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Volume-Based Thermodynamics: A Prescription for Its Application and Usage in Approximation and Prediction of Thermodynamic Data

Leslie Glasser*,† and H. Donald Brooke Jenkins*,‡

†Nanochemistry Research Institute, Department of Applied Chemistry, Curtin University, Perth 6845, Western Australia

‡Department of Chemistry, University of Warwick, Coventry, West Midlands CV4 7AL, United Kingdom

ABSTRACT: Thermodynamics, as both thermochemistry and thermophysics, is fundamental and central to the science of matter and, in particular, of condensed materials. While extensive data resources for thermodynamic quantities do exist, none of the experimental, simulation, or theoretical studies can keep pace with the rate of synthesis of new materials or provide reliable data for hypothesized materials. Correlation methods can fill this gap. We describe a range of recently developed correlation methods that rely on volume to predict thermodynamic quantities. In parallel with these, thermodynamic difference rules, which describe how properties of materials (say, of a group of solvates) may be inferred from corresponding properties of materials that neighbor them in composition, have recently been reviewed.

PREAMBLE: IMPORTANCE AND CURRENT STATUS OF VOLUME-BASED THERMODYNAMICS

Thermodynamics, as both thermochemistry and thermophysics, is fundamental and central to the science of matter and, in particular, of condensed materials. In principle, thermodynamics provides relations between its parameters (such as energy, entropy, etc.) while the parameters themselves are obtained by experimental measurement, statistical thermodynamic theory, simulations of various kinds, or correlations among related materials.

A large literature and an impressive set of databases[1−6] of values of the more familiar parameters (e.g., entropy, lattice energy, compressibility, etc.) exist, but neither experiment nor simulation can keep pace with the synthesis of new materials (e.g., the CAS has recently announced the 50 millionth addition to its chemical database). Experiment is unavailable for hypothesized materials, and computerized simulations may be both difficult and expensive, whether for real or hypothesized materials. For these reasons, correlation techniques of various kinds have always had a place in estimating data values and checking reported results. Indeed, correlation techniques have a long history, going back in modern times even to Mendeleev, who predicted the properties of undiscovered elements by relating them to their neighbors in his periodic table.

This paper reviews those techniques that correlate thermodynamic parameters with formula-unit volume [which we call volume-based thermodynamics and thermoelasticity (VBT)], principally for ionic materials, while those techniques that correlate parameters among related hydrated or solvated materials [termed thermodynamic difference rules (TDR)] have been reviewed independently.[7]

The most suitable form of correlation uses some well-known quantity as a surrogate for the parameter sought; in this context, formula-unit volume, V_m, is among the most accessible of physical quantities, as it can be obtained through diffraction techniques (favored as being the most precise), from density, or by a variety of estimation methods. Molar volume, V_{molar}, is related to V_m through the equation $V_m = V_{molar}/L$, where L is the Avogadro constant. There are many sources of data on V_m, in printed and electronic format, free or commercial.[3,8−16] For these reasons, VBT offers a valuable entry point into thermodynamic estimation and prediction. An early proponent of volume as a physical measure was Linus Pauling, who related bond properties to bond lengths (which are components of volume).

Estimation of Formula-Unit Volume and Molar Volume. Methods for estimating V_m and molar volume are illustrated in Scheme 1.

Wherever possible, V_m should be estimated from diffraction data using the volume of the unit cell divided by Z, the integral number of formula units in the unit cell.[17]

Surprisingly often in the older literature and even in some current databases, Z is not reported but must be inferred, perhaps using space group information,[18] by comparison with related materials, or by estimation of the volume. Alternatively and conveniently, V_m can be estimated from the combination of molar mass, M, and density, ρ, independent of Z:

$$\begin{aligned} V_m/\mathrm{nm}^3 &= \frac{(V_{cell}/\mathrm{nm}^3)}{Z} \\ &= \frac{(V_{cell}/\mathrm{cm}^3\cdot\mathrm{mol}^{-1})}{602.2\cdot Z} \\ &= \frac{(M/\mathrm{g}\cdot\mathrm{mol}^{-1})}{602.2\cdot(\rho/\mathrm{g}\cdot\mathrm{cm}^{-3})} \end{aligned} \quad (1)$$

where the factor 602.2 converts between $\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$ and nm^3 per formula unit using the Avogadro constant.

It should be noted that the formula unit may consist of a group of identical molecules that are not related by symmetry (but in

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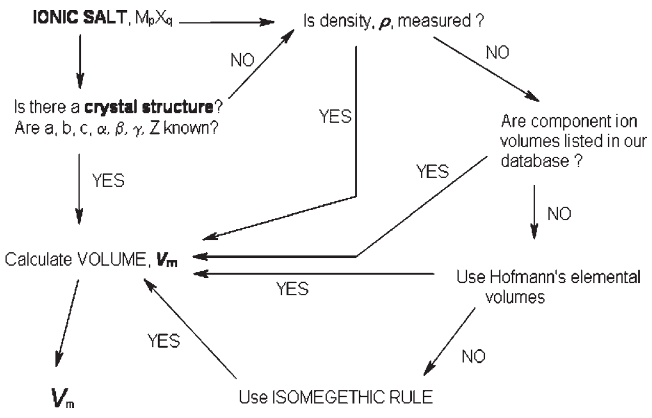
Scheme 1



only about 10 % of crystal structures), and this must be taken into account when assessing V_m.

