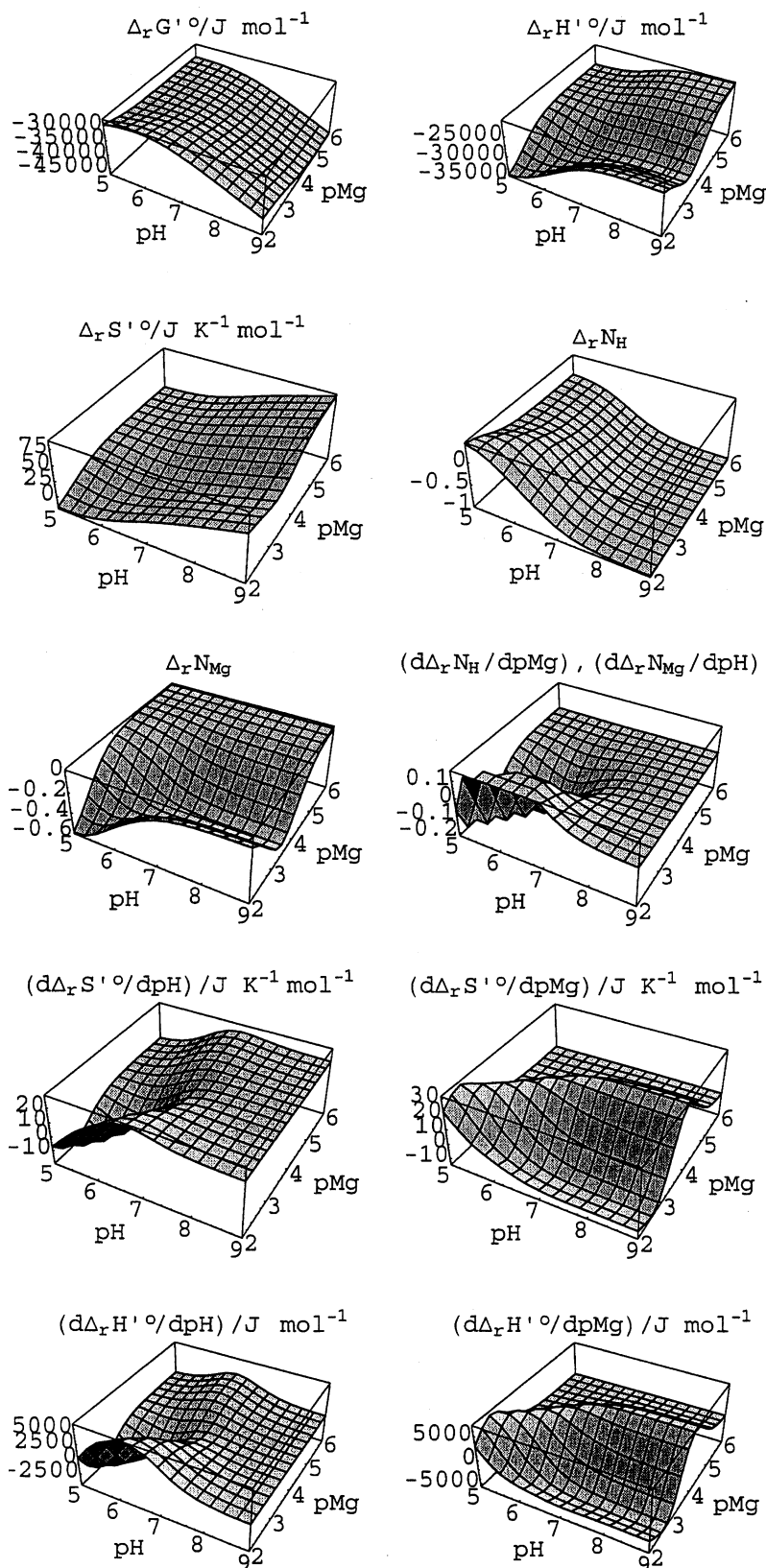


Figure 2. Transformed thermodynamic properties for $\text{ATP} + \text{H}_2\text{O} = \text{ADP} + \text{P}_i$ at 298.15 K and 0.25 M ionic strength. The function for $\Delta_r G'^\circ$ has been used to calculate all these plots. Four of the Maxwell equations yield $\Delta_r H'^\circ$, $\Delta_r S'^\circ$, $\Delta_r N_H$, and $\Delta_r N_{Mg}$. A fifth Maxwell relation is the reciprocal relation between $\Delta_r N_H$ and $\Delta_r N_{Mg}$. The last four plots can each be calculated in two ways, as shown by eqs 16–19.

in the inverse transform. Thus the Gibbs energy G can be defined in terms of the transformed Gibbs energy G' by use of the following Legendre transform:

$$G = G' + n_c(\text{H})\mu(\text{H}^+) + n_c(\text{Mg})\mu(\text{Mg}^{2+}) \quad (21)$$

This approach has been used to write three computer programs¹⁸ to calculate $\Delta_r G_j^\circ(298.15 \text{ K})$ and $\Delta_r H_j^\circ(298.15 \text{ K})$ for the species of a reactant, depending on whether the reactant consists of one, two, or three species. This approach requires separate measurement (or estimation) of the pK' s of the reactant.

