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Estimation of thermodynamic data for metallurgical applications

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Abstract

The ever growing need to develop new materials for specific applications is leading to increased demand for thermodynamic values which have not been measured so far. This necessitates the use of estimated values for evaluating the feasibility or suitability of different proposed processes for producing materials with particular compositions and properties. Methods for estimating thermodynamic properties of inorganic and metallic substances are presented in this paper. A general categorization into estimation methods for heat capacities, entropies and enthalpies of formation has been used. Some comparisons of estimated values with experimental data are presented and possible future developments in estimation techniques are discussed. © 1998 Elsevier Science B.V.

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1. Introduction

The present-day availability of advanced, user-friendly commercial software considerably facilitates the thermodynamic calculation of reaction equilibria, even in very complex systems. However, published data for many substances and systems of practical interest are still not complete, especially in the ever-widening field of materials chemistry, where reliable thermodynamic data not only for *stable* but also for *metastable* phases are becoming increasingly important.

When such data are lacking, it is necessary to estimate the missing values with reasonable accuracy. For stoichiometric inorganic compounds, this task is not as difficult as it might appear, for many of the principles which are applicable have been well established for a considerable time. For solution phases, however, methods available are generally more complex, and software incorporating various solution models has been written with the aim of providing missing data from the more limited information available.

Experience is required to enable the best choice of estimation method to be made in each particular case, and if necessary to develop new methods. A selection of current methods used to estimate thermodynamic values for both pure stoichiometric substances and solution phases of different types, as well as some examples of their application, are given in this paper. Due to space limitation, only condensed phases are discussed. Further examples and more detailed descriptions of individual estimation methods can be found in Chapter 3 of Ref. [1].

2. Pure inorganic substances

2.1. Heat capacities

For most materials applications, it is sufficient to be able to estimate heat capacities at room temperature

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and above. Heat capacities at lower temperatures will not be considered here.

2.1.1. Solids

Kellogg [2] originally suggested a method for estimating the heat capacity of predominantly ionic, solid compounds at 298 K. It is analogous to Latimer's method for the estimation of standard entropies [3] and consists in adding together contributions from the cationic and anionic groups in the compound (here denoted as θ(cat) and θ(an)). Using the then available compiled experimental data, Kellogg derived average values of θ(cat) for the metallic ions independent of their valency and of θ(an) for the anions, depending on valency. The estimated heat capacities at 298 K were then obtained by summing the various contributions, i.e. $C_p(298\ \mathrm{K})=\Sigma\theta$.

Kubaschewski and Ünal [4] revised the tables of Kellogg from an analysis of a larger set of experimental $C_p(298\ \mathrm{K})$ data. Within the scatter of the individual values, and in contrast to Kellog's findings, it was found possible to represent the θ(an) contributions by a single number for each anion independent of valency. (See Tables 1 and 2 below).

A further analysis carried out, here, on newer data for oxide species has enabled still more anions to be taken into account. As an example, the heat capacity of 1 mol of calcium aluminate at room temperature

Table 1
Cationic contributions to the heat capacity at 298 K

Metal	$\theta_{(cat)}$ (J/K)	Metal	$\theta_{(cat)}$ (J/K)	Metal	$\theta_{(cat)}$ (J/K)	Metal	$\theta_{(cat)}$ (J/K)
Ag	25.73	Fe	25.94	Mn	23.43	Sn	23.43
Al	19.66	Ga	(20.92)	Na	25.94	Sr	25.52
As	25.10	Gd	23.43	Nb	23.01	Ta	23.01
Ba	26.36	Ge	20.08	Nd	24.27	Th	25.52
Be	(9.62)	Hf	25.52	Ni	(27.61)	Ti	21.76
Bi	26.78	Hg	25.10	P	14.23	Tl	27.61
Ca	24.69	Ho	23.01	Pb	26.78	U	26.78
Cd	23.01	In	24.27	Pr	24.27	V	22.18
Ce	23.43	Ir	(23.85)	Rb	26.36	Y	(25.10)
Co	28.03	K	25.94	Sb	23.85	Zn	21.76
Cr	23.01	La	(25.52)	Se	21.34	Zr	23.85
Cs	26.36	Li	19.66	Si	—		
Cu	25.10	Mg	19.66	Sm	25.10		

Table 2
Anionic contributions to the heat capacity at 298 K

Anion	θ(an) (J/K)	Anion	θ(an) (J/K)	Anion	θ(an) (J/K)	Anion	θ(an) (J/K)
Br	25.94	CO_3	58.58	Cr_2O_4	125.33	Si_2O_5	106.79
Cl	24.69	NO_3	64.43	Fe_2O_4	126.05	TiO_3	74.45
F	22.80	OH	30.96	GeO_3	72.08	TiO_4	92.52
H	8.79	SO_4	76.57	HfO_3	78.47	Ti_2O_5	124.69
I	26.36	Al_2O_4	98.52	MoO_4	92.77	UO_4	107.11
O	18.41	Al_2O_6	135.46	Nb_2O_6	155.99	VO_4	89.2
P	(23.43)	BO_2	41.19	PO_4	75.72	V_2O_6	143.08
S	24.48	B_2O_6	111.20	SeO_3	73.32	V_2O_7	163.5
Se	26.78	B_4O_7	134.26	SiO_3	62.93	WO_4	97.49
Si	(24.68)	CrO_4	92.27	SiO_4	78.34	ZrO_3	75.06
Te	27.20						

may be estimated:

$$C_p(298\mathrm{K}) = 3\theta(\mathrm{Ca}) + 1\theta(\mathrm{Al_2O_6}) = 74.07 + 135.46 = 209.53\ \mathrm{J/K\cdot mol} \qquad (1)$$

which compares with the measured value of 205.43 J/K·mol.

The heat capacity of solids at the melting point is roughly the same, per ion or atom, for all compounds. Kelley [5] took this value to be 29.3 J/K·mol. Kubaschewski [4], with more recent experimental evidence, increased this average to (30.3±2.1) J/K·mol. Not included in the evaluation of the mean deviation were the data for those substances which undergo a solid–solid transformation below the melting point, nor for those that have a melting point below ca. 420 K. If one includes the first transformation rather than considering the melting point alone, the average value turns out to be closer to Kelley's original value 29.3 J/K·mol – a point that should be noted. These observations taken together with the values in Tables 1 and 2 may be used to recommend the estimation of the constants in a heat-capacity equation of the type

$$C_p = a + b \times 10^{-3}T + c \times 10^5 T^{-2} \qquad (2)$$

Earlier estimated C_p vs. T relations [5] were often a two-term linear expression. However, the introduction of a T^{-2} term enables the pronounced curvature at lower temperatures (above 298 K) and around the Debye temperature to be described more accurately. When values of c in Eq. (2) as obtained from different experiments are compiled, they show a considerable scatter, due more to the inaccuracy of the differentiation of experimental enthalpy data than to the actual relations. A mean value of $c/n = -4.12$ J/K was obtained from the T^{-2} terms of some 200 inorganic substances [4].

Expressions for the constants in Eq. (2) were derived [4] as follows:

$$a = \frac{T_m \times 10^{-3}(\Sigma\theta + 1.125n) - 0.298n \times 10^5 T_m - 2.16n}{T_m \times 10^{-3} - 0.298} \qquad (3)$$

$$b = \frac{6.125n + 10^5 n T_m - \Sigma\theta}{T_m 10^{-3} - 0.298} \qquad (4)$$

$$c = -4.12n \qquad (5)$$

Here, T_m is the absolute melting temperature of the compound and n the number of atoms in the molecule.

If C_p(298 K) is known from low-temperature measurements, the experimental value should, of course, be used instead of $\Sigma\theta$, the estimated value. Adjustment of the estimated equation can also be made if the heat capacities of compounds similar in mass and chemical nature to the one under consideration are known. Although the average value of $C_p(T_m)/n$ increases somewhat with molecular weight, the scatter in the data and the smallness of the effect make it difficult to justify a two-term expression in terms of log M.

Hoch [6–9] has shown that the high-temperature heat-capacity data of solids can be represented by the equation

$$C_p = 3\boldsymbol{R}F(\theta_D/T) + bT + dT^3 \qquad (6)$$

where $F(\theta_D/T)$ is the Debye function, b is equivalent to the electronic heat capacity, and d reflects only the contribution of the anharmonic vibrations within the lattice. The equation is valid in the temperature range between θ_D and the melting point. By plotting the experimental heat-capacity data for a number of metals and ceramics using Eq. (6) in the rearranged form

$$\frac{C_p - 3\boldsymbol{R}F(\theta_D/T)}{T} = b + dT^3 \qquad (7)$$

Hoch was able to derive values for the electronic heat capacity, b, and for the heat capacity due to the anharmonic vibrations, d, from the intercepts and slopes, respectively, of the linear plots. For insulating materials, b=0 and the line passes through the origin. Using this approach, a very satisfactory description of the heat capacities of Nb, Ta, Cr, Re, Mo, W, Cu, Al, UO_2, UO_{2+x}, US, UN, UC, and Al_2O_3 was obtained. Eq. (7), thus, appears useful as a general equation for estimating the heat-capacity data for solids, where values are scarce or rather unreliable.

Lacking any information about the heat capacity of a compound, C_p may be assumed to be zero for *condensed reactions* without affecting most calculations too seriously. This postulate regarding the additivity of the heat capacities of the elements or the reactants to give the heat capacities of the compound or the products in a reaction is known as Neumann and Kopp's rule. It has been found to be approximately valid for a large number of reactions and so has been used frequently. Neumann–Kopp's rule holds good, especially for alloy phases.