Even when direct volume information is unavailable, there are a number of successful procedures by which V_m may be estimated. The most direct is simple summation of ion or group volumes, for which there are now considerable resources.[19−22] This summation replaces the earlier process of summation of volumes obtained from thermochemical radii; such radii were developed to provide a link between the size of nonspherical species (such as the planar nitrate anion) and thermochemical estimation using the Kapustinskii equation.

In another more direct summation process, the formula-unit volumes of components of which the material may be considered to consist are summed:[23,24] for example, ilmenite, $FeTiO_3$, may be considered as $FeO \cdot TiO_2$ for this purpose.

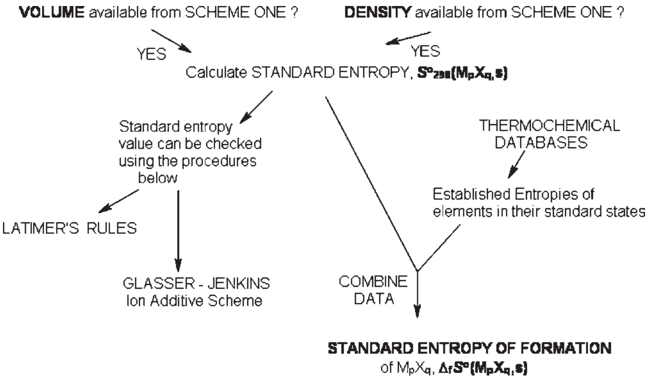
A very powerful but perhaps less reliable procedure is to use the "isomegethic rule",[20,25] which states that "ionic salts of the same empirical chemical formula having identical charge states (i.e., lattice ionic strength factors, I) will have approximately equal formula unit volumes, V_m". It follows that, since their formulas are identical and their volumes are approximately equal, so also will be their densities, ρ, lattice potential energies, U_{POT}, and standard absolute entropies, S°_m (see below).

Volume-Based Thermodynamics. The present authors, together with colleagues, have over recent years developed a number of VBT correlations that have gained considerable attention in providing bases for predicting and understanding thermodynamic quantities. The most direct of these are the correlations of standard molar entropy, S°_m, under ambient conditions with formula-unit volume (see Scheme 2)[26,27] for organic and inorganic solids and, separately, for ionic liquids,[28] i.e.,

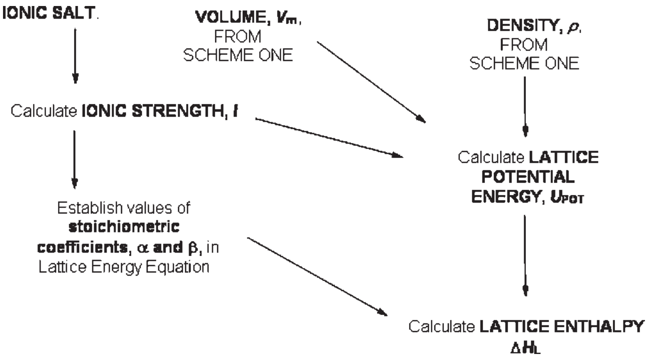
$$S^\circ_m = kV_m + c \qquad (2)$$

The constants k and c are specific for a given group of materials (ionic solids, ionic hydrates, minerals,[26] organic solids and liquids,[27] or ionic liquids[28]) and may be further improved by selection of closely related materials to form the correlation. A possibly more reliable elaboration for a mineral may be made by summing the entropies of component oxides with a correction term for the difference between the volume of the mineral and the volume sum of the component oxides.[29]

Scheme 2



Scheme 3



A step up in VBT sophistication is a volume-based procedure for the evaluation of lattice potential energies, U_{POT} (see Scheme 3). Lattice energies are of central importance in the estimation of enthalpies of formation via thermochemical cycles. Initially, Mallouk et al.[30] demonstrated that the lattice energy for simple binary ionic solids is related to the inverse cube root of the formula-unit volume, on the basis of the Kapustinskii lattice energy equation:

$$U_{POT} = \frac{Bz_+z_-n}{r_+ + r_-}\left(1 - \frac{\rho}{r_+ + r_-}\right) \qquad (3)$$

where n is the number of ions in the formula unit, r_+ and r_- are the cation and anion radii, respectively, and B and ρ are constants.

However, the charge product, z_+z_-, in Kapustinskii's lattice energy equation can be generalized for any ionic material by use of an ionic strength factor,[31] $I = {}^1/_2\sum_{i=1}^{t} n_i z_i^2$, allowing an extended VBT lattice energy correlation to be established:[31−35]

$$U_{POT} = 2I\left(\frac{\alpha}{V_m^{1/3}} + \beta\right) \qquad (4a)$$

where α and β are fitted constants.