TABLE 2: Transformed Thermodynamic Properties of ATP + H₂O = ADP + P_i at Temperatures of 298.15 and 313.15 K at 0.25 M Ionic Strength

		298.15 K			313.15 K		
		pH 5	pH 7	pH 9	pH 5	pH 7	pH 9
$\Delta_r G^\circ$ (J mol ⁻¹)	pMg 2	-29632	-30801	-41475	-29375	-31039	-42348
	pMg 4	-32497	-34998	-45443	-32777	-35327	-46331
	pMg 6	-32562	-36022	-46684	-32867	-36666	-47948
$\Delta_r H^\circ$ (J mol ⁻¹)	pMg 2	-34809	-26422	-24410	-34668	-25709	-23830
	pMg 4	-26768	-28204	-27508	-27121	-28684	-28005
	pMg 6	-26386	-23164	-21468	-26660	-23269	-21661
$\Delta_r S^\circ$ (J K ⁻¹ mol ⁻¹)	pMg 2	-17.36	14.69	57.24	-16.90	17.02	59.14
	pMg 4	19.21	22.79	60.15	18.06	21.22	58.52
	pMg 6	20.72	43.12	84.58	19.82	42.78	83.94
$\Delta_r N_H$	pMg 2	0.396	-0.734	-0.997	0.392	-0.764	-0.997
	pMg 4	-0.017	-0.668	-0.995	-0.012	-0.674	-0.995
	pMg 6	-0.038	-0.741	-0.996	-0.040	-0.763	-0.997
$\Delta_r N_{Mg}$	pMg 2	-0.605	-0.162	-0.082	-0.624	-0.136	-0.057
	pMg 4	-0.026	-0.319	-0.366	-0.034	-0.372	-0.419
	pMg 6	0.000	-0.006	-0.007	0.000	-0.007	-0.010
$\partial \Delta_r N_H / \partial \text{pMg}$, $\partial \Delta_r N_{Mg} / \partial \text{pH}$	pMg 2	-0.071	0.149	0.002	0.000	0.149	0.002
	pMg 4	-0.048	-0.096	-0.001	-0.061	-0.099	-0.001
	pMg 6	-0.001	-0.003	0.000	0.000	-0.004	0.000
$\partial \Delta_r S^\circ / \partial \text{pH}$ (J K ⁻¹ mol ⁻¹)	pMg 2	-7.18	26.19	19.28	-4.78	25.74	19.26
	pMg 4	-1.12	15.43	19.15	-1.70	15.53	19.14
	pMg 6	1.49	23.22	19.27	1.33	22.99	19.25
$\partial \Delta_r S^\circ / \partial \text{pMg}$ (J K ⁻¹ mol ⁻¹)	pMg 2	21.28	-8.13	-9.27	17.38	-7.03	-7.55
	pMg 4	3.39	28.14	30.05	3.94	26.19	26.62
	pMg 6	0.04	0.78	1.05	0.04	0.94	1.26
$\partial \Delta_r H^\circ / \partial \text{pH}$ (J mol ⁻¹)	pMg 2	118	3619	60	852	3484	54
	pMg 4	-428	788	28	-604	821	27
	pMg 6	225	2694	57	179	2624	53
$\partial \Delta_r H^\circ / \partial \text{pMg}$ (J mol ⁻¹)	pMg 2	2892	-3349	-3229	1699	-3014	-2705
	pMg 4	861	6572	6871	1027	5974	5821
	pMg 6	9	201	270	11	248	335

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Appendix

calcdGmatMgT[speciesmat_] := Module[{dGzero,dHzero,dGzeroT,zi,nH,nMg,pHterm,stdGMg,pMgterm,coeffis,isterm,gpfns} (*This program produces the function of T, pH, pMg and ionic strength (is) that gives the standard transformed Gibbs energy of formation of a reactant (sum of species). The input speciesmat is a matrix that gives the standard Gibbs energy of formation, the standard enthalpy of formation, the electric charge, the number of hydrogen atoms, and the number of magnesium atoms in each species. There is a row in the matrix for each species of the reactant. gpfns is a list of the functions for the species. Energies are expressed in kJ mol⁻¹ in the program, but the output is changed to J mol⁻¹ in the last line.*)

```
{dGzero,dHzero,zi,nH,nMg} = Transpose[speciesmat];
pHterm = nH*8.31451*t*Log[10]*pH/1000;
stdGMg=(t/298.15)*(-455.3)+(1-t/298.15)*(-467.00);
pMgterm = nMg*(-stdGMg+8.31451*(t/1000)*Log[10]*pMg);
coeffis=(9.20483*t)/10^3-(1.284668*t^2)/10^5+(4.95199*t^3)/10^8;
dGzeroT=(t/298.15)*dGzero+(1-t/298.15)*dHzero;
isterm = coeffis*((zi^2)-nH-4*nMg)*(is^5)/(1 + 1.6*is^5);
gpfns=dGzeroT+pHterm+pMgterm-isterm;
-8.31451*t*Log[Apply[Plus,Exp[-1*gpfns]/(8.31451*(t/1000))]]]
```

