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Thermochimica Acta 448 (2006) 82–106
thermochimica acta
www.elsevier.com/locate/tca

The energetics of metabolism in hydrothermal systems: Calculation of the standard molal thermodynamic properties of magnesium-complexed adenosine nucleotides and NAD and NADP at elevated temperatures and pressures

Douglas E. LaRowe*, Harold C. Helgeson

Department of Earth and Planetary Science, University of California, 307 McCone Hall, Berkeley, CA 94720, USA

Received 28 October 2005; received in revised form 14 June 2006; accepted 14 June 2006

Abstract

Calculation of the thermodynamic properties of biomolecules at high temperatures and pressures is fundamental to understanding the energetics of metabolism in hydrothermal systems. Perhaps the most direct interaction between hyperthermophilic microbes and their aquatic and mineralogic habitat involves conversion of environmentally available redox potential into biochemically useful energy. Although chemical thermodynamics can be used to quantify this process, little is known about the thermodynamic properties of the biomolecules involved, especially at high temperatures. However, recent advances in theoretical biogeochemistry make it possible to calculate these properties using the limited experimental data available in the literature, together with group additivity and correlation algorithms, reference model compounds and reactions, and the revised-HKF equations of state. This approach permits calculation of the standard molal thermodynamic properties and equations of state parameters for magnesium-complexed adenosine nucleotides, nicotinamide adenine dinucleotides (NADs), and nicotinamide adenine dinucleotide phosphates (NADPs) as a function of pressure and temperature. The thermodynamic properties and revised-HKF equations of state parameters generated in the present study can be used to carry out comprehensive mass transfer and Gibbs energy calculations to quantify the energetics of microbial energy production in hydrothermal systems.

Keywords: Magnesium adenosine nucleotides; NAD; NADP; Thermodynamics; Temperature; Pressure

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1. Introduction

Much has been learned about the numerous organic and inorganic compounds that thermophilic and hyperthermophilic microbes metabolize in hydrothermal systems to obtain energy [1–12]. Similarly, the discovery and identification of novel enzymes [13–19], genes [20,21], membranes [22–26], and metabolic strategies [27–29], as well as the search for new organisms that can tolerate ever more extreme environments [4,30–36] have received considerable attention in recent years. Yet, little is understood about the chemical and thermodynamic factors responsible for stabilizing the biomolecules involved in the energetics of metabolism at elevated temperatures and pressures [2,37,121]. Because *in vivo* Mg^{2+} activity,[1] pH, and cellular redox couples such as nicotinamide adenine dinucleotide (NAD) and nicotinamide adenine dinucleotide phosphate (NADP) are essential to the generation of ATP and other forms of biochemical energy, quantifying their chemical and thermodynamic interactions with minerals and other biomolecules as a function of temperature and pressure is essential to understanding the energetics of metabolism in hydrothermal systems. In

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* Corresponding author. Tel.: +1 510 642 8978; fax: +1 510 642 8975.
E-mail address: larowe@berkeley.edu (D.E. LaRowe).

[1] The term pMg is sometimes used in the biochemical literature to characterize the concentration of the aqueous magnesium cation or the total concentration of aqueous magnesium in solution. Using the former definition, pMg is related to the activity of the magnesium cation, $a_{Mg^{2+}}$, by $pMg = -\log a_{Mg^{2+}}$.

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doi:10.1016/j.tca.2006.06.008

particular, the exergonic hydrolysis reaction of ATP to ADP, which is coupled to otherwise endergonic reactions to make the overall reaction favorable, is known to proceed only in the presence of a divalent cation [38–43]. Of the many metal cations that form complexes with nucleotides, nucleic acids and enzymes, perhaps none is more essential than Mg^{2+} [38–41,43–47]. In particular, Mg^{2+} forms complexes with nucleotides such as ADP and ATP to make Mg–ADP and Mg–ATP species. Furthermore, biological redox compounds such as NAD and NADP that are connected to the external redox environment are linked to the flow of electrons required for the phosphorylation of ADP to ATP and other synthesis reactions. The relative stabilities of these redox molecules and Mg-nucleotides are controlled by the chemical potentials of H^+, O_2, H_2, and other components that are shared among biomolecules and the aqueous and mineralogic environment in which hyperthermophilic microbes thrive. Quantifying these interactions requires in addition to the thermodynamic properties of the electron donors and geochemical species, those of the biomolecules essential for the conversion of food into biochemically useful energy, i.e., growth. The purpose of the present communication is to address this challenge by developing a comprehensive and internally consistent set of thermodynamic properties and equations of state parameters for the variously protonated Mg-complexed adenosine nucleotides, NAD, and NADP at high temperatures and pressures.

Since the pioneering calorimetric studies of Mg-adenosine nucleotides, NAD, and NADP by Smith and Alberty [48], Burton [49], Burton and Wilson [50], Racker [51], and Engel and Dalziel [52], considerable attention has been devoted to measuring the thermodynamic properties of reaction for the reduction of NAD [53,54] and NADP [55,56], as well as the hydrolysis of MgATP [57–74] at or near 25 °C and 1 bar. More recently, Ould-Moulaye [75] has generated a comprehensive set of thermodynamic properties of Mg-adenosine nucleotides at 25 °C and 1 bar. Although the thermodynamic properties of reaction for the redox reaction between reduced and oxidized NAD (NAD_{red} and NAD_{ox}, respectively) and NADP ($NADP_{red}$ and $NADP_{ox}$, respectively) have been reported in the literature, the standard molal thermodynamic properties of the individual species have not been determined, nor is much known about the relative stabilities of these species at higher temperatures and pressures.

Most experimental thermodynamic data reported in the literature for Mg-adenosine nucleotides are restricted to 25 °C and 1 bar, although some experimental heats of reaction are available up to 125 °C [76,77]. No other experimental data are available for Mg-adenosine nucleotides at or approaching the temperatures and pressures obtaining in submarine hydrothermal vent systems. Similarly, there is a paucity of experimental thermodynamic data reported in the literature for NAD and NADP compounds at any temperature and pressure. Nevertheless, experimental low-temperature thermodynamic data reported in the literature for reference model compounds and reactions among them can be combined with the revised HKF equations of state [78–83] and correlation and group additivity algorithms to estimate the thermodynamic properties of Mg-adenosine nucleotides and variously charged NAD and NADP species at elevated temperatures and pressures. To ensure internal consistency and compatibility with the most recent experimental data reported in the literature, this approach requires reassessment of the values of the standard molal Gibbs energies and enthalpies of formation, (ΔG_f° and ΔH_f°) and third law entropies, S°, at 25 °C and 1 bar for the Mg-adenosine nucleotides given by Ould-Moulaye et al. [75].

For the cases in which few or no experimental data are available in the literature from which to generate or derive the standard molal thermodynamics properties at 25 °C and 1 bar and the revised HKF equations of state parameters for Mg-adenosine, NAD, and NADP species, extensive use of experimental data reported in the literature for crystalline and aqueous reference model compounds and reactions are used in a first approximation to estimate these properties and parameters. Although the resulting estimates of these thermodynamic properties may have greater uncertainties associated with them than experimentally measured values, they can be used as provisional estimates to better understand the biogeochemistry of hydrothermal systems until more experimental calorimetric data become available in the literature. The conventions and strategies used for this purpose are described below.

2. Standard state conventions

The standard state adopted for H_2O is one of unit activity of the pure liquid at any pressure and temperature. In contrast, that for aqueous species corresponds to unit activity of the species in a hypothetical one molal solution referenced to infinite dilution at any pressure and temperature. The standard molal thermodynamic properties of charged aqueous species are consistent with the hydrogen ion convention [84,85,80], which can be expressed as

$$\Xi_i = \Xi_i^{abs} - Z_i \Xi_{H^+}^{abs} \tag{1}$$

where Ξ_i and Ξ_i^{abs} stand for any given conventional and absolute standard molal property, or equations of state parameters of the ith aqueous species, $\Xi_{H^+}^{abs}$ denotes the corresponding absolute standard molal property of the hydrogen ion, and Z_i represents the charge of the subscripted species. Hence, $\Xi_{H^+} = 0$ at all temperatures and pressures.

Standard molal Gibbs energies and enthalpies are expressed in the present communication as apparent standard molal Gibbs energies and enthalpies of formation (ΔG° and ΔH°, respectively) in accord with [86,84]

$$\Delta G^\circ \equiv \Delta G_f^\circ + (G_{P,T}^\circ - G_{P_r,T_r}) \tag{2}$$

and

$$\Delta H^\circ \equiv \Delta H_f^\circ + (H_{P,T}^\circ - H_{P_r,T_r}) \tag{3}$$

where ΔG_f° and ΔH_f° refer to the standard molal Gibbs energy and enthalpy of formation from the elements in their stable form at the reference pressure (P_r) and temperature (T_r) of 1 bar and 298.15 K, and $(G_{P,T}^\circ - G_{P_r,T_r})$ and $(H_{P,T}^\circ - H_{P_r,T_r})$ stand for the differences in the standard molal Gibbs energy and enthalpy of the aqueous species at the pressure (P) and temperature (T) of interest, and those at P_r and T_r. These parenthetical differences can be quantified using Eqs. (A.1) and (A.2), respectively, in Appendix A.

3. Magnesium-complexed adenosine nucleotides

The magnesium-complexed adenosine nucleotides considered in the present study consist of variously protonated complexes of magnesium and adenosine mono-, di-, and triphosphates. In addition to their chemical formulas, specific species are referred to below by adding Mg and/or H at the beginning of the acronyms representing the ionized reference species for adenosine mono-, di-, and triphosphate, as in MgAMP, $HADP^{2-}$, and $MgHATP^-$, etc. Values of the standard molal Gibbs energies and enthalpies of formation (ΔG_f° and ΔH_f°, respectively) and the standard molal third law entropies (S°), volumes (V°), and isobaric heat capacities (C_p°) adopted in the present study for these species are given in Table 1, together with values of the revised-HKF equations of state parameters[2] required to calculate values of the apparent molal Gibbs energies and enthalpies (ΔG° and ΔH°, respectively) and S°, V°, and C_p° at elevated temperatures and pressures.

3.1. Standard molal Gibbs energies, enthalpies, and third law entropies at 25 °C and 1 bar

Values of ΔG_f° and ΔH_f° for the Mg-complexed adenosine nucleotides considered in present study were calculated using specific statements of the generic equations listed in the second column of Table 2, together with experimental values of the standard molal enthalpies and Gibbs energies of reaction (ΔH_r° and ΔG_r°) taken from Table 3 for the reactions listed in column 1 of Table 2. The values of S° at 25 °C and 1 bar for the Mg-complexed adenosine nucleotides were calculated from their corresponding values of ΔG_f° and ΔH_f° from

$$S^\circ = \frac{\Delta H_f^\circ - \Delta G_f^\circ}{T} - \sum_i \nu_i S_i^\circ \tag{4}$$

where ν_i denotes the number of moles of the ith element in one mole of the species and S_i° represents the standard molal third-law entropy of the ith element in its stable state at 25 °C and 1 bar. The values of S_i° used in these calculations were taken from [87].

3.2. Equations of state parameters

Calculation of the standard molal thermodynamic properties of aqueous species as a function of temperature and pressure using the revised HKF equations of state requires values of the species-dependent solvation and non-solvation parameters in the equations (see Appendix A Section A.2). These parameters can be generated by regressing experimental values of the standard molal isobaric heat capacity (C_p°), volume (V°), and isothermal compressibility (κ_T°) for a given species with the revised HKF equations of state as a function of temperature. It can be demonstrated that reliable values of the solvation parameter, ω, can be retrieved from calorimetric data only if values of C_p° above ~100 °C are available in the literature for the aqueous species of interest [80–83,88]. In the absence of experimental high-temperature calorimetric and densimetric data, experimentally derived low-temperature values of C_p° can be combined with the revised-HKF equations of state and iterative trial values of ω to generate values of the c_1 and c_2 parameters in the equations discussed below. Furthermore, correlation algorithms reported in the literature (e.g., [89]) can be combined with values of V° at 25 °C and 1 bar to calculate values of the a_1, a_2, a_3, and a_4 non-solvation parameters for the species of interest.

3.2.1. ω, c_1 and c_2

In the absence of experimental high-temperature calorimetric data, estimated values of c_1 and c_2 for Mg-complexed adenosine nucleotides can be obtained by regressing low-temperature experimentally derived values of C_p° using two rearranged versions of Eq. (A.31), together with trial values of the solvation parameter ω. For $P = P_r$, Eq. (A.31) reduced to

$$\Delta C_{P,n}^\circ = C_p^\circ - \omega T X, \tag{5}$$

where

$$\Delta C_{P,n}^\circ = c_1 + \frac{c_2}{(T-\Theta)^2}. \tag{6}$$

Taking account of experimental and theoretical considerations [80–82,89], a series of trial values of ω in Eq. (5) for the Mg-adenosine nucleotides were specified for each species until the distribution of the calculated values of $\Delta C_{p,n}^\circ$ became linear functions of

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[2] The revised-HKF equations of state are summarized in Appendix A.

Table 1
Summary of the standard molal thermodynamic properties at 25 °C and 1 bar and the revised HKF equations of state parameters required to calculate the standard molal thermodynamic properties as a function of temperature and pressure of selected magnesium-adenosine nucleotides (see text)

Compound	Formula	ΔG_f° [a]	ΔH_f° [a]	S° [b]	C_p° [b,d]	V° [c,d]	a_1 (×10)[e]	a_2 (×10^{-2})[a]	a_3 [f]	a_4 (×10^{-4})[g]	c_1 [b]	c_2 (×10^{-4})[g]	ω (×10^{-5})[a]
MgAMP	$MgC_{10}H_{12}N_5O_7P$	−1505110	−2082860	174.4	482.8	158.14	9.7119	456.504	−78.4132	−7.2446	801.91	−76.41	18
$MgADP^-$	$MgC_{10}H_{12}N_5O_{10}P_2^-$	−2374520	−3058220	233.2	585.7	189.17	10.087	531.962	−80.1633	−10.364	733.20	−16.30	13
MgHADP	$MgC_{10}H_{13}N_5O_{10}P_2$	−2403560	−3061190	320.2	675.6	199.93	10.303	575.287	−81.1683	−12.155	1023.3	−81.07	20
Mg_2ADP^+	$Mg_2C_{10}H_{12}N_5O_{10}P_2^+$	−2838010	−3510500	172.8	667.1	174.77	9.7952	473.231	−78.8015	−7.9370	698.06	−5.853	2.1
$MgATP^{2-}$	$MgC_{10}H_{12}N_5O_{13}P_3^{2-}$	−3236780	−4042910	236.8	628.2	193.48	10.252	565.191	−80.9340	−11.738	1071.2	−109.2	24
$MgHATP^-$	$MgC_{10}H_{13}N_5O_{13}P_3^-$	−3267680	−4038360	355.7	882.0	208.97	10.465	607.810	−81.9227	−13.500	1320.5	−107.0	24
MgH_2ATP	$MgC_{10}H_{14}N_5O_{13}P_3$	−3289460	−4060490	354.5	1118	208.63	10.433	601.517	−81.7767	−13.239	1517.1	−100.9	21
Mg_2ATP	$Mg_2C_{10}H_{12}N_5O_{13}P_3$	−3701180	−4488400	202.2	854.1	191.55	10.253	565.212	−80.9349	−11.739	1298.3	−96.70	27

[a] $J\,mol^{-1}$.
[b] $J\,K^{-1}\,mol^{-1}$.
[c] $cm^3\,mol^{-1}$.
[d] Calculated from the revised HKF equations of state parameters generated in the present study.
[e] $J\,mol^{-1}\,bar^{-1}$.
[f] $J\,K\,mol^{-1}\,bar^{-1}$.
[g] $J\,K\,mol^{-1}$.