This calculation becomes even more powerful and all-encompassing as the lattice energy increases beyond about 5000 $kJ \cdot mol^{-1}$ for ionic materials, at which point the Coulombic forces among the ions overwhelm all other forces of attraction. In this situation, the equation takes the following simple form:

$$U_{POT} = AI(2I/V_m)^{1/3} \qquad (4b)$$

where A = 121.39 $kJ \cdot mol^{-1} \cdot nm$ is the standard electrostatic Madelung constant of the Kapustinskii equation. It is remarkable that this equation contains *no* adjustable parameters whatsoever and depends on only the chemical formula, its integer charges, and the formula-unit volume.

A further enhancement of the calculation of lattice energy is the conversion of energy to enthalpy, as is generally required in thermochemical applications:[36]

$$\Delta_L H = U_{POT} + \sum_{i=1}^{n} s_i\left(\frac{c_i}{2} - 2\right)RT \qquad (5)$$

where $\Delta_L H$ is the lattice enthalpy, s_i is the number of ions of type i, n is the number of ion types in the formula unit, and c_i is defined according to whether ion i is monatomic ($c_i = 3$), linear polyatomic ($c_i = 5$), or nonlinear polyatomic ($c_i = 6$).

In the field of thermoelasticity, early work established linear relations between the logarithm of the bulk modulus, K_T, and the logarithm of the pair volume of ions, V_{pr}, but with widely differing slopes within classes of materials. However, the logarithms can be eliminated since the compressibility, β (which is the reciprocal of the bulk modulus), is linearly correlated with the pair volume within classes of materials.[37,56]

Acceptance of VBT and TDR. Since VBT and TDR are widely applicable across materials chemistry, providing otherwise unavailable data estimates, it is unsurprising that they have received wide acceptance in chemistry, being applied in areas such as energetic materials,[38] ionic liquids,[28,39] inorganic synthesis,[40−42] and explosives development.[41]

EXAMPLES OF THE APPLICATION OF VBT

We will estimate the thermodynamic properties of K_2PtCl_6 as a convenient example material.

Calculations of Volumes. *Example 1: For the Salt K_2PtCl_6, Obtain the Formula-Unit Volume, $V_m(K_2PtCl_6)/nm^3$.* Crystal structure data for the salt K_2PtCl_6 is available from a number of sources.[9] The crystal is cubic in the $Fm\bar{3}m$ space group (No. 225) with $Z = 4$. The variation in cell constant that may arise is seen in the following dated data:[9] a/nm = 0.966 (1926); 0.975 ± 3 (1928); 0.9754 (1933); 0.9745 (1935); 0.973 (1951); 0.9755 (precision result, 1955).

Using eq 1, we calculate that:

$$V_m/\text{nm}^3 = \frac{V_{cell}}{Z} = \frac{a^3}{Z} = \frac{(0.9755)^3}{4} = \frac{0.9283}{4} = 0.2321$$

The volume based on the above cell constants ranges from 0.2254 nm^3 to 0.2321 nm^3 (a range of about 2 %).

Example 2: Use the Measured Density of the K_2PtCl_6 Crystal To Determine $V_m(K_2PtCl_6)/nm^3$. The measured density of K_2PtCl_6 (M = 485.99 g·mol^{-1}) is cited[9] as 3.34 g·cm^{-3}. Using eq 1 gives:

$$V_m/\text{nm}^3 = \frac{(M/\text{g}\cdot\text{mol}^{-1})}{602.2\cdot(\rho/\text{g}\cdot\text{cm}^{-3})} = \frac{485.99}{602.2\cdot 3.34}$$
$$= 0.2416\ (4.1\ \%)$$

The Handbook of Chemistry and Physics,[3] on the other hand, cites a value of 3.50 for ρ/g·cm^{-3}. This more recent result leads to:

$$V_m/\text{nm}^3 = \frac{485.99}{602.2\cdot 3.50} = 0.2306\ (-0.7\ \%)$$

The latter value is very close to the volume obtained from diffraction data (see Example 1).

Example 3: Using Ion Volumes Given in VBT Tables,[32] Estimate $V_m(K_2PtCl_6)/nm^3$. Using the ion volume data $V(K^+)/\text{nm}^3 = 0.00394$ and $V(PtCl_6^{2-})/\text{nm}^3 = 0.219 \pm 0.009$ (given in Tables 4 and 5, respectively, of our published VBT tables[32]), we have:

$$\begin{aligned} V_m(K_2PtCl_6)/\text{nm}^3 &\approx 2[V(K^+)/\text{nm}^3] + [V(PtCl_6^{2-})/\text{nm}^3] \\ &= 2(0.00394) + (0.219 \pm 0.009) \\ &= 0.2269 \pm 0.009\ (-2.3\ \%) \end{aligned}$$

This estimated ion-sum volume is 2.3 % smaller than the diffraction value (see Example 1).

Example 4: Using Hofmann's Elemental Volumes,[19] Estimate $V_m(K_2PtCl_6)/nm^3$. Using the volumes of elements in molecular solids cited in Hofmann's paper (in Å^3), we have:

$$\begin{aligned} &V_m(K_2PtCl_6)/\text{nm}^3 \\ &\approx \left\{ 2[V(K)/\text{Å}^3] + [V(Pt)/\text{Å}^3] + 6[V(Cl)/\text{Å}^3] \right\}/1000 \\ &= [2(36 \pm 3) + (38 \pm 2) + 6(25.8 \pm 0.3)]/1000 \\ &= 0.265 \pm 0.01\ (+12\ \%) \end{aligned}$$

Since Hoffman's values were obtained from a general survey of crystal structure data, including organic solids, they are expected to be less reliable for ionic solids.

