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Extensions and Corollaries of the Thermodynamic Solvate Difference Rule[†]

H. Donald B. Jenkins[‡] and Joel F. Liebman[*,§]

Department of Chemistry, University of Warwick, Coventry CV4 7AL, West Midlands, U.K., and Department of Chemistry and Biochemistry, University of Maryland, Baltimore County, Baltimore, Maryland 21250

The ever-growing requirement to develop new materials for highly specific applications is making major demands for thermodynamic data which have not, to date, been measured. This, in turn, means that, increasingly, estimated values are required to make thermodynamic interpretations and feasibility studies of reactions involving these materials. In this vein, four further extensions of, and insights into, the Thermodynamic Solvate Difference Rule, are presented here and tested. The result is the provision of valuable, albeit approximate, rules useful for many areas of organic/inorganic chemisty to predict thermodynamic data in cases where experimental data have not yet been determined. These extended rules take the form $P\{\mathrm{M_pX_q}\cdot\mathrm{jL,p}\} + P\{\mathrm{M'_pX'_{q'}}\cdot\mathrm{kL,p}\} \approx P\{\mathrm{M_pX_q}\cdot\mathrm{dL,p}\} + P\{\mathrm{M'_pX'_{q'}}\cdot\mathrm{sL,p}\}$ where $\mathrm{j} + \mathrm{k} = \mathrm{d} + \mathrm{s}$ and the salt $\mathrm{M'_pX'_q}$ can be the same as $\mathrm{M_pX_q}$. *P* represents any of the individual thermodynamic properties: $\Delta_fH°$, $\Delta_fG°$, $\Delta_fS°$, $S°$, etc. Also $P\{\mathrm{M_pX_q}\cdot\mathrm{jL,p}\} + P\{\mathrm{M'_pX'_{q'}}\cdot\mathrm{kL,p}\} \approx P\{\mathrm{M_pX_q}\cdot\mathrm{kL,p}\} + P\{\mathrm{M'_pX'_{q'}}\cdot\mathrm{jL,p}\}$ For salts $\mathrm{M_pX_q}$, $\mathrm{M'_pX'_q}$, and $\mathrm{M'_rX'_s}$ and then for multiple salts compounded from these, where one salt is considered to be the "solvent" of the other, and vice-versa, then $P\{\mathrm{M_pX_q}\cdot\mathrm{jM'_rX'_s,s}\} \approx P\{\mathrm{M_pX_q,s}\} + j\cdot\Theta_P\{M'_rX'_s,\mathrm{s-s}\}$ $P\{\mathrm{M'_rX'_s}\cdot\mathrm{dM_pX_q,s}\} \approx P\{\mathrm{M'_rX's,s}\} + \mathrm{d}\cdot\Theta_P\{\mathrm{M_pX_q,s-s}\}$ where $\Theta_P\{\mathrm{M'_rX'_s,\ s-s}\}$ and $\Theta_P\{\mathrm{M_pX_q,s-s}\}$ are constants, independent of the nature of $\mathrm{M_pX_q}$ and $\mathrm{M'_rX'_s}$, respectively. Thus, salts may be permuted as being regarded as solvent and solvate. A cascading rule can be established as follows $P\{\mathrm{M_pX_q}\cdot\mathrm{M'_pX'_q}\cdot\mathrm{jM'_rX'_s,s}\} \approx P\{\mathrm{M_pX_q}\cdot\mathrm{M'_pX'_q,s}\} + \mathrm{j}\cdot\Theta_P\{\mathrm{M'_rX'_s,s-s}\} \approx P\{\mathrm{M_pX_q,s}\} + \Theta_P\{\mathrm{M'_pX'_q,s-s}\} + j\cdot\Theta_P\{\mathrm{M'_rX'_s,s-s}\}$ and permutations thereon. Developed and applied initially for inorganic compounds, the rule is shown to extend into the arena of organic thermochemistry.

Introduction

Recently, one of us established the thermodynamic solvate difference rule[1−3]

$$P\{\mathrm{M_pX_q}\cdot n\mathrm{L,p}\} \approx P\{\mathrm{M_pX_q}\cdot m\mathrm{L,p}\} + (n-m)\cdot\Theta_P\{\mathrm{L,p-p}\} \tag{1}$$

$$P\{\mathrm{M_pX_q}\cdot n\mathrm{L,p}\} \approx P\{\mathrm{M_pX_q}\} + n\cdot\Theta_P\{\mathrm{L,p-p}\} \tag{2}$$

where L represents the bound solvent molecule (including H_2O, SO_2, and NH_3 as well as other ligands; see Table 1, ref 2); *P* includes the key properties $\Delta_fH°$, $\Delta_fG°$, $\Delta_fS°$, $S°$, V_m, and U_{POT}; and p refers to the phase, either solid, liquid, or (occasionally) gas. We recognize $m = 0$ as being the condensed-phase unsolvated parent, and $\Theta_P\{\mathrm{L,p-p}\}$ is the approximately constant incremental contribution per mole of the bound solvent, L, to the property, $P\{\mathrm{M_pX_q,p}\}$ of interest. M and X are the cation and anion of the solvated material, respectively, and p and q refer to their number as defined by the stoichiometry, in this solvate. For any given solvate, $\mathrm{M_pX_q}$ may also represent salts of varying stoichiometries. The rules represented by eqs 1 and 2 can be used to estimate the value of the property, P ($= \Delta_fH°$, $\Delta_fG°$, $\Delta_fS°$, $S°$, etc.), for any solvate provided that: (i) the values of $\Theta_P\{\mathrm{L,p-p}\}$ and *P* for the parent compound ($\mathrm{M_pX_q}$) are known or (ii) the values of *P* for the parent compound ($\mathrm{M_pX_q}$) and one solvate, $P\{\mathrm{M_pX_q}\cdot n\mathrm{L,p}\}$ are known or (iii) the values of *P* for two solvates, $P\{\mathrm{M_pX_q}\cdot n\mathrm{L,p}\}$ and $P\{\mathrm{M_pX_q}\cdot m\mathrm{L,p}\}$, are known. In cases (ii) and (iii), $\Theta_P\{\mathrm{L,p-p}\}$ can be evaluated. Conversely, the value of the property, *P*, for the parent compound ($\mathrm{M_pX_q}$), if unknown, can be inferred knowing either (i) the value of $\Theta_P\{\mathrm{L,p-p}\}$ and *P* for one solvate, $P\{\mathrm{M_pX_q}\cdot n\mathrm{L,p}\}$, or (ii) the values of *P* for two solvates, $P\{\mathrm{M_pX_q}\cdot n\mathrm{L,p}\}$ and $P\{\mathrm{M_pX_q}\cdot m\mathrm{L,p}\}$, in which case $\Theta_P\{\mathrm{L,p-p}\}$ can be established.

As earlier said, this rule is truly general and powerful and is shown here to have application for organic thermochemistry as well as in the inorganic arena, the area of its usage so far.

