Scaling of Equilibrium Properties of Inorganic Substances

A. A. Bondi
Shell Development Co., Emeryville, Calif. 94608

Theoretical models suggest scaling rules for a wide range of technically important physical properties of ionically and covalently bonded solids and melts. The properties so treated are the melting point, critical constants, Debye temperature, density, thermal expansion coefficient, and the usual elastic moduli. Scaling with universal pure numbers as expected by theory turns out to be possible only rarely, if at all. Instead, one must accept specific trends of the scaling factors that can be grouped by chemical families and therefore still be useful for the estimation of physical properties from composition data. Since the chemical bonding mode in most inorganic compounds is neither fully ionic nor fully covalent, definition of the interaction energy in the scaling parameters is least reliable when the usual coulombic potential is assumed, and is most reliable when a phenomenological definition is adopted, namely, the experimentally easily accessible energy of atomization. While perfectly feasible in crystals composed of simple ions, only the coulombic potential can be used for scaling the properties of substances containing complex ions. Other inherent limitations to the property estimation of inorganic substances, such as the well-known uncertainties of ion radii, will also be discussed.

This work is to provide chemists with means to estimate the magnitude of equilibrium properties of ionically and covalently bonded inorganic solids and melts from a knowledge of their structural organization. Incidentally, this work is to encourage the use of similitude principles for the correlation of physical property data in the absence of quantitatively reliable theories.

The scope of these examples for the use of similitude principles has been restricted to the scaling of equilibrium properties by readily accessible interparticle energy and distance measures. The properties selected for illustration of the principle are the Debye frequency of the crystal, the elastic constants, thermal expansion, and the melting point. Application of the technique to the technically very interesting rate properties is an obvious extension that is currently under way.

General Principles

The exact molecular theories of solids and liquids are quite awkward to use for the calculation of physical properties. Moreover, they are not applicable for other than monatomic species. Hence it is generally more convenient to make the independent and dependent variables in the equations dimensionless with the molecule properties occurring in the equations. In all first-order approximations only three molecular parameters appear: the equilibrium potential energy, u_o, between neighboring molecules, their equilibrium distance r_o, and the mass per molecule, m.

These parameters can be calculated in principle from the electronic properties of atoms. In practice they are available from various experimental data, especially if one deals with monatomic systems. In the sense of the present treatment, ionic and covalent solids or melts are considered to be composed of monatomic species, except for cases where one or more lattice positions per unit cell are occupied by complex ions. The complication caused by such ions will be discussed separately.

In purely ionic systems (ignoring, in the present approximation, the repulsion component of u_o), $u_o = (Ze)^2/d_{ij}$, where Z = effective valence acting between neighbor atoms i and j, e = elementary charge, and d_{ij} is their equilibrium distance, generally available from X-ray crystallography. In the absence of experimental data, d_{ij} can be estimated from the usual ionic radii. Conversion of the indicated Coulomb energy to lattice energy requires the Madelung constant which is available for many crystals (*14*).

Only few crystals and melts are held together by ionic forces alone or by covalent bonding alone. One generally deals with mixed bonding. Since purely covalent bond energies can be estimated from electronegativity data, one can estimate the total bonding energy if one knows the fractional ionic bonding. Such estimates are generally made by comparing the observed interatomic distance $d_{ij}(o)$ with the appropriate sum of the ionic radii. Then one can estimate the interatomic energy u_o from the sum of these two energy components divided by one half of the coordination number, n_c.

A totally different approach is to identify u_o as the measured energy of atomization, E_a, and set $u_o = 2\ E_a/n_c$, and proceed with a phenomenological rather than a theoretical definition of the molecule parameter. Then one would use the experimentally observed zero-point volume, V_o (*4*), as measure of the interatomic distance. This approach is restricted to solids or melts composed of monatomic species, since the internal cohesion of a complex ion—also measured in E_a—may not contribute substantially to the system's cohesive forces. With substances containing complex ions one may be restricted to estimates based on the assumption of purely coulombic interaction.

Comparisons of the generalized—i.e., dimensionless—properties with theory will be limited to comparison with the predictions of the Mie-Grueneisen equations of state and their derivatives. They are based on the assumption of central force fields and of a pair potential

$$\phi(r) = (A/r^m) - (B/r^n) \tag{1}$$

Whenever covalent bonding makes a substantial contribution, the exponents m and n can have only qualitative significance (*12*), and deviations from theory might be substantial.