Example 5: Use the Isomegethic Rule To Estimate Unknown Volume Data for Salts or Individual Ions. Our ion volume tabulations[32] can be used as a convenient source of ion volume data for use with the isomegethic rule.[20,25] Although this rule is generally formulated in terms of neutral compounds, it satisfactorily handles ionic volume relationships for charged species.

Although an ion volume for our chosen example anion, $V(PtCl_6^{2-})/\text{nm}^3 = 0.219 \pm 0.009$, is included in Table 5 in ref 32, let us assume that this datum is *not* known for the purpose of illustrating the isomegethic rule. We describe how we can use the rule to estimate a value for $V(PtCl_6^{2-})$ using selected remaining ion volume data from Table 5.

"Isomegethically" we can write, for example:

$$V(PtCl_6^{2-}) + V(MX_6^{2-}) \approx V(PtX_6^{2-}) + V(MCl_6^{2-})$$

where M is any element for which $V(MCl_6^{2-})$ and $V(MX_6^{2-})$, the volumes of the hexachloride ion and one other hexahalogen ion, respectively, are known. The halogen X (X ≠ Cl) must be one for which the volume of the corresponding *hexahaloplatinate* ion, $V(PtX_6^{2-})$, is also available. In the choice of PtX_6^{2-}, X can be F, Br, or I. Once this choice of X is made, the nature of the counterion MX_6^{2-} whose volume we need is determined. The availability of volume data for MX_6^{2-} ions depends very much on X. Table 5 in ref 32 includes volumes for the following ions:

- 22 hexafluoride ions MF_6^{2-}, with M = Am, Ce, Co, Cr, Ge, Hf, Mn, Ni, Os, Pb, Pd, Pt, Re, Rh, Ru, Si, Sn, Tc, Th, Ti, U, or Zr;
- 21 hexachloride ions MCl_6^{2-}, with M = Ce, Ge, Ir, Mn, Mo, Nb, Os, Pb, Pd, Pu, Re, Ru, Se, Sn, Tc, Te, Th, Ti, U, W, or Zr;
- 12 hexabromide ions MBr_6^{2-}, with M = Mo, Os, Pd, Po, Pt, Re, Se, Sn, Tc, Te, Ti, or W;
- 5 hexaiodide ions MI_6^{2-}, with M = Po, Re, Sn, Tc, or Te. The underlined ions are ones for which diffraction data exist for at least two representative salts containing the anion, thus making it possible to estimate an error for the volume listed.

Two examples of the use of the isomegethic rule to estimate $V(PtCl_6^{2-})/\text{nm}^3$ are given. Table 1 shows the results obtained using $V(PtBr_6^{2-})/\text{nm}^3 = 0.258 \pm 0.006$ in the following

Table 1. Estimates of the Volume of the Solid-State Ion $PtCl_6^{2-}$ Based on $V(PtBr_6^{2-})/nm^3 = 0.258 \pm 0.006$

M	$[V(MCl_6^{2-}) - V(MBr_6^{2-})]/nm^3$	difference	$V(PtCl_6^{2-})/nm^3$
Mo	$[(0.225 \pm 0.007) - (0.266 \pm 0.003)]$	-0.041 ± 0.009	0.217 ± 0.011
Os	$[(0.223 \pm 0.008) - (0.261 \pm 0.004)]$	-0.038 ± 0.011	0.220 ± 0.013
Pd	$[(0.218 \pm 0.008) - (0.247 \pm 0.0014)]$	-0.029 ± 0.016	0.229 ± 0.017
Re	$[(0.224 \pm 0.007) - (0.263 \pm 0.003)]$	-0.039 ± 0.010	0.219 ± 0.012
Se	$[(0.229 \pm 0.007) - (0.267 \pm 0.004)]$	-0.038 ± 0.008	0.220 ± 0.010
Sn	$[(0.234 \pm 0.006) - (0.274 \pm 0.004)]$	-0.040 ± 0.009	0.218 ± 0.010
Tc	$[(0.219 \pm 0.002) - (0.259 \pm 0.001)]$	-0.040 ± 0.002	0.218 ± 0.006
Te	$[(0.244 \pm 0.005) - (0.286 \pm 0.002)]$	-0.042 ± 0.005	0.216 ± 0.008
Ti	$[(0.221 \pm 0.009) - (0.256 \pm 0.003)]$	-0.035 ± 0.009	0.223 ± 0.011
W	$[(0.222 \pm 0.001) - (0.263 \pm 0.006)]$	-0.041 ± 0.006	0.217 ± 0.008
		mean volume of $PtCl_6^{2-}/nm^3$:	0.219 (0.0 %)
		standard deviation/nm^3:	0.004

equation:

$$\begin{aligned} V(PtCl_6^{2-})/nm^3 &\approx \{V(PtBr_6^{2-}) + [V(MCl_6^{2-}) - V(MBr_6^{2-})]\}/nm^3 \\ &= (0.258 \pm 0.006) + [V(MCl_6^{2-}) - V(MBr_6^{2-})]/nm^3 \end{aligned}$$