Theory and Application

Applications in Inorganic Chemistry. Application to Alkali Metal and Alkaline Earth Hydroxylamine Complexes. Consider the solvent or ligand NH_2OH. Experimental values of the standard enthalpy of formation, $\Delta_fH°(\mathrm{M(NH_2OH)}_n\mathrm{X_q,\ s})$ of a number of alkali metal and alkaline earth hydroxylamine complexes have been established from solution calorimetry[4] where X is either ClO_4 or NO_3 and M = Li, Ca, Mg, or Ba for selected values of *n* in the range $6 \geq n \geq 0$. Table 1 tabulates these experimental data reported, and Figure 1 shows an overall difference plot of $[\Delta_fH°(\mathrm{M(NH_2OH)}_n\mathrm{X_q,\ s}) - \Delta_fH°(\mathrm{MX_q,\ s})]/\mathrm{kJ\cdot mol^{-1}}$ versus *n* for all the salts listed. Constraining the line to pass through the origin, we find the analytical form

$$[\Delta_fH°(\mathrm{M(NH_2OH)}_n\mathrm{X_q,s}) - \Delta_fH°(\mathrm{MX_q,s})]/\mathrm{kJ\cdot mol^{-1}} \approx \Theta_{\mathrm{Hf}}\{\mathrm{NH_2OH,s-s}\}n \approx -133.0n$$

Individual plots can be made for each separate family of salts and can also be used to estimate missing data.

The rather low correlation coefficient of $R^2 = 0.977$ is similar in magnitude to that obtained[2] from the data on the related 270 ammoniates (where R^2 was 0.932). Difference plots made for individual hydroxylamine series in Table 1 show far less scatter

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[*] Corresponding author. Tel.: 1-410-455-2549. Fax: 1-410-455-2608. E-mail: jliebman@umbc.edu.
[†] Part of the special issue "Robin H. Stokes Festschrift".
[‡] University of Warwick.
[§] University of Maryland.

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Table 1. Values of Standard Enthalpies of Formation for Metal Hydroxylamine Complexes $\Delta_f H°(M(NH_2OH)_nX_2, s)$/kJ·mol^{-1} and $\Delta_f H°(MX_2, s)$/kJ·mol^{-1} (M = Mg, Ca, Ba) and $\Delta_f H°(M(NH_2OH)_nX, s)$/kJ·mol^{-1} and $\Delta_f H°(MX, s)$ (M = Li)/kJ·mol^{-1} and their Difference Functions $[\Delta_f H°(M(NH_2OH)_nX_2, s) - \Delta_f H°(MX_2, s)]$/kJ·mol^{-1} and $[\Delta_f H°(M(NH_2OH)_nX, s) - \Delta_f H°(MX, s)]$/kJ·mol^{-1}, Respctively[a]

	kJ·mol^{-1}				
M	X	$\Delta_f H°(M(NH_2OH)_nX_2, s)$	$\Delta_f H°(MX_2, s)$	$[\Delta_f H°(M(NH_2OH)_nX_2, s) - \Delta_f H°(MX_2, s)]$	n
Mg	ClO_4	− 898.3	− 568.9	−329.4	2
Mg	ClO_4	− 1332.2	− 568.9	− 763.3	6
Mg	NO_3	− 1092.4	− 790.7	− 301.7	2
Ca	ClO_4	− 1156.5	− 736.8	− 419.7	3
Ca	ClO_4	− 1533.9	− 736.8	− 797.1	6
Ca	NO_3	− 1230.1	− 938.4	− 291.7	2
Ba	ClO_4	− 897.9	− 800.0	− 97.9	1
Ba	ClO_4	− 1159.8	− 800.0	− 359.8	3

		kJ·mol^{-1}			
M	X	$\Delta_f H°(M(NH_2OH)_nX, s)$	$\Delta_f H°(MX, s)$	$[\Delta_f H°(M(NH_2OH)_nX, s) - \Delta_f H°(MX, s)]$	n
Li	ClO_4	−799.1	−381.0	−418.1	3
Li	NO_3	−608.8	−483.1	−125.7	1

[a] All data are from ref 4.

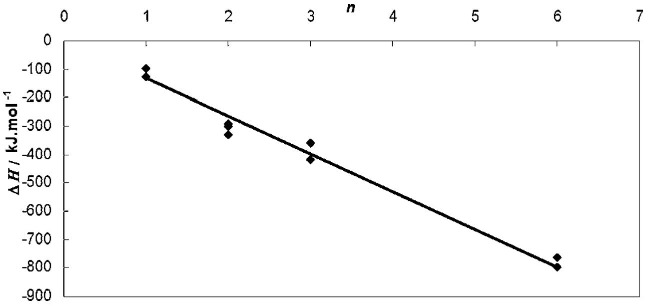

Figure 1. Plot of $[\Delta_f H°(M(NH_2OH)_nX_q, s) - \Delta_f H°(MX_q, s)]$ ($q = 1$ or 2) $= \Delta H$/kJ·mol^{-1} as ordinate versus number of NH_2OH ligands, n, in the complex as abscissa, having a correlation coefficient $R^2 = 0.977$ and analytical form: $[\Delta_f H°(M(NH_2OH)_nX_q, s) - \Delta_f H°(MX_q, s)] = \Theta_{Hf}\{NH_2OH, s{-}s\}n = -133.0n$ (the line is constrained to pass through the origin).

than our "global" plot above, thus, for example, a plot of $[\Delta_f H°(Ca(NH_2OH)_n(ClO_4)_2, s)]$/kJ·mol^{-1} versus n (= 0, 3, 6) has a correlation coefficient $R^2 = 0.9991$ and the analytical form

$$[\Delta_f H°(Ca(NH_2OH)_n(ClO_4)_2, s)]/\mathrm{kJ\cdot mol^{-1}} \approx \Theta_{Hf}\{NH_2OH, s{-}s\}n + \Delta_f H°(X/Ca(ClO_4)_2, s) \approx -132.9n - 743.9 \quad (3)$$

Evaluation of Θ_{Hf}\{L, s−s\} from Alternative Routes. It has been noted previously[2] that a *linear* relationship exists in general between $\Theta_{Hf}\{L, s{-}s\}$ and $\Delta_f H°(L, s)$, the enthalpy of formation of the solid ligand, L (see plot in Figure 4, ref 2). Using only eq 34 of ref 2 and the known[5,6] enthalpy of formation of hydroxylamine, $\Delta_f H°(NH_2OH, s)$/kJ·mol^{-1} = − 114.2, we would have predicted (without the use of any other data) that $\Theta_{Hf}\{NH_2OH, s{-}s\}$/kJ·mol^{-1} = 1.041(− 114.2) − 9.28 = − 128.2, very close to the experimental value (−133.0 kJ·mol^{-1}) returned by the data in Figure 1 above. This means of course that for any ligand for which $\Delta_f H°(L,s)$ is available we can estimate quite reliably the gradient of the difference plot, $\Theta_{Hf}\{L, s{-}s\}$, and—with a little further exploration—there is no doubt we can derive, more generally, $\Theta_P\{L, s{-}s\}$ from known values of $P(L, s)$, etc.

Ambiguous as well as irrelevant as to whether N- and/or O-coordination is involved, the rule is well-obeyed. Likewise left unanswered is the effect, or rather seemingly negligible effect, of the structure of the $M(NH_2OH)_nX_q$ (i.e., $MX_q \cdot n(NH_2OH)$) complex or in general of the $M_pX_q \cdot nL$ complex. For example, whether the M has tetrahedral or octahedral coordination of the ligands L and group(s) X or whether N or O is the coordinating atom from the hydroxylamine or is uncoordinated, save the anion, seemingly has rather negligible effect. These observations may largely be the result of taking the differences in the thermodynamic property P for the solvate and parent materials. The thermodynamics associated with the individual parent are effectively eliminated. This idea is further exemplified when we consider organic materials in relation to the difference rule later in this paper.