Debye Frequency

The heat capacity and several other physical properties of condensed phases can be estimated if their Debye frequency is known. Assuming that the crystal lattice acts as a simple harmonic oscillator assembly, the Debye frequency ω_D would be given by

$$\omega_D \sim (1/2\,\pi d_{ij})(mnu_o/\mu)^{1/2} \tag{2}$$

where μ is the reduced mass of the oscillating atoms. In the framework of the present system of generalized properties, the generalized Debye frequency is

$$\omega_D d_{ij}(\mu/E_a)^{1/2} = \text{const} \tag{3}$$

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[1] Present address, Shell Development Co., P.O. Box 481, Houston, Tex. 77001

for a family of crystals within which n_c, m, and n are invariant. In purely ionic lattices the generalized Debye frequency is

$$\omega_D(d_{ij}^3\mu)^{1/2}/Ze = \text{const} \qquad (4)$$

for a family of compounds within which n_c, m, n, and the fraction f_i of ionic bonding are constant.

Typical results are presented in Tables I and II. Within the reliability limits imposed by comparatively sparse sampling in several compound classes, one can discern trends that are in order-of-magnitude agreement with expectation from the simple theory back of Equation 2. The error limits of heat capacity and related predictions based on these generalizations should be tolerable for most engineering applications, if the standard deviations from the correlation mean are valid indications of likely prediction errors.

Effects of anharmonicity and of lattice defects on the heat capacity at $T > \theta_D$ must be estimated separately, of course. It should be noted that predictions of both of these also depend strongly on the assumed lattice energy (*10*).

Elastic Constants

The Mie-Grueneisen relations yield for the bulk modulus B_o at 0K the generalized form (*9*)

$$B_oV_o/u_s = \tfrac{1}{3}\,(m\cdot n/m - n)\,\{[(n/3) + 1](v_o/v^{n/3} - [(m/3) + 1](v_o/v)^{m/3}\} = F_1(m,n,\rho^*) \qquad (5)$$

where ρ^* is the packing density of the condensed phase. The same general form of relation holds for the other elastic moduli since Poisson's ratio at 0K is likewise a function of m,n,ρ^*. At a fixed value of the zero-point packing density, $F_1(m,n)$ takes on the numerical values shown in Figure 1.

For molecular crystals one finds that the generalized elastic moduli depend very strongly on the packing densi-

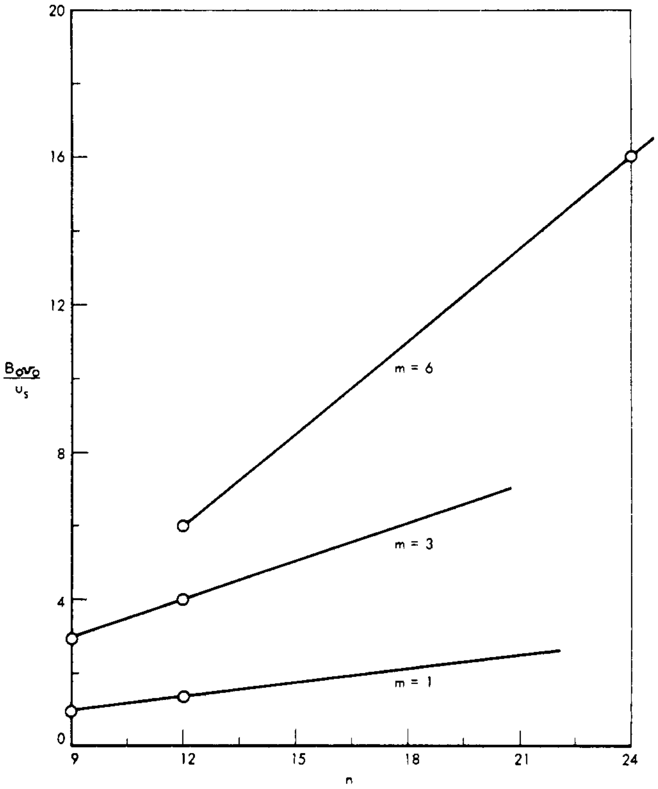

Figure 1. Theoretical Relation Between the Generalized Bulk Modulus B_oV_o/u_s and m,n according to Equation 5 at $V_o/V = 1$