Glossary

$\Delta_r C_{P_i}^\circ$	standard transformed heat capacity of formation of a reactant (J K ⁻¹ mol ⁻¹)
G	Gibbs energy of a system (J)
$\Delta_r G_j$	Gibbs energy of formation of species j (J mol ⁻¹)
$\Delta_r G_j^\circ$	standard Gibbs energy of formation of species j (J mol ⁻¹)
$\Delta_r G^\circ$	standard Gibbs energy of reaction for a chemical reaction (J mol ⁻¹)
G'	transformed Gibbs energy of a system (J)
$\Delta_r G_j'$	transformed Gibbs energy of formation of a species j (J mol ⁻¹)
$\Delta_r G'^\circ$	standard transformed Gibbs energy of formation of a species i or reactant j (J mol ⁻¹)
$\Delta_r G'$	transformed Gibbs energy of reaction (J mol ⁻¹)
$\Delta_r G'^\circ$	standard transformed Gibbs energy of reaction (J mol ⁻¹)
H	enthalpy of a system (J)
\bar{H}_j	molar enthalpy of species j (J mol ⁻¹)
$\Delta_r H_j^\circ$	standard enthalpy of formation of species j (J mol ⁻¹)
$\Delta_r H^\circ$	standard enthalpy of reaction (J mol ⁻¹)
H'	transformed enthalpy of a system (J)
$\Delta_r H'$	transformed enthalpy of formation of species j or reactant i (J mol ⁻¹)
$\Delta_r H'^\circ$	standard transformed enthalpy of formation of a species j or reactant i (J mol ⁻¹)
$\Delta_r H'^\circ$	standard transformed enthalpy of reaction (J mol ⁻¹)
I	ionic strength (M)
K	equilibrium constant for a chemical reaction
K'	apparent equilibrium constant for a biochemical reaction

n_j	amount of species j (mol)
n_i'	amount of reactant i at specified pH (mol)
$n_c(i)$	amount of component i (mol)
N_{iso}	number of different species in an isomer group
$N_{\text{H}}(j)$	number of hydrogen atoms in species j
$N_{\text{Mg}}(j)$	number of magnesium atoms in species j
\bar{N}_{H}	average number of hydrogen atoms in a reactant
\bar{N}_{Mg}	average number of magnesium atoms in a reactant
$\Delta_r N_{\text{H}}$	change in number of hydrogen ions bound in a reaction
$\Delta_r N_{\text{Mg}}$	change in number of magnesium ions bound in a reaction
P	pressure (bars)
pH	$-\log[\text{H}^+]$
pMg	$-\log[\text{Mg}^{2+}]$
pK	$-\log K$
R	gas constant (8.31451 J K ⁻¹ mol ⁻¹)
S	entropy of a system (J K ⁻¹)
\bar{S}_j	molar entropy of a species j (J K ⁻¹ mol ⁻¹)
$\Delta_f S_j^\circ$	standard entropy of formation of species j (J K ⁻¹ mol ⁻¹)
$\Delta_r S^\circ$	standard entropy of reaction (J K ⁻¹ mol ⁻¹)
S'	transformed entropy of a system (J K ⁻¹)
\bar{S}_j	molar entropy of species j (J K ⁻¹ mol ⁻¹)
$\Delta_f S'^\circ$	standard transformed entropy of formation of a species i or reactant j (J K ⁻¹ mol ⁻¹)
$\Delta_r S'^\circ$	standard transformed entropy of reaction (J K ⁻¹ mol ⁻¹)
T	temperature (K)
V	volume (m ³)
z_i	charge number
α	coefficient in the Debye–Huckel limiting law written in terms of $\ln \gamma$
μ_j	chemical potential of species j (J mol ⁻¹)

ν_i'	stoichiometric number for reactant i
ξ'	extent of reaction for a biochemical reaction (mol)

Supporting Information Available: A *Mathematica* notebook containing the calculations described in this article. Three-dimensional plots are also provided for the transformed thermodynamic properties of $\text{ATP} + 2\text{H}_2\text{O} = \text{ADP} + 2\text{P}_i$. This material is available free of charge via the Internet at <http://pubs.acs.org>

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