Table 2
Summary of equations and reactions used to calculate values of ΔG_f° and ΔH_f° for selected aqueous Mg-complexed adenosine mono-, di-, and triphosphate nucleotide species at 25 °C and 1 bar

Reactions for which values of ΔG_r° and ΔH_r° are available in the literature		Equations used to calculate values of ΔG_f° and ΔH_f° for the indicated species
$AMP^{2-} + Mg^{2+} \rightleftharpoons MgAMP^\circ$	(I)	$\Xi^\circ_{MgAMP^\circ} = \Xi^\circ_{AMP^{2-}} + \Xi^\circ_{Mg^{2+}} + \Delta\Xi^\circ_{r(1)}$
$ADP^{3-} + Mg^{2+} \rightleftharpoons MgADP^-$	(II)	$\Xi^\circ_{MgADP^-} = \Xi^\circ_{ADP^{3-}} + \Xi^\circ_{Mg^{2+}} + \Delta\Xi^\circ_{r(2)}$
$HADP^{2-} + Mg^{2+} \rightleftharpoons MgHADP^\circ$	(III)	$\Xi^\circ_{MgHADP^\circ} = \Xi^\circ_{HADP^{2-}} + \Xi^\circ_{Mg^{2+}} + \Delta\Xi^\circ_{r(3)}$
$ATP^{4-} + Mg^{2+} \rightleftharpoons MgATP^{2-}$	(IV)	$\Xi^\circ_{MgATP^{2-}} = \Xi^\circ_{ATP^{4-}} + \Xi^\circ_{Mg^{2+}} + \Delta\Xi^\circ_{r(4)}$
$HATP^{3-} + Mg^{2+} \rightleftharpoons MgHATP^-$	(V)	$\Xi^\circ_{MgHATP^-} = \Xi^\circ_{HATP^{3-}} + \Xi^\circ_{Mg^{2+}} + \Delta\Xi^\circ_{r(5)}$
$H_2ATP^{2-} + Mg^{2+} \rightleftharpoons MgH_2ATP^\circ$	(VI)	$\Xi^\circ_{MgH_2ATP^\circ} = \Xi^\circ_{MgHATP^-} + \Delta\Xi^\circ_{r(6)}$
$MgADP^- + Mg^{2+} \rightleftharpoons Mg_2ADP^+$	(VII)	$\Xi^\circ_{Mg_2ADP^+} = \Xi^\circ_{MgADP^-} + \Xi^\circ_{Mg^{2+}} + \Delta\Xi^\circ_{r(7)}$
$MgATP^{2-} + Mg^{2+} \rightleftharpoons Mg_2ATP^\circ$	(VIII)	$\Xi^\circ_{Mg_2ATP^\circ} = \Xi^\circ_{MgATP^{2-}} + \Xi^\circ_{Mg^{2+}} + \Delta\Xi^\circ_{r(8)}$

The symbol Ξ° stands for ΔG_f° and ΔH_f° for the subscripted species and $\Delta\Xi_r^\circ$ denotes ΔG_r° and ΔH_r° for the indicated reaction in column 1. Values of $\Delta\Xi_r^\circ$ for Reactions (I)–(VII) are listed in Table 3. Values of ΔG_f° or ΔH_f° for AMP^{2-}, ADP^{3-}, $HADP^{2-}$, ATP^{4-}, and $HATP^{3-}$ were taken from LaRowe and Helgeson [120].

$1/(T-\Theta)^2$ at 1 bar. The values of C_p° required to evaluate Eq. (5) for each of the nucleotides considered in the present study were calculated by taking finite difference derivatives (δ) of values of ΔH° for these species in accord with

$$C_p^\circ = \left(\frac{\partial H^\circ}{\partial T}\right)_p \approx \left(\frac{\delta H^\circ}{\delta T}\right)_p = \frac{\Delta H^\circ_{T_2} - \Delta H^\circ_{T_1}}{T_2 - T_1}, \tag{7}$$

where T_1 and T_2 designate lower and higher temperatures, respectively. The values of ΔH° at different temperatures required to evaluate Eq. (7) for the Mg-complexed nucleotides were calculated using the equations listed in Table 4, together with experimental values of ΔH_r° taken from the literature for the reactions shown in Table 4.

It follows from Eq. (6) that values of c_1 and c_2 for Mg-complexed adenosine nucleotides correspond to the intercepts and slopes, respectively, of straight lines fitted to the resulting values of $\Delta C^\circ_{p,n}$ as a function of $1/(T-\Theta)^2$. For example, the filled circular symbols in Fig. 1 represent values of $\Delta C^\circ_{P,n}$ for MgATP, $MgADP^-$, MgHADP, Mg_2ADP^+, $MgATP^{2-}$, $MgHATP^-$, MgH_2ATP, and Mg_2ADP calculated from Eq. (5) using experimentally derived values of C_p°. It can be seen in Fig. 1 that the straight lines

Table 3
Summary of standard molal thermodynamic properties for selected aqueous Mg-phosphate and Mg-nucleotide reactions at 25 °C and 1 bar

Reaction	$\Delta G_r^{\circ\,a}$	$\Delta H_r^{\circ\,a}$
Monophosphates		
$Mg^{2+} + AMP^{2-} \rightarrow MgAMP$	-15930^b	11300^b
$Mg^{2+} + HPO_4^{2-} \rightarrow MgHPO_4$	-15460^c	12220^c
Diphosphates		
$Mg^{2+} + ADP^{3-} \rightarrow MgADP^-$	-26540^b, -24390^d, $-26650^{e,h}$	$19000^{c,h}$, 17990^d
$Mg^{2+} + HP_2O_7^{3-} \rightarrow MgHP_2O_7^-$	-25810^c	11800^c
$Mg^{2+} + HADP^{2-} \rightarrow MgHADP$	$-14270^{b,h}$, -140204^d	$12500^{b,h}$, 3800^d
$Mg^{2+} + H_2P_2O_7^{2-} \rightarrow Mg_2H_2P_2O_7$	-16560^c	11090^c
$Mg^{2+} + MgADP^- \rightarrow Mg_2ADP^+$	-9620^f, $-9510^{e,h}$	13700^e
Triphosphates		
$Mg^{2+} + ATP^{4-} \rightarrow MgATP^{2-}$	-35280^b, -33260^d, $-33750^{e,h}$	22890^b, 21340^d, $18200^{e,h}$
$Mg^{2+} + P_2O_7^{4-} \rightarrow MgP_2O_7^{2-}$	-41100^c	13310^c
$Mg^{2+} + HATP^{3-} \rightarrow MgHATP^-$	-20460^d, $-20720^{b,h}$	9210^d, $16900^{b,h}$
$Mg^{2+} + MgATP^{2-} \rightarrow Mg_2ATP$	-15350^b, $-10410^{e,h}$	10800^b, $20460^{e,h}$
$Mg^{2+} + MgP_2O_7^{2-} \rightarrow Mg_2P_2O_7$	-22320^c	3810^c
$Mg^{2+} + H_2P_2O_7^{2-} \rightarrow Mg_2H_2P_2O_7$	-16560^c	11090^c
$Mg^{2+} + H_2ATP^{2-} \rightarrow MgH_2ATP$	-16560^g	11090^g

[a] $\mathrm{J\,mol^{-1}}$.
[b] [57].
[c] [99].
[d] [46].
[e] These values are consistent with higher temperature experimental ΔH_r° values give by [77] and the revised HKF equations of state parameters derived from them.
[f] [100].
[g] Taken to be the same as that for $Mg^{2+} + H_2P_2O_7^{2-} \rightarrow MgH_2P_2O_7$.
[h] Values adopted in the present study.

Table 4
Summary of equations and reactions used to calculate values of ΔH° as a function of temperature for selected aqueous Mg-complexed adenosine mono-, di-, and triphosphate nucleotide species

Reactions from which values of ΔH_r° were used to calculate values of ΔH° for selected Mg-nucleotides		Equations used to calculate values of ΔH° for the indicated Mg-nucleotides as a function of temperature
$ADP^{3-} + Mg^{2+} \rightleftharpoons MgADP^-$	(i)	$\Delta H^\circ_{MgADP^-} = \Delta H^\circ_{ADP^{3-}} + \Delta H^\circ_{Mg^{2+}} + \Delta H^\circ_{r1}$
$MgADP^- + Mg^{2+} \rightleftharpoons Mg_2ADP^+$	(ii)	$\Delta H^\circ_{Mg_2ADP^+} = \Delta H^\circ_{MgADP^-} + \Delta H^\circ_{Mg^{2+}} + \Delta H^\circ_{r2}$
$H_2ADP^{2-} + H^+ \rightleftharpoons H_3ADP^0$	(iii)	$\Delta H^\circ_{MgHADP^0} = \Delta H^\circ_{MgADP^-} + \Delta H^\circ_{r3}$
$ATP^{4-} + Mg^{2+} \rightleftharpoons MgATP^{2-}$	(iv)	$\Delta H^\circ_{MgATP^{2-}} = \Delta H^\circ_{ATP^{4-}} + \Delta H^\circ_{Mg^{2+}} + \Delta H^\circ_{r4}$
$MgATP^{2-} + Mg^{2+} \rightleftharpoons Mg_2ATP^0$	(v)	$\Delta H^\circ_{Mg_2ATP^0} = \Delta H^\circ_{MgATP^{2-}} + \Delta H^\circ_{Mg^{2+}} + \Delta H^\circ_{r5}$
		$\Delta H^\circ_{MgAMP^0} = \Delta H^\circ_{AMP^{2-}} + \Delta H^\circ_{Mg^{2+}} + \Delta H^\circ_{r5}$
$H_2ATP^{2-} + H^+ \rightleftharpoons H_3ATP^-$	(vi)	$\Delta H^\circ_{MgHATP^-} = \Delta H^\circ_{MgATP^{2-}} + \Delta H^\circ_{r6}$
$H_3ATP^- + H^+ \rightleftharpoons H_4ATP^0$	(vii)	$\Delta H^\circ_{MgH_2ATP^0} = \Delta H^\circ_{MgHATP^-} + \Delta H^\circ_{r7}$

The values of ΔH_r° for Reactions (i), (ii), (iv), and (v) were taken from [77]. Those for Reactions (iii) and (vii) were calculated using the SUPCRT92 software package [93] and the standard molal enthalpies of formation and revised HKF equation of state parameters for AMP^{2-}, ADP^{3-}, $HADP^{2-}$, ATP^{4-}, $HATP^{3-}$, H_2ATP^{2-}, H_3ATP^-, and H_4ATP taken from LaRowe and Helgeson [120]. The values of ΔH° for Mg^{2+} were taken from SUPCRT92.

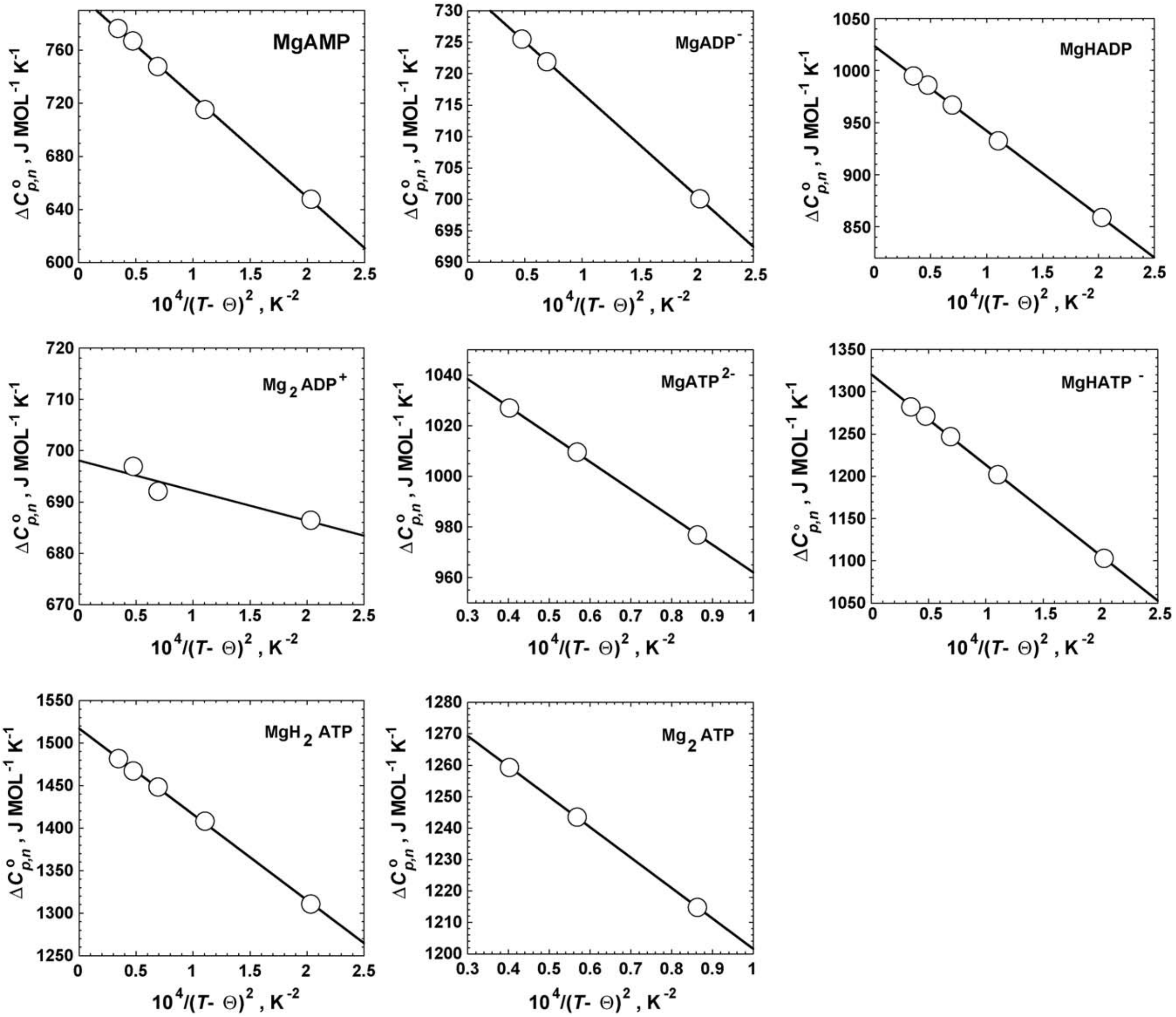


Fig. 1. $\Delta C^\circ_{P,n}$ for selected aqueous Mg-adenosine nucleotides as a function of $10^4/(T-\Theta)^2$ at 1 bar. The symbols represent values of $\Delta C^\circ_{P,n}$ computed from Eqs. (5) and (6) using values of ω taken from Table 1 and values of C°_p calculated as discussed in Section 3.2.1. The regression lines denote fits of Eq. (6) to the data.

representing the revised HKF equations of state are closely consistent with the experimentally derived values of $\Delta C^\circ_{P,n}$ as a function of $1/(T-\Theta)^2$.