The mean value from Table 1 is a highly accurate result with a small standard deviation. In the same vein, using $V(PtF_6^{2-})/nm^3 = 0.119 \pm 0.012$ as the reference and the relation

$$\begin{aligned} V(PtCl_6^{2-})/nm^3 &\approx \{V(PtF_6^{2-}) + [V(MCl_6^{2-}) - V(MF_6^{2-})]\}/nm^3 \\ &= (0.119 \pm 0.012) + [V(MCl_6^{2-}) - V(MF_6^{2-})]/nm^3 \end{aligned}$$

we find a mean volume of 0.226 nm^3 (2.7 %) for $PtCl_6^{2-}$, with a standard deviation of 0.018 nm^3. Use of this second set of data gives rise to a larger uncertainty because there is rather greater volume variability among cubic fluorometalates, as also among fluorides in general.

Thermodynamic Calculations. The relative error quoted in parentheses following each estimate below is based on the use of the corresponding NBS value[43] as the reference, unless otherwise specified.

Example 6: Calculate the Standard Entropy of K_2PtCl_6, $S^\circ_{298}(K_2PtCl_6)/J \cdot K^{-1} \cdot mol^{-1}$, Using the Volume Correlation (eq 2). The current literature value[43] is $S^\circ_{298} = 333.88\ J \cdot K^{-1} \cdot mol^{-1}$. The following experimental values for $S^\circ_{298}(K_2PtCl_6)/J \cdot K^{-1} \cdot mol^{-1}$ have been published: 333.9,[44] 329.7,[44] 333.9,[44] and 333.9.[43]

Inserting various estimates of $V_m(K_2PtCl_6)/nm^3$ into eq 2 and using the fitted values of the constants k and c for ionic solids,[26] we obtain the following values:

For the maximum volume, $V_m(K_2PtCl_6) = 0.2321\ nm^3$,

$$\begin{aligned} S^\circ_{298}(K_2PtCl_6) &\approx kV_m + c \\ &\approx (1360\ J \cdot K^{-1} \cdot mol^{-1} \cdot nm^{-3})(0.2321\ nm^3) + (15\ J \cdot K^{-1} \cdot mol^{-1}) \\ &= 330.7\ J \cdot K^{-1} \cdot mol^{-1}\ (-1\ \%) \end{aligned}$$

For the minimum volume, $V_m = 0.2254\ nm^3$

$$\begin{aligned} S^\circ_{298}(K_2PtCl_6) &\approx kV_m + c \\ &\approx (1360\ J \cdot K^{-1} \cdot mol^{-1} \cdot nm^{-3})(0.2254\ nm^3) + (15\ J \cdot K^{-1} \cdot mol^{-1}) \\ &= (321.5 \pm 12.2)\ J \cdot K^{-1} \cdot mol^{-1}\ (-3.7\ \%) \end{aligned}$$

Using Single-Ion Entropies. Latimer's rules[45] can be applied using data from his Appendix III, adding the appropriate elemental entropy contributions corrected for cation charge. Thus:

$$\begin{aligned} S^\circ_{298}(K_2PtCl_6)/J \cdot K^{-1} \cdot mol^{-1} \\ &\approx [2S(K) + S(Pt) + 6S(Cl)]/J \cdot K^{-1} \cdot mol^{-1} \\ &= 2(38.5) + 63.6 + 6(33.9) \\ &= 344.0\ (+2.9\ \%) \end{aligned}$$

Marcus[46] lists a series of single ion entropies that yield the following result:

$$\begin{aligned} S^\circ_{298}(K_2PtCl_6)/J \cdot K^{-1} \cdot mol^{-1} \\ &\approx [2S(K^+) + S(PtCl_6^{2-})]/J \cdot K^{-1} \cdot mol^{-1} \\ &= 2(36.9) + 316.3 \\ &= 390.1\ (+17\ \%) \end{aligned}$$

The database of recently estimated single-ion entropies[47] is useful for obtaining values for S°_{298} for compounds made up of the ions listed there, but it cannot be applied directly to this example since it does not contain data for the $PtCl_6^{2-}$ ion. We illustrate a way forward in such a case, provided that there is available at least one example salt containing a $PtCl_6^{2-}$ anion that has a known experimental standard entropy and contains a countercation featured in our single-ion database. The single-ion contribution for $S(PtCl_6^{2-})$ can thus be established and then used to predict the standard entropy of the target salt, K_2PtCl_6.