2.1.2. Liquids

The heat capacities of molten inorganic substances do not differ greatly from those of the corresponding solid materials and the heat capacity of an inorganic liquid amounts from 29.3 to ca. 33.5 J/K·mol, to some extent depending on the atomic weight of the substance concerned. The value 31.4 may be used if measurements are not available; alternatively, the atomic heats of the liquid constituent elements may be taken additively.

Hoch and Venardakis, in a series of publications, e.g. [10,11], have analysed experimental heat-capacity data for a number of liquid metals, oxides and halides. They suggest that the experimental data indicate anharmonic contributions to the heat capacity of the liquids close to the melting point. As the temperature is raised, the anharmonic contributions decrease and the heat capacity at very high temperatures is made up of two parts – a term which corresponds to the Debye function, and a linear term which can be assigned to the electronic heat capacity.

The equation derived by Hoch and Venardakis, to describe the heat capacity of liquid inorganic substances of various types at high temperatures, is

$$C_\mathrm{p} = 3\boldsymbol{R}F(\theta_\mathrm{D}/T) + gT + hT^{-2} \qquad (8)$$

where g is the electronic heat capacity and h the anharmonic term.

Eq. (8) was applied to a wide variety of metallic and inorganic materials and the fit was very good in all cases, although scatter in the published enthalpy data result in values of the anharmonic contribution, h, ranging from 4% for Al_2O_3 to 18% for Fe. Because of its apparent generality, Eq. (8) seems suitable for estimating high temperature heat-capacity values for other liquid metals and inorganic compounds where the available data are scarce.

More recently, Hoch has shown [12] that, within the experimental error, the term $dh/m\theta^2$ is constant, where d and h correspond to the appropriate constants in the equations for the heat capacity of solids and liquids, respectively, and m the mass per atom in a compound. Thus, if $C_\mathrm{p}(L)$ is unknown for a particular compound, the constant value of $dh/m\theta^2$ can be used to estimate h, using the known value of d. The resulting error in $C_\mathrm{p}(L)$ will be relatively small because only a correction term is calculated. The general constancy of $dh/m\theta^2$ is illustrated by the values given in Table 3 for a range of materials.

Table 3
Relation between the anharmonic terms for substances in the solid and liquid state

Substance	θ_D	d	h	Mass/atom	$dh/m\theta^2$
Li	344	4.60E-8	1.41E+6	7	7.81E-8
Pb	105	8.79E-9	1.81E+6	207	6.98E-9
In	109	2.96E-8	3.30E+5	115	7.15E-9
Bi	117	8.28E-9	5.99E+5	209	1.73E-9
Ti(α)	420	4.90E-9	6.11E+7	48	3.53E-8
Fe(gam)	470	1.61E-9	3.26E+7	56	4.25E-9
Mo	380	7.66E-10	4.58E+7	96	2.53E-9
Al_2O_3	895	5.02E-10	9.54E+7	20	2.93E-9
UO_2	590	1.39E-9	2.28E+8	90	1.01E-8
NaCl	1074	8.43E-9	1.28E+7	29	4.97E-8
$CaCl_2$	989	4.14E-9	1.59E+7	37	2.81E-8
$MnCl_2$	882	7.53E-9	7.30E+6	42	2.27E-8
MgF_2	1460	1.70E-9	1.85E+7	21	4.59E-9

2.2. Enthalpies and entropies of transformation

A knowledge of enthalpies of transition is more important than that of variation in heat capacity since the former have a relatively greater effect on the value of the Gibbs energy of a substance. Fortunately, the methods available for estimating their value, given a knowledge of the molecular structure of the substance, are fairly reliable.

2.2.1. Fusion

2.2.1.1. Entropy of fusion as a function of temperature of fusion. For the elements, several authors have reported simple linear correlations between the entropy of fusion and the melting temperature for elements of a given structure. Such correlations have been used, for example, by Saunders, Miodownik and Dinsdale in producing sets of values for the SGTE Unary Database [13].

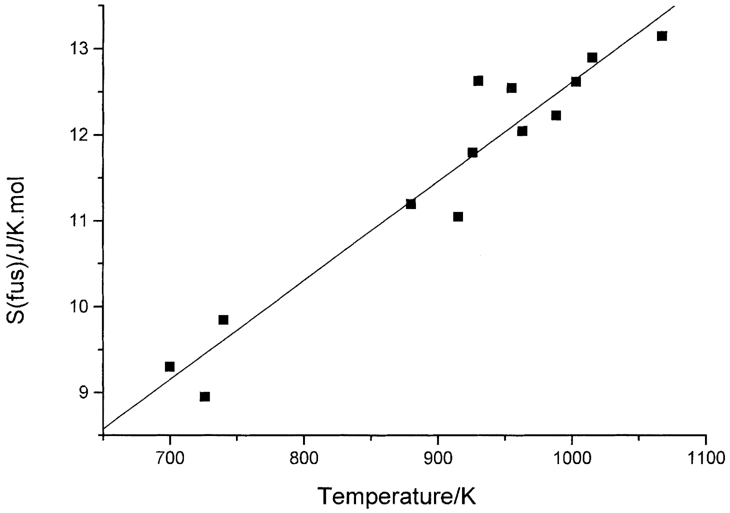

Fig. 1. Entropy of fusion vs. temperature of fusion for alkali metal halides.

The correlations have been tested further here for inorganic compounds of a given structure and are found to hold quite well for alkali chlorides, bromides and iodides with the NaCl structure (Fig. 1) and for some transition metal monosilicides with the B20 structure (Fig. 2).

2.2.1.2. Enthalpy of fusion from the enthalpy of the solid at the melting point. Kazragis et al. [14] have demonstrated for the elements that a simple relation exists between the enthalpy of fusion and the enthalpy of the solid at the melting point. These authors also propose an equation to represent the entropy of fusion:

$$\begin{aligned}\Delta S_{\mathrm{fus}} = {} & S(298\,\mathrm{K}) + A[0.023a(\log T_{\mathrm{m}} - 2.4742) \\ & + 10^{-3}b(T_{\mathrm{m}} - 298) \\ & + 0.005c(1.1261 - 10^{5}/T_{\mathrm{m}}^{2})] \end{aligned} \tag{9}$$

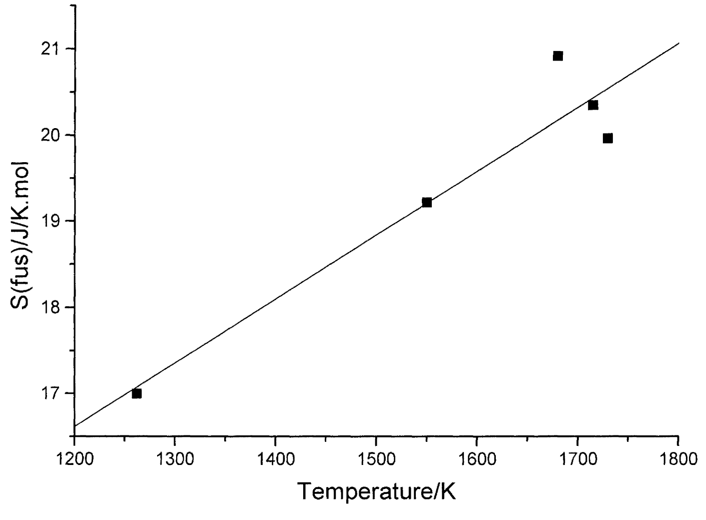

Fig. 2. Entropy of fusion vs. temperature of fusion for transition metal monosilicides.

where A is the atomic mass, and a, b and c are coefficients in the heat-capacity equation

$$C_p = a + bT + cT^{-2}$$

The correlation ΔH_m vs. $H(T_m){-}H_{298}$ has been tested both for a group of inorganic compounds with the same structure (Fig. 3) and for inorganic compounds with different structures (Fig. 4). The latter included oxides, halides, carbides, etc. selected at random. The alkali halides give a very good linear correlation (Fig. 3) and even though there is a fairly large scatter from linearity for the different types of compound plotted together (Fig. 4), the correlation appears to offer good general possibilities for estimating unknown enthalpies of fusion.

For practical applications, enthalpies of fusion are small compared with the total heat content of a

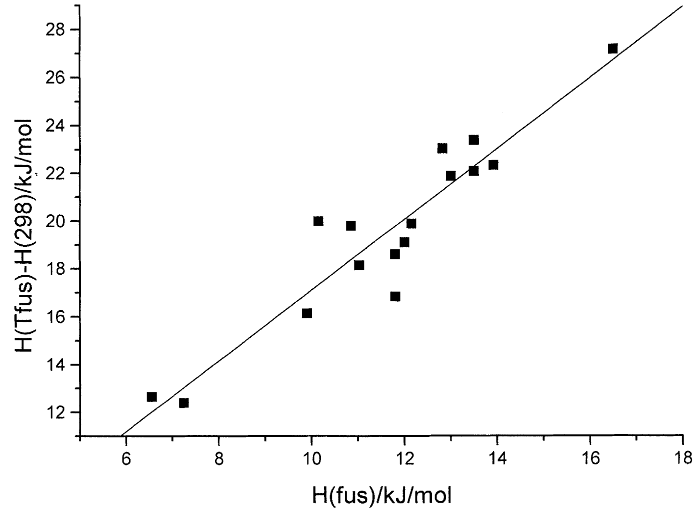

Fig. 3. Enthalpy of fusion vs. enthalpy at the melting point for alkali metal halides.