Application to Hydrate Families. Likewise unanswered, in the case of hydrates, $M_pX_q \cdot mH_2O$ and $M_pX_q \cdot nH_2O$, was why only specific values of m and n are found and their properties reported in the chemical literature. For example, standard enthalpies of formation of $CuSO_4$ as the anhydrous salt and the mono-, tri-, and pentahydrate are all long known,[5] while the data for the di- and tetrahydrate are unreported. Indeed, one might well have anticipated the latter since in the pentahydrate one of the water molecules is uncoordinated to the cation (the other four being tetrahedrally bound to it) and resides within the voids in the structure. Haruhiko[7] has made a detailed study of the three-stage thermal dehydration of this pentahydrate and found the individual decomposition enthalpies to be in accord with those predicted from the standard enthalpy of formation data (and hence from the difference rule). In another study,[8] discussion is made of the dihydrate, $CuSO_4 \cdot 2H_2O$ dehydration, although no thermodynamic formation data are given. While one might infer that this absence of thermodynamic data is due to lack of interest in certain species, in fact some of these species have seemingly evaded synthesis[9] (these last authors having suggested the existence of a hemihydrate, yet again, seemingly unstudied by experimental thermodynamicists).

Consider now the reactions

$$CuSO_4 \cdot H_2O(s) + CuSO_4 \cdot 5H_2O(s) \rightarrow 2CuSO_4 \cdot 3H_2O(s) \quad (4)$$

$$CuSO_4 \cdot H_2O(s) + CuSO_4 \cdot 5H_2O(s) \rightarrow CuSO_4 \cdot 2H_2O(s) + CuSO_4 \cdot 4H_2O(s) \quad (5)$$

The thermodynamic solvate difference rule immediately suggests thermoneutrality for *both* reactions. More precisely, a corollary of this rule is that

$$P\{M_pX_q \cdot jL, p\} + P\{M_pX_q \cdot kL, p\} \approx P\{M_pX_q \cdot dL, p\} + P\{M_pX_q \cdot sL, p\} \quad (6)$$

whenever j + k = d + s. Taking the necessary thermochemical data of all the copper(II) sulfate hydrates from ref 6, we find

$$\Delta H\circ_{\text{reaction}}(4)/\text{kJ}\cdot\text{mol}^{-1} = 2\Delta_f H^\circ(\text{CuSO}_4\cdot 3\text{H}_2\text{O, s}) - \Delta_f H^\circ(\text{CuSO}_4\cdot 5\text{H}_2\text{O, s}) - \Delta_f H^\circ(\text{CuSO}_4\cdot \text{H}_2\text{O, s}) = 2(-1684.31) - [-1085.83 + (-2279.65)] = -3.14 \quad (7)$$

$$\Delta G\circ_{\text{reaction}}(4)/\text{kJ}\cdot\text{mol}^{-1} = 2\Delta_f G^\circ(\text{CuSO}_4\cdot 3\text{H}_2\text{O, s}) - \Delta_f G^\circ(\text{CuSO}_4\cdot 5\text{H}_2\text{O, s}) - \Delta_f G^\circ(\text{CuSO}_4\cdot \text{H}_2\text{O, s}) = 2(-1399.96) - [-1879.745 + (-918.11)] = -2.07 \quad (8)$$

$$\Delta S\circ_{\text{reaction}}(4)/\text{kJ}\cdot\text{mol}^{-1} = 2S^\circ(\text{CuSO}_4\cdot 3\text{H}_2\text{O, s}) - S^\circ(\text{CuSO}_4\cdot 5\text{H}_2\text{O, s}) - S^\circ(\text{CuSO}_4\cdot \text{H}_2\text{O, s}) = 2(221.3) - [300.4 + 146.0] = -3.8 \quad (9)$$

$$\Delta C_{p,\text{reaction}}(4)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 2C_p{}^\circ(\text{CuSO}_4\cdot 3\text{H}_2\text{O, s}) - C_p{}^\circ(\text{CuSO}_4\cdot 5\text{H}_2\text{O, s}) - C_p{}^\circ(\text{CuSO}_4\cdot \text{H}_2\text{O, s}) = 2(205.0) - [280.0 + 134.0] = -4 \quad (10)$$

The rule represented by eq 6 is very well obeyed.

However, there are no data and no report for the tetrahydrate (one implication being that it does not occur) which would mean that reaction 5 is significantly endothermic (i.e., $\Delta H^\circ(5) > 0$) and endoergic (i.e., $\Delta G^\circ(5) > 0$), with no explanation for *why* this hydrate is particularly unstable.

Consider now the magnesium sulfate hydrates. The mono-, di-, tetra-, hexa-, and heptahydrates are all thermochemically characterized as is the anhydrous species. However the mono, 1.25, di-, tri-, tetra-, penta-, hexa-, and heptahydrates can all be prepared (see Table 1 in ref 29). Above 298 K, only the mono-, hexa-, and heptahydrates form solid stable phases in aqueous solution. The penta-, tetra-, tri-, and di- and nonstoichiometric hydrates are considered to be metastable.[11] The 2.5 hydrate is, apparently, formed during the decomposition of the heptahydrate under specific pressure conditions.[12] A considerable number of, often quite different, hydrate intermediate stages have been found during studies[13−16] on the examination of the decomposition of the heptahydrate, and these have included the 1.4 and 0.5 hydrates.[10] An undecahydrate has also been characterized.[17] The existence or otherwise of intermediate hydrates is largely controlled by the partial pressure of the water vapor released on decomposition. Thus, absence of thermodynamic data for a given hydrate certainly does not imply its nonexistence. In addition, Haruhiko[7] and others have studied deuterated forms, $\text{CuSO}_4\cdot n\text{D}_2\text{O}$. To estimate the thermodynamics of these deuterates using the difference rule, resort can be made to the known[6,2] data for $\Delta_f H^\circ(\text{CuSO}_4\text{, s})$ and $\Theta_{\text{Hf}}\{\text{D}_2\text{O, s}-\text{s}\}$ ($= -307.8\ \text{kJ}\cdot\text{mol}^{-1}$, Table 1, ref 2, although based only on three example salts) and the use of eq 2, L = D_2O, and $\Delta_f H^\circ(\text{CuSO}_4\cdot n\text{D}_2\text{O,s})$ can then be estimated.

From the solvate difference rule, we predict that the reactions

$$\text{MgSO}_4\cdot 2\text{H}_2\text{O(s)} + \text{MgSO}_4\cdot 6\text{H}_2\text{O(s)} \rightarrow 2\text{MgSO}_4\cdot 4\text{H}_2\text{O(s)} \quad (11)$$

$$\text{MgSO}_4\cdot 2\text{H}_2\text{O(s)} + \text{MgSO}_4\cdot 6\text{H}_2\text{O(s)} \rightarrow \text{MgSO}_4\cdot 3\text{H}_2\text{O(s)} + \text{MgSO}_4\cdot 5\text{H}_2\text{O(s)} \quad (12)$$

are expected to be thermoneutral. The first reaction is exothermic by 10 kJ·mol^{-1} (i.e., $\Delta H^\circ_{\text{reaction}}(11)/\text{kJ}\cdot\text{mol}^{-1} = -10$) with insufficient data in the literature to calculate corresponding Gibbs energy, entropy, or heat capacity changes for reaction 11. In the related absence of data[18] for reaction 12, we cannot quantitatively determine anything about this reaction. However, as evidenced by the absence of Gibbs energy data for the tetrahydrate (as well as the other quantities above), we cannot assume lack of stability or anything else because the tetrahydrate most assuredly is known and its enthalpy of formation available in our tables. Further, the existence of the monohydrate belies any assumption that "odd" hydrates are necessarily, but enigmatically, more stable for copper(II) sulfates in that both "even" and "odd" hydrates are known for magnesium species. Indeed, we do mean "odd hydrates" for MgSO_4 in that enthalpy of formation, Gibbs energy, and absolute entropies are known for both crystalline and amorphous monohydrate! The two sets of values differ by 27 kJ·mol^{-1}, 24 kJ·mol^{-1}, and 12 J·mol^{-1}·K^{-1}. The direct application of the thermodynamic difference rule, at first sight, would have suggested the sets of values would be the same for the two solid forms (Table 2). That there is a difference suggests that we need to distinguish between $\Theta_P\{\text{s}-\text{s}\}$ and $\Theta_P\{\text{am}-\text{s}\}$, where am = amorphous. Unless we do this, there is an inherent limitation as to the accuracy of the preferred rule. It also suggests a first principles proof would be lacking unless structural details are suppressed (or cancel out).