3.2.2. a_1, a_2, a_3, and a_4

No experimental volumetric and compressibility data are available in the literature for Mg-adenosine nucleotides. Nevertheless, estimates of the a_1, a_2, a_3, and a_4 parameters can be generated from correlation algorithms reported by Shock and Helgeson [89]. For example, the a_1 and a_2 parameters can be calculated from

$$a_1 = 0.013684\left(\frac{\Delta V^\circ_{\mathrm{n}}}{41.8393}\right) + 0.1765 \tag{8}$$

and

$$a_2 = 2601[\sigma(0.0239006) - a_1] \tag{9}$$

where $\Delta V^\circ_{\mathrm{n}}$ and σ are given by

$$\Delta V^\circ_{\mathrm{n}} = V^\circ - \Delta V^\circ_{\mathrm{s}} \tag{10}$$

and

$$\sigma = 1.07143\Delta V^\circ_{\mathrm{n}} + 3. \tag{11}$$

The values of $\Delta V^\circ_{\mathrm{s}}$ required to evaluate Eq. (10) were calculated using the independently derived values of ω for the species given in Table 1, together with the relation $\Delta V^\circ_{\mathrm{s}} = -\omega Q$, where Q refers to volumetric Born function (see [82]). The a_4 and a_3 parameters can be calculated using [89]

$$a_4 = 27790 - 4.134a_2 \tag{12}$$

and

$$a_3 = \xi(0.0239006) - \left(\frac{a_4}{2601}\right) \tag{13}$$

where

$$\xi = 70.15(\Delta V^\circ_{\mathrm{n}} - \sigma). \tag{14}$$

The values of V° at 25 °C and 1 bar for the ith Mg-complexed adenosine nucleotide, $V^\circ_{\text{Mg-nucleotide}_i}$, which are required to evaluate Eq. (10), can be calculated from

$$V^\circ_{\text{Mg-nucleotide}_i} = V^\circ_{\mathrm{Mg}^{2+}} + V^\circ_{\text{nucleotide}_i} + \Delta V^\circ_{\mathrm{r}} \tag{15}$$

where $V^\circ_{\text{nucleotide}_i}$ and $V^\circ_{\mathrm{Mg}^{2+}}$ refer to the standard molal volumes of the ith adenosine nucleotide and Mg^{2+}, respectively, and $\Delta V^\circ_{\mathrm{r}}$ represents the standard molal volume of the association reaction for the ith nucleotide (nucleotide$_i$) and Mg^{2+}. A generic representation of this reaction can be written as

$$\text{nucleotide}_i^{Z_i} + \mathrm{Mg}^{2+} \rightleftharpoons \text{Mg-nucleotide}_i^{(Z_i+2)} \tag{16}$$

Although values of $\Delta V^\circ_{\mathrm{r}}$ for association reactions like those represented by Reaction (16) are not available in the literature, values of $\Delta V^\circ_{\mathrm{r}}$ for these reactions can be taken in a first approximation to be equal to those of $\Delta V^\circ_{\mathrm{r}}$ for reactions involving analogous association of Mg^{2+} with a variety of ionized organic acids (OA) reported in the literature. Values of $\Delta V^\circ_{\mathrm{r}}$ for the latter reactions can be calculated using

$$\Delta V^\circ_{\mathrm{r}} = V^\circ_{\mathrm{Mg-(OA)_2}} - V^\circ_{\mathrm{Mg}^{2+}} - 2V^\circ_{\mathrm{OA}^-}, \tag{17}$$

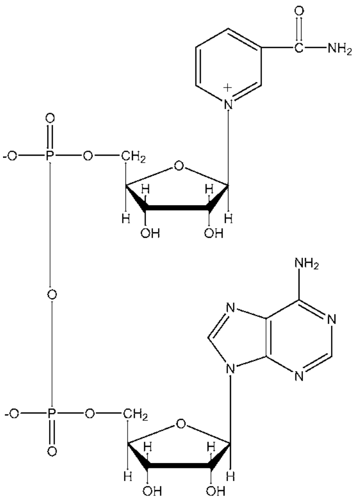
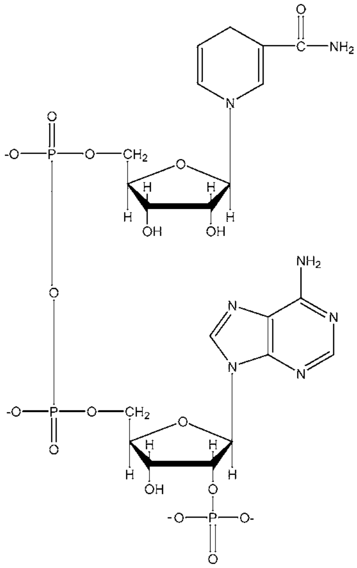
and

$$\Delta V^\circ_{\mathrm{r}} = V^\circ_{\mathrm{Mg-(OA)^+}} - V^\circ_{\mathrm{Mg}^{2+}} - V^\circ_{\mathrm{OA}^-} \tag{18}$$

where OA^-, $Mg-(OA)_2$, and $Mg-(OA)^+$ stand for ionized organic acid, magnesium-complexed di-organic acid, and magnesium-complexed organic acid, respectively.

Values of $\Delta V^\circ_{\mathrm{r}}$ at 25 °C and 1 bar for Eqs. (17) and (18) were computed using values of V° for Mg^{2+}, nine $Mg-(OA)_2$ compounds, and eight $Mg-(OA)^+$ species. The experimental values of V° for the Mg-organic acids and organic acids used in the calculations were taken from [90–92]. The average values of $\Delta V^\circ_{\mathrm{r}}$ at 25 °C and 1 bar computed from these equations are 3.43 and −9.89, respectively, with standard deviations of ±2.00 and ±0.02. These values were taken in a first approximation to be equivalent to those for the analogous nucleotide reactions. Eq. (15) was then used to calculate the values of $V^\circ_{\text{Mg-nucleotide}_i}$ given in Table 1.

Table 5
Idealized structures of selected nicotinamide adenine dinucleotide species

NAD^{-}_{ox}	$NADP^{4-}_{red}$
	
$C_{21}H_{26}N_7O_{14}P_2^{-}$	$C_{21}H_{26}N_7O_{17}P_3^{4-}$

4. Nicotinamide-adenine dinucleotides

The aqueous nicotinamide-adenine dinucleotides (NADs) considered in the present study are variously protonated compounds consisting of one adenosine nucleotide monophosphate and one nicotinamide nucleotide monophosphate joined by a phosphodiester bond. An idealized structural representation of oxidized NAD is shown in Table 5. Because nicotinamide nucleotides have two biologically relevant oxidation states, both the reduced and oxidized forms of nicotinamide-adenine dinucleotides, (NAD_{red} and NAD_{ox}, respectively[3]) are considered in the present communication. The generic acronyms NAD_{red} and NAD_{ox} stand for all of the differently charged varieties of each type of dinucleotides. Particular charged species are referred to by $H_nNAD_{red}^{(n-2)}$ and $H_nNAD_{ox}^{(n-1)}$ for values of $n = 0, 1$, or 2, which represents the number of moles of hydrogen atoms bonded to the respective base species, NAD_{red}^{2-} and NAD_{ox}^{-}. The same nomenclature is used to refer to the reduced and oxidized nicotinamide nucleotide monophosphates ($H_nNicMP_{red}^{(n-2)}$) and ($H_nNicMP_{ox}^{(n-1)}$). Although few experimentally determined thermodynamic properties have been reported in the literature for these species, the standard molal thermodynamic properties and revised HKF equations of state parameters for nicotinamide adenine dinucleotides can be estimated from the corresponding properties of the constituent mononucleotides using reference model reactions. The standard molal Gibbs energies, enthalpies, third law molal entropies, volumes, and heat capacities for nicotinamide adenine dinucleotides adopted in the present study are given in Table 6 together with the revised HKF equations of state parameters.

4.1. *Standard molal Gibbs energies, enthalpies, and third law entropies at* 25 °C *and 1 bar*

The values of ΔG_f°, ΔH_f°, and S° at 25 °C and 1 bar for aqueous H_2NAD_{red} were calculated from the standard molal Gibbs energies and enthalpies of formation and third law entropies of its constituent nucleotides, H_2AMP and H_2NicMP_{red}, using the corresponding standard molal thermodynamic properties of reaction for

$$H_2AMP + H_2NicMP_{red} \rightleftharpoons H_2NAD_{red} + H_2O, \tag{19}$$

in accord with

$$\Xi^\circ_{H_2NAD_{red}} = \Xi^\circ_{H_2NicMP_{red}} + \Xi^\circ_{H_2AMP} + \Delta\Xi^\circ_r - \Xi^\circ_{H_2O}. \tag{20}$$

The subscripted symbol Ξ° in Eq. (20) refers to ΔG_f°, ΔH_f°, or S° of the indicated species, and $\Delta\Xi^\circ_r$ stands for the corresponding standard molal thermodynamic property of reaction. Because no experimental values of $\Delta\Xi^\circ_r$ for Reaction (19) are available in the

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[3] Because nicotinamide-adenine dinucleotide species of different overall charges are considered in the present study, the abbreviations used to refer to them differ slightly from those commonly used in the biochemical literature.

Table 6

Summary of the revised HKF equations of state parameters and the standard molal thermodynamic properties at 25 °C and 1 bar of selected aqueous nicotinamide mono- and dinucleotides and ribose-5-phosphate species

Compound	Formula	ΔG°_f[a]	ΔH°_f[a]	S°[b]	C°_p[b]	V°[c]	a_1 (×10)[d]	a_2 (×10^{-2})[a]	a_3[e]	a_4 (×10^{-4})[f]	c_1[b]	c_2 (×10^{-4})[f]	ω (×10^{-5})[a]
Mononucleotides													
H_2NicMP_{red}	$C_{11}H_{17}N_2O_8P$	−1379150	−1933540	367.7	363.3	198.9	10.2127	557.1858	−80.747	−11.407	606.1	−66.99	12
$HNicMP^-_{red}$	$C_{11}H_{16}N_2O_8P^-$	−1357390	−1915550	355.1	340.4	199.4	10.2391	562.4681	−80.868	−11.625	625.7	−78.49	14
$NicMP^{2-}_{red}$	$C_{11}H_{15}N_2O_8P^{2-}$	−1323090	−1919060	228.2	119.1	172.9	9.87591	489.5062	−79.178	−8.609	384.3	−68.62	14
$H_2NicMP^+_{ox}$	$C_{11}H_{16}N_2O_8P^+$	−1401620	−1904000	411.5	331.9	199.0	10.2144	557.4883	−80.755	−11.419	599.2	−78.99	12
$HNicMP_{ox}$	$C_{11}H_{15}N_2O_8P$	−1379860	−1886010	398.8	309.1	190.0	10.2408	562.7706	−80.877	−11.638	618.8	−90.50	14
$NicMP^-_{ox}$	$C_{11}H_{14}N_2O_8P^-$	−1345550	−1889520	272.0	87.78	173.0	9.87759	489.8087	−79.186	−8.6216	377.4	−80.63	14
Dinucleotides													
H_2NAD_{red}	$C_{21}H_{29}N_7O_{14}P_2$	−2216430	−3266560	682.0	914.2	346.4	−10.074	1037.896	−168.43	−8.0241	1361	−124.3	21
$HNAD^-_{red}$	$C_{21}H_{28}N_7O_{14}P_2^-$	−2207650	−3274510	625.9	824.7	341.0	−10.778	1036.191	−167.79	−7.9534	1366	−142.5	28
NAD^{2-}_{red}	$C_{21}H_{27}N_7O_{14}P_2^{2-}$	−2194260	−3276600	574.0	741.4	335.8	−10.916	1035.846	−167.64	−7.9391	1386	−159.4	35
$H_2NAD^+_{ox}$	$C_{21}H_{28}N_7O_{14}P_2^+$	−2238900	−3237020	725.9	882.8	346.5	−10.072	1038.199	−168.44	−8.0366	1354	−136.3	21
$HNAD_{ox}$	$C_{21}H_{27}N_7O_{14}P_2$	−2230110	−3244970	669.4	793.7	341.1	−10.776	1036.493	−167.80	−7.9659	1359	−154.6	28
NAD^-_{ox}	$C_{21}H_{26}N_7O_{14}P_2^-$	−2216730	−3247060	617.6	710	335.9	−10.914	1036.149	−167.65	−7.9517	1379	−171.4	35
Ribose-5-phosphates													
R5P	$C_5H_{11}O_8P$	−1636080	−2037740	261.5	379.1	120.1	28.0625	289.1098	−92.066	−0.32468	494.1	−67.94	-2.5
$R5P^-$	$C_5H_{10}O_8P^-$	−1623700	−2045690	192.8	251.5	110.3	20.5932	270.8726	−84.898	0.42928	477.7	−94.01	3.8
$R5P^{2-}$[g]	$C_5H_9O_8P^{2-}$	−1582570	−2041480	68.99	31.38	83.78	8.64373	241.6946	−73.429	1.6355	430.4	−137.7	12.4

[a] J mol^{-1}.

[b] J K^{-1} mol^{-1}.

[c] cm^3 mol^{-1}.

[d] J mol^{-1} bar^{-1}.

[e] J K mol^{-1} bar^{-1}.

[f] J K mol^{-1}.

[g] LaRowe and Helgeson [120]. The revised HKF equations of state parameters and standard molal thermodynamic properties at 25 °C and 1 bar for $R5P^-$ and R5P were estimated using $\Xi^\circ_{R5P^-} = \Xi^\circ_{R5P^{2-}} - \Delta\Xi^\circ_r$ and $\Xi^\circ_{R5P} = \Xi^\circ_{R5P^-} - \Delta\Xi^\circ_r$. The values of $\Delta\Xi^\circ_r$ were taken in a first approximation to be equal to that for Reactions (41) and (40), respectively.