Table I. Generalized Debye Frequencies[a] of Ionically and Covalently Bonded Solids

Substance	Lattice	bcc[b]	fcc	hcp
Metallic elements	$\omega_D a(M/\Delta H_s)^{1/2}$	0.93 ± 0.07	1.13 ± 0.075	0.87 ± 0.1
Alkali halides, MgO, etc.	$\omega_D d_{ij}(\bar{M}/E_a)^{1/2}$	0.348 ± 0.024		
	$\omega_D d_{ij}(\bar{M}/E_L)^{1/2}$	0.303 ± 0.04		
Sulfide, oxides	$\omega_D d_{ij}(\bar{M}/E_a)^{1/2}$	0.122 ± 0.012		

[a]From data of ref. *1*. [b]And simple cubic.

Table II. Generalized Bulk Moduli[a].(B_oV_o/E_a) of Metal Oxides, Sulfides, and Carbides (at Room Temperature)

Cubic crystals									
MgO:	1.75								
CaO:	1.80	CaS:	1.70	MnS:	2.26	FeO:	1.97	Fe_3O_4:	2.16
SrO:	2.45			ZrO_2:	2.05	NiO:	2.38		
ThO_2:	2.1	UO_2:	2.0			CoO:	2.42		
Hexagonal crystals									
BeO:	2.65								
ZnO:	2.80	ZnS:	3.00						
		CdS:	3.44						
Rhombic crystals									
Al_2O_3:	2.08								
MnO:	2.05								
Triagonal crystals									
Fe_2O_3:	1.24								
Tetragonal crystals									
TiO_2:	2.1								

[a] From data of ref. *8*.

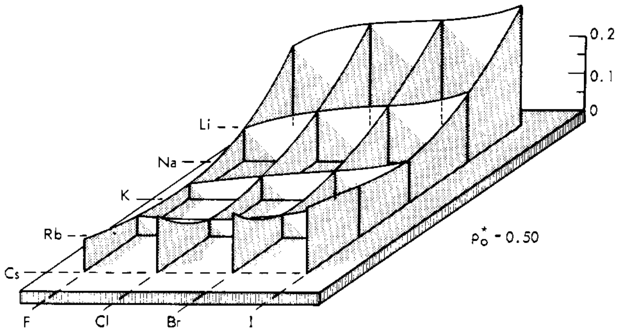

Figure 2. Topography of zero-point packing density of alkali halide crystals, from data of ref. *4*

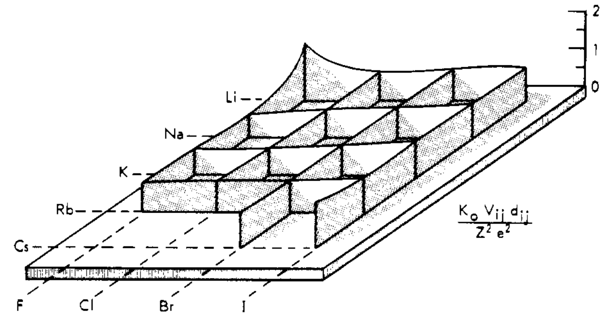

Figure 4. Generalized coulombic bulk moduli of alkali halides
Note the different effectiveness of phenomenological and coulombic reducing parameter in producing a uniform generalized modulus

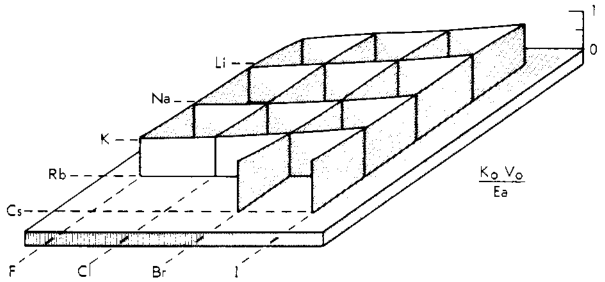

Figure 3. Generalized phenomenological bulk moduli of alkali halides
Note the different effectiveness of phenomenological and coulombic reducing parameter in producing a uniform generalized modulus