Table 2. Standard Enthalpies of Formation, $\Delta_f H^\circ$/kJ·mol^{-1}, Standard Gibbs Energies, $\Delta_f G^\circ$/kJ·mol^{-1}, and Absolute Entropies S°/J·K^{-1}·mol^{-1} for $\text{MgSO}_4\cdot\text{H}_2\text{O}$ in Its Crystalline and Amorphous Forms[a]

	$\Delta_f H^\circ$ kJ·mol^{-1}	$\Delta_f G^\circ$ kJ·mol^{-1}	S° J·K^{-1}·mol^{-1}
$\text{MgSO}_4\cdot\text{H}_2\text{O(s)}$	− 1602.1	− 1428.7	126.4
$\text{MgSO}_4\cdot\text{H}_2\text{O(am)}$	−1574.9	− 1404.9	138.1

[a] All data are from ref 6.

Application to Investigate Internal Bonding. Another aspect of the difference rule manifests itself when considering the compound Mg(OH)_2, in which the water is more intimately bound than is the case within the hydrate $\text{MgO}\cdot\text{H}_2\text{O}$. From the difference rule, we can estimate that $\Delta G_{\text{reaction}}$ (13) for the process

$$\text{MgO(s)} + \text{H}_2\text{O(g)} \rightarrow \text{MgO}\cdot\text{H}_2\text{O(s)} \quad (13)$$

is given by[3]

$$\Delta G_{\text{reaction}}(13)/\text{kJ}\cdot\text{mol}^{-1} = [\Theta_{\text{Gf}}\{\text{H}_2\text{O, s}-\text{s}\} - \Delta_f G(\text{H}_2\text{O, g})] \approx [242.2 - (-228.06)] = -13.8 \quad (14)$$

and corresponding to the average value for conversion of gaseous to hydrated water in the majority of hydrates (Table 6, column 4, in ref 3). In contrast, $\Delta G_{\text{reaction}}$ (13) for the process in which gaseous water is constitutively bound into the lattice of Mg(OH)_2 in the process

$$\text{MgO(s)} + \text{H}_2\text{O(g)} \rightarrow \text{Mg(OH)}_2\text{(s)} \quad (15)$$

$$\Delta G_{\text{reaction}}(15)/\text{kJ}\cdot\text{mol}^{-1} = [\Delta_f G(\text{Mg(OH)}_2\text{, s}) - \Delta_f G(\text{MgO, s}) - \Delta_f G(\text{H}_2\text{O, g})] \approx [-833.6 - (-568.9) - (-228.06)] = -36.1 \quad (16)$$

where an additional 22 kJ·mol^{-1} of Gibbs energy stability over that of monohydrate formation is identified.

Application Using Data Involving Multiple Inorganic Salts. Relationships Involving Hydrates of More than One Parent. To the extent that $\Theta_P\{\text{L, p}-\text{p}\}$ may be assumed to be a constant, another immediate corollary is

$$P\{\text{M}_\text{p}\text{X}_\text{q}\cdot\text{jL, p}\} + P\{\text{M}'_\text{r}\text{X}'_\text{s}\cdot\text{kL, p}\} \approx P\{\text{M}_\text{p}\text{X}_\text{q}\cdot\text{kL, p}\} + P\{\text{M}'_\text{r}\text{X}'_\text{s}\cdot\text{jL, p}\} \quad (17)$$

for two arbitrary salts $\text{M}_\text{p}\text{X}_\text{q}$ and $\text{M}'_{\text{r}'}\text{X}'_\text{s}$, and so is

$$P\{M_pX_q\cdot jL, p\} + P\{M'_rX'_s\cdot kL, p\} \approx P\{M_pX_q\cdot dL, p\} + P\{M'_rX'_s\cdot sL, p\} \quad (18)$$

for arbitrary salts with arbitrary solvation as long as the total number of solvent molecules $j + k = d + s$ once again. Many examples may be given where the best agreement may probably be expected for those cases where X and X′ are the same. After all, the value of P was shown to have some dependence on the type of salt, e.g., “sulfates”. Use of the difference rule in the form of eqs 17 and 18 can be used to produce the missing data for $\Delta_fH°$ for the tri- and pentahydrates of $MgSO_4$ discussed above in relation to reaction 12, such that

$$\Delta_fH°(MgSO_4\cdot 3H_2O, s)/kJ\cdot mol^{-1} = \Delta_fH°(MgS_2O_3\cdot 3H_2O, s) + \Delta_fH°(MgSO_4\cdot 6H_2O, s) - \Delta_fH°(MgS_2O_6\cdot 6H_2O, s) = [-1948.1 - 3087.0 - (-2848.5)] = -2186.6 \quad (19)$$

This equation represents a use of the newly reported aspect of the Difference Rule as illustrated in both eqs 17 and 18, namely, that using solvates of *more than one parent* can establish needed relationships. The rule, in this form, considerably increases the scope for cross-checking data as well as providing estimates of elusive data for limited, and other, solvate data sets.

$$\Delta_fH°(MgSO_4\cdot H_2O, s)/kJ\cdot mol^{-1} = \frac{1}{2}[\Delta_fH°(MgSO_4\cdot 2H_2O, s) + \Delta_fH°(MgSO_4\cdot 4H_2O, s)] = \frac{1}{2}[(-1896.2 + (-2496.6)] = -2196.4 \quad (20)$$

$$\Delta_fH°(MgSO_4\cdot 5H_2O, s)/kJ\cdot mol^{-1} = \frac{1}{2}[\Delta_fH°(MgSO_4\cdot 6H_2O, s) + \Delta_fH°(MgSO_4\cdot 4H_2O, s)] = \frac{1}{2}[(-3087.0) + (-2496.6)] = -2791.8 \quad (21)$$

Averaging the values for $\Delta_fH°(MgSO_4\cdot 3H_2O,s)/kJ\cdot mol^{-1}$ gives a value of −2191.5 and renders the calculation of $\Delta H°_{reaction}(12)$ for reaction 12 now possible, leading to confirmation of thermoneutrality: $\Delta H°_{reaction}(12)/kJ\cdot mol^{-1} \sim -0.6$, almost thermoneutral.