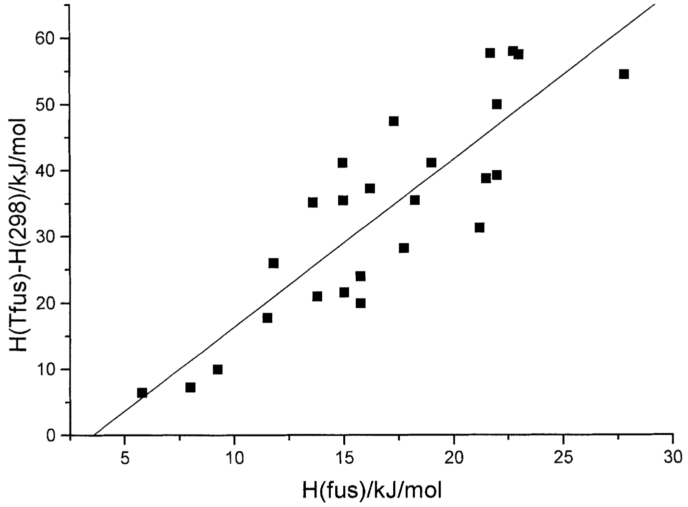

Fig. 4. Enthalpy of fusion vs. enthalpy at the melting point for a selection of inorganic compounds with different structures.

material, and even an approximate estimate is adequate for calculating equilibria involving liquid species. For this purpose, entropies and enthalpies of fusion may be estimated by comparison with similar compounds in the Periodic Table.

2.3. Entropy and entropy changes

2.3.1. Standard entropies

2.3.1.1. Elements. Although the standard entropies of nearly all elements in their stable structures are known more or less accurately, reliable estimation methods are still required to obtain values of the entropies of metals in metastable or non-stable structures. If such information were available, the calculation of alloy phase equilibria could be significantly refined. From an analysis of the phase equilibria, in a large number of binary alloy systems, Kaufman and Bernstein [15] have derived approximate entropy (and enthalpy) differences between the stable and metastable structures of many metallic elements. In particular, the fcc, bcc and hcp structures have been considered. Fig. 5 illustrates such differences for the hcp and bcc structures across the second and third Long Periods of the Periodic Table.

Thermodynamic data for transformations between other metastable structures and the stable structures of the pure elements are still needed as are the equivalent data for compounds such as oxides, carbides, nitrides, etc. which play an important role in many areas of materials technology. Curves such as those shown in Fig. 5, together with standard entropy values for the stable phases of the elements, enable standard entropy data for the elements in metastable structures to be derived.

2.3.1.2. Inorganic compounds. Latimer's method for obtaining the standard entropies of predominantly ionic compounds from the empirically found values for the anion and cation contributions [3], has been updated by Mills [16] from an analysis of experimental data for ca. 300 compounds. The overall standard deviation of the resulting $S_{obs}-S_{est}$ values, 5.4 J/

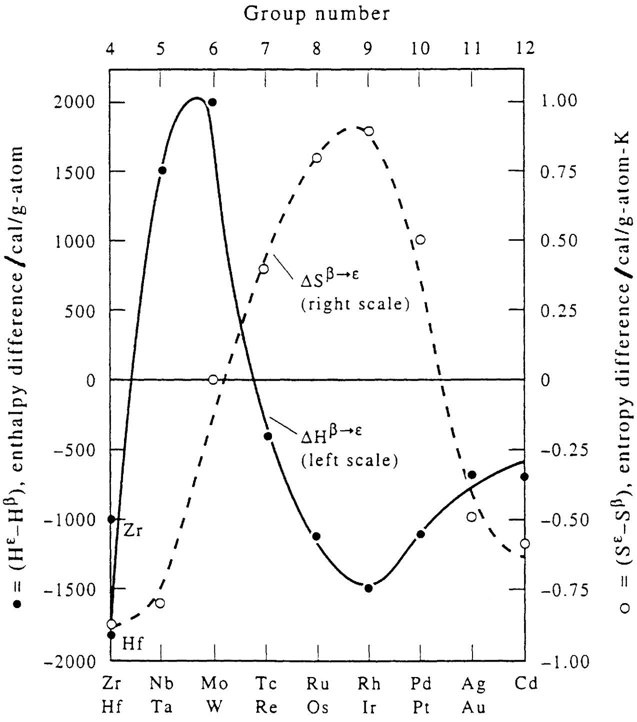

Fig. 5. Enthalpy and entropy differences between the hcp(ϵ) and bcc(β) forms of the transition metals.

K·mol, is smaller than that associated with Latimer's earlier values. The data presented by Mills, for the cationic and anionic contributions to the standard entropy of inorganic compounds of general formula MX_a, were calculated for {M} and n{X} and are listed in Tables 4 and 5.

To obtain the standard entropy of a solid compound from these tables, the appropriate value for its cation in Table 4 is multiplied by the number of cations in the molecule and added to the anion contribution, obtained by multiplying the value given in Table 5 according to the charge on the cation by the number of anions in a formula weight. Thus, the standard entropy of $Al_2(SO_4)_3$ is obtained as $S(298\ \mathrm{K})=(2\times 23.4)+(3\times 64.2)=239.4$ J/K·mol.

Although Latimer originally devised the method, described above, for application to predominantly ionic compounds, Mills has also demonstrated its

Table 4
'Latimer' entropy contributions {M}

M	{M} (J/K mol)	M	{M} (J/K mol)	M	{M} (J/K mol)	M	{M} (J/K mol)
Ag	57.6±2.5	Fe	35.0±7.8	Nd	60.7	Sm	60.2
Al	23.4±6.7	Ga	40.0±2.5	Ni	35.1±5.0	Sn	58.2±7.6
As	45.2±4.6	Gd	56.0	Os	50±8	Sr	48.7±2.5
Au	58.5±2.0	Ge	49.8±3.3	P	39.5	Ta	53.8
B	23.5	Hf	53.0	Pb	72.2±5.0	Tb	55.2
Ba	62.7±3.0	Hg	59.4±5.4	Pd	45.6±2.2	Tc	(42)
Be	12.6±4.2	Ho	56.0	Pm	(61)	Te	69
Bi	65.0±9.2	In	55.0±6.0	Pr	61.1	Th	59.9±0.8
Ca	39.1±2.9	Ir	50.0	Pt	39.3±1.5	Ti	39.3±8.0
Cd	50.7±3.4	K	46.4±0.8	Rb	59.2±0.5	Tl	72.1±2.7
Ce	61.9	La	62.3	Re	42±6.5	Tm	52.3
Co	34.1±3.3	Li	14.6±3.8	Rh	(46)	U	64.0±5.2
Cr	32.9±5.9	Lu	51.5	Ru	53±8	V	36.8±6.3
Cs	67.9±3.7	Mg	23.4±4.2	S	48	W	40.9±3.3
Cu	44.0±5.0	Mn	43.8±6.7	Sb	58.9±8.3	Y	50.4±4.2
Dy	54.8	Mo	35.9±5.2	Sc	36.0±1.3	Yb	54.0
Er	54.8	Na	37.2±3.8	Se	60.5	Zn	42.8±6.3
Eu	60.2	Nb	48.1±2.5	Si	35.2	Zr	37.2±9.6

Table 5
'Latimer' entropy contributions ^{n}{X} as a function of the charge number, n, of the cations

X	^{n}{X} (J/K·mol)						
	n=1	n=2	n=2.67	n=3	n=4	n=5	n=6
O^{2-}	4.5	2.9	0.4	2.4	3.2	7.1	12.7
S^{2-}	20.6	18.4		20.1	17.0	22.4	
Se^{2-}	35.5	32.8		34.1	30.9		
Te^{2-}	38.3	41.9		44.1	40.1		
F^{-}	20.8	17.0		18.3	20.3	22.4	27.2
Cl^{-}	36.3	31.8		30.3	34.4		37.2
Br^{-}	50.3	45.7		44.7	50.8		
I^{-}	58.3	53.5		54.8	53.9	59.4	
CO_3^{2-}	62.4	46.6					
SO_4^{2-}	80.0	69.5		64.2			
NO_3^{-}	86.0	74.0					
NO_2^{-}	70.6	(61)					
SO_3^{2-}	42.9						

usefulness for estimating standard entropy values for non-ionic compounds. Values of the {X} contributions to the standard entropy of metallic borides, carbides, silicides, nitrides, phosphides, arsenides and antimonides were derived from the more limited data available for such substances and the uncertainties associated with the resulting values were not much larger than those found for ionic compounds. Mills attributed this consistency to the similarity of crystal structure and bonding characteristics for most compounds of an element X with a given stoichiometry.

Table 6 presents the newly updated values obtained from an analysis of a large number of such compounds contained in the SGTE Pure Substances Database [17]. The classification into different MX_a types, as employed by Mills, has been retained here. However, because of the stoichiometric ranges shown by a number of the compounds involved, the values presented in Table 6 should only be considered useful in providing a guide to the magnitude of missing entropy data.