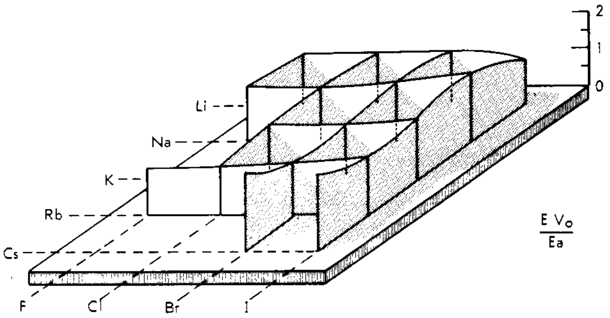

Figure 5. Generalized tensile moduli of alkali halides

ty (*5*). Hence it seemed worthwhile to examine the packing density of a few ionic crystals before trying to correlate their elastic moduli. The packing density of ionic crystals is defined as

$$\rho^*_{ij} = (4\,\pi/3)\, \rho_{ij} N_A (r_i^3 + r_j^3)/M \qquad (6)$$

where ρ is the measured density of the salt (ij), M its molecular weight, r the ion radii, and N_A Avogadro's number.

The packing density data of the alkali halides have been plotted in Figure 2. Qualitatively these data exhibit the expected pattern for the fluorides and chlorides in that a minimum of the right magnitude ($\sim$0.52) appears at the point of equisized anion and cation. However, this trough does not continue diagonally toward the bottom row as one would expect if the ions were hard spheres. Instead, the trough continues parallel to the bottom row, suggesting that the increasing polarizability permits close squeezing of the heavy ions resulting in higher-than-expected density.

The corresponding graphs of the generalized elastic moduli (at 0K) of the alkali halides (Figures 3-5) show very little dependence on composition and none that can be related to the packing density. This observation suggests that one should be able to estimate the zero-point moduli in other families of ionic crystals once the modulus of one "family" member has been determined. A few random examples from other compound families have been collected in Table II.

The elastic moduli of the metallic elements span a range of about two orders of magnitude which are effectively collapsed into a range spanning about a factor of two by their dimensionless representation. This range is still wider than that for the ionic crystals and, in addition, forms a curious pattern when mapped onto the periodic table, as shown on Figures 6 and 7. There are a few unexplained reversals in relative magnitude between adjacent elements as one moves from the bulk to the tensile modulus. Since the possibility of measurement errors cannot be excluded, it is perhaps premature to look for any sophisticated explanations for the waves on these graphs. Yet, until the accuracy of the data is established and the strange oscillations have been give a rational background, it will be hard to predict the elastic properties of still unmeasured elements or of alloys.

The step from the zero-point moduli to their numerical value at any other temperature is most easily performed by the Wachtmann-Anderson equation

$$B(T) = B_0 - 2\,\alpha_s T B_0 (B_1 - 1)^2 \exp(-\theta_D/2\,T) \qquad (7)$$

where α_s is the cubic thermal expansion coefficient and B_1 is the dimensionless pressure coefficient dB/dP. Both of these coefficients can also be represented as functions of m, n, and ρ^*. The thermal expansion coefficient in generalized form is

$$\alpha u_s/C_v = [(n + m + 1)/2][(m - n)/(m{\cdot}n)] \times [n/3\,(v_s/v)^{n/3} - (m/3)\,(v_s/v)]^{-1} \qquad (8)$$

the qualitative predictions of which are in good agreement with experimental data as shown by comparison of the numbers in Table III with the numbers taken from Figure 8.

However, a troublesome aspect is that the generalized expansion coefficient moves with temperature much as the closely related Grueneisen constant does. The thermal expansion coefficient estimated from the generalized relations is therefore only approximate at least at $T < \theta_D/2$. At $T \geq \theta_D$, the generalized α_s is reasonably constant, and its magnitude is also tolerably well represented as a family constant as shown by the data of Table IV.

A relation between B_1 and m,n has been presented by Spetzler (*13*) as:

$$B_i = 2 + [(m + n)/3] - [(m + 3)(n + 3)/9](P/B_0) \qquad (9)$$

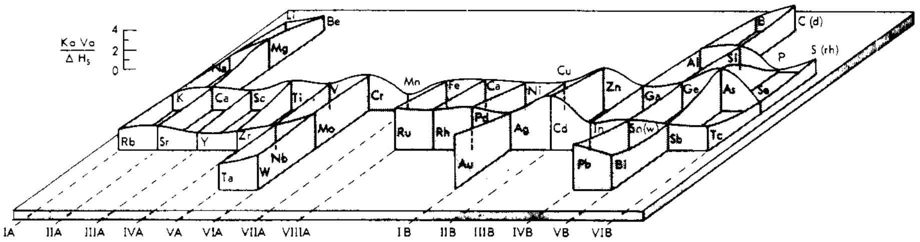

Figure 6. Generalized bulk moduli of those elements for which data are available (7)