Accordingly, consider now $CuSO_4\cdot 2H_2O$. We may approximate its enthalpy of formation in numerous ways, e.g., by assuming thermoneutrality for the reaction

$$2CuSO_4\cdot H_2O(s) \rightarrow CuSO_4(s) + CuSO_4\cdot 2H_2O(s) \quad (22)$$

or by assuming thermoneutrality for the reaction

$$CuSO_4(s) + MgSO_4\cdot 2H_2O(s) \rightarrow MgSO_4(s) + CuSO_4\cdot 2H_2O(s) \quad (23)$$

From reaction 22 we assume that

$$\Delta H\circ_{reaction}(22)/kJ\cdot mol^{-1} = \Delta_fH°(CuSO_4\cdot 2H_2O, s) + \Delta_fH°(CuSO_4, s) - 2\Delta_fH°(CuSO_4\cdot H_2O, s) \approx 0 \quad (24)$$

so that

$$\Delta_fH°(CuSO_4\cdot 2H_2O, s)/kJ\cdot mol^{-1} \approx 2\Delta_fH°(CuSO_4.H_2O, s) - \Delta_fH°(CuSO_4, s) = [2(-1085.83) - (-771.36)] = -1400.3 \quad (25)$$

while from reaction 23 we find

$$\Delta_fH°(CuSO_4\cdot 2H_2O, s)/kJ\cdot mol^{-1} \approx \Delta_fH°(MgSO_4\cdot 2H_2O, s) + \Delta_fH°(CuSO_4, s) - \Delta_fH°(MgSO_4, s) = [-(1896.2) + (-771.36) - (-1284.9)] = -1382.7 \quad (26)$$

in reasonably good agreement to within 18 kJ·mol^{-1}.

Some Limitations of the Application. In the section above, we have seen typical levels of uncertainty in predicted values as generated by the difference rule. At this point, therefore, we need to inject a note of caution. For inorganic applications, similar uncertainties to the above, of the order of 18 kJ·mol^{-1}, in predicted ΔG values would create an uncertainty of almost 3 orders of magnitude in any predicted solubilities. This would then render such solubility prediction as meaningless from a solution chemistry point of view (Editor Ken Marsh informs us that Robin Stokes (to whom this article is dedicated) often expressed his concern that it takes only small differences in the Gibbs energy to change the solubility by a large amount). Broad predictive schemes, such as this one, cannot be expected to account for factors such as changes in coordination number, steric hindrance, or other important chemical behavior. Nevertheless, when experimental data are simply not available, resorting to derivations such as this one, based on a theoretical model, is much better than having nothing at all. In cases where thermodynamics is silent by virtue of lack of data, then the thermodynamic difference rule may be used to offer useful indicative results.

Application to Minerals and Double Salts. Mineralogical Applications and the Cascade Rule. In the mineralogical arena and in usage designed to probe the interrelation of thermodynamics for multiple complex inorganic salts, the difference rule also has its place. Consider Table 3 which assembles data for the free energy of formation of various materials based on $Cu(OH)_2(s)$ and $CuSO_4(s)$. Using this data and taking $M_pX_q = CuSO_4(s)$ and $M'_rX'_s = Cu(OH)_2(s)$, we can demonstrate that a further general rule exists, namely

$$P\{M_pX_q\cdot jM'_rX'_{s,}s\} \approx P\{M_pX_q, s\} + j \quad \Theta_P\{M'_rX'_{s,}s{-}s\} \quad (27)$$

In this case, the salt $M'_rX'_s$ is considered to “solvate” M_pX_q, thereby taking the role of L, the bound solvent, in eq 2, for example. Equally well we might regard the salt M_pX_q as “solvating” $M'_rX'_s$ so that

$$P\{M'_rX'_s\cdot dM_pX_q, s\} \approx P\{M'_rX'_s, s\} + d \quad \Theta_P\{M_pX_q, s{-}s\} \quad (28)$$

These rules can be employed for compounds involving multiple salts to estimate unknown data once $\Theta_P\{M_pX_q, s{-}s\}$ and $\Theta_P\{M'_rX'_s, s{-}s\}$ have been established.

Table 3. Standard Gibbs Energies, $\Delta_fG°/kJ\cdot mol^{-1}$, for $CuSO_4/Cu(OH)_2$ Salts

compound	$\Delta_fG°$ kJ·mol^{-1}
$Cu(OH)_2(s)$	− 359.0[a]
$CuSO_4(s)$	− 661.8[b]
$CuSO_4\cdot 2Cu(OH)_2(s)$ “antlerite”	− 1446.6[b]
$CuSO_4\cdot 3Cu(OH)_2(s)$ “brochantite”	− 1817.7[b]
$CuSO_4\cdot 3Cu(OH)_2\cdot H_2O(s)$ “langite”	− 2044.0[b]
$Cu(OH)_2\cdot (1/2)CuSO_4(s)$	= −1446.6/2 = −723.3[c]
$Cu(OH)_2\cdot (1/3)CuSO_4(s)$	= −1817.7/3 = −605.9[c]

[a] Ref 19. [b] Ref 6. [c] Derived from values elsewhere in this table.

Table 4. Experimentally Determined Standard Enthalpies of Formation[a], $\Delta_f H°$/kJ·mol^{-1} of 1-Bromoalkanes, $CH_3CH_2(CH_2)_nBr$[b], in the Gaseous and Liquid Phases[c]

		kJ·mol^{-1}			
1-bromoalkane[a]	n	A[b]	B[b]	C	D
CH_3Br	–	− 35.4	− 59.8	–	–
CH_3CH_2Br	0	− 61.9	− 90.5	0	0
$CH_3CH_2CH_2Br$	1	− 87.0	− 121.9	− 25.1	− 31.4
$CH_3CH_2(CH_2)_2Br$	2	−107.1	− 143.8	− 45.2	− 53.3
$CH_3CH_2(CH_2)_3Br$	3	− 128.9	− 170.2	− 66.1	− 79.7
$CH_3CH_2(CH_2)_4Br$	4	− 148.2	− 194.2	− 86.3	− 103.7
$CH_3CH_2(CH_2)_5Br$	5	−167.8	− 218.4	− 105.9	− 127.9
$CH_3CH_2(CH_2)_6Br$	6	− 189.3	− 245.1	− 127.4	− 154.6
$CH_3CH_2(CH_2)_{10}Br$	10	− 269.9	− 344.7	− 208.0	− 254.2
$CH_3CH_2(CH_2)_{14}Br$	14	−350.2	− 444.5	− 288.3	− 354.0

[a] The various 1-bromoalkanes (save methyl bromide/bromomethane) are all written as $CH_3CH_2(CH_2)_nBr$ rather than as $CH_3(CH_2)_pBr$ ($p = n + 1$) to emphasize that they are formally derived from ethyl bromide, not methyl bromide, by the addition of CH_2 groups. [b] Values assembled from data in Pedley.[28] [c] A = [$\Delta_f H°(CH_3CH_2(CH_2)_nBr,g)$]. B = [$\Delta_f H°(CH_3CH_2(CH_2)_nBr,l)$]. C = [$\Delta_f H°(CH_3CH_2(CH_2)_nBr,g) - \Delta_f H°(CH_3CH_2Br,g)$]. D = [$\Delta_f H°(CH_3CH_2(CH_2)_nBr,l) - \Delta_f H°(CH_3CH_2Br,l)$].

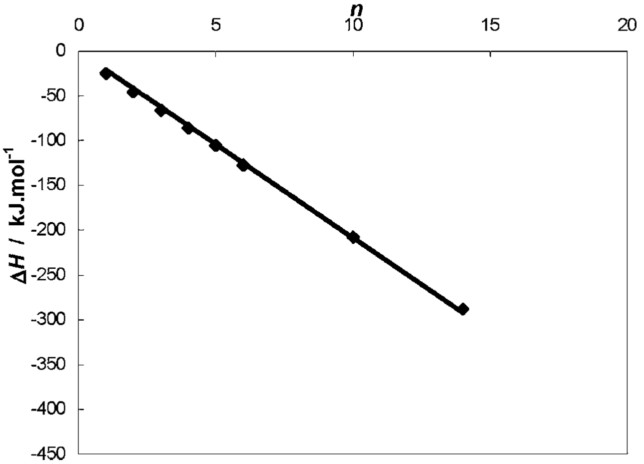

Figure 2. Plot of [$\Delta_f H°(CH_3CH_2(CH_2)_nBr, g) - \Delta_f H°(CH_3CH_2Br, g)$] = ΔH/kJ·mol^{-1} as ordinate versus number of additional methylene groups beyond CH_3CH_2Br, n, present in the linear 1-bromoalkane chain, as abscissa. (The line is constrained to pass through the origin.)