The entropy of a related salt is known:[43] $S^\circ_{298}(Na_2PtCl_6) = 312.0\ J \cdot K^{-1} \cdot mol^{-1}$. Using different databases, we can then establish the following estimates:

According to Latimer,[45] $S(Na^+)/J \cdot K^{-1} \cdot mol^{-1} = 31.4$ and $S(K^+)/J \cdot K^{-1} \cdot mol^{-1} = 38.5$. Hence,

$$\begin{aligned} S(K_2PtCl_6)/J \cdot K^{-1} \cdot mol^{-1} &= 2(38.5 - 31.4) + 312.0 \\ &= 326.2\ (-2.4\ \%) \end{aligned}$$

According to Mills (as quoted by Spencer[48]), $S(Na^+)/J \cdot K^{-1} \cdot mol^{-1} = 37.2$ and $S(K^+)/J \cdot K^{-1} \cdot mol^{-1} = 46.4$. Thus,

$$\begin{aligned} S(K_2PtCl_6)/J \cdot K^{-1} \cdot mol^{-1} &= 2(46.4 - 37.2) + 312.0 \\ &= 330.4\ (-1.1\ \%) \end{aligned}$$

Table 2. Literature Estimates of $U_{\mathrm{POT}}(\mathrm{K_2PtCl_6})/\mathrm{kJ\cdot mol^{-1}}$ and Methodologies Used

author (year of publication)	$U_{\mathrm{POT}}(\mathrm{K_2PtCl_6})/\mathrm{kJ\cdot mol^{-1}}$	method of calculation
Jenkins and Pratt (1977)[51]	1468	direct minimization method
DeJonge (1976)[52]	1337	extended Born−Landé equation
	1323	Born−Landé
Burgess and Cartwright (1975)[53]	1521	Born−Mayer equation
Lister, Nyburg and Poyntz (1974)[54]	1521	Kapustinskii equation
	1572	Kapustinskii equation
	1450	simple Born−Landé equation
	1274	extended Born−Landé equation
	1327	extended Born−Landé equation
	1461	empirical method
Hartley (1972)[55]	1598	Kapustinskii equation
	1540	simple Born−Landé equation
mean of tabulated values	1449	

According to Marcus,[46] $S(\mathrm{Na^+})/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = 22.5$ and $S(\mathrm{K^+})/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = 36.9$, so

$$\begin{aligned} S(\mathrm{K_2PtCl_6})/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} &= 2(36.9 - 22.5) + 312.0 \\ &= 340.8\ (+2.1\ \%) \end{aligned}$$

According to Glasser and Jenkins,[47] $S(\mathrm{Na^+})/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = 37.2$ and $S(\mathrm{K^+})/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = 50.5$. Hence

$$\begin{aligned} S(\mathrm{K_2PtCl_6})/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} &= 2(50.5 - 37.2) + 312.0 \\ &= 338.6\ (+1.4\ \%) \end{aligned}$$

Example 7: Calculate the Standard Entropy of K_2PtCl_6, S°_{298}(K_2PtCl_6)/J·K^{-1}·mol^{-1}, Using Density. The experimental density for $\mathrm{K_2PtCl_6}$ ($M = 485.99\ \mathrm{g\cdot mol^{-1}}$), $\rho(\mathrm{K_2PtCl_6})/\mathrm{g\cdot cm^{-3}}$, is cited[3] as being $3.50\ \mathrm{g\cdot cm^{-3}}$. Inserting the values into eq 2 and using the fitted constants appropriate for an ionic solid,[26] we obtain:

$$\begin{aligned} S^{\circ}_{298}(\mathrm{K_2PtCl_6})/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} &\approx k'\left[\frac{M/\mathrm{g\cdot mol^{-1}}}{\rho/\mathrm{g\cdot cm^{-3}}}\right] + c' \\ &= 2.258\left(\frac{485.99}{3.50}\right) + 15 \\ &= 328.5\ (-1.6\ \%) \end{aligned}$$

Example 8: Calculate the Ionic Strength, I, for the Salt K_2PtCl_6. The salt is of the $\mathrm{M_2X}$ type,[49] containing two cations, each with +1 charge, and an anion with a −2 charge. Thus:

$$I = {}^{1}/\sum n_i z_i^2 = [2(+1)^2 + 1(-2)^2]/2 = 6/2 = 3$$

Example 9: Estimate the Lattice Potential Energy, U_{POT}(K_2PtCl_6)/kJ·mol^{-1}, Using the Volume-Based Equation. Numerous estimates of $U_{\mathrm{POT}}(\mathrm{K_2PtCl_6})$ have been made, as shown in Table 2. For the calculation, we use eq 4a:

$$U_{\mathrm{POT}}(\mathrm{K_2PtCl_6})/\mathrm{kJ\cdot mol^{-1}} \approx 2I\left(\frac{\alpha}{V_{\mathrm{m}}{}^{1/3}} + \beta\right)$$

where α and β are coefficients chosen depending on the stoichiometry of the salt in question. Since $\mathrm{K_2PtCl_6}$ is an $\mathrm{M_2X}$ salt (see Example 8),[49] α and β take the values $165.3\ \mathrm{kJ\cdot mol^{-1}\cdot nm}$ and $-29.8\ \mathrm{kJ\cdot mol^{-1}}$. Accordingly, use of $V_{\mathrm{m}}/\mathrm{nm^3} = 0.2313$ gives:

$$\begin{aligned} &U_{\mathrm{POT}}(\mathrm{K_2PtCl_6})/\mathrm{kJ\cdot mol^{-1}} \\ &\approx 2I\left(\frac{\alpha/\mathrm{kJ\cdot mol^{-1}\cdot nm}}{(V_{\mathrm{m}}/\mathrm{nm^3})^{1/3}} + \beta/\mathrm{kJ\cdot mol^{-1}}\right) \\ &= (2)(3)\left[\frac{165.3}{(0.2313)^{1/3}} - 29.8\right] \\ &= 1437\ (-0.8\ \%) \end{aligned}$$