Table 7
Summary of the equations and reference model reactions used to calculate values of ΔG°_f, ΔH°_f, and S° at 25 °C and 1 bar and the revised HKF equations of state parameters for selected nicotinamide adenine mono- and dinucleotide species

Equations used to calculate values of ΔG°_f, ΔH°_f, S°, and equations of state parameters for the indicated species[a]	Reference model reactions used to calculate $\Delta\Xi^\circ_r$ for the adjacent equations	
$\Xi^\circ_{\mathrm{HNAD^-_{red}}} = \Xi^\circ_{\mathrm{H_2NAD_{red}}} + \Delta\Xi^\circ_r$	$\mathrm{H_4P_2O_7^0 \rightleftharpoons H_3P_2O_7^- + H^+}$	(a)
$\Xi^\circ_{\mathrm{NAD^{2-}_{red}}} = \Xi^\circ_{\mathrm{HNAD^-_{red}}} + \Delta\Xi^\circ_r$	$\mathrm{H_3P_2O_7^- \rightleftharpoons H_2P_2O_7^{2-} + H^+}$	(b)
$\Xi^\circ_{\mathrm{HNAD_{ox}}} = \Xi^\circ_{\mathrm{NAD^-_{ox}}} + \Delta\Xi^\circ_r$	$\mathrm{H_2P_2O_7^{2-} + H^+ \rightleftharpoons H_3P_2O_7^-}$	(c)
$\Xi^\circ_{\mathrm{H_2NAD^+_{ox}}} = \Xi^\circ_{\mathrm{HNAD_{ox}}} + \Delta\Xi^\circ_r$	$\mathrm{H_3P_2O_7^- + H^+ \rightleftharpoons H_4P_2O_7^0}$	(d)
$\Xi^\circ_{\mathrm{HNicMP^-_{red}}} = \Xi^\circ_{\mathrm{H_2NicMP_{red}}} + \Delta\Xi^\circ_r$	$\mathrm{H_2AMP \rightleftharpoons HAMP^- + H^+}$	(e)*
$\Xi^\circ_{\mathrm{HNicMP^-_{ox}}} = \Xi^\circ_{\mathrm{H_2NicMP_{ox}}} + \Delta\Xi^\circ_r$		
$\Xi^\circ_{\mathrm{NicMP^{2-}_{red}}} = \Xi^\circ_{\mathrm{HNicMP^-_{red}}} + \Delta\Xi^\circ_r$	$\mathrm{HAMP \rightleftharpoons AMP^{2-} + H^+}$	(f)*
$\Xi^\circ_{\mathrm{NicMP^{2-}_{ox}}} = \Xi^\circ_{\mathrm{HNicMP^-_{ox}}} + \Delta\Xi^\circ_r$		

[a] The symbol Ξ° stands for ΔG°_f, ΔH°_f, S° and the revised HKF equations of state parameters for the subscripted species, and $\Delta\Xi^\circ_r$ denotes ΔG°_r, ΔH°_r, ΔS°_r, and the equations of state parameters for the adjacent reference model reactions. Values of ΔG°_f, ΔH°_f, S° and the revised HKF equations of state parameters for the species involved in reference model Reactions (a)–(d) above were taken from SUPCRT92 [93]. Those for the species in Reactions (e) and (f) were taken from LaRowe and Helgeson [120].

* It has been observed that the values of ΔG°_r, ΔH°_r, and ΔS°_r for the deprotonation reactions of mononucleotides containing different nucleic-acid bases have virtually the same values [120].

literature, and because Reaction (19) constitutes a dehydration reaction involving two phosphate groups bonded to two nucleosides, $\Delta\Xi^\circ_r$ in Eq. (20) was estimated in the present study by taking it to be equal in a first approximation to $\Delta\Xi^\circ_r$ for the analogous condensation of two phosphoric acids into diphosphoric acid given by

$$\mathrm{H_3PO_4 + H_3PO_4 \rightleftharpoons H_4P_2O_7 + H_2O} \tag{21}$$

which is consistent with

$$\Delta\Xi^\circ_r = \Xi^\circ_{\mathrm{H_4P_2O_7}} - 2\Xi^\circ_{\mathrm{H_3PO_4}} + \Xi^\circ_{\mathrm{H_2O}}. \tag{22}$$

The values of Ξ° for the indicated species used to calculate $\Delta\Xi^\circ_r$ in Eq. (22) were taken from SUPCRT92 [93]. The values of ΔG°_f, ΔH°_f, and S° at 25 °C and 1 bar for $\mathrm{HNAD^-_{red}}$ and $\mathrm{NAD^{2-}_{red}}$ were calculated using the equations and reference model reactions shown in Table 7, together with experimental data taken from the references cited in the footnotes to Table 7.

Values of the standard molal Gibbs energy and enthalpy and third law entropy for $\mathrm{NAD^-_{ox}}$ can be calculated from the corresponding properties of $\mathrm{NAD^{2-}_{red}}$ and experimental values of ΔG°_r, ΔH°_r, and ΔS°_r reported in the literature for the reduction of $\mathrm{NAD^-_{ox}}$ to $\mathrm{NAD^{2-}_{red}}$ by the oxidation of ethanol (C_2H_6O) to acetaldehyde (C_2H_4O), i.e.,

$$\mathrm{C_2H_6O + NAD^-_{ox} \rightleftharpoons C_2H_4O + NAD^{2-}_{red} + H^+}. \tag{23}$$

The requisite values of ΔG°_f, ΔH°_f, and S° for $\mathrm{NAD^-_{ox}}$ were computed from

$$\Xi^\circ_{\mathrm{NAD^-_{ox}}} = \Xi^\circ_{\mathrm{C_2H_6O}} + \Delta\Xi^\circ_r - \Xi^\circ_{\mathrm{C_2H_4O}} - \Xi^\circ_{\mathrm{NAD^{2-}_{red}}} \tag{24}$$

where Ξ° represents values of ΔG°_f, ΔH°_f, or S° of the subscripted species and $\Delta\Xi^\circ_r$ denotes the corresponding standard molal reaction property of Reaction (23) given by [94]. The values of ΔG°_f, ΔH°_f, and S° 25 °C and 1 bar for ethanol and acetaldehyde used to evaluate Eq. (24) were taken from [95] and [96], respectively. Values of ΔG°_f, ΔH°_f, and S° for $\mathrm{HNAD_{ox}}$ and $\mathrm{H_2NAD^+_{ox}}$ were calculated from the equations given in Table 7 using values of the standard molal properties of reaction for the reference model reactions shown in this table.

The values of $\Xi^\circ_{\mathrm{H_2NicMP_{red}}}$ required to evaluate Eq. (20) are not available in the literature. Despite this, values of ΔG°_f and ΔH°_f can be calculated from estimated values of ΔG°_f and ΔH°_f for crystalline $\mathrm{H_2NicMP_{red}}$ ($\Delta G^\circ_{f\,(cr)}$ and $\Delta H^\circ_{f(cr)}$) and the corresponding standard molal properties of solution ($\Delta G^\circ_{f\,(sol)}$ and $\Delta H^\circ_{f\,(sol)}$) using

$$\Delta G^\circ_f = \Delta G^\circ_{f\,(cr)} - \Delta G^\circ_{sol} \tag{25}$$

$$\Delta H^\circ_f = \Delta H^\circ_{f(cr)} - \Delta H^\circ_{sol}. \tag{26}$$

A value of S° for aqueous $\mathrm{H_2NicMP_{red}}$ at 25 ° C and 1 bar can then be computed by combined the resulting values of ΔG°_f, ΔH°_f, and $S^\circ$of the elements with Eq. (4). The values of $\Delta G^\circ_{f(cr)}$ and $\Delta H^\circ_{f(cr)}$ for $\mathrm{H_2NicMP_{red}}$ required to evaluate Eqs. (25) and (26) were estimated by equating them in a first approximation to the corresponding standard molal Gibbs energies and enthalpies of the reference model reaction given by

$$\mathrm{nicotinamide_{red(cr)} + R5P_{(cr)} \rightleftharpoons H_2O + H_2NicMP_{red\,(cr)}}, \tag{27}$$

for which

$$\Xi^{\circ}_{\mathrm{H_2NicMP_{red\,(cr)}}} = \Xi^{\circ}_{\mathrm{nicotinamide_{red\,(cr)}}} + \Xi^{\circ}_{\mathrm{R5P_{(cr)}}} - \Xi^{\circ}_{\mathrm{H_2O}} + \Delta\Xi^{\circ}_{\mathrm{r}}. \tag{28}$$

The subscripts nicotinamide$_{\mathrm{red\,(cr)}}$ and R5P$_{\mathrm{(cr)}}$ in Eq. (28) denote crystalline reduced nicotinamide and ribose-5-phosphate, respectively. The symbol $\Delta\Xi^{\circ}_{\mathrm{r}}$ in this equation stands for $\Delta G^{\circ}_{\mathrm{r}}$ or $\Delta H^{\circ}_{\mathrm{r}}$ of Reaction (27), which were taken to be equal to the corresponding values for the reference model reaction represented by

$$\mathrm{adenine_{(cr)}} + \mathrm{R5P_{(cr)}} \rightleftharpoons \mathrm{H_2AMP_{(cr)}} + \mathrm{H_2O}, \tag{29}$$

which is consistent with

$$\Delta\Xi^{\circ}_{\mathrm{r}} = \Xi^{\circ}_{\mathrm{H_2AMP_{(cr)}}} + \Xi^{\circ}_{\mathrm{H_2O}} - \Xi^{\circ}_{\mathrm{adenine_{(cr)}}} - \Xi^{\circ}_{\mathrm{R5P_{(cr)}}}. \tag{30}$$

The values of $\Delta G^{\circ}_{\mathrm{f}}$ and $\Delta H^{\circ}_{\mathrm{f}}$ for H$_2$AMP$_{\mathrm{(cr)}}$ were estimated using

$$\Xi^{\circ}_{\mathrm{H_2AMP_{(cr)}}} = 2\,\Xi^{\circ}_{\mathrm{adenosine_{(cr)}}} + \Xi^{\circ}_{\mathrm{H_3PO_4\,(cr)}} - \Xi^{\circ}_{\mathrm{adenine_{(cr)}}} - \Xi^{\circ}_{\mathrm{R5P_{(cr)}}}, \tag{31}$$

and those for R5P$_{\mathrm{(cr)}}$ were calculated from

$$\Xi^{\circ}_{\mathrm{R5P_{(cr)}}} = \Xi^{\circ}_{\mathrm{R5P_{(aq)}}} - \Delta\Xi^{\circ}_{\mathrm{sol}}. \tag{32}$$

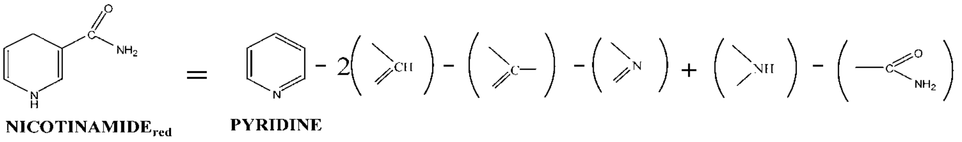
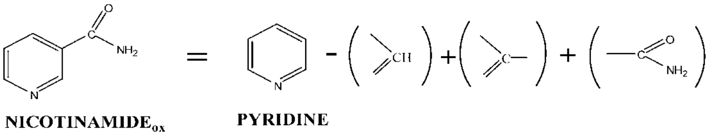
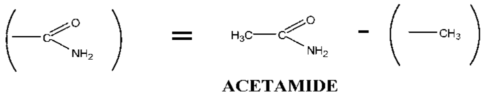
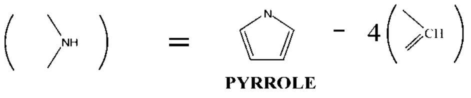
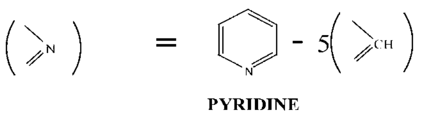
using values of $\Delta\Xi^{\circ}_{\mathrm{sol}}$ computed from

$$\Delta\Xi^{\circ}_{\mathrm{sol_{R5P}}} = \Xi^{\circ}_{\mathrm{sol\ adenosine}} + \Xi^{\circ}_{\mathrm{sol\ H_3PO_4}} - \Xi^{\circ}_{\mathrm{sol\ adenine}}. \tag{33}$$

The values for $\Delta G^{\circ}_{\mathrm{f}}$ and $\Delta H^{\circ}_{\mathrm{f}}$ used in these calculations for H$_3$PO$_{4\,\mathrm{(cr)}}$, adenosine$_{\mathrm{(cr)}}$, adenine$_{\mathrm{(cr)}}$, and the Gibbs energies and enthalpies of solution for these species were taken from LaRowe and Helgeson [120]. The calculated values of $\Delta G^{\circ}_{\mathrm{f}}$ and $\Delta H^{\circ}_{\mathrm{f}}$ for R5P$_{\mathrm{(aq)}}$ are given in Table 6. Values of $\Delta H^{\circ}_{\mathrm{f\,(cr)}}$ for nicotinamide$_{\mathrm{red}}$, are available in the literature, but values of $\Delta G^{\circ}_{\mathrm{f\,(cr)}}$ and $S^{\circ}_{\mathrm{(cr)}}$ are not. As a first approximation, the value of the standard molal third law entropy of reduced nicotinamide ($S^{\circ}_{\mathrm{Nic_{red\,(cr)}}}$) can be calculated using the group additivity algorithm depicted in Table 8. Combining this estimate with a value of $\Delta H^{\circ}_{\mathrm{f\,(cr)}}$ for crystalline nicotinamide$_{\mathrm{red}}$ given in Table 9, a provisional value of $\Delta G^{\circ}_{\mathrm{f\,(cr)}}$ can be computed using a rearranged version of Eq. (4) and values of S° of the elements taken from [87]. The C°_{p} power function coefficients for the reference model compounds acetamide and pyridine given in Table 9 were determined by regressing experimental values of C°_{p} for these compounds with Eq. (A.4). These regressions are shown in Fig. 2.

Table 8

Summary of group additivity algorithms used to calculate the standard molal heat capacity (C°_{p}) power function coefficients in Eq. (A.4) and the indicated standard molal thermodynamic properties at 25 °C and 1 bar for selected crystalline compounds and groups

	$\Delta H^{\circ}_{\mathrm{f}}$, S°, a, b, c
	S°, a, b, c
	$\Delta H^{\circ}_{\mathrm{f}}$, S°, a, b, c
	V°
	$\Delta H^{\circ}_{\mathrm{f}}$, S°, a, b, c

Values for the properties and parameters of the groups used in these algorithms are given in Table 10, and those for the reference model compounds are given in Table 9.

Table 9
Summary of standard molal heat capacity (C_p°) power function coefficients for Eq. (A.4) and the standard molal thermodynamic properties at 25 °C and 1 bar of selected crystalline and liquid reference model compounds

Compound	Formula	$\Delta G_f^{\circ a,b}$	$\Delta H_f^{\circ a}$	$S^{\circ c}$	$C_p^{\circ c}$	$V^{\circ d}$	a^c	$b\,(\times 10^3)^e$	$c\,(\times 10^{-5})^f$
Acetamide$_{(cr)}$	C_2H_5NO	−188540	−314220[g]	115.0[h]	89.24	50.96[i]	3.940[j]	275.4[j]	2.821[j]
Pyridine$_{(cr)}$	C_5H_5N	184060	90140[k]	136.2[l]	115.80	64.4[m]	4.561[j]	373.2[j]	0[j]
Pyridine$_{(lq)}$	C_5H_5N	181460	99960[n]	177.9[o]	132.7[o]	80.86[p]	42.84[o]	269.2[o]	8.544[o]
Piperidine$_{(cr)}$	$C_5H_{10}N$	103660	−103970[k]	146.9[o]	137.4[o]	80.71[q]	−55.23[o]	612.1[o]	9.000[o]
Piperidine$_{(lq)}$	$C_5H_{10}N$	101550	−87280[r]	210.0[o]	179.7[o]	99.40[s]	10.13[o]	413.7[o]	41.13[o]
Pyrrole	C_4H_5N					53.9[p]			
H_2AMP[t]	$C_{10}H_{14}N_5O_7P$	−1090410	−1641130	363.1	356.5	214.51	15.94	1132	2.699
H_2CMP[t]	$C_9H_1 4N_3O_8P$	−1451350	−1959330	411.7	347.2	198.14	78.32	933.5	−8.389
Ribose-5-phosphate[t]	$C_5H_{11}O_8P$	−1615410	−2032250	211.0	253.3	135.4	−1.079	835.5	4.648
Nicotinamide$_{red}$	$C_6H_8N_2O$	9740	−202880[u]	138.2[v]	131.0[v]	105.26[v]	−121.2[v]	754.0[v]	24.33[v]
Nicotinamide$_{ox}$	$C_6H_6N_2O$	21760	−142470[w]	169.9[v]	125.3[v]	96.97[v]	−84.35[v]	603.8[v]	26.38[v]
H_2NicMP$_{red}$[t]	$C_{11}H_{17}N_2O_8P$	−1367390	−1938340	312.1	344.4		−106.8	1411	27.03

[a] J mol^{-1}.
[b] Calculated from the values given for ΔH_f° and S° using Eq. (4) and values of S° of the elements taken from [87].
[c] J K^{-1} mol^{-1}.
[d] cm^3 mol^{-1}.
[e] J K^{-2} mol^{-1}.
[f] J K mol^{-1}.
[g] Average of values given by [101,102], and [103].
[h] [101].
[i] Calculated from density data given in [104].
[j] Calculated by regressing experimental C_p° data from [104] (acetamide) and [105] (pyridine) with Eq. (A.4).
[k] Metastable crystal value calculated using values of ΔH_f° for the liquid together with those for ΔH_{melt} and C_p° of liquid and crystalline phases.
[l] [105].
[m] Calculated from the group additivity algorithm represented by (pyridine) = (($\geq$ N) + 5 ($\geq$ C)) using the values of V° for the groups given by [106]. The symbols $\geq$ N and $\geq$ C denote aromatic nitrogen and carbon atoms, respectively.
[n] Calculated using the average of values given by [107] and [108].
[o] LaRowe and Helgeson [120].
[p] Calculated from a value for density given by [109].
[q] Calculated from the group additivity algorithm represented by (pyridine) = (>NH) + 5 (>CH$_2$). The value of V° for (>NH) was calculated as shown in the algorithm in Table 8, and that for (>CH$_2$) is taken from [100]. The symbols (>NH) and (>CH$_2$) denote saturated cyclic nitrogen and carbon atoms, respectively.
[r] Average of values given by [110] and [111].
[s] Calculated using density data given by [110].
[t] See text for discussion of these species.
[u] Average of values given by [112] and [113].
[v] Calculated using the algorithms depicted in Table 8 together with the groups shown in Table 10.
[w] Average of literature values given by [112] and [113].