From data in Table 2, we can establish plots of $\Delta_f G°(CuSO_4 \cdot kCu(OH)_2,s)$ versus k ($k = 0$, 2 and 3) and of $\Delta_f G°(Cu(OH)_2 \cdot sCuSO_4,s)$ versus s ($s = 1/k = 0$, 0.333, 0.5), both having correlation coefficients $R^2 = 0.9998$ with parameters

$$\Delta_f G°(CuSO_4 \cdot kCu(OH)_2, s)/kJ \cdot mol^{-1} = -386.3k - 664.8 \quad (29)$$

$$\Delta_f G°(Cu(OH)_2 \cdot sCuSO_4, s)/kJ \cdot mol^{-1} = -730.4s - 359.9 \quad (30)$$

and with intercepts close to the values (Table 2) of $\Delta_f G°(CuSO_4, s)$ and $\Delta_f G°(Cu(OH)_2, s)$, respectively, as is required by the difference rule. The above rules 27 and 28 therefore provide a scope for the estimation of much missing data for complex salts and for minerals. These rules can be "cascaded" further to treat more complex examples such as the compound $CuSO_4 \cdot 3Cu(OH)_2 \cdot H_2O(s)$, for which data are available (Table 3), which can be considered also to be a hydrate of $CuSO_4 \cdot 3Cu(OH)_2(s)$ where

$$\Delta_f G°(CuSO_4 \cdot 3Cu(OH)_2 \cdot H_2O, s) - \Delta_f G°(CuSO_4 \cdot 3Cu(OH)_2 s)/kJ \cdot mol^{-1} = \Theta_{Gf}\{H_2O, s{-}s\} \approx (-2044.0 - (-1817.7)) \approx -226.3 \quad (31)$$

$\Theta_{Gf}\{H_2O, s{-}s\}$ has earlier been established (from data on 93 salts, see Table 1 ref 2) to be −242.4 kJ·mol^{-1}, reasonably close to the value calculated in eq 31 considering the complexity of the material. A further extension of the above is the development of a Cascade Rule in the form

$$P\{M_pX_q \cdot M'_pX'_q \cdot jM'_rX'_s, s\} \approx P\{M_pX_q \cdot M'_pX'_q, s\} + j \cdot \Theta_P\{M'_rX'_s, s{-}s\} \approx P\{M_pX_q, s\} + \Theta_P\{M'_pX'_q, s{-}s\} + j \cdot \Theta_P\{M'_rX'_s, s{-}s\} \quad (32)$$

and permutations thereon.

Applications in Organic Chemistry. Application to 1-Bromoalkanes. The apparent independence of structure may appear surprising. Consider the case where $p = q = 1$, M = CH_3CH_2 (rather than CH_3[26,27]), X = Br (although this is quite arbitrary), and L = CH_2. Most assuredly, in this case, the $MX \cdot nL$ species are *not* salts, and CH_2 is *not* a typical ligand. Yet, here again, the Difference Rule works where it is "assumed" that CH_2 is a ligand and the 1-bromoalkanes are solvates! Here there are enthalpy of formation data[29] for both the gas and liquid phases of 1-bromoalkanes ($CH_3CH_2(CH_2)_nBr$) for $n = 0$, 1, 2, 3, 4, 5, 6, 10, and 14 (see Table 4). We consider now making a "difference plot" of [$\Delta_f H°(CH_3CH_2(CH_2)_nBr$, g) − $\Delta_f H°(CH_3CH_2Br$, g)]/kJ·mol^{-1} versus n, tantamount to regarding gaseous 1-bromoethane, CH_3CH_2Br, as the "parent", unsubstitued material, the -(CH_2)- methylene groups as the "ligand", and the gaseous 1-bromoalkanes ($n = 1$ to 6, 10, and 14), listed in Table 4, column 1, as the "solvated" material. The gradient of the plot would, by analogy, correspond to $\Theta_{Hf}\{CH_2, g{-}g\}$, which in turn should correspond to the gaseous "methylene increment" associated with such a homologous series.[29,30] Such a plot is made in Figure 2.

The plot has gradient $\Theta_{Hf}\{CH_2, g{-}g\}$/kJ·mol^{-1} = − 20.9 and correlation coefficient $R^2 = 0.999$, so that

$$[\Delta_f H°(CH_3CH_2(CH_2)_nBr, g) - \Delta_f H°(CH_3CH_2Br, g)]/kJ \cdot mol^{-1} = \Theta_{Hf}\{CH_2, g{-}g\} = -20.9n \quad (33)$$

Figure 3 shows a difference plot for the corresponding liquid species.

$$[\Delta_f H°(CH_3CH_2(CH_2)_nBr, l) - \Delta_f H°(CH_3CH_2Br, l)]/kJ \cdot mol^{-1} = \Theta_{Hf}\{CH_2, l-l\}n = -25.5n \quad (34)$$

Thus for which the correlation coefficient is $R^2 = 0.999$.

This leads to the relationship

$$[\Theta_{Hf}(CH_2, g{-}g) - \Theta_{Hf}\{CH_{2,}l{-}l\}]/kJ \cdot mol^{-1} = -20.9 - (-25.5) = 4.6 \quad (35)$$

discussed below.

Thus we see the application of the Difference rule in *organic* thermochemistry. It is acknowledged here that the above results are similar to classic organic textbook examples derived from organic group additivity rules, and it is true that the difference rule could equally well be considered as an extension into the inorganic arena of well-known group additivity rules. The important point here though is that the two different starting points: the organic group additivity approach and the inorganic difference rule (which has its origins in the observed patterns in thermodynamic data arising initially in the inorganic hydrates) converge to yield similar

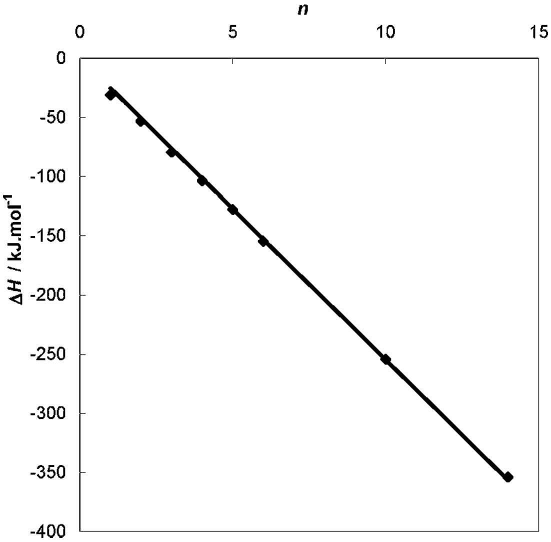

Figure 3. Plot of $[\Delta_f H°(CH_3CH_2(CH_2)_nBr, l) - \Delta_f H°(CH_3CH_2Br, l)] = \Delta H$ as ordinate versus number of additional methylene groups beyond CH_3CH_2Br, n, present in the linear 1-bromoalkane chain, as abscissa. (The line is constrained to pass through the origin.)

conclusions and so are thereby both mutually strengthened as theoretical concepts.