Richter and Vreuls [18] have estimated standard entropy values for solid and molten salts within a mean deviation of ca. 3.5% based on the linear dependence of the entropy on the radius, r(c), of the cation constituent of the compound. The linear extrapolation to zero of r(c) leads to the anionic contribution of the molar entropy depending on the cationic charge. Evaluation of cationic contributions to the entropy can be made from experimental data and the method has the advantage that its application is not restricted to ionic compounds only. Table 7 pre-

Table 6
'Latimer' entropy contributions {X} for metallic borides, carbides, silicides, nitrides, phosphides, arsenides and antimonides

X	{X} (J/K mol)					
	in $MX_{0.33}$	in $MX_{0.5}$	in $MX_{0.7\pm1}$	in MX	in MX_2	in MX_3
B		−(18.4±4)	−9.5	−(6.5±3)	−(2.1±3)	
C		−(13.6±10)	−(6.5±4)	−(9.6±5)	(10.8±5)	
Si	−(4.5±8)		(5.8±4)	(6.5±4)	(12.2±3)	
N		−16.8(±10)	−1.5	−(4.6±5)		(20±5)
P	−(2.2±3)	(6.3±5)	(7.2±5)	(10.6±5)		
As		(43.8±6)	(23.0±8)	(27.8±10)		
Sb		(40±10)	(26.6±8)	(40.4±5)	(36±8)	

Table 7
Anionic contributions to the entropy of solid salts at 298 K as a function of cation charge

Anion	S(298 K) (J/K mol)			Monovalent cation	Divalent cation
	Monovalent cation	Divalent cation	Anion cation		
F^-	8.9	18.6	$Cr_2O_4^{2-}$	—	84.7
Cl^-	37.8	30.5	$Fe_2O_4^{2-}$	—	96.3
Br^-	51.6	47.0	MoO_4^{2-}	—	84.3
I^-	65.9	53.9	O^{2-}	6.4	2.5
H^-	2.1	—	O_2^{2-}	21.9	—
OH^-	25.1	18.3	O_2^-	76.0	—
NO_3^-	83.6	66.1	PO_4^{3-}	—	60.3
ClO_4^-	105.8	—	S^{2-}	31.3	18.1
AlF_6^{3-}	114.2	—	SiO_3^{2-}	43.4	39.9
$AlCl_6^{3-}$	229.0	—	SiO_4^{4-}	—	40.2
$Al_2O_4^{2-}$	—	57.0	SO_4^{2-}	84.8	68.7
$B_2O_4^{2-}$	—	61.8	TiO_3^{2-}	—	51.6
$B_4O_7^{2-}$	117.6	94.8	TiO_4^{4-}	—	62.6
$B_6O_{10}^{2-}$	156.9	—	WO_4^{2-}	—	85.6
CO_3^{2-}	63.3	44.4			

Table 8
Cationic contributions to the entropy of solid salts at 298 K

Cation	S(298 K) (J/K mol)	Cation	S(298 K) (J/K mol)
Ag^+	55.3	Li^+	19.7
Ba^{2+}	59.3	Mg^{2+}	26.7
Be^{2+}	13.2	Mn^{2+}	48.1
Ca^{2+}	39.5	Na^+	34.0
Cd^{2+}	51.3	Ni^{2+}	33.3
Co^{2+}	44.8	Pb^{2+}	72.7
Cs^+	62.1	Rb^+	55.9
Cu^{2+}	41.5	Sn^{2+}	60.9
Fe^{2+}	52.2	Sr^{2+}	52.9
Hg^{2+}	67.1	Tl^+	68.3
K^+	46.4	Zn^{2+}	47.9

sents the anionic contribution to the standard entropy of solid salts at 298 K as a function of the cation charge and Table 8 presents the cationic contributions as evaluated by Richter and Vreuls.

2.3.2. *Entropies of mixing of non-metallic solution phases*

In deriving entropies of mixing for non-metallic solutions, it should always be remembered that a mixture of cations contains not only the configurational entropy arising from the random distribution of cations on the cation sub-lattice, but also a thermal entropy term related to heat capacity changes. For example, in the formation of spinels from their constituent oxides, Jacob and Alcock [19] found that the configurational term is always accompanied by a thermal entropy of formation which must be added to the configurational entropy to obtain the total entropy of formation. Such thermal terms arising from the changes in the vibrational structure of the cations and their surrounding oxygen ions on formation of an inter-oxide compound should always be considered.

In the spinel studies, it was found that the thermal entropy of formation of spinels, such as Fe_3O_4, $FeAl_2O_4$, FeV_2O_4 and $FeCr_2O_4$ could be represented by the equation

$$\Delta_f S = -7.32 + \Delta S^M \text{ J/mol} \quad (10)$$

where −7.32 entropy units originate from the non-configurational source.

2.4. *Enthalpies of formation*

2.4.1. *General*

Information on the enthalpies of formation of the substances taking part in a reaction are essential to obtain reliable evaluation of Gibbs energy values, and hence allow calculation of particular chemical equilibria of interest. However, the methods available for estimating enthalpies of formation are often not very exact and apply to a relatively small group of compounds only. Consequently, all possible methods should be used to estimate a single value. Since the variation of enthalpies of formation with temperature is generally small, the values can often be assumed to be temperature-independent, provided no phase transformation takes place.

2.4.1.1. Empirical relations. In a series of papers, Hisham and Benson [22–29] have compiled information on the enthalpies of formation of a wide variety of inorganic compounds and derived empirical relations to enable known values to be calculated to within close limits, and missing values to be estimated, for particular groups of compounds. Some of the equations that have been derived are presented below.

2.4.2. *Polyvalent metal oxides [22]*

For polyvalent oxides, MO_z, which have three or more well-defined stoichiometric valence states, the following relation holds:

$$-\Delta_f H^0_{298} = az + bz^2 \quad (11)$$

The authors present values of a and b for 15 metals

2.4.3. *Metal oxyhalide compounds [24]*

Examination of 35 solid metal oxyhalides, MO_xX_y, showed that their standard enthalpies of formation can be correlated quantitatively with the enthalpies of formation of the corresponding oxides and halides of the same oxidation states by the equation:

$$\begin{aligned}\Delta_f H^0_{298}(MO_xX_y) &= a[(2x/z)\Delta_f H^0_{298}(MO_{z/2}) \\ &\quad + (y/z)\Delta_f H^0_{298}(MX_z)] + C \quad (12)\end{aligned}$$

where $z=2x+y$ is the formal oxidation state of the metal and $MO_{z/2}$ and MX_z are the corresponding oxide and halide of the same oxidation state *z*. *C* is a correction factor in kJ/mol.

For main and first transition-metal compounds, $a=1$ and $C=0$. For trivalent-state lanthanides, $a=2.155\pm 0.12$ and $C=1078.6\pm5.4$ or 1047.7 ± 5.0 kJ/mol. For tetravalent oxychlorides, $a=1$ and $C=20.9$ kJ/mol. For penta- and hexavalent compounds, $a=1$ and $C=0$.

2.4.4. Double salts with the formula MX_aY_b [25]

The standard enthalpies of formation of double salts of the type MX_aY_b can be calculated additively from the enthalpies of formation of their binary salts MX_c and MY_d.

For divalent metals the relation takes the form:

$$\Delta_f H^0_{298}(MXY) = 1/2\Delta_f H^0_{298}(MX_2) + 1/2\Delta_f H^0_{298}(MY_2) + C \quad (13)$$

where $C=-13.4$ or -17.6 kJ/mol

From an analysis of the more limited amount of data, available for trivalent and tetravalent metals, a simple additivity relation is again found

$$\Delta_f H^0_{298}(MX_aY_b) = (ax/z)\Delta_f H^0_{298}(MX_{z/x}) + (by/z)\Delta_f H^0_{298}(MY_{z/y}) + C \quad (14)$$

where *x*, *y*, and *z* are the formal valencies of X, Y, and M, respectively, i.e. $z=ax+by$, and $C=0$.

2.4.5. Oxides, carbonates, sulphates, hydroxides and nitrates [26]

The standard enthalpies of formation of any three compounds for a particular metal oxidation state can be correlated quantitatively by two-parameter linear equations.

For mono- and divalent compounds

$$\Delta_f H^0_{298}(SO_4) - \Delta_f H^0_{298}(O) = 1.36[\Delta_f H^0_{298}(CO_3) - \Delta_f H^0_{298}(O)] - 13.4\,\mathrm{kJ/mol} \quad (15)$$

For monovalent compounds

$$\Delta_f H^0_{298}(OH) - \Delta_f H^0_{298}(O) = 0.463[\Delta_f H^0_{298}(SO_4) - \Delta_f H^0_{298}(O)] - 9.6\,\mathrm{kJ/mol} \quad (16)$$

and

$$\Delta_f H^0_{298}(NO_3) - \Delta_f H_{298}(O) = 1.02[\Delta_f H^0_{298}(SO_4) - \Delta_f H^0_{298}(O)] - 234.7\,\mathrm{kJ/mol} \quad (17)$$

For divalent compounds

$$\Delta_f H^0_{298}(OH) - \Delta_f H^0_{298}(O) = 0.318[\Delta_f H^0_{298}(SO_4) - \Delta_f H^0_{298}(O)] + 94.6\,\mathrm{kJ/mol} \quad (18)$$

and

$$\Delta_f H^0_{298}(NO_3) - \Delta_f H^0_{298}(O) = 1.025[\Delta_f H^0_{298}(SO_4) - \Delta_f H^0_{298}(O)] - 500.4\,\mathrm{kJ/mol} \quad (19)$$

where $\Delta_f H^0_{298}(O)$, $\Delta_f H^0_{298}(SO_4)$, $\Delta_f H^0_{298}(CO_3)$, $\Delta_f H^0_{298}(NO_3)$, and $\Delta_f H^0_{298}(OH)$ are the standard enthalpies of formation in kJ/mol of the oxide, sulphate, carbonate, nitrate, and hydroxide, respectively, of the metal.