The values of $\Delta G^\circ_{f\,(sol)}$ and $\Delta H^\circ_{f\,(sol)}$ used to evaluate Eqs. (25) and (26) for H_2NicMP$_{red}$ were taken in a first approximation to be the same as that for H_2CMP, which is a similar nucleotide. The latter values were calculated from

$$\Xi^\circ_{sol_{H_2CMP}} = 2\Xi^\circ_{sol_{cytidine}} + \Xi^\circ_{sol_{H_3PO_4}} - \Xi^\circ_{sol_{cytosine}} - \Xi^\circ_{sol_{ribose}} \tag{34}$$

which takes into account the solubilities of each bonded molecular constituent of H_2CMP. The values of Ξ°_{sol} at 25 °C and 1 bar for cytidine, H_3PO_4, cytosine, and ribose used in the calculations were taken from LaRowe and Helgeson [120].

Values of ΔG_f°, ΔH_f°, and S° for HNicMP$^-_{red}$ and NicMP$^{2-}_{red}$ were calculated from equations given in Table 7. The calculated values of ΔG_f°, ΔH_f°, and S° for the aqueous nicotinamide mononucleotides are given in Table 6.

4.2. *Equations of state parameters*

Experimental values of C_p°, V°, and κ_T° are not available in the literature for any of the nicotinamide adenine nucleotides. Nevertheless, provisional estimates of the revised HKF equations of state parameters for these species can be calculated from those of their constituent molecules using reference model reactions.

The values of the equations of state parameters corresponding to ω, c_1, c_2, a_1, a_2, a_3, and a_4 for H_2NAD$_{red}$ given in Table 11 were calculated from a version of Eq. (20) in which the subscripted symbol Ξ° stands for values of the equations of state parameters and $\Delta\,\Xi_r^\circ$ refers to the parameters for Reaction (21).

The values of ω, c_1, c_2, a_1, a_2, a_3, and a_4 for H_2NAD$^+_{ox}$ were calculated from the oxidized analog of Eq. (20), which can be written as

$$\Xi^\circ_{H_2NAD^+_{ox}} = \Xi^\circ_{H_2NicMP^+_{ox}} + \Xi^\circ_{H_2AMP} + \Delta\,\Xi_r^\circ - \Xi^\circ_{H_2O} \tag{35}$$

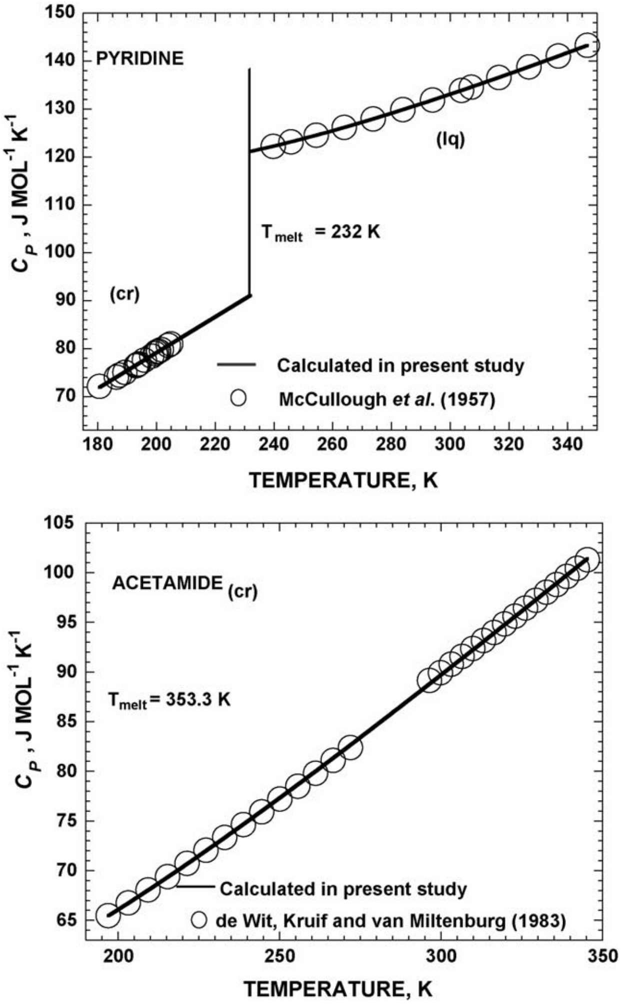


Fig. 2. Standard molal heat capacities (C_p°) of crystalline acetamide and crystalline and liquid pyridine as a function of temperature at 1 bar. The symbols denote experimental values of C_p°. The regression lines represent fits of the standard molal heat capacity power function (Eq. (A.4)) to the data.

where $\Delta\Xi_r^\circ$ was taken in a first approximation to be equivalent to that in Eq. (22). The corresponding equations of state parameters for $\mathrm{HNAD}_{\mathrm{red}}^{-}$, $\mathrm{NAD}_{\mathrm{red}}^{2-}$, $\mathrm{HNAD}_{\mathrm{ox}}$, and $\mathrm{NAD}_{\mathrm{ox}}^{-}$ were calculated from equations listed in Table 7 using values of $\Delta\Xi_r^\circ$ for the reference model reactions shown in this table.

The values of the equations of state parameters for the reduced and oxidized aqueous nicotinamide nucleotides ($\mathrm{Nic}_{\mathrm{red}}$ and $\mathrm{Nic}_{\mathrm{ox}}$) required to evaluate the algorithms discussed above were estimated from those of cytidine monophosphate (CMP) and other reference model compounds for which experimentally derived equations of state parameters are available [120]. The values of ω and c_2 for aqueous $\mathrm{H_2NicMP_{red}}$, $\mathrm{HNicMP}_{\mathrm{red}}^{-}$, and $\mathrm{NicMP}_{\mathrm{red}}^{2-}$ were taken to be equal in a first approximation to those for aqueous $\mathrm{H_2CMP}$, HCMP^{-}, and CMP^{2-}, respectively. The values of c_1 for $\mathrm{H_2NicMP_{red}}$, $\mathrm{HNicMP}_{\mathrm{red}}^{-}$, and $\mathrm{NicMP}_{\mathrm{red}}^{2-}$ were computed using those of ω and c_2, together with rearranged versions of Eqs. (5) and (6). The values of C_p° at 25 °C and 1 bar required to calculate values of c_1 for these species were generated by estimating their standard molal isobaric heat capacities of solution from

$$C^\circ_{p\,\mathrm{H_2NicMP_{red}}} = C^\circ_{p\,\mathrm{H_2NicMP_{(cr)}}} + \Delta C^\circ_{p\,\mathrm{sol}} \tag{36}$$

$$C^\circ_{p\,\mathrm{HNicMP}^-_{\mathrm{red}}} = C^\circ_{p\,\mathrm{H_2NicMP_{red}}} + \Delta C^\circ_{p,\mathrm{r}} \tag{37}$$

and

$$C^\circ_{p\,\mathrm{NicMP}^{2-}_{\mathrm{red}}} = C^\circ_{p\,\mathrm{HNicMP}^-_{\mathrm{red}}} + \Delta C^\circ_{p,\mathrm{r}}. \tag{38}$$

The requisite values of $\Delta C^\circ_{p,\mathrm{sol}}$ and $\Delta C^\circ_{p,\mathrm{r}}$ in these equations were taken in a first approximation to be equal to those of the reference model reactions represented by

$$\mathrm{H_2CMP_{(cr)}} \rightleftharpoons \mathrm{H_2CMP_{(aq)}} \tag{39}$$

$$\mathrm{H_2CMP} \rightleftharpoons \mathrm{HCMP^-} + \mathrm{H^+} \tag{40}$$

and

$$\mathrm{HCMP^-} \rightleftharpoons \mathrm{CMP^{2-}} + \mathrm{H^+}, \tag{41}$$

respectively, which were computed from

$$\Delta C^{\circ}_{\mathrm{p,sol}} = C^{\circ}_{\mathrm{p,H_2CMP_{(aq)}}} - C^{\circ}_{\mathrm{p,H_2}\mathit{CMP}_{\mathrm{(cr)}}}, \tag{42}$$

$$\Delta C^{\circ}_{\mathrm{p,r}} = C^{\circ}_{\mathrm{p,HCMP^-}} - C^{\circ}_{\mathrm{p,H_2CMP_{(aq)}}}, \tag{43}$$

and

$$\Delta C^{\circ}_{\mathrm{p,r}} = C^{\circ}_{\mathrm{p,CMP^{2-}}} - C^{\circ}_{\mathrm{p,HCMP^-}}. \tag{44}$$

The values of C°_{p} for the aqueous cytidine nucleotides were taken from LaRowe and Helgeson [120] and that of $C^{\circ}_{\mathrm{p\,(cr)}}$ for $\mathrm{H_2NicMP_{red\,(cr)}}$ was calculated from Eq. (28). The value of $\Delta C^{\circ}_{\mathrm{p\,sol}}$ at 25 °C and 1 bar for $\mathrm{H_2CMP}$ was computed by combining the value of $C^{\circ}_{\mathrm{p\,(aq)}}$ for $\mathrm{H_2CMP}$ given in Ref. [120] with

$$\Delta C^{\circ}_{\mathrm{p\,sol}} = C^{\circ}_{\mathrm{p\,aq}} - C^{\circ}_{\mathrm{p\,cr}} \tag{45}$$

and that of $C^{\circ}_{\mathrm{p\,(cr)}}$ calculated from

$$C^{\circ}_{\mathrm{p\,H_2CMP_{(cr)}}} = C^{\circ}_{\mathrm{p\,cytidine_{(cr)}}} + C^{\circ}_{\mathrm{p\,H_3PO_4\,(cr)}} - C^{\circ}_{\mathrm{p\,H_2O}} + \Delta C^{\circ}_{\mathrm{p,r}}. \tag{46}$$

The values of $C^{\circ}_{\mathrm{p\,(cr)}}$ used in these calculations for the subscripted species on the right side of Eq. (46) correspond to those given by LaRowe and Helgeson [120], and the value of $\Delta C^{\circ}_{\mathrm{p,r}}$ For Reaction (46) was taken to be equal in a first approximation to that for Reaction (29).

The values of c_1, c_2, and ω for the oxidized nicotinamide nucleotides can be computed using the corresponding values for $\mathrm{H_2NicMP_{red}}$ and a reference model group additivity algorithm that takes explicit account of the difference in the oxidation state of the reduced and oxidized nicotinamide bases in $\mathrm{H_2NicMP_{red}}$ and $\mathrm{H_2NicMP^+_{ox}}$. This difference in redox state was taken in a first approximation to equal to that per carbon between cyclohexane and benzene. Accordingly, values of c_1, c_2, and ω for $\mathrm{H_2NicMP^+_{ox}}$ were calculated from

$$\Xi^{\circ}_{\mathrm{H_2NicMP^+_{ox}}} = \Xi^{\circ}_{\mathrm{H_2NicMP_{red}}} - \tfrac{1}{6}\,\Xi^{\circ}_{\mathrm{cyclohexane}} + \tfrac{1}{6}\,\Xi^{\circ}_{\mathrm{benzene}} \tag{47}$$

where Ξ° stands for values for the equations of state parameters of the indicated species. Values of the revised-HKF parameters for aqueous cyclohexane and benzene were taken from [97] and [89], respectively. The values of c_1, c_2, and ω for $\mathrm{HNicMP_{ox}}$ and $\mathrm{NicMP^-_{ox}}$ given in Table 6 were then computed using the procedure described above for $\mathrm{HNicMP^-_{red}}$ and $\mathrm{NicMP^{2-}_{red}}$ and the equations and reference model reactions for these species listed in Table 7.