Application to Obtain Physical Thermodynamic Properties. Application to Enthalpies of Vaporization, Fusion, and Sublimation. Further, subtraction of eq 34 from eq 33 leads us to

$$[\Delta_f H°(CH_3(CH_2)_nBr, g) - \Delta_f H°(CH_3(CH_2)_nBr, l] - [\Delta_f H°(CH_3CH_2Br, g) - \Delta_f H°(CH_3CH_2Br, l)]/kJ \cdot mol^{-1} \approx [\Theta_{Hf}\{CH_2, g-g\} - \Theta_{Hf}\{CH_2, l-l\}]n = [\Delta_{vap}H°(CH_3CH_2(CH_2)_nBr, l) - \Delta_{vap}H°(CH_3CH_2Br, l)] \approx \Theta_{Hvap}\{CH_2, l-l\}n \quad (36)$$

implying that a Difference plot can also be made from enthalpies of vaporization, $\Delta_{vap}H°$, of the appropriate liquids. A plot of $[\Delta_{vap}H°(CH_3CH_2(CH_2)_mBr, l) - \Delta_{vap}H°(CH_3CH_2Br, l)]/kJ \cdot mol^{-1}$ versus m for the 1-bromoalkanes has a gradient $\Theta_{Hvap}\{CH_2, l-l\} = 4.8\ kJ \cdot mol^{-1}$ and a correlation coefficient $R^2 = 0.999$. It should be noted that the difference in the gradients of Figures 2 and 3 is

$$[\Theta_{Hf}\{CH_2, g-g\} - \Theta_{Hf}\{CH_2, l-l\}]/kJ \cdot mol^{-1} = 4.6 \quad (37)$$

In other words, we have successfully regarded CH_3CH_2Br as the basic substrate (parent) onto which additional $(CH_2)_m$ ligands are attached.

The thermodynamic terms associated with the structural element of the parent structure cancel out, while those associated with the "ligand" portion remain and contribute to the value of the gradient of the plot, Θ_{Hf}. Although specific for the case of X = Br, the features are, however, quite general and so extends the treatment of inorganic salts also. There are no enthalpies of formation data for bromide species $CH_3(CH_2)_nBr$ with values of n other than those listed in Table 4. There are also no data showing any equilibration between species with differing values of n and/or X = Br with species with other X; i.e., reactions that take the form

$$CH_3(CH_2)_jBr(g) + CH_3(CH_2)_kBr(g) \rightarrow CH_3(CH_2)_dBr(g) + CH_3(CH_2)_sBr(g) \quad (38)$$

where j + k = d + s or

$$CH_3(CH_2)_jBr(g) + CH_3(CH_2)_kOH(g) \rightarrow CH_3(CH_2)_kBr(g) + CH_3(CH_2)_jOH(g) \quad (39)$$

We doubt many chemists would infer the absence of such species as $CH_3(CH_2)_8Br$ and $CH_3(CH_2)_9Br$, and indeed both are well-established compounds to the organic chemist. It would appear in these cases the barrier for interconversion is simply too high.

In our discussion of 1-bromoalkanes and cycloalkanes, we chose the methylene group, CH_2, for explicit emphasis. This was done to parallel our discussion of species containing water, i.e. hydrates with H_2O, because of their formally analogous stoichiometry as nonmetal dihydrides. However, there are many other organic groups with their so-related (near) additivity of enthalpic and entropic contributions, as well as other thermochemical quantities such as heat capacity. Such groups include CH_3 and CH, the latter in distinct manifestations such as found in tertiary carbon $C-H(C)_3$, in branched alkanes, and in terminal alkynes $C_t-(H)$ and in benzene derivatives, polynuclear hydrocarbons, and aromatics in general, $C_B-(H)$. We may thus recognize our solvate difference rule as being related to the group additivity methodology as pioneered by Benson and his co-workers[20-25] for the gas phase and more recently extended to liquids and solids. In that it is groups, and not only atoms and bonds, it may even be said that molecular mechanics (MM) of organic compounds is conceptually related to both the Benson group and our solvate difference rule.

Application to Gas Phase Complexes and Clusters. We may even discuss those species in which the MX is *absent*. There are gas phase complexes of pure H_2O and those of pure CH_2. The former complexes are very labile, the structures floppy, species with different stoichiometries or should we say clusters with differing degrees of oligomerization readily interconverting and few ever studied at ambient temperature. Water is either extensively polymerized as in the liquid phase or in the multiple forms of ice or else is significantly depolymerized in the gas phase. Water clusters have also been prepared characterized by a variety of degrees of oligomerization and structures.[31] They are generally unstable and interconvert readily with each other and with the monomer: nonetheless, the lower members, at least, have consequences to atmospheric solar absorption and hence climate.

The clusters of CH_2 are generally much more stable with some conformational flexibility[32,33] (recall the puckering of the cyclobutane, the psuedorotation of cyclopentane, the rapidly interconverting chairs of cyclohexane, and the anomalous stability of cyclotetradecane corresponding to n = 4, 5, 6, 14). The dependence of stability on n has also been recognized: we recognize this as the differing strain energies of the cycloalkanes. However, interconversion between species with different values of n is essentially unknown except as a conceptual guide and mathematical model for strain energies[34] rather than recognized as a phenomenon of biomedical or chemical import.[35] The reader will note the word "generally". The n = 1 case of CH_2 is methylene, a highly reactive species and "the most indiscriminate reagent in organic chemistry",[36] paralleling the textbook description of water as "the universal solvent" and hence ligand L.

The revelation in this paper that standard enthalpies of vaporization, $\Delta_{vap}H°$, are indeed candidates for the application of the difference rule and thus that the difference property, P, can also be $\Delta_{vap}H°$ no doubt also means that related properties of fusion and sublimation can be treated similarly (i.e., P can also be $\Delta_{vap}G°$, $\Delta_{vap}S°$, $\Delta_{fus}H°$, $\Delta_{fus}G°$, $\Delta_{fus}S°$, $\Delta_{sub}H°$, $\Delta_{sub}G°$, and $\Delta_{\text{sub}}S°$). This observation extends the potential use of this important rule.

Application to Mixed Inorganic/Organic Materials. Application to Trialkylphosphates. We consider next some inorganic compounds having organic ligands. Enthalpies of vaporization, $\Delta_{\text{vap}}H°$, have recently been determined[37] for a series of trialkylphosphates, $(R{-}O)_3{-}P = O$ where R = CH_3 (TMP); CH_3CH_2 (TEP); $CH_3(CH_2)_3$ (TBP); $CH_3(CH_2)_4$ (TAP); $CH_3(CH_2)_5$ (THP); as well as for branched chain trialkylphosphates, R = $(CH_3)_2CHCH_2$ (TiBP); R = $(CH_3)_3CCH_2$ (TsBP), $(CH_3)_2CH(CH_2)_2$ (TiAP); and R = $(CH_3)_3C(CH_2)_2$ (TsAP). It is noteworthy that no values are reported for tripropylphosphate (TPP, $CH_3(CH_2)_2{-}O)_3{-}P{=}O$), nor any higher trialkylphosphates (e.g., triheptyl (THpP), trinonyl (TNP),..., etc), nor for any "hybrids" or "mixed" species having alkyl chains of differing lengths (e.g., methyldiethylphosphate, $(CH_3CH_2{-}O)_2(CH_3{-}O)P{=}O$ (MDEP) or butyldipropylphosphate $(CH_3(CH_2)_3{-}O)(CH_3(CH_2)_2{-}O)_2P{=}O$ (BDPP)). Here we can establish the validity of the difference rule using $\{\Delta_{\text{vap}}H°[(CH_3CH_2(CH_2)_n{-}O)_3P{=}O, l] - \Delta_{\text{vap}}H°[(CH_3CH_2{-}O)_3P{=}O, l]\}$ values using the basic data for the series $n = 0$ (TEP), $n = 2$ (TBP), $n = 3$ (TAP), and $n = 4$ (THP) and noting that the *total* number of -CH_2- "ligands", m, involved in the compounds is equal to $3n$ in each case. By adopting (TEP), $(CH_3CH_2{-}O)_3P{=}O$ as the "parent" rather than (TMP) $(CH_3{-}O)_3P{=}O$, we are, as discussed in the case of the alkyl bromides above, once again avoiding the use of the first member of the homologous series as the reference (parent) compound. Plotting against m rather than n, we find that