2.4.6. Halides [28]

The standard enthalpies of formation of any three solid halides, MX_n, MY_n, and MZ_n of any metal M with formal valence *n* (including cations such as NH_4^+), can be correlated by the general equation

$$\Delta_f H^0_{298}(MX_n) - \Delta_f H^0_{298}(MY_n) = a[\Delta_f H^0_{298}(MX_n) - \Delta_f H^0_{298}(MZ_n)] + bn \quad (20)$$

The coefficients *a* and *b* are the same for any particular main or subgroup of a given valence state. Values of *b* vary over a wide range, but *a* is always close to unity.

For any given group, maximum deviations are found to be no more than ±12.5 kJ/mol.

2.4.6.1. Enthalpies of formation of double oxides. Many methods are presented in the literature for estimating enthalpies of formation of double oxides. These are becoming increasingly important as new materials are developed. Some of the methods are specific to small groups of materials, others can be applied to a wider range of substances. Slough [30] has made a comparison of the methods available for estimating such values and has tabulated the results obtained. A summary of some of these methods is presented below.

2.4.7. *Plots involving the ratio of ionic charge to ionic radius*

Using the basic assumption that van der Waals and polarization forces are of major importance in determining the enthalpy change on reaction of two different oxides, Slough has developed a useful procedure for estimating this change [31]. He found that for many double oxide combinations, good linear plots of C/R against $\Delta_f H^0_{298}$ from the component oxides were obtained. (C is the charge number and R the crystal ionic radius of the cation.) Ferrates, titanates, tungstates, vanadates, zirconates, silicates, selenites and borates were all analysed in this way. Deviations of individual points from the linear plots were usually $\leq$20 kJ/mol. Fig. 6 illustrates plots obtained for certain borates and silicates.

Since the ionic charge of the cation is of major importance in applying this method, double oxides, formed from metal oxides in which covalent bonding predominates (e.g. BeO, Ag_2O, or Cu_2O), do not fit into the plots concerned.

2.4.8. *Statistical analysis methods*

Schwitzgebel et al. [32] have produced a general relation for the estimation of enthalpies of formation of double oxides based on a statistical correlation of existing data. This relation takes the form

$$\Delta_f H^0_{298}\,\mathrm{kJ/mol} = -4.184b(K_\alpha - A_\beta)^{n\beta} \qquad (21)$$

where $\Delta_f H^0_{298}$ is the enthalpy of formation from the component oxides, K_α represents the base strength of the oxide α or alternatively, the stability of the cation in the double oxide combination, A_β represents the acid strength of oxide β. The exponent $n\beta$ is taken to be a characteristic of the anion resulting from the double oxide combination. The cation and anion parameter values given by Schwitzgebel et al. are reproduced in Tables 9 and 10.

Table 9
Cation parameters

α	K_α	α	K_α
Ag^+	8.97	Li^+	15.39
Al^{3+}	4.37	Mg^{2+}	8.68
Ba^{2+}	18.18	Mn^{2+}	9.10
Be^{2+}	4.93	Mn^{3+}	5.47
Bi^{3+}	7.75	Na^+	19.97
Ca^{2+}	13.10	Ni^{2+}	7.46
Cd^{2+}	8.53	Pb^{2+}	9.34
Ce^{4+}	9.05	Rb^+	24.60
Co^{2+}	8.95	Sb^{3+}	3.24
Cs^+	25.31	Sn^{4+}	1.41
Cu^+	4.08	Sr^{2+}	15.74
Cu^{2+}	4.53	Th^{4+}	7.73
Fe^{2+}	8.25	U^{4+}	6.79
Fe^{3+}	4.29	Zn^{2+}	6.56
K^+	23.73	Zr^{4+}	9.87

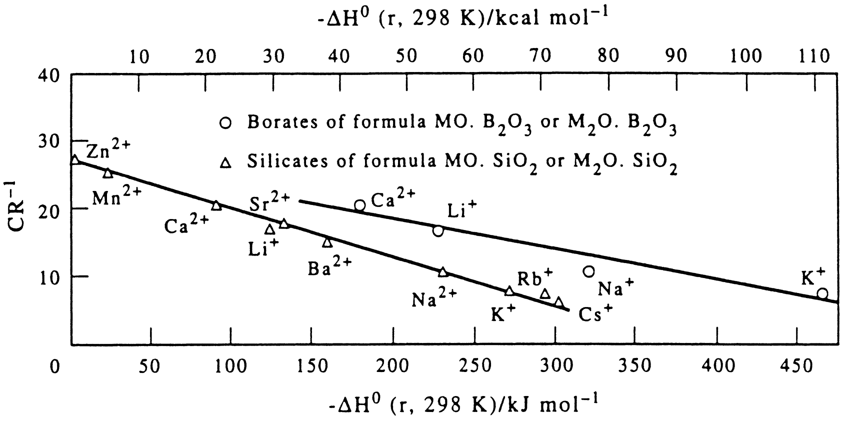

Fig. 6. Enthalpy of formation of certain borates and silicates as a function of the cation charge to radius ratio.

Table 10
Anion parameters

β	A_β	$n\beta$
SO_4^{2-}	−9.77	1.45
CO_3^{2-}	0.00	1.43
SO_3^{2-}	−2.60	1.44
$Fe_2O_4^{2-}$	7.45	1.39
CrO_4^{2-}	0.13	1.43
$V_2O_6^{2-}$	1.55	1.47
TiO_3^{2-}	5.13	1.40
WO_4^{2-}	0.87	1.48
MoO_4^{2-}	−2.87	1.38
$Al_2O_4^{2-}$	5.24	1.38

2.4.8.1. Additivity of bond energies – 'Le Van's method'. Le Van [33] has described a method for estimating enthalpies of formation of oxyacids based essentially upon the assumption of additivity of bond energies. This allows $\Delta_f H^0_{298}$ for an oxyacid salt to be expressed in terms of two characteristic parameters, P and Q, as given by the relation

$$\Delta_f H^0_{298}\,\text{kJ/mol} = [n(p)P + n(q)Q + 4.184(4(n(q))^2 + 4.184(n(p))^2] \qquad (22)$$

where $n(p)$ represents the number of anions, $n(q)$ the number of cations, and the characteristic parameters P and Q refer to anion and cation, respectively. Values of the parameters P and Q are given in Tables 11 and 12.

2.4.8.2. Comparison of data for similar compounds. Slobodin et al. [34] calculated enthalpies of formation for selected ortho-vanadates from a comparison of $\Delta_f H^0_{298}$ values for various compounds with the same

Table 11
Values of the parameter Q

Cation	Q	Cation	Q	Cation	Q	Cation	Q
Ag^+	−92	Cs^+	−444	Li^+	−452	Sb^{3+}	−393
Al^{3+}	−916	Cu^+	−84	Mg^{2+}	−741	Sn^{2+}	−406
Ba^{2+}	−883	Cu^{2+}	−213	Mn^{2+}	−523	Sn^{4+}	−544
Be^{2+}	−653	Fe^{2+}	−372	Na^+	−448	Sr^{2+}	−862
Bi^{3+}	−469	Fe^{3+}	−423	$NH4^+$	−326	Th^{4+}	−1435
Ca^{2+}	−858	Hg^+	−121	Ni^{2+}	−331	Ti^{2+}	−544
Cd^{2+}	−385	Hg^{2+}	−167	Pb^{2+}	−352	Tl^+	−205
Ce^{4+}	−1239	In^{3+}	−649	Pd^{2+}	−205	U^{4+}	−958
Co^{2+}	−343	K^+	−448	Ra^{2+}	−891	$UO2^{2+}$	−1292
Cr^{2+}	−728	La^{3+}	−1213	Rb^+	−444	Zn^{2+}	−439

Table 12
Values of the parameter P

Anion	P	Anion	P	Anion	P	Anion	P
$Al_2O_4^{2-}$	−1494	CrO_4^-	−565	$H_3P_2O_7^-$	−2121	TiO_3^{2-}	−795
AsO_4^{3-}	−460	$Cr_2O_4^{2-}$	−1075	SO_4^{2-}	−569	UO_4^{2-}	−1318
$HAsO_4^{2-}$	−607	IO_3^-	−109	ReO_4^-	−657	VO_3^-	−762
$H_2AsO_4^-$	−753	MnO_4^-	−393	SeO_4^{2-}	−305	VO_4^{2-}	−975
BO_2^-	−653	MoO_4^{2-}	−732	SiO_3^{2-}	−795	WO_4^{2-}	−845
BO_3^-	−515	NO_2^-	+29	SnO_3^{2-}	−381	ZnO_2^{2-}	−13
$B_4O_7^{2-}$	−2853	NO_3^-	−67	SO_3^{2-}	−314		
BrO_3^-	+84	PbO_3^{2-}	−84	HSO_3^-	−444		
ClO^-	+50	$PO4_4^-$	−854	HSO_4^-	−724		
ClO_2^-	+63	HPO_4^{2-}	−983	$S_2O_3^{2-}$	−314	$HCOO^-$	−285
ClO_3^-	+34	$H_2PO_4^-$	−1146	$S_2O_5^{2-}$	−644	CH_3COO^-	−326
ClO_4^-	+21	HPO_3^{2-}	−623	$S_2O_6^{2-}$	−908	$CH_3CH_2COO^-$	−352
CNO^-	−13	$H_2PO_3^-$	−799	$S_2O_8^{2-}$	−1105		
CO_3^{2-}	−356	$P_2O_7^{4-}$	−1766	$S_4O_6^{2-}$	−950		
HCO_3^-	−544	$H_2P_2O_7^{2-}$	−2004	SrO_3^{2-}	−335		

cation and the ortho-, EO_4(n-), anion. Thus the sulphates, phosphates, molybdates, and orthovanadates of di- and trivalent elements were chosen for comparison, and calculations were made using the relation

$$A = \Delta\Delta_f H^0_{298}/rm \tag{23}$$

where $\Delta\Delta_f H^0_{298}$ is the difference between the experimental and additive value for formation of the particular compound from the corresponding oxides (referred to one EO_4(n-) group), r the radius of the cation, and m the number of cations per EO_4(n-) group.