The a_1, a_2, a_3, and a_4 equations of state parameters for the nicotinamide mononucleotides were calculated using Eqs. (8)–(14). The values of V° at 25 °C and 1 bar required to evaluate these equations for each of the nicotinamide mononucleotides species were computed from estimated values of their respective standard molal crystalline volumes (V°_{cr}) using volumes of solution ($\Delta V^{\circ}_{\mathrm{sol}}$) and the relation,

$$V^{\circ} = V^{\circ}_{\mathrm{cr}} + \Delta V^{\circ}_{\mathrm{sol}}. \tag{48}$$

The values of V°_{cr} and $\Delta V^{\circ}_{\mathrm{sol}}$ in Eq. (48) for the nicotinamide mononucleotides were computed from the corresponding values for their constituent molecules and reference model compounds. For example, the value of V° for aqueous $\mathrm{H_2NicMP_{red}}$($V^{\circ}_{\mathrm{H_2NicMP_{red}}}$) was calculated from

$$V^{\circ}_{\mathrm{H_2NicMP^{\circ}_{red}}} = V^{\circ}_{\mathrm{H_2NicMP_{red(cr)}}} + \Delta V^{\circ}_{\mathrm{sol}}. \tag{49}$$

The requisite value of $\Delta V^{\circ}_{\mathrm{sol}}$ in this equation was taken to be equal in a first approximation to that of $\Delta V^{\circ}_{\mathrm{sol}}$ for $\mathrm{H_2CMP}$, which was calculated from values of $\Delta V^{\circ}_{\mathrm{sol}}$ for its constituent molecules. A provisional value of $\Delta V^{\circ}_{\mathrm{sol}}$ for $\mathrm{H_2CMP}$ can be estimated from

$$\Delta V^{\circ}_{\mathrm{sol\,H_2CMP}} = 2\Delta V^{\circ}_{\mathrm{sol\,cytidine}} + \Delta V^{\circ}_{\mathrm{sol\,H_3PO_4}} - \Delta V^{\circ}_{\mathrm{sol\,cytosine}} - \Delta V^{\circ}_{\mathrm{sol\,ribose}}. \tag{50}$$

Similarly, the standard molal volume of $\mathrm{H_2NicMP_{red\,(cr)}}$ ($V^{\circ}_{\mathrm{H_2NicMP_{red\,(cr)}}}$) at 25 °C and 1 bar in Eq. (49) was calculated from

$$V^{\circ}_{\mathrm{H_2NicMP_{red\,(cr)}}} = V^{\circ}_{\mathrm{Nic_{red\,(cr)}}} - 2\Delta V^{\circ}_{\mathrm{adenine_{(cr)}}} + 2V^{\circ}_{\mathrm{adenosine_{(cr)}}} + V^{\circ}_{\mathrm{H_3PO_4\,(cr)}} - V^{\circ}_{\mathrm{ribose_{(cr)}}} \tag{51}$$

using the value of V° for $\mathrm{Nic_{red\,(cr)}}$ computed from the group additivity algorithm for this species shown in Table 8. Values of a_1, a_2, a_3, and a_4 for $\mathrm{HNicMP^-_{red}}$ and $\mathrm{NicMP^{2-}_{red}}$ were calculated from the equations for these species listed in Table 7, but those of $\Delta\Xi^{\circ}_{\mathrm{r}}$

in these equations were generated in a first approximation from the corresponding parameters for the species in Reactions (40) and (41), together with

$$\Delta\Xi_r^\circ = \Xi_{HCMP^-}^\circ + \Xi_{H^+}^\circ - \Xi_{H_2CMP}^\circ \tag{52}$$

and

$$\Delta\Xi_r^\circ = \Xi_{CMP^{2-}}^\circ + \Xi_{H^+}^\circ - \Xi_{HCMP^-}^\circ, \tag{53}$$

respectively. The symbol Ξ° in these equations stands for the values of a_1, a_2, a_3, or a_4 for the indicated species, and $\Delta\Xi_r^\circ$ in Eqs. (52) and (53) refers to the corresponding parameters for Reactions (43) and (44), respectively. Values of these parameters for the cytidine nucleotides are given by LaRowe and Helgeson [120]. However, those for H_2NicMP_{ox} were calculated by first evaluating

$$V_{H_2NicMP_{ox}}^\circ = V_{H_2NicMP_{ox\,(cr)}}^\circ + \Delta V_{sol}^\circ. \tag{54}$$

The value of ΔV_{sol}° in this equation was taken to be equal in a first approximation to that calculated from Eq. (50). The a_1, a_2, a_3, and a_4 parameters for $HNicMP_{ox}$ and $NicMP_{ox}^-$ were computed from the equations for these species listed in Table 7 using values of $\Delta\Xi_r^\circ$ generated from Eqs. (52) and (53) (Table 10).

5. Standard molal thermodynamic properties at 25 °C and 1 bar and equations of state parameters for nicotinamide adenine dinucleotide phosphates (NADPs)

The reduced and oxidized nicotinamide adenosine dinucleotide phosphates, which are generically referred to by the acronyms $NADP_{red}$ and $NADP_{ox}$, respectively, are structurally identical to NAD_{red} and NAD_{ox} except that the OH groups located on the 2′ carbon in the ribose ring that is bonded to the adenine base is replaced with a phosphate group (see Table 5 for the idealized chemical structure). The $NADP_{red}$ and $NADP_{ox}$ species considered in the present communication include the variously charged reduced and oxidized species referred to as $H_nNADP_{red}^{(n-4)}$ and $H_nNADP_{ox}^{(n-3)}$ for values of $n = 0, 1, 2, 3$, or 4, which represents the number of protons bonded to the phosphate oxygens in the respective base species, $NADP_{red}^{4-}$ and $NADP_{ox}^{3-}$. Because few experimental data are available for these various species, provisional values of ΔG_f°, ΔH_f°, S°, and the equations of state parameters for the NADPs were determined by combining the corresponding properties and parameters for the molecules that comprise these species with reference model reaction properties and parameters. The standard molal thermodynamic properties and revised HKF equations of state parameters for the reduced NADP species given in Table 11 were estimated using

$$\Xi_{H_4NADP_{red}}^\circ = \Xi_{H_2NAD_{red}}^\circ + \Xi_{H_3PO_4}^\circ + \Delta\Xi_r^\circ - \Xi_{H_2O}^\circ \tag{55}$$

$$\Xi_{H_3NADP_{red}^-}^\circ = \Xi_{HNAD_{red}^-}^\circ + \Xi_{H_3PO_4}^\circ + \Delta\Xi_r^\circ - \Xi_{H_2O}^\circ \tag{56}$$

$$\Xi_{H_2NADP_{red}^{2-}}^\circ = \Xi_{NAD_{red}^{2-}}^\circ + \Xi_{H_3PO_4}^\circ + \Delta\Xi_r^\circ - \Xi_{H_2O}^\circ \tag{57}$$

$$\Xi_{HNADP_{red}^{3-}}^\circ = \Xi_{H_2NADP_{red}^{2-}}^\circ + \Delta\Xi_r^\circ \tag{58}$$

and

$$\Xi_{NADP_{red}^{4-}}^\circ = \Xi_{HNADP_{red}^{3-}}^\circ + \Delta\Xi_r^\circ \tag{59}$$

where

$$\Delta\Xi_r^\circ = \Xi_{H_2R5P}^\circ + \Xi_{H_2O}^\circ - \Xi_{H_3PO_4}^\circ - \Xi_{ribose}^\circ. \tag{60}$$

The values of $\Delta\Xi_r^\circ$ in Eq. (60) were taken in a first approximation to be equivalent to those of $\Delta\Xi_r^\circ$ in Eqs. (55)–(57). Similarly,

$$\Delta\Xi_r^\circ = \Xi_{H_2PO_4^-}^\circ - \Xi_{H_3PO_4}^\circ \tag{61}$$

and

$$\Delta\Xi_r^\circ = \Xi_{HPO_4^{2-}}^\circ - \Xi_{H_2PO_4^-}^\circ \tag{62}$$

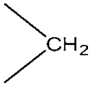
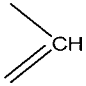
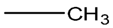
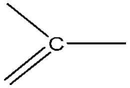
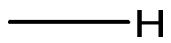
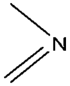
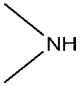
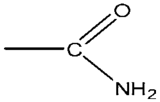
were used to calculate values of $\Delta\Xi_r^\circ$ for Eqs. (58) and (59), respectively. The symbols Ξ° and $\Delta\Xi_r^\circ$ in Eqs. (55)–(62) stand for values of the standard molal Gibbs energies and enthalpies of formation, standard molal entropies, and the solvation and non-solvation revised HKF equations of state parameters for the subscripted species, which are given in Tables 6 and 11.

The standard molal Gibbs energies and enthalpies of formation and third law entropies of the completely deprotonated oxidized NADP species ($NADP_{ox}^{3-}$) were calculated from those of $NADP_{red}^{4-}$, 2-propanol (C_3H_8O), acetone (C_3H_6O), and the corresponding reaction properties for

$$C_3H_8O + NADP_{ox}^{3-} \rightleftharpoons C_3H_6O + NADP_{red}^{4-} + H^+. \tag{63}$$

Table 10

Summary of standard molal heat capacity (C_p°) power function coefficients for Eq. (A.4) and the standard molal thermodynamic properties at 25 °C and 1 bar of crystalline groups used to calculate the corresponding properties and parameters for the compounds and groups shown in Table 8

Group	ΔG_f° [a,b]	ΔH_f° [a]	S° [c]	C_p° [c]	V° [d]	a [c]	$b\,(\times 10^3)$ [e]	$c\,(\times 10^{-5})$ [f]
 [g]	4535	−26510	32.3	23.8	14.6	−7.3	93.7	2.8
 [g]	21630	6908	21.7	19.8	10.5	−1.5	71.5	0
 [h]	−4740	−48310	55.6	60.17	16.6	70.25	32	−17.4
 [g]	18600	15700	−4.0	0.24	12.9	−24.1	59	6.15
					5.54[i]			
					4.16[i]			
 [j]	75930	55600	28	16.9	11.9[i]	12.3	15.4	0
 [j]	81010	28600[k]	−14.7[l]	18.5[l]	7.71[j]	−19[l]	144[l]	−4.81[l]
	−183790	−265900	59.40	29.1	34.36	−66.32	243.6	20.23

[a] $\mathrm{J\,mol^{-1}}$.

[b] Calculated from the values given for ΔH_f° and S° using Eq. (4), together with values of S° taken from [87].

[c] $\mathrm{J\,K^{-1}\,mol^{-1}}$.

[d] $\mathrm{cm^3\,mol^{-1}}$.

[e] $\mathrm{J\,K^{-2}\,mol^{-1}}$.

[f] $\mathrm{J\,K\,mol^{-1}}$.

[g] [100].

[h] Average of values for ($-CH_{3\,\mathrm{even}}$) and ($-CH_{3\,\mathrm{odd}}$) given by [100].

[i] [106].

[j] Calculated from algorithm 4 in Table 8.

[k] Calculated from the group additivity algorithm represented by (>NH) = piperidine − 5(>CH_2). The value of ΔH_f° used in this algorithm was taken from Table 9, and that for (>CH_2) from [100].

[l] [120].

Table 11

Summary of the revised HKF equations of state parameters and standard molal thermodynamic properties at 25 °*C* and 1 bar for selected aqueous reduced (red) and oxidized (ox) nicotinamide adenosine dinucleotide phosphates

Compound	Formula	ΔG_f° [a]	ΔH_f° [a]	S° [b]	C_p° [b,c]	V° [c,d]	a_1 (×10) [e]	a_2 (×10^{-2}) [a]	a_3 [f]	a_4 (×10^{-4}) [g]	c_1 [b]	c_2 (×10^{-4}) [g]	ω (×10^{-5}) [a]
NAD-phosphates													
H_4NADP_{red}	$C_{21}H_{30}N_7O_{17}P_3$	−3100490	−4270300	694.5	1009	378.35	−100.226	1357.804	−101.694	−31.055	1291.8	−54.94	18
$H_3NADP_{red}^{-}$	$C_{21}H_{29}N_7O_{17}P_3^{-}$	−3091700	−4278250	638.5	919.0	372.96	−100.930	1356.098	−101.054	−30.985	1296.6	−73.18	24
$H_2NADP_{red}^{2-}$	$C_{21}H_{28}N_7O_{17}P_3^{2-}$	−3078310	−4280340	586.6	836.2	367.72	−101.068	1355.754	−100.903	−30.970	1316.1	−90.04	32
$HNADP_{red}^{3-}$	$C_{21}H_{27}N_7O_{17}P_3^{3-}$	−3065930	−4288290	518.4	708.8	350.51	−108.537	1337.516	−93.735	−30.216	1299.6	−116.1	38
$NADP_{red}^{4-}$	$C_{21}H_{26}N_7O_{17}P_3^{4-}$	−3024800	−4284090	394.6	495.0	323.81	−120.487	1308.338	−82.2666	−29.010	1252.3	−159.8	47
$H_4NADP_{ox}^{+}$	$C_{21}H_{29}N_7O_{17}P_3^{+}$	−3128310	−4235750	773.2	982.9	378.46	−100.224	1358.106	−101.702	−31.068	1284.9	−66.94	18
H_3NADP_{ox}	$C_{21}H_{28}N_7O_{17}P_3$	−3119530	−4243700	717.1	893.4	373.07	−100.929	1356.401	−101.063	−30.997	1289.7	−85.19	24
$H_2NADP_{ox}^{-}$	$C_{21}H_{27}N_7O_{17}P_3^{-}$	−3106140	−4245790	665.2	810.6	367.83	−101.066	1356.056	−100.911	−30.983	1309.1	−102.0	32
$HNADP_{ox}^{2-}$	$C_{21}H_{26}N_7O_{17}P_3^{2-}$	−3093750	−4253740	597.1	683.2	350.62	−108.535	1337.819	−93.7434	−30.229	1292.7	−128.2	38
$NADP_{ox}^{3-}$	$C_{21}H_{25}N_7O_{17}P_3^{3-}$	−3052630	−4249530	473.2	469.4	323.92	−120.485	1308.641	−82.275	−29.023	1246.7	−171.8	47

[a] $J\,mol^{-1}$.

[b] $J\,K^{-1}\,mol^{-1}$.

[c] $cm^3\,mol^{-1}$.

[d] Calculated from the revised HKF equations of state parameters generated in the present study.

[e] $J\,mol^{-1}\,bar^{-1}$.

[f] $J\,K\,mol^{-1}\,bar^{-1}$.

[g] $J\,K\,mol^{-1}$.

Table 12

Summary of the reactions (left column) and corresponding equations (right column) used to calculate values of ΔG_f°, ΔH_f° and S° for selected oxidized NADP species

Reactions from which the equations used to calculate ΔG_f°, ΔH_f°, and S° for the indicated species were derived		Equations used to calculate values of ΔG_f°, ΔH_f°, and S° for the indicated species
$NADP_{ox}^{3-} + H^+ \rightleftharpoons HNADP_{ox}^{2-}$	(A)	$\Xi^\circ_{HNADP_{ox}^{2-}} = \Xi^\circ_{NADP_{ox}^{3-}} + \Delta\Xi^\circ_{r\,1A}$
$HNADP_{ox}^{2-} + H^+ \rightleftharpoons H_2NADP_{ox}^{-}$	(B)	$\Xi^\circ_{H_2NADP_{ox}^{-}} = \Xi^\circ_{HNADP_{ox}^{2-}} + \Delta\Xi^\circ_{r\,2A}$
$H_2NADP_{ox}^{-} + H^+ \rightleftharpoons H_3NADP_{ox}$	(C)	$\Xi^\circ_{H_3NADP_{ox}} = \Xi^\circ_{H_2NADP_{ox}^{-}} + \Delta\Xi^\circ_{r\,3A}$
$H_3NADP_{ox} + H^+ \rightleftharpoons H_3NADP_{ox}^{+}$	(D)	$\Xi^\circ_{H_4NADP_{ox}^{+}} = \Xi^\circ_{H_3NADP_{ox}} + \Delta\Xi^\circ_{r\,4A}$
Reference model reactions from which values of $\Delta\Xi_r^\circ$ were calculated		Equations used to calculate $\Delta\Xi_r^\circ$
$H_2P_2O_7^{2-} + H^+ \rightleftharpoons H_3P_2O_7^{-}$	(E)	$\Delta\Xi^\circ_{r\,1B} = \Xi^\circ_{H_3P_2O_7^{-}} - \Xi^\circ_{H_2P_2O_7^{2-}}$
$H_3P_2O_7^{-} + H^+ \rightleftharpoons H_4P_2O_7^{\circ}$	(F)	$\Delta\Xi^\circ_{r\,2B} = \Xi^\circ_{H_4P_2O_7^{\circ}} - \Xi^\circ_{H_3P_2O_7^{-}}$
$HPO_4^{2-} + H^+ \rightleftharpoons H_2PO_4^{-}$	(G)	$\Delta\Xi^\circ_{r\,3B} = \Xi^\circ_{H_2PO_4^{-}} - \Xi^\circ_{HPO_4^{2-}}$
$H_2PO_4^{-} + H^+ \rightleftharpoons H_3PO_4^{\circ}$	(H)	$\Delta\Xi^\circ_{r\,4B} = \Xi^\circ_{H_3PO_4^{\circ}} - \Xi^\circ_{H_2PO_4^{-}}$

The symbol Ξ° represents ΔG_f°, ΔH_f° and S° for the subscripted species, and $\Delta\Xi_r^\circ$ stands for ΔG_r°, ΔH_r°, and ΔS_r° for the reaction of interest. Values of ΔG_f°, ΔH_f° and S° for the mono- and diphosphate species used in the reference model reaction are taken from SUPCRT92 [93]. The values of $\Delta\Xi_r^\circ$ for Reactions (E)–(H) were taken in a first approximation to be equal to those of Reactions (A)–(D).