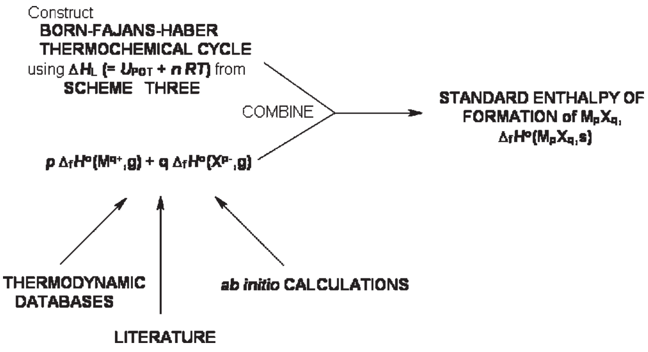
where the relative deviation in parentheses is with respect to the mean of the values in Table 2. Using the alternative volumes $V_{\mathrm{m}}/\mathrm{nm^3} = 0.2306$, 0.2416, and 0.2269 ± 0.0090 generated within Example 2 leads to the following estimates for $U_{\mathrm{POT}}(\mathrm{K_2PtCl_6})/\mathrm{kJ\cdot mol^{-1}}$: 1439 (−0.7 %); 1413 (−2.5 %), and 1447 ± 21 (−0.1 %). The direct minimization approach[50] represents the most sophisticated of the approaches listed in Table 2 and gives a result close to the average (+1.3 % relative deviation from the mean of the tabulated values).

Example 10: Estimate the Lattice Potential Energy, U_{POT}(K_2PtCl_6)/kJ·mol^{-1}, Using the Density-Based Equation. Lattice energy can also be estimated by using our density-based version[35] of eq 4a, which takes the form:

$$\begin{aligned} &U_{\mathrm{POT}}(\mathrm{K_2PtCl_6})/\mathrm{kJ\cdot mol^{-1}} \\ &\approx 2I\left\{\frac{\alpha/\mathrm{kJ\cdot mol^{-1}\cdot nm}}{\left[\dfrac{(M/\mathrm{g\cdot mol^{-1}})}{602.2\cdot(\rho/\mathrm{g\cdot cm^{-3}})}\right]^{1/3}} + \beta/\mathrm{kJ\cdot mol^{-1}}\right\} \\ &= (2)(3)\left\{\frac{165.3}{\left[\dfrac{485.99}{(602.2)(3.50)}\right]^{1/3}} - 29.8\right\} = 1438\ (-0.8\ \%) \end{aligned}$$

where the relative deviation in parentheses is with respect to the mean of the values in Table 2.

Scheme 4



Example 11: Calculate the Number of RT Terms Required for Conversion of $U_{POT}(K_2PtCl_6)/kJ\cdot mol^{-1}$ into a Lattice Enthalpy Term, $\Delta_L H(K_2PtCl_6,s)/kJ\cdot mol^{-1}$, Suitable for Incorporation into a Born—Fajans—Haber Enthalpy Cycle. Using eq 5,

$$\Delta_L H = U_{POT} + \sum_{i=1}^{n} s_i\left(\frac{c_i}{2} - 2\right)RT$$

we obtain

$$\begin{aligned}&\Delta_L H(K_2PtCl_6, s)\\ &= U_{POT}(K_2PtCl_6) + [(2)(3/2 - 2) + (1)(6/2 - 2)]RT\\ &= U_{POT}(K_2PtCl_6) + 0RT\end{aligned}$$

Example 12: Assemble Gas-Phase Enthalpies of Formation, $\Delta_f H°(K^+,g)/kJ\cdot mol^{-1}$ and $\Delta_f H°(PtCl_6^{2-},g)/kJ\cdot mol^{-1}$, for Insertion into the Appropriate Born—Fajans—Haber Enthalpy Cycle (Scheme 4) in Order To Estimate $\Delta_f H°(K_2PtCl_6,s)$. Quoted experimental values for $\Delta_f H°(K_2PtCl_6,s)/kJ\cdot mol^{-1}$ are −1187.4,[45] −1229.3,[43] and −1261.3.[5] A datum for $\Delta_f H°(K^+,g)/kJ\cdot mol^{-1}$ can be found in the NBS tabulation (514.26 at STP), while Jenkins and Pratt[50] cite a value of −792 for $\Delta_f H°(PtCl_6^{2-},g)/kJ\cdot mol^{-1}$. From the thermochemical cycle shown in Figure 1, we obtain:

$$\begin{aligned}&\Delta_f H°(K_2PtCl_6, s)/kJ\cdot mol^{-1}\\ &= [2\Delta_f H°(K^+, g) + \Delta_f H°(PtCl_6^{2-}, g)\\ &\quad - U_{POT}(K_2PtCl_6) - nRT]/kJ\cdot mol^{-1}\\ &= (2)(514.26) + (-792) - 1438 - (0)(RT)/kJ\cdot mol^{-1}\\ &= -1202\ (-2.3\ \%)\end{aligned}$$