Slobodin et al. found, for the four types of salt selected, and using Ba^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+}, Fe^{2+}, Ni^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+} as the cations concerned, that the values of A for compounds with the same cation vary almost linearly and that the straight lines joining the values of A for compounds with the same cation are parallel. (see Fig. 7). This enables missing values to be estimated with a fair degree of certainty. The method can presumably be applied in a similar manner to other compounds.

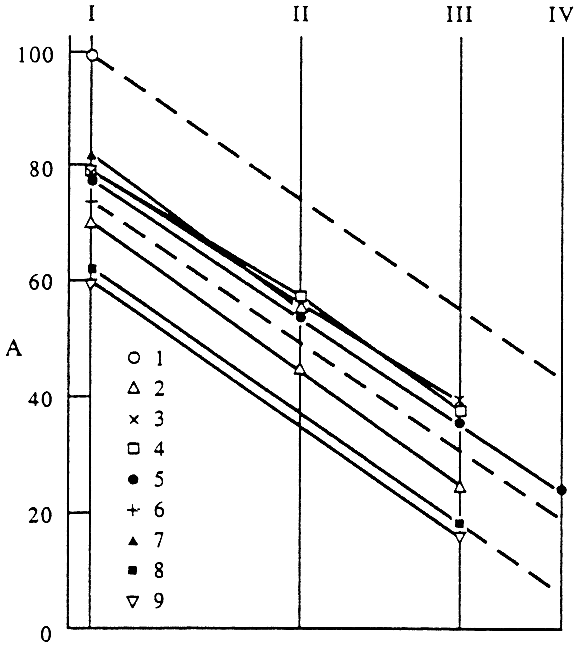

Fig. 7. Dependence of the parameter A for various compounds with the same cation on the anionic groups: (I) sulphates; (II) phosphates; (III) molybdates; (IV) vanadates; (1) Cr^{3+}; (2) Al^{3+}; (3) Sr^{2+}; (4) Ba^{2+}; (5) Ca^{2+}; (6) Fe^{3+}; (7) Mg^{2+}; (8) Ni^{2+}; (9) Fe^{2+}.

3. Alloys

It is important to emphasise that an alloy system must be considered as a whole when evaluating thermochemical data critically. Consideration of phases individually, and not in relation to neighbouring phases, has often led to inconsistencies when the resulting data are used to calculate phase equilibria in a given system. Several methods of approximating the thermodynamic properties of alloy phases are described in Chapters 1 and 4 of [1]. Here, some more recent published methods for calculating thermodynamic values of alloys from available physical property information are presented.

3.1. Homologous series

A certain relationship appears to exist between the enthalpy of formation of metal compounds and the atomic number of the metal in compounds of the same stoichiometric proportion and the same common radical. Depending on the compounds concerned, the curves obtained from this correlation may show sharp maxima and/or minima, but missing values can nevertheless be predicted from the curves with a fair degree of reliability.

More recently, Pettifor [20] has reorganised the Periodic Table of the elements into a single string instead of the normal Periods and Groups – the relative ordering being given by what Pettifor terms the 'Mendeleev number'. The resulting sequence is illustrated in Fig. 8.

The purpose of the re-ordering was to permit a better classification of the structures of binary compounds. Using this new arrangement of the Periodic Table, enthalpies of formation of particular types of compound with particular structures can be plotted as a function of the Mendeleev number. Such a plot has been made by Stolten [21] for metal nitrides and carbides with the cubic NaCl structure Fig. 9. A similar plot for the transition metal silicides, M_5Si_3, with the $D8_m$ structure is presented in Fig. 10.

The values lie on a smooth curve, rather than on the more irregularly-shaped curves resulting from the

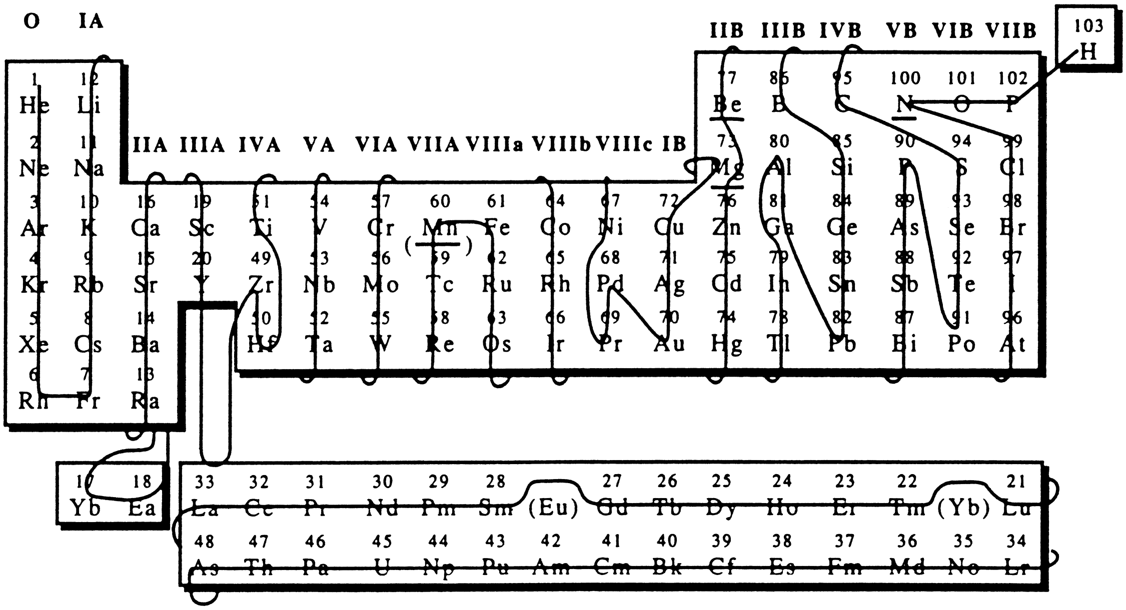

Fig. 8. The Pettifor single string rearrangement of the Periodic Table in the sequence of the Mendeleev number.

'conventional' Periodic arrangement. This enables not only missing values to be estimated for compounds which are known to exist, but also values which correspond to compounds in a metastable structure. Such information is particularly important in calculating the stability ranges of phases formed from mixtures of compounds.

3.2. The 'Miedema method' for enthalpies of mixing and formation

In the Wigner–Seitz model of the alkali metals each atom is segregated into a volume within which all the electrons on the atom are treated as being localized and in normal atomic states except one electron, which is in an *s* state and is treated as the electron giving rise to the electrical conductivity of the metal. This electron has a wave function which is different from that in the isolated atom. The *s* wave function at the periphery of the cell occupied by each atom joins smoothly with the *s* wave function in neighbouring cells, thus permitting easy movement of *s* electrons among the cells. This gives rise to metallic conduction.

When an alloy is formed between two elements, the cells containing the metallic ions will differ from one metallic species to the other. The nature of these species and their relative attraction for valence electrons, which is reflected in the Pauling electronegativities, makes an important contribution in a negative sense to the enthalpy of formation of alloys according to Miedema [35]. Counteracting this effect is the mismatch of conduction electron wave functions and electron densities at the joining plane between two cells containing different metallic ions. This density term (Δm) leads to a positive contribution to the enthalpy of mixing. The enthalpy of formation of an intermetallic compound can thus be expressed in a simplified form by the equation

$$\Delta_f H^0_{298} = -A(E_A - E_B)^2 + B(\Delta m) \qquad (24)$$

Miedema identifies the first term, following the model of metallic contact potentials in free electron theory, with the difference in work function for the two metals, and shows that the electron density term can be related to the respective compressibilities of the metals forming the compound

$$m = B/V$$

where V is the molar volume.