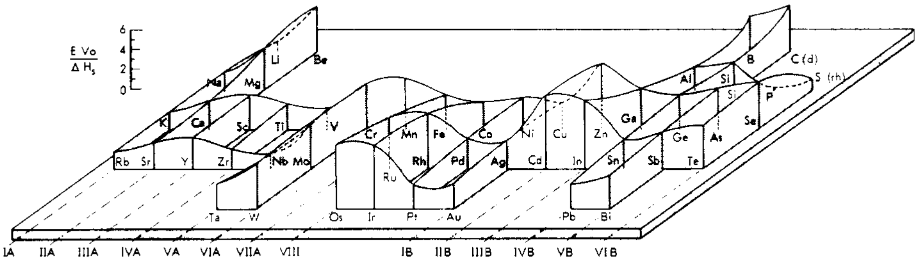

Figure 7. Generalized tensile moduli of those elements for which data are available (7)

Table III. Generalized Tensile Moduli[a] E_0V_0/E_a of Metal Oxides, Sulfides, and Carbides

	E_0V_0/E_a
Cubic metal oxides, sulfides, Be_2C[b]	2.9 ± 0.26
Hexagonal metal oxides, sulfides	2.7 ± 0.17

[a] Far fewer tensile modulus data are available for oxides, sulfides, etc., than bulk modulus data, and many seem far less reliable and consistent with each other. The data used here are from ref. (8) and (3). [b] Other carbides, regardless of crystalline structure, 5 ± 1 seemingly.

Table IV. Generalized Cubic Thermal Expansion Coefficient of Various Solids at $T \gtrsim \theta_D$

Compounds	$\alpha_s E_a/C_v$	$\alpha_s(Ze)^2/d_{ij}C_v$
Alkali and earth-alkali halides and oxides (other than fluorides)	1.3 ± 0.24	1.0 ± 0.21
Alkali and earth-alkali fluorides	2.2 ± 0.1	1.7 ± 0.1
Heavy metal carbides and nitrides	0.58 ± 0.09	
Diamond	0.43	
Molecular crystals composed of rigid molecules ($\alpha_s \Delta H_s/C_v{}^s$) (for comparison)	0.44 ± 0.04	

which simplifies to the first term when $P < B_0$. The predicted dependence of B_1 on n,m at that condition is shown in Figure 9. The few available experimental data for ionic and covalent crystals, shown in Table V, are in qualitative agreement with prediction, at least in comparison with data on molecular crystals. However, the quantitative agreement with the usually postulated 1:9 or similar power laws leaves much to be desired. Prediction is therefore more safely based on comparisons with similar solids, and the guidance from theory should only be used for adjustments.

Substitution of the estimated magnitudes of α_s and B_1 and their uncertainties in the Anderson-Wachtmann equation leads to the uncertainties in the elastic moduli at $T > 0K$ indicated in Table VI. The comparatively small relative effect of even large uncertainties on the magnitude of the moduli is due to the small change of the elastic moduli with temperature.