Values of ΔG_f°, ΔH_f° and S° for $NADP_{ox}^{3-}$ in this reaction can be calculated from

$$\Xi^\circ_{NADP_{ox}^{3-}} = \Xi^\circ_{NADP_{red}^{4-}} + \Xi^\circ_{C_3H_6O} - \Xi^\circ_{C_3H_8O} + \Delta\Xi_r^\circ, \tag{64}$$

where Ξ° refers to ΔG_f°, ΔH_f°, or S° of the indicated species, and $\Delta\Xi_r^\circ$ stands for the corresponding properties of reaction taken from [98]. The standard molal thermodynamic properties of aqueous acetone and 2-propanol were taken from [95] and [97], respectively, and those for $NADP_{red}^{4-}$ are given in Table 6. The standard molal Gibbs energies, enthalpies, and third law entropies for the other $NADP_{ox}$ species were calculated using the equations and reference model reactions shown in Table 12.

The revised HKF equations of state parameters for $H_4NADP_{ox}^{+}$, H_3NADP_{ox}, $H_2NADP_{ox}^{-}$, $HNADP_{ox}^{2-}$, and $NADP_{ox}^{3-}$ were computed from

$$\Xi^\circ_{H_4NADP_{ox}^{+}} = \Xi^\circ_{H_2NAD_{ox}^{+}} + \Xi^\circ_{H_3PO_4} + \Delta\Xi_r^\circ - \Xi^\circ_{H_2O}, \tag{65}$$

$$\Xi^\circ_{H_3NADP_{ox}} = \Xi^\circ_{HNAD_{ox}} + \Xi^\circ_{H_3PO_4} + \Delta\Xi_r^\circ - \Xi^\circ_{H_2O}, \tag{66}$$

$$\Xi^\circ_{H_2NADP_{ox}^{-}} = \Xi^\circ_{NAD_{ox}^{-}} + \Xi^\circ_{H_3PO_4} + \Delta\Xi_r^\circ - \Xi^\circ_{H_2O}, \tag{67}$$

$$\Xi^\circ_{HNADP_{ox}^{2-}} = \Xi^\circ_{H_2NADP_{ox}^{-}} + \Delta\Xi_r^\circ, \tag{68}$$

and

$$\Xi^\circ_{NADP_{ox}^{3-}} = \Xi^\circ_{HNADP_{ox}^{2-}} + \Delta\Xi_r^\circ. \tag{69}$$

The values of $\Delta\Xi_r^\circ$ for Eqs. (65)–(67) were taken to be equal in a first approximation to those calculated from Eq. (64). Similarly, the values of $\Delta\Xi_r^\circ$ in Eqs. (68) and (69) were provisionally considered to be equivalent to those for reference model Reactions (C), (D), (G) and (H), respectively, in Table 12.

6. Uncertainties

Because so few relevant experimental data are available in the literature, it is difficult to assess the uncertainties associated with the values of the standard molal thermodynamic properties and revised HKF equations of state parameters generated in the present study for aqueous Mg-adenosine and nicotinamide adenine nucleotides. However, in a first approximation uncertainties associated with ΔG_f°, ΔH_f°, S°, C_p° and V° at 25 °C and 1 bar and the ω, a_1, a_2, a_3, a_4, c_1, and c_2 parameters of the species considered above can be estimated by propagating the uncertainties associated with the experimental data used to calculate values of these properties and parameters.

6.1. Mg-adenosine nucleotides

6.1.1. ΔG_f°, ΔH_f°, S°, C_p° and V° at 25 °C and 1 bar

The uncertainties associated with the values of ΔG_f°, ΔH_f°, and S° adopted in the present study for aqueous Mg-adenosine nucleotides at 25 °C and 1 bar can be assessed by combining the uncertainties associated with those of the adenosine nucleotides taken from LaRowe and Helgeson [120] and the experimentally determined values of ΔG_r°, ΔH_r°, and ΔS_r° for these species given in Table 3. Uncertainties assessed in this manner for the values of ΔG_f° and ΔH_f° for Mg-adenosine nucleotides are ±2900 J mol^{-1} and those associated with the values of S° are ±12 J mol^{-1} K^{-1}. Due to the dearth of calorimetric data in the literature, similar calculations could not be carried out for the values of C_p° and V° of the Mg-adenosine nucleotides at 25 °C and 1 bar.

6.1.2. Revised HKF equations of state parameters

Uncertainties associated with the revised HKF equations of state non-solvation parameters can be estimated by taking into account the extent to which the straight lines in Fig. 1 represent the experimentally derived values of $\Delta C_{P,n}^\circ$ as a function of $1/(T-\Theta)^2$. It can be deduced from this that figure that the lines represent all of the symbols corresponding to experimentally derived values within 10 J mol^{-1} K^{-1} or less, which is of the order of the experimental uncertainty.

The uncertainties associated with the values of ΔG_f°, ΔH_f°, S°, C_p° and V° for Mg-adenosine nucleotides at elevated temperatures and pressures can be estimated by taking into account the maximum additive uncertainties associated with the equations of state parameters for these species given in Table 1. For example, using the maximum error in the equations of state parameters for MgATP^{2-} as a function of temperature and pressure, the uncertainties associated with values of the Gibbs energy for this species under different conditions can be assessed. The maximum uncertainty in the HKF parameters for MgATP^{2-} combine to yield an uncertainty of ±2900 J mol^{-1} for ΔG° at 150 °C and 5 bar. At 150 °C and 800 bar, the uncertainty decreases to nearly ±840 J mol^{-1}. Combining the uncertainty in ΔG_f° for MgATP^{2-} at 25 °C and 1 bar, results in a total maximum uncertainty of the order of ±4000 kJ mol^{-1} at elevated temperatures and pressures.

6.2. Nicotinamide adenine dinucleotides

Because so few experimental thermodynamic data are available in the literature for the nicotinamide adenine dinucleotides, the relative uncertainties associated with values of ΔG_f°, ΔH_f° , S°, C_p° and V° and the revised HKF equations of state parameters adopted in the present study cannot be easily determined. Nonetheless, uncertainties associated with the corresponding thermodynamic properties and parameters of the constituent nucleotides that comprise these dinucleotides can be used to estimate the relative uncertainties associated with nicotinamide adenine dinucleotides species. For example, if the relative uncertainties associated with the standard molal thermodynamic properties at 25 °C and 1 bar and the HKF equations of state parameters for the nucleotides taken from LaRowe and Helgeson [120] are of the same magnitude for those of the nicotinamide adenine dinucleotides, then the maximum uncertainty of ΔG° for $\mathrm{NAD}_{\mathrm{red}}^{2-}$ at 150 °C and 5 bar is 5000 J mol^{-1} and at 150 °C and 800 bar it is around 2900 J mol^{-1}.

7. Concluding remarks

The estimated revised HKF equations of state parameters, together with the standard molal thermodynamic properties of Mg-complexed adenosine nucleotides and nicotinamide nucleotide mono- and diphosphates at 25 °C and 1 bar computed above make it possible to characterize a wide variety of reactions among minerals, biomolecules, and other aqueous species at elevated temperatures and pressures. Calculations of this kind can be used to guide experimental studies of the relative stabilities of aqueous biomolecules by identifying possible metastable equilibrium states and providing a basis for comparison of the relative chemical affinities (A) of various irreversible reactions. However, assessing the accuracy of the estimation strategies employed to compute the standard molal thermodynamic properties and revised HKF equations of state parameters for the species considered in the present study requires more calorimetric, densimetric, and sound velocity data. Of particular interest in this regard is the experimental determination of the standard molal heat capacities and volumes of the Mg-adenosine nucleotides and nicotinamide adenine dinucleotides at temperatures in excess of 25 °C and preferably beyond 100 °C. In the interim, the standard molal thermodynamic properties and revised HKF equations of state parameters generated in the present study from the group additivity algorithms and reference model compounds summarized above provide a provisional comprehensive and internally consistent framework for thermodynamic investigation of biogeochemical systems at elevated temperatures and pressures. The properties and parameters generated in the present study can be used to quantify mass transfer among microorganisms and their environment under a wide variety of temperature and pressure conditions. Furthermore, fundamental biochemical processes such as the polymerization of RNA and DNA and the energetics of the ATP–ADP cycle can now be investigated for extremophiles and mesophiles alike.

The equations of state parameters and standard molal thermodynamic properties at 25 °C and 1 bar generated in the present study are being incorporated in a biogeochemical analog of the SUPCRT92 [93] software package to be called OBIGT (OrganoBioGeoTherm). This software package will be available at no cost from the Laboratory of Theoretical Geochemistry and Biogeochemistry (otherwise known as Prediction Central) at http://www.affinity.berkeley.edu.

Acknowledgments

The research summarized above represents part of the Ph.D. dissertation of the senior author at the University of California, Berkeley. The research was supported by the National Science Foundation (NSF Grants EAR-9613753 and EAR-0309829), the Department of Energy (DOE Grant DE-FG03-85ER13419 and DE-FG02-03ER15418), and the Committee on Research at the University of California, Berkeley. The senior author is also indebted to the ARCS Foundation and Graduate Opportunity Program at the University of California, Berkeley. We also would like to thank Laurent Richard, Jeff Dick, and Doug Clark for helpful discussions, encouragement, and assistance during the course of this study. Furthermore, DEL would like to thank Don Depaolo, Mark Bukowinski, John Baross, and Doug Clark for serving on his oral examination committee. We are especially grateful to Juliana Boerio-Goates for sharing with us the results of her heat capacity data for ribose in advance of publication. Finally, we would like to thank Fred Mackenzie, Chris Measures, and the Department of Oceanography at the University of Hawaii, Manoa for their hospitality and support during HCH's 2002–2003 sabbatical year.

Appendix A. Thermodynamic relations

The differences in Gibbs energies and enthalpies between the pressure and temperature of interest (P, T) and the reference pressure and temperature (P_r, T_r) in Eqs. (2) and (3) can be expressed by writing

$$G^\circ_{P,T} - G^\circ_{P_r,T_r} = -S^\circ_{P_r,T_r}(T - T_r) + \int_{T_r}^{T} C^\circ_{p_r}\,\mathrm{d}T - T\int_{T_r}^{T} C^\circ_{p_r}\,\mathrm{d}\ln T + \int_{P_r}^{P} V^\circ\,\mathrm{d}P, \tag{A.1}$$

and

$$H^\circ_{P,T} - H^\circ_{P_r,T_r} = \int_{T_r}^{T} C^\circ_{p_r}\,\mathrm{d}T + \int_{P_r}^{P} V^\circ\,\mathrm{d}P - \left(T\int_{P_r}^{P}\left(\frac{\partial V^\circ}{\partial T}\right)_{p}\mathrm{d}P\right)_{T}, \tag{A.2}$$

which are consistent with

$$S^\circ = S^\circ_{P_r,T_r} + \int_{T_r}^{T} C^\circ_{p_r}\,\mathrm{d}\ln T - \left(\int_{P_r}^{P}\left(\frac{\partial V^\circ}{\partial T}\right)_{p}\mathrm{d}P\right)_{T} \tag{A.3}$$

where $C^\circ_{p_r}$ stands for the isobaric molal heat capacity of the species at the reference pressure, $(\partial V^\circ/\partial T)_p$ represents its standard molal expansibility, and $S^\circ_{P_r,T_r}$ refers to the standard molal entropy of the species at the reference pressure and temperature.

A.1. Crystalline compounds

Consideration of a wide range of experimental data indicates that in the absence of lambda phase transitions the standard molal heat capacities at 1 bar of crystalline organic compounds including amino acids [114] can be represented as a function of temperature by the Maier–Kelley power function [115], which can be written as

$$C^\circ_{p_r} = a + bT + cT^{-2} \tag{A.4}$$

where a, b, and c stand for temperature-independent coefficients of the species of interest.

Combining Eq. (A.4) with Eqs. (A.1)–(A.3) and integrating the heat capacity terms leads to

$$G^\circ_{P,T} - G^\circ_{P_r,T_r} = -S^\circ_{P_r,T_r}(T - T_r) + a\left(T - T_r - T\ln\left(\frac{T}{T_r}\right)\right) - \left(\frac{(c - bT_r^2T)(T - T_r)^2}{2T_r^2T}\right) + \int_{P_r}^{P} V^\circ\,\mathrm{d}P, \tag{A.5}$$

$$H^\circ_{P,T} - H^\circ_{P_r,T_r} = a(T - T_r) + \frac{b}{2}(T^2 - T_r^2) - c\left(\frac{1}{T} - \frac{1}{T_r}\right) + \int_{P_r}^{P} V^\circ\,\mathrm{d}P - \left(T\int_{P_r}^{P}\left(\frac{\partial V^\circ}{\partial T}\right)_{p}\mathrm{d}P\right)_{T}, \tag{A.6}$$

and

$$S^\circ = S^\circ_{P_r,T_r} + a\ln\left(\frac{T}{T_r}\right) + b(T - T_r) - \frac{c}{2}\left(\frac{1}{T^2} - \frac{1}{T_r^2}\right) - \left(\int_{P_r}^{P}\left(\frac{\partial V^\circ}{\partial T}\right)_{p}\mathrm{d}P\right)_{T} \tag{A.7}$$

As in the case of minerals [116] and organic crystals [114,100], the standard molal volumes of crystalline molecules are insensitive to the changes in temperature and pressure considered in the present study, which range from 0 °C and 1 bar to 150 °C and 800 bar. Therefore, as a first approximation we can write

$$V^\circ = V^\circ_{P_r,\,T_r} \tag{A.8}$$

which can be used to evaluate the volume integrals in Eqs. (A.5)–(A.7) for crystalline compounds.

A.2. Aqueous Species

The conventional standard molal properties of aqueous species are expressed in the revised-HKF equations of state [78–83,88,89,93,117,118] as the sum of structural (non-solvation) and solvation contributions, which can be expressed as

$$\Xi^\circ = \Delta\Xi_n^\circ + \Delta\Xi_s^\circ \tag{A.9}$$

where Ξ° stands for any conventional standard molal property of an aqueous species, and $\Delta\Xi_n^\circ$ and $\Delta\Xi_s^\circ$ refer to the conventional non-solvation and solvation contributions to that property, respectively.