Miedema et al. [35–39] have published a series of papers in which they have demonstrated that experimental enthalpies of formation for solid and liquid

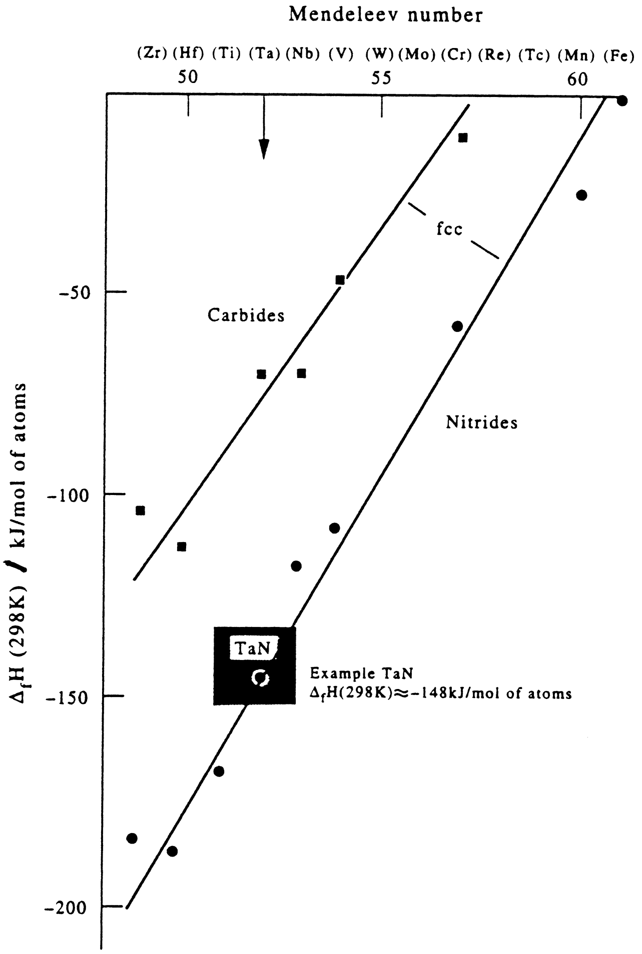

Fig. 9. Enthalpies of formation of carbides and nitrides with the cubic NaCl structure plotted using the Pettifor arrangement of the Periodic Table.

binary alloys of transition metals can be accounted for within reasonable limits. The expression they derive for the enthalpy of formation is

$$\Delta_f H \approx [-Pe(\Delta\phi^*)^2 + Q_0(\Delta n_{WS}^{1/3})^2] \qquad (25)$$

where P and Q are constants having nearly the same values for widely different alloy systems (e.g. intermetallic compounds of two transition metals or liquid alloys of two non-transition metals), ϕ^* is obtained by adjusting the experimental work functions, and n is obtained from estimates of the charge density at the Wigner–Seitz boundary.

For regular liquid or solid solutions, the concentration dependence of $\Delta_f H$ contains the product $c_A^s c_B^s$. For ordered compounds, the area of contact between dissimilar cells is larger than the statistical value. Near the equiatomic composition, experimental results show that the ordering energy of alloys $(f(c_A^s, c_B^s))$ is, quite generally, of the order of 1/3 of the total enthalpy of formation.

Consideration of the physical origin of the two terms in Eq. (25) suggests that in addition to the ordering function, there is another factor, $g(c_A, c_B)$, that varies somewhat with the relative concentration of the two metals. Concentration dependent values of $\Delta_f H$ can thus be derived using the more general expression

$$\Delta_f H/N_0 = f(c_A^s, c_B^s).g(c_A, c_B)[-Pe(\Delta\phi^*)^2 + Q_0(\Delta n_{WS}^{1/3})^2] \qquad (26)$$

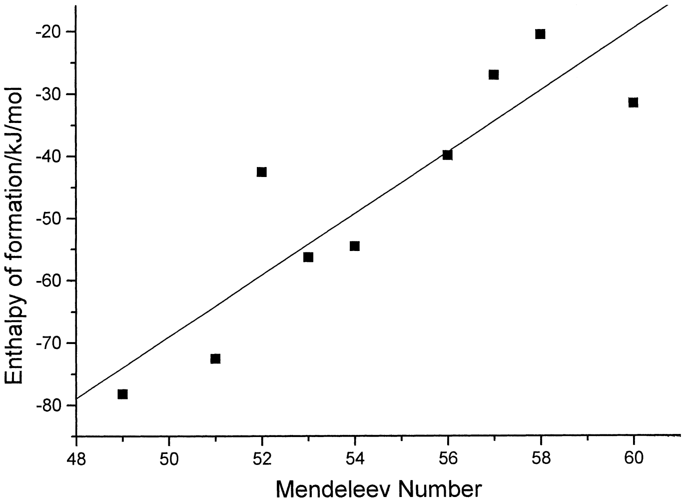

Fig. 10. Enthalpies of formation of transition metal silicides, M_5Si_3, with the $D8_m$ structure plotted using the Pettifor arrangement of the Periodic Table.

N_0 is Avogadro's number, $\Delta_f H$ is expressed per gram atom of alloy, and

$$g(c_A, c_B) = 2(c_A V_A^{2/3} + c_B V_B^{2/3})/(V_A^{2/3} + V_B^{2/3}). \tag{27}$$

Table 13 presents the values of ϕ^*, $n_{WS}^{1/3}$ and $V_m^{2/3}$ selected by Miedema et al. [26] and used in calculating enthalpies of formation.

The method due to Miedema, described above, has the great advantage that enthalpies of formation can be calculated for many alloy systems where no experimental information whatsoever is available.

3.3. Properties of mixing 'free volume' theory

In a recent series of papers [40–42], Tanaka, Gokcen and Morita have described how the thermodynamic properties of mixing in liquid binary alloys can be derived from physical properties using the 'free volume' theory proposed by Shimoji and Niwa [43], the first approximation of the regular solution model as described by Gokcen [44], and a consideration of the configuration and vibration of the atoms in the alloys.

Assuming that an atom vibrates harmonically in its cell surrounded by its nearest-neighbours, the following equations may be used to calculate the excess properties of mixing:

$$\Delta G^E = \Delta H - T\Delta S^E \tag{28}$$

$$\Delta H = N_{AB}\Omega_{AB}/Z \tag{29}$$

with

$$N_{AB} = ZN_0 X_A X_B (1 - X_A X_B \Omega_{AB}/kT) \tag{30}$$

$$\Delta S^E = \Delta S^E_{conf} + \Delta S^E_{nonconf} \tag{31}$$

$$\Delta S^E_{conf} = -X_A^2 X_B^2 \Omega_{AB}^2/2kT^2 \tag{32}$$

$$\begin{aligned}\Delta S^E_{nonconf} &= 3/2kN_0\{X_A \ln(v_A/v_{AA}) \\ &\quad + X_B \ln(v_B/v_{BB})\} \\ &= 3/2kN_0\{2X_A \ln(L_A/L_{AA}) \\ &\quad + 2X_B \ln(L_B/L_{BB}) + X_A \ln(U_{AA}/U_A) \\ &\quad + X_B \ln(U_{BB}/U_B)\}\end{aligned} \tag{33}$$

where N_{AB} is the number of A–B pairs; Z the coordination number; Ω_{AB} the exchange energy; k the Boltzman's constant; N_0 the Avogadro number; X_A, X_B are mol fractions; v_A, v_B, v_{AA} and v_{BB} are free volumes; L_A, L_B, L_{AA} and L_{BB} are the distances which the interatomic potential extends in a cell; and U_A, U_B, U_{AA} and U_{BB} are the potential energy depths in a cell. In these equations, the suffices AA and BB denote pure elements and A and B the states of A and B atoms in an A–B alloy.

By differentiation and rearrangement, the above equations can also be used to derive partial thermo-

Table 13
Parameters of Eq. (1) to be used in calculating enthalpies of formation of alloys

Metal	ϕ^* (V)	$n_{\mathrm{WS}}^{1/3}$	$V_{\mathrm{m}}^{2/3}$ (cm^2)	Metal	ϕ^* (V)	$n_{\mathrm{WS}}^{1/3}$	$V_{\mathrm{m}}^{2/3}$ (cm^2)
Sc	3.25	1.27	6.1	Li	2.85	0.98	5.5
Ti	3.65	1.47	4.8	Na	2.70	0.82	8.3
V	4.25	1.64	4.1	K	2.25	0.65	12.8
Cr	4.65	1.73	3.7	Rb	2.10	0.60	14.6
Mn	4.45	1.61	3.8	Cs	1.95	0.55	16.8
Fe	4.93	1.77	3.7	Cu	4.55	1.47	3.7
Co	5.10	1.75	3.5	Ag	4.45	1.39	4.7
Ni	5.20	1.75	3.5	Au	5.15	1.57	4.7
Y	3.20	1.21	7.3	Ca	2.55	0.91	8.8
Zr	3.40	1.39	5.8	Sr	2.40	0.84	10.2
Nb	4.00	1.62	4.9	Ba	2.32	0.81	11.3
Mo	4.65	1.77	4.4	Be	4.20	1.60	2.9
Tc	5.30	1.81	4.2	Mg	3.45	1.17	5.8
Ru	5.40	1.83	4.1	Zn	4.10	1.32	4.4
Rh	5.40	1.76	4.1	Cd	4.05	1.24	5.5
Pd	5.45	1.67	4.3	Hg	4.20	1.24	5.8
La	3.05	1.09	8.0	Al	4.20	1.39	4.6
Hf	3.55	1.43	5.6	Ga	4.10	1.31	5.2
Ta	4.05	1.63	4.9	In	3.90	1.17	6.3
W	4.80	1.81	4.5	Tl	3.90	1.12	6.6
Re	5.40	1.86	4.3	Sn	4.15	1.24	6.4
Os	5.40	1.85	4.2	Pb	4.10	1.15	6.9
Ir	5.55	1.83	4.2	Sb	4.40	1.26	6.6
Pt	5.65	1.78	4.4	Bi	4.15	1.16	7.2
Th	3.30	1.28	7.3	Si	4.70	1.50	4.2
U	4.05	1.56	5.6	Ge	4.55	1.37	4.6
Pu	3.80	1.44	5.2	As	4.80	1.44	5.2

dynamic properties of mixing:

$$\Delta\bar{H}_{\mathrm{B}} = \Omega_{\mathrm{AB}} \tag{34}$$

$$\begin{aligned}\Delta\bar{S}^{\mathrm{E}}_{\mathrm{B}} = \Delta\bar{S}^{\mathrm{E}} &= 3/2kN_0[(L_{\mathrm{AA}} - L_{\mathrm{BB}})^2]/L_{\mathrm{AA}}L_{\mathrm{BB}} \\ &\quad + \{4U_{\mathrm{AA}}U_{\mathrm{BB}} - 2\Omega_{\mathrm{AB}}(U_{\mathrm{AA}} + U_{\mathrm{BB}}) \\ &\quad - (U_{\mathrm{AA}} + U_{\mathrm{BB}})^2\}/2U_{\mathrm{AA}}U_{\mathrm{BB}}\}\end{aligned} \tag{35}$$

where U_{AA} and U_{BB} can be obtained from:

$$U_{ii} = -2\pi^2 L_{ii}^2 M_{ii}\nu_{ii}^2/N_0 \quad (i = \mathrm{A\ or\ B}) \tag{36}$$

with M_{ii} being the atomic weight, L_{ii} half the nearest-neighbour distance, given by

$$L_{ii} = 1/2(2^{1/2}v_{ii}/N_0)^{1/3} \quad (i = \mathrm{A\,or\,B}) \tag{37}$$

where v_{ii} is the molar volume. ν_{ii} is the frequency of an atom, which can be evaluated using the following equation proposed by Iida and Guthrie [45]:

$$\nu_{ii} = 2.8 \times 10^{12}\beta_{ii}(T_{\mathrm{m}'ii}/M_{ii}v_{ii}^{2/3})^{1/2} \quad (i = \mathrm{A\ or\ B}) \tag{38}$$

where $T_{\mathrm{m}'ii}$ is the melting point and β_{ii} the coefficient required to transform the solid-state frequency to that in the liquid state at the melting point. Value of β_{ii} can be obtained from experimental data for the surface tension of the pure elements in the liquid state.

It can be seen from the above equations that, if the partial enthalpy of mixing is known, both the partial excess entropy and partial excess Gibbs energy of mixing can be calculated. Using these equations, Tanaka et al. have demonstrated the relation between enthalpy and excess entropy of mixing in liquid binary alloys. The necessary enthalpy of mixing data for the calculations were obtained both from published experimental values and also by use of the Miedema method described above. In addition, an equation allowing for the influence of temperature on the enthalpy–entropy relation was derived.

Tanaka et al. have used the free volume theory to calculate successfully activity coefficients of solutes at infinite dilution in liquid iron-base binary alloys [42].

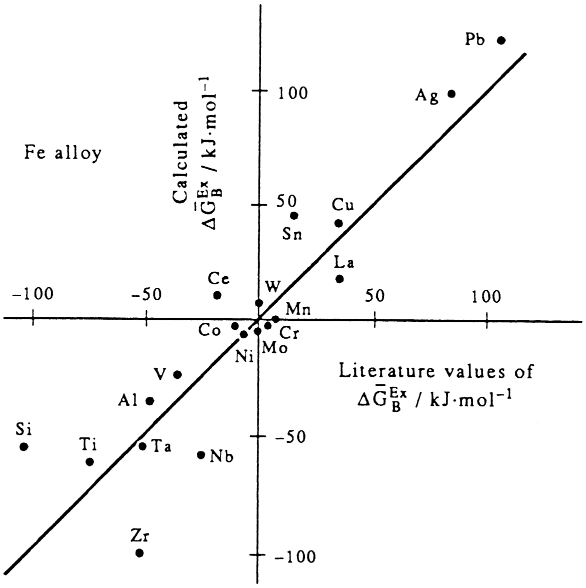

Fig. 11. Calculated partial excess Gibbs energy values for solutes in dilute solution in liquid Fe-base binary alloys.

Some results of these calculations are shown in Fig. 11.

3.4. Correlation methods

In the CALPHAD modelling of phase diagrams as well as in analysing the cohesive and thermal behaviour of materials, it is necessary to have information on various kinds of properties. The requirements have been discussed, in particular, in a series of papers by Fernandez Guillermet and Grimvall [46–48] and a summarised form is presented in the Group 5 report contained in 'Proceedings of the 1995 Ringberg Workshop on Unary Data' [49]. The requirements are of three kinds:

3.4.1. Thermophysical properties of single phases

- Molar volume (V_m) or average volume per atom (Ω)
- Isothermal (B_T) and isentropic (B_S) bulk moduli; other elastic $\hat{E}$ constants, and the 'elastic' Debye temperature (θ_E)
- The pressure derivative ($B'=(\partial B/\partial T)_T$) and the temperature of the bulk modulus ($\partial B/\partial T$)
- The thermal expansion coefficient $\alpha=1/V_m(\partial V_m/\partial T)_P$
- The heat capacity at constant pressure (C_P) as a function of temperature; in particular, the low temperature C_P values and the related Debye temperature (θ_C) and electronic heat capacity (γ_e)
- The total entropy (S_T) as a function of temperature, and the related entropy Debye temperature (θ_S)

3.4.2. Thermophysical properties of two phases

- Equilibrium temperatures for solid–solid phase equilibria (T_{tr}), enthalpies (ΔH_{tr}) and entropies (ΔS_{tr}) of transformation
- Equilibrium temperatures for solid–liquid equilibrium (T_{fus}), enthalpies (ΔH_{fus}) and entropies (ΔS_{fus}) of fusion
- Enthalpies of formation ($\Delta_f H^0_{298}$) of compounds at 298 K
- Cohesive energies (E_{coh}) of elements (Me) and compounds (MeX), i.e. the enthalpy changes for the reactions

$$\mathrm{Me(st)} \rightarrow \mathrm{Me(g)}$$

$$\mathrm{MeX(st)} \rightarrow \mathrm{Me(g)} + \mathrm{X(g)}$$

at 0 K and 1 atm, respectively. In these equations 'st' and 'g' refer to the stable modification and the gaseous monoatomic state, respectively.

For many stable phases, the above properties are known from experimental measurements and can be obtained from standard evaluations of thermodynamic data. However, in the case of metastable phases, usually there are no experimental data available and methods to predict these quantities and to judge the reliability of existing estimates are needed. A brief summary of the predictive methods, based on established trends in the thermodynamic quantities of elements and compounds, is given here.

3.4.3. Properties related to cohesion and the equation of state (EOS) of solids

Many of the properties reviewed in the previous section depend upon the bonding behaviour of the solid. The way in which they co-vary has been studied both empirically and theoretically. Examples of the empirical approach are the relations between B_T and $1/\Omega$, and that between E_{coh} and B_T which have been established for elements and compounds. Additional relations are provided by models of the binding energy vs. distance function. For instance, the Lennard–Jones type of expression $E(\Omega)=a/\Omega^m+b/\Omega^n$ predicts that the dimensionless ratio $\beta=E_{\mathrm{coh}}/B_{\mathrm{T}}\Omega$ depends only on the parameters '*m*' and '*n*'. The EOS developed by Rose et al.[50] predicts that the pressure derivative B'_{T} is related in a simple way to the quantity β.

A useful combination of thermodynamic quantities is the well-known Gühneisen parameter

$$\gamma_{\mathrm{G}} = \alpha V_{\mathrm{m}} B_{\mathrm{T}}/C_V \tag{39}$$

$\gamma_{\mathrm{G}}(298)$ has been shown to remain fairly constant within a given class of substances.

Recently, it has been shown [46–48] that correlations involving the vibrational entropy of elements and compounds can be established by using the effective force constant k_{S}, defined by

$$k_{\mathrm{S}} = (k_{\mathrm{B}}\theta_{\mathrm{S}}/h)^2 M_{\mathrm{eff}} \tag{40}$$

where M_{eff} is the logarithmically averaged atomic mass in a formula unit of the compound, and the characteristic energy E_{S}

$$E_{\mathrm{S}} = k_{\mathrm{S}}\Omega^{2/3} \tag{41}$$

which is related to the lattice vibrations. It has been found that E_{S} co-varies with $\Delta_{\mathrm{f}}H^0_{298}$ and E_{coh} in the case of transition metal carbides and nitrides.

4. Neural network scanning of databases

There are thousands of compounds for which thermodynamic data are unavailable. With the present extensive computer databases it should be possible to estimate missing values relatively easily by making use of the computer to exploit trends in the Periodic Table and to develop empirical correlations among properties. As discussed at the 1995 Ringberg Workshop on Unary Data [49], what is required is:

1. The addition of some other properties to our databases. These properties, although of importance in their own right, should be added because they can act as independent variables in the correlations. These include, in addition to those listed above:
   - Electronegativities
   - Ionic and atomic radii
   - A description of the structural units involved (ex: K_2SO_4 contains K and SO_4 ions)
   - A description of structure and bond types.
2. The development of software which can readily access the data for a class of compounds, set up property spreadsheets, and search for multivariate correlations. Physical principles would guide the user in the choice of variables, etc.
3. The development of neural networks accessing the above databases. The user would present the program with a property to be estimated, along with a number of other properties with which it might be correlated. Some idea of the expected correlations would also be given as a starting point. The network would then learn (i.e. refine the correlations) by looking at all compounds within a class of compounds from the database. As new data on a compound or data on new compounds became available, they could be fed to the program to refine the neural network. With a neural network for each property, we would have a true expert system for property estimations.

Many of the estimation methods described in this paper are indeed currently being programmed and linked for use with the SGTE Databases as a source of reference data wherever needed. They will be available as a software product shortly [51].

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