$$\{\Delta_{\text{vap}}H°[(CH_3CH_2(CH_2)_n - O)_3P{=}O, l] - \Delta_{\text{vap}}H°[(CH_3CH_2 - O)_3P{=}O, l]\}/\text{kJ}\cdot\text{mol}^{-1} \approx \Theta_{\text{Hvap}}\{CH_{2,}l{-}l\}m = 3.8m \quad (40)$$

with correlation coefficient $R^2 = 0.997$ (based on the data in column 5 of ref 31).[38] As might be anticipated, the value $\Theta_{\text{Hvap}}\{CH_2, l{-}l\}(= 3.8\ \text{kJ}\cdot\text{mol}^{-1})$ is similar in magnitude to the value ($\Theta_{\text{Hvap}}\{CH_2, l{-}l\} = 4.8\ \text{kJ}\cdot\text{mol}^{-1}$) determined above for the alkyl bromides. A value for the missing $\Delta_{\text{vap}}H°[(CH_3(CH_2)_2{-}O)_3P{=}O, l]$ (TPP, $n = 1$, $m = 3$) can now be established using the rule, and $\Delta_{\text{vap}}H°$ for further (higher) homologues can also be estimated, e.g., $m = 15$ (triheptyl phosphate, THpP). *More significantly, however*, if we interpolate $\Delta_{\text{vap}}H°$ values for other values of m = 1, 2, 4, 5, 7, 8,..., etc., these will correspond to estimates of $\Delta_{\text{vap}}H°$ for diethyl(propyl)phosphate (DEPP) when $m = 1$; ethyldipropylphosphate (EDPP) when $m = 2$; butyldipropylphosphate (BDPP) when $m = 4$, etc. Thus, the difference rule can be used to estimate *mixed R chain data* from experimental data only from compounds where each of the three alkyl chains is of identical length. This again illustrates the versatility of the difference rule approach.

In general, we conclude that the absence of a solvate with a given stoichiometry (i.e., n value) may reflect a low energy barrier separating solvates with a nearby stoichiometry or, and this is most likely, a lack of interest by the scientific community to the extent that the compound has received no attention or else that experimental conditions (pressure and temperature, etc.) have not been chosen conducive to its appearance.

Applications in Other Areas. In the case of highly energetic materials, inclusion of solvate molecules often significantly influences the sensitivity of such materials, and it is anticipated this rule may find application there also.

Conclusion

The additivity principle, which implies that a polyatomic group (or "ligand") exhibits the same contribution, independent of its microenvironment, remains highly attractive since it substantially simplifies interpretation of experimental data and enables further extensions and inferences to be made which lead to thermodynamic data which are close to measured quantities and the experimental reality. Accordingly, the problems arising from the paucity of thermochemical data for contemporary compounds and novel materials of scientific interest and importance are ameliorated.

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(26) Note here that M is chosen to be CH_3CH_2 rather than CH_3 (although in the case of the 1-bromoalkanes, this makes little difference to the outcome).[27] The choice is influenced by the well-known observation that the Me-Et difference in a property is quite often slightly anomalous when compared to those between the higher homologues, a situation exacerbated when the alkyl group is affixed to a significantly electropositive element, e.g., Li and Zn. Cf. the discussions in: Slayden, S. W.; Liebman, J. F. Thermochemistry of Organolithium Compounds. In *The Chemistry of Organic Lithium Compounds*; Rappoport, Z., Marek, I., Eds.; Wiley: Chichester, 2004; pp 121−136. Liebman, J. F.; Slayden, S. W. Thermochemistry of Organozinc Compounds. In *The Chemistry of Organozinc Compounds*; Rappoport, Z., Marek, I., Eds.; Wiley: Chichester, 2006; pp 135−145.

(27) The plot of the difference function: $[\Delta_f H°(CH_3CH_2(CH_2)_n Br, g) - \Delta_f H°(CH_3CH_2Br, g)]$ as ordinate versus number of methylene groups, n, in the linear 1-bromoalkane chain as abscissa has a correlation coefficient, $R^2 = 0.995$, and analytical form: $[\Delta_f H°(CH_3CH_2(CH_2)_n Br, g) - \Delta_f H°(CH_3CH_2Br, g)] = \Theta_{Hf}\{CH_2, g-g\}\ n = -21.5\ n$ where $\Theta_{Hf}\{CH_2, g-g\}/kJ \cdot mol^{-1} = -21.5$ is (like that discussed in the text using $CH_3CH_2Br(l)$ as the "parent" and for which $\Theta_{Hf}\{CH_2, g-g\}/kJ \cdot mol^{-1} = -20.9$) close to that determined for the CH_2 increment for these species of (-20.67 ± 0.05) kJ·mol^{-1}.[29] If an analogous plot for the liquids is made, viz.: $[\Delta_f H°(CH_3(CH_2)_n Br, l) - \Delta_f H°(CH_3Br, l)]/kJ \cdot mol^{-1} = \Theta_{Hf}\{CH_2, l-l\}n$, then $\Theta_{Hf}\{CH_2, l-l\}/kJ \cdot mol^{-1} = -26.1$ (which compares closely to that found for the "CH_3CH_2Br" plot made in the text, where $\Theta_{Hf}\{CH_2, l-l\}/kJ \cdot mol^{-}{}_{1} = -25.5$, also $[\Theta_{Hf}\{CH_2, g-g\} - \Theta_{Hf}\{CH_2, l-l\}]/kJ \cdot mol^{-1} = 4.6$ (see eq 34 in text).

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(35) (a) The reversible dimerization of olefins to form cyclobutanes (substituted counterparts of $2 \cdot (n = 2) \rightarrow n = 4$) is a rare example of this interconversion of an import. A recent review of the biomedical consequences of this is discussed in: (b) Friedel, M. G. Gierlich, J.; Carell, T. Cyclobutane Pyrimidine Dimers as UV-Induced DNA Lesions. In *The Chemistry of Cyclobutanes*; Rappoport, Z., Liebman, J. F., Eds.; Wiley: Chichester; 2005, pp 1031−1058.

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(38) It is worth noting here that in the case of the phosphates if $\{\Delta_{vap}H°[(CH_3(CH_2)_n-O)_3P{=}O, l] - \Delta_{vap}H°[(CH_3-O)_3P{=}O, l]\}/kJ \cdot mol^{-1}$ is used as the difference function (i.e., it is based on trimethyl phosphate, TMP), the result is much the same, since $\Theta_{Hvap}\{CH_2, l-l\}/kJ \cdot mol^{-1}$ now equals 3.9 and the correlation coefficient for the fit is $R^2 = 0.998$.

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