A.2.1. Charged aqueous species

The solvation contributions to the standard molal heat capacity, volume, isothermal compressibility, and entropy of a charged aqueous species can be expressed in terms of Born transfer theory as [88]

$$\Delta C_{\mathrm{p,s}}^\circ = \omega TX + 2TY\left(\frac{\partial\omega}{\partial T}\right)_{\mathrm{p}} - T\left(\frac{1}{\epsilon}-1\right)\left(\frac{\partial^2\omega}{\partial T^2}\right)_{\mathrm{p}}, \tag{A.10}$$

$$\Delta V_{\mathrm{s}}^\circ = -\omega Q + \left(\frac{1}{\epsilon}-1\right)\left(\frac{\partial\omega}{\partial P}\right)_T, \tag{A.11}$$

$$\Delta\kappa_{T,\mathrm{s}}^\circ = \omega N + 2Q\left(\frac{\partial\omega}{\partial P}\right)_T - \left(\frac{1}{\epsilon}-1\right)\left(\frac{\partial^2\omega}{\partial P^2}\right)_T, \tag{A.12}$$

and

$$\Delta S_{\mathrm{s}}^\circ = \omega Y + \left(\frac{1}{\epsilon}-1\right)\left(\frac{\partial\omega}{\partial T}\right)_{\mathrm{p}}, \tag{A.13}$$

where $\Delta C_{\mathrm{p},s}^\circ$, $\Delta V_{\mathrm{s}}^\circ$, $\Delta\kappa_{T,s}^\circ$, and $\Delta S_{\mathrm{s}}^\circ$ refer to the standard molal heat capacity, volume, isothermal compressibility, and entropy of solvation, ϵ stands for the dielectric constant of H_2O, ω designates the conventional Born coefficient, and X, Y, N, and Q denote the Born functions defined in [82]. Values of X, Y, N, and Q have been tabulated [78] and discussed in detail by [82].

The non-solvation contributions to the heat capacity ($\Delta C_{\mathrm{p},n}^\circ$), volume ($\Delta V_{\mathrm{n}}^\circ$), and isothermal compressibility ($\Delta\kappa_{T,n}^\circ$) of an aqueous species are given by

$$\Delta C_{P,n}^\circ = c_1 + \frac{c_2}{(T-\Theta)^2} - \left(\frac{2T}{(T-\Theta)^3}\right)\left(a_3(P-P_{\mathrm{r}}) + a_4\ln\left(\frac{\Psi+P}{\Psi+P_{\mathrm{r}}}\right)\right), \tag{A.14}$$

$$\Delta V_{\mathrm{n}}^\circ = \sigma + \frac{\xi}{T-\Theta} = a_1 + \frac{a_2}{\Psi+P} + \left(a_3 + \frac{a_4}{\Psi+P}\right)\left(\frac{1}{T-\Theta}\right), \tag{A.15}$$

and

$$-\Delta\kappa_{T,\mathrm{n}}^\circ = \left(\frac{\partial\sigma}{\partial P}\right)_T + \left(\frac{\partial\xi}{\partial P}\right)_T\left(\frac{1}{T-\Theta}\right), \tag{A.16}$$

where

$$\sigma = a_1 + \frac{a_2}{\Psi+P}, \tag{A.17}$$

$$\xi = a_3 + \frac{a_4}{\Psi+P}, \tag{A.18}$$

$$\left(\frac{\partial\sigma}{\partial P}\right)_T = \frac{-a_2}{(\Psi+P)^2}, \tag{A.19}$$

and

$$\left(\frac{\partial\xi}{\partial P}\right)_T = \frac{-a_4}{(\Psi+P)^2} \tag{A.20}$$

where c_1, c_2, a_1, a_2, a_3, a_4, σ, and ξ represent species-dependent non-solvation parameters and Ψ and Θ denote solvent parameters equal to 2600 bar and 228 K, respectively. The revised-HKF equations for the standard molal heat capacity, volume, and entropy, and the standard molal enthalpy and Gibbs energy of formation of charged species are given by

$$\begin{aligned} C_{\mathrm{p}}^{\circ} = \Delta C_{P,n}^{\circ} + \Delta C_{P,s}^{\circ} = c_1 + \frac{c_2}{(T-\Theta)^2} - \left(\frac{2T}{(T-\Theta)^3}\right)\left(a_3(P-P_{\mathrm{r}}) + a_4 \ln\left(\frac{\Psi+P}{\Psi+P_{\mathrm{r}}}\right)\right) \\ + \omega TX + 2TY\left(\frac{\partial\omega}{\partial T}\right)_{\mathrm{p}} - T\left(\frac{1}{\epsilon}-1\right)\left(\frac{\partial^2\omega}{\partial T^2}\right)_{\mathrm{p}}, \end{aligned} \tag{A.21}$$

$$V^{\circ} = \Delta V_{\mathrm{n}}^{\circ} + \Delta V_{\mathrm{s}}^{\circ} = \sigma + \frac{\xi}{T-\Theta} = a_1 + \frac{a_2}{\Psi+P} + \left(a_3 + \frac{a_4}{\Psi+P}\right)\left(\frac{1}{T-\Theta}\right) - \omega Q + \left(\frac{1}{\epsilon}-1\right)\left(\frac{\partial\omega}{\partial P}\right)_T, \tag{A.22}$$

$$\kappa_T^{\circ} = \Delta\kappa_{T,n}^{\circ} + \Delta\kappa_{T,s}^{\circ} = -\left(\frac{\partial\sigma}{\partial P}\right)_T - \left(\frac{\partial\xi}{\partial P}\right)_T\left(\frac{1}{T-\Theta}\right) + \omega N + 2Q\left(\frac{\partial\omega}{\partial P}\right)_T - \left(\frac{1}{\epsilon}-1\right)\left(\frac{\partial^2\omega}{\partial P^2}\right)_T, \tag{A.23}$$

$$\begin{aligned} S^{\circ} = S_{P_{\mathrm{r}},T_{\mathrm{r}}} + c_1 \ln\left(\frac{T}{T_{\mathrm{r}}}\right) - \frac{c_2}{\Theta}\left[\left(\frac{1}{T-\Theta}\right) - \left(\frac{1}{T_{\mathrm{r}}-\Theta}\right) + \frac{1}{\Theta}\ln\left(\frac{T_{\mathrm{r}}(T-\Theta)}{T(T_{\mathrm{r}}-\Theta)}\right)\right] \\ + \left(\frac{1}{T-\Theta}\right)^2\left(a_3(P-P_{\mathrm{r}}) + a_4\ln\left(\frac{\Psi+P}{\Psi+P_{\mathrm{r}}}\right)\right) + \omega Y - \left(\frac{1}{\epsilon}-1\right)\left(\frac{\partial\omega}{\partial T}\right)_{\mathrm{p}} - \omega_{P_{\mathrm{r}},T_{\mathrm{r}}} Y_{P_{\mathrm{r}},T_{\mathrm{r}}}, \end{aligned} \tag{A.24}$$

$$\begin{aligned} \Delta H^{\circ} = \Delta H_{\mathrm{f}}^{\circ} + c_1(T-T_{\mathrm{r}}) - c_2\left(\left(\frac{1}{T-\Theta}\right) - \left(\frac{1}{T_{\mathrm{r}}-\Theta}\right)\right) + a_1(P-P_{\mathrm{r}}) + a_2\ln\left(\frac{\Psi+P}{\Psi+P_{\mathrm{r}}}\right) \\ + \left(\frac{2T-\Theta}{(T-\Theta)^2}\right)\left(a_3(P-P_{\mathrm{r}}) + a_4\ln\left(\frac{\Psi+P}{\Psi+P_{\mathrm{r}}}\right)\right) + \omega\left(\frac{1}{\epsilon}-1\right) + \omega TY - T\left(\frac{1}{\epsilon}-1\right)\left(\frac{\partial\omega}{\partial T}\right)_{\mathrm{p}} \\ - \omega_{P_{\mathrm{r}},T_{\mathrm{r}}}\left(\frac{1}{\epsilon_{P_{\mathrm{r}},T_{\mathrm{r}}}}-1\right) - \omega_{P_{\mathrm{r}},T_{\mathrm{r}}} T_{\mathrm{r}} Y_{P_{\mathrm{r}},T_{\mathrm{r}}}, \end{aligned} \tag{A.25}$$

and

$$\begin{aligned} \Delta G^{\circ} = \Delta G_{\mathrm{f}}^{\circ} - S_{P_{\mathrm{r}},T_{\mathrm{r}}}(T-T_{\mathrm{r}}) - c_1\left(T\ln\left(\frac{T}{T_{\mathrm{r}}}\right) - T + T_{\mathrm{r}}\right) \\ + a_1(P-P_{\mathrm{r}}) + a_2\ln\left(\frac{\Psi+P}{\Psi+P_{\mathrm{r}}}\right) - c_2\left(\left(\left(\frac{1}{T-\Theta}\right) - \left(\frac{1}{T_{\mathrm{r}}-\Theta}\right)\right)\left(\frac{\Theta-T}{\Theta}\right) - \frac{T}{\Theta^2}\ln\left(\frac{T_{\mathrm{r}}(T-\Theta)}{T(T_{\mathrm{r}}-\Theta)}\right)\right) \\ + \left(\frac{1}{T-\Theta}\right)\left(a_3(P-P_{\mathrm{r}}) + a_4\ln\left(\frac{\Psi+P}{\Psi+P_{\mathrm{r}}}\right)\right) + \omega\left(\frac{1}{\epsilon}-1\right) - \omega_{P_{\mathrm{r}},T_{\mathrm{r}}}\left(\frac{1}{\epsilon_{P_{\mathrm{r}},T_{\mathrm{r}}}}-1\right) + \omega_{P_{\mathrm{r}},T_{\mathrm{r}}} Y_{P_{\mathrm{r}},T_{\mathrm{r}}}(T-T_{\mathrm{r}}), \end{aligned} \tag{A.26}$$

respectively.

A.2.2. Neutral aqueous species

As in the case of other neutral aqueous species [83,117], the effective Born coefficient (ω) of the various nucleotides are taken to be independent of temperature and pressure. [4] Therefore, the non-solvation contributions to the standard molal properties of these species can be expressed as

$$\Delta C_{P,s}^{\circ} = \omega TX, \tag{A.27}$$

$$\Delta V_{\mathrm{s}}^{\circ} = -\omega Q, \tag{A.28}$$

$$\Delta\kappa_{T,\mathrm{s}}^{\circ} = \omega N, \tag{A.29}$$

and

$$\Delta S_{\mathrm{s}}^{\circ} = \omega Y. \tag{A.30}$$

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[4] The effective Born coefficients for neutral aqueous species account for dipole-dipole interactions arising from the presence of the neutral aqueous molecules in a structured solution [81,88,119].

It follows that Eqs. (A.21)–(A.26) can be expressed for neutral nucleotides as

$$C_{\mathrm{p}}^{\circ} = \Delta C_{P,n}^{\circ} + \Delta C_{P,s}^{\circ} = c_1 + \frac{c_2}{(T-\Theta)^2} - \left(\frac{2T}{(T-\Theta)^3}\right) X \left(a_3(P-P_{\mathrm{r}}) + a_4 \ln\left(\frac{\Psi+P}{\Psi+P_{\mathrm{r}}}\right)\right) + \omega T X, \tag{A.31}$$

$$V^{\circ} = \Delta V_{\mathrm{n}}^{\circ} + \Delta V_{\mathrm{s}}^{\circ} = a_1 + \frac{a_2}{\Psi+P} + \left(a_3 + \frac{a_4}{\Psi+P}\right)\left(\frac{1}{T-\Theta}\right) - \omega Q, \tag{A.32}$$

$$\kappa_T^{\circ} = \Delta\kappa_{T,n}^{\circ} + \Delta\kappa_{T,s}^{\circ} = -\left(\frac{\partial\sigma}{\partial P}\right)_T - \left(\frac{\partial\xi}{\partial P}\right)_T \left(\frac{1}{T-\Theta}\right) + \omega N, \tag{A.33}$$

$$\begin{aligned} S^{\circ} = {} & S_{P_{\mathrm{r}},T_{\mathrm{r}}} + c_1 \ln\left(\frac{T}{T_{\mathrm{r}}}\right) - \frac{c_2}{\Theta}\left[\left(\frac{1}{T-\Theta}\right) - \left(\frac{1}{T_{\mathrm{r}}-\Theta}\right) + \frac{1}{\Theta}\ln\left(\frac{T_{\mathrm{r}}(T-\Theta)}{T(T_{\mathrm{r}}-\Theta)}\right)\right] \\ & + \left(\frac{1}{T-\Theta}\right)^2 \left(a_3(P-P_{\mathrm{r}}) + a_4\ln\left(\frac{\Psi+P}{\Psi+P_{\mathrm{r}}}\right)\right) + \omega(Y_{P,T} - Y_{P_{\mathrm{r}},T_{\mathrm{r}}}), \end{aligned} \tag{A.34}$$

$$\begin{aligned} \Delta H^{\circ} = {} & \Delta H_{\mathrm{f}}^{\circ} + c_1(T-T_{\mathrm{r}}) - c_2\left(\left(\frac{1}{T-\Theta}\right) - \left(\frac{1}{T_{\mathrm{r}}-\Theta}\right)\right) + a_1(P-P_{\mathrm{r}}) + a_2\ln\left(\frac{\Psi+P}{\Psi+P_{\mathrm{r}}}\right) \\ & + \left(\frac{2T-\Theta}{(T-\Theta)^2}\right)\left(a_3\,(P-P_{\mathrm{r}}) + a_4\ln\left(\frac{\Psi+P}{\Psi+P_{\mathrm{r}}}\right)\right) + \omega\left(\frac{1}{\epsilon} - 1\right) \\ & + \omega\left(TY_{P,T} - T_{\mathrm{r}}Y_{P_{\mathrm{r}},T_{\mathrm{r}}} - \left(\frac{1}{\epsilon_{P_{\mathrm{r}},T_{\mathrm{r}}}} - 1\right) + \left(\frac{1}{\epsilon_{P,T}} - 1\right)\right), \end{aligned} \tag{A.35}$$

and

$$\begin{aligned} \Delta G^{\circ} = {} & \Delta G_{\mathrm{f}}^{\circ} - S_{P_{\mathrm{r}},T_{\mathrm{r}}}(T-T_{\mathrm{r}}) - c_1\left(T\ln\left(\frac{T}{T_{\mathrm{r}}}\right) - T + T_{\mathrm{r}}\right) + a_1(P-P_{\mathrm{r}}) \\ & + a_2 X \ln\left(\frac{\Psi+P}{\Psi+P_{\mathrm{r}}}\right) - c_2\left(\left(\left(\frac{1}{T-\Theta}\right) - \left(\frac{1}{T_{\mathrm{r}}-\Theta}\right)\right)\left(\frac{\Theta-T}{\Theta}\right) - \frac{T}{\Theta^2}\ln\left(\frac{T_{\mathrm{r}}(T-\Theta)}{T(T_{\mathrm{r}}-\Theta)}\right)\right) \\ & + \left(\frac{1}{T-\Theta}\right)\left(a_3(P-P_{\mathrm{r}}) + a_4\ln\left(\frac{\Psi+P}{\Psi+P_{\mathrm{r}}}\right)\right) + \omega\left(Y_{P_{\mathrm{r}},T_{\mathrm{r}}}(T-T_{\mathrm{r}}) + \left(\frac{1}{\epsilon_{P,T}} - 1\right) - \left(\frac{1}{\epsilon_{P_{\mathrm{r}},T_{\mathrm{r}}}} - 1\right)\right). \end{aligned} \tag{A.36}$$

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