Example 13: Estimate the Standard Entropy of Formation, $\Delta_f S°(K_2PtCl_6,s)/J\cdot K^{-1}\cdot mol^{-1}$, from the Estimates Made for $S°_{298}(K_2PtCl_6,s)/J\cdot K^{-1}\cdot mol^{-1}$ in Example 6 . $\Delta_f S°(K_2PtCl_6,s)/J\cdot K^{-1}\cdot mol^{-1}$ is given by:

$$\begin{aligned}&\Delta_f S°_{298}(K_2PtCl_6, s)/J\cdot K^{-1}\cdot mol^{-1}\\ &= [S°_{298}(K_2PtCl_6, s) - 2S°_{298}(K, s) - S°_{298}(Pt, s)\\ &\quad - 3S°_{298}(Cl_2, g)]/J\cdot K^{-1}\cdot mol^{-1}\\ &= 333.9 - (2)(64.7) - 41.63 - (3)(222.956)\\ &= -506.0\end{aligned}$$

Example 14: Using the Estimated Data for the Standard Enthalpy of Formation, $\Delta_f H°(K_2PtCl_6,s)$ /kJ·mol^{-1}, from Example 12 and the Standard Entropy of Formation, $\Delta_f S°(K_2PtCl_6,s)/J\cdot K^{-1}\cdot mol^{-1}$, from Example 13, Calculate the Standard Gibbs Energy of Formation, $\Delta_f G°(K_2PtCl_6,s)/kJ\cdot mol^{-1}$, for K_2PCl_6 at 298.15 K (see Scheme 5). The estimate $\Delta_f H°(K_2PtCl_6,s)/kJ\cdot mol^{-1}$ = −1202 from Example 12 and the estimate $\Delta_f S°(K_2PtCl_6,s)/J\cdot K^{-1}\cdot mol^{-1}$ = −506.0 from Example 13 allow us to estimate $\Delta_f G°(K_2PtCl_6,s)$ at T = 298.15 K using the following equation:

$$\begin{aligned}\Delta_f G°(K_2PtCl_6, s) &= \Delta_f H°(K_2PtCl_6, s) - T\Delta_f S°(K_2PtCl_6, s)\\ &= -1051\ kJ\cdot mol^{-1}\ (-2.6\ \%)\end{aligned}$$

Experimental values for $\Delta_f G°(K_2PtCl_6,s)/kJ\cdot mol^{-1}$ are −1037.2,[44] −1107.92,[45] −1078.5,[43] and −1108.4.[5]

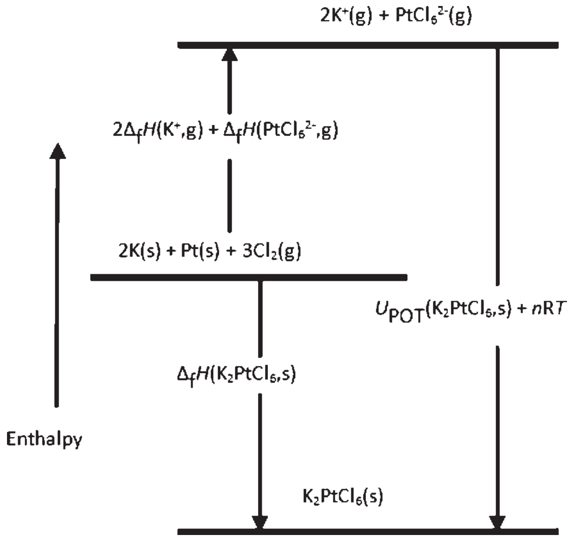
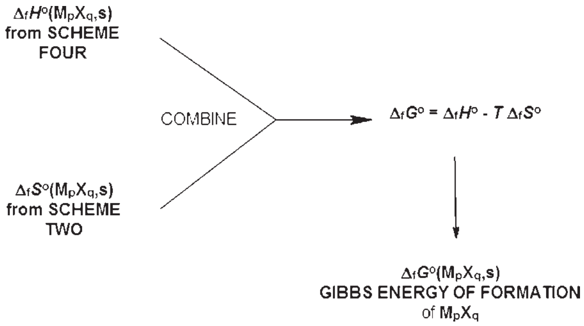


Figure 1. Thermochemical enthalpy cycle for the formation of $K_2PtCl_6(s)$.

Scheme 5



■ CONCLUSIONS

We have here demonstrated how (experimental or estimated) volume and density data can be employed to estimate many standard thermodynamic quantities to usable accuracy by means of correlation relations that require little expertise and only the simplest of calculational tools. A further example can be found in ref 57.

■ AUTHOR INFORMATION

Corresponding Author

*L.G.: tel, +61 8 9266-3126; fax, +61 8 9266-4699; e-mail, leslieglasser@yahoo.co.uk. H.D.B.J.: tel, +44 2476-523-265 or +44

2476-466-747; fax, +44 2476-524-112 or +44 2476-466-747; e-mail, h.d.b.jenkins@warwick.ac.uk.

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