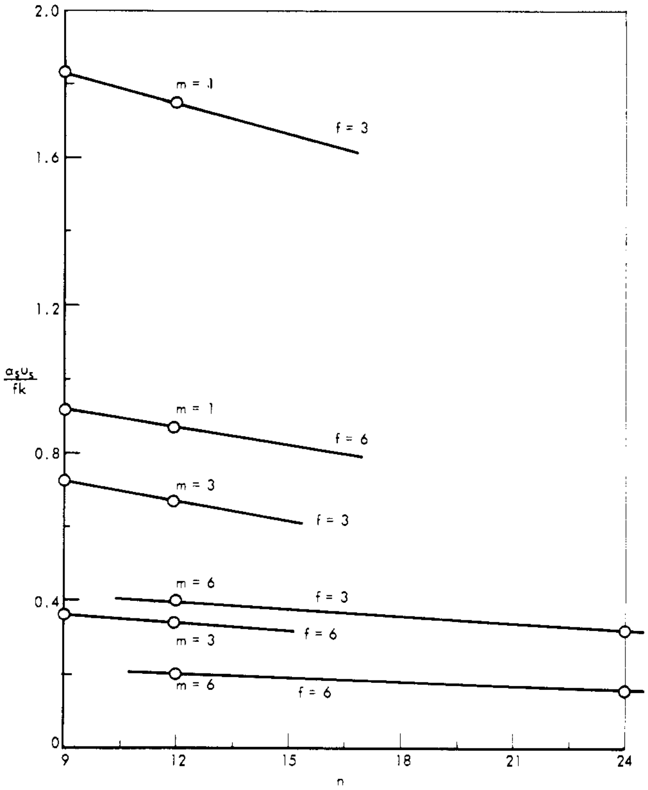

Figure 8. Theoretical relation between the generalized expansion coefficient $a_s u_s/fk$ (taking $C_v = fk$) and m,n according to Equation 8 at $V_s/V = 1$

Melting Point

The most commonly determined property of solids, the melting temperature T_m, is not easily related to molecular properties of the system because of its composite nature. Thermodynamically it is the temperature at which liquid and solid phases are in equilibrium, at a fixed pressure, hence

$$T_m = \Delta H_m/\Delta S_m \quad (10)$$

where ΔH_m, ΔS_m are the changes in enthalpy and entropy, respectively, accompanying the phase change at T_m.

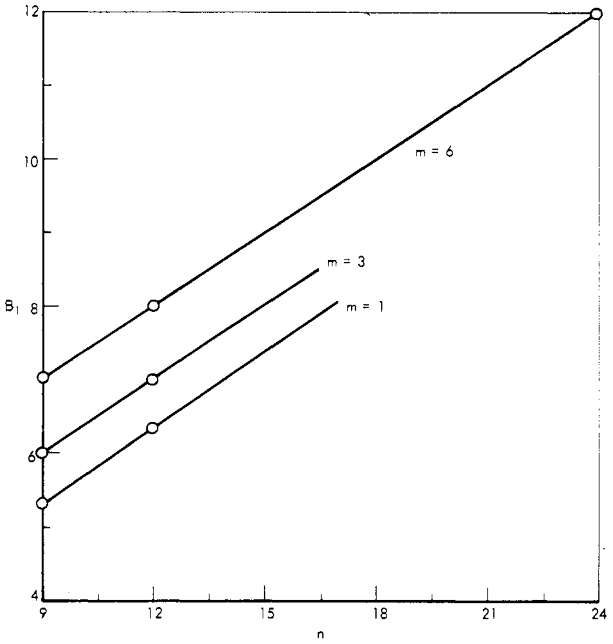

Figure 9. Theoretical relation between B_1 and m,n according to Equation 9

Table V. Pressure Coefficient B_1 of the Bulk Modulus of Crystalline Solids[a]

bcc	fcc		Diamond
Li: 3.6	Cu: 5.6	Mg: 4.3	C:
Na: 3.6	Ag: 6.2		Si: 4.2
K: 4.0	Au: 6.4	Cd: 6.3	Ge: 4.4
Fe: 5.1	Al: 5.8		
Alkali halides:	5.2 ± 0.2		
Cubic metal oxides:	3.8 ± 0.3		
Molecular crystals:	8 ± 1		

[a] Most of the data are from Ref. (2) and (6). [b] Except for Cd and related oxides.

Since ΔS_m is a measure of the change in order at T_m, one can expect ΔS_m to remain constant within a series of substances composed of atoms, rigid ions, or rigid molecules of the same geometry (5). Hence within such families, $T_m \sim \Delta H_m$. Furthermore, if $\Delta V_m/V$ is constant in that family as well, then $\Delta H_m \sim \Delta u_o$, and $\Delta u_o/u_o$ = const and thus $T_m \sim u$. For such families of compounds then, a generalized melting point, kT_m/u_s = const, should be obtained.

Again, for monatomic substances of that type kT_m/u_o should be a function of m,n only; specifically, Moelwyn Hughes (9) derived for $P = 0$

$$kT_m/u_s = -[2m\cdot n/3(n+m+1)(m-n)] \times [(m+3/n+3)^{n/n-m} - (m+3/n+3)^{m/n-m}] \quad (11)$$

The generalized melting points so estimated are presented in Figure 10 as a function of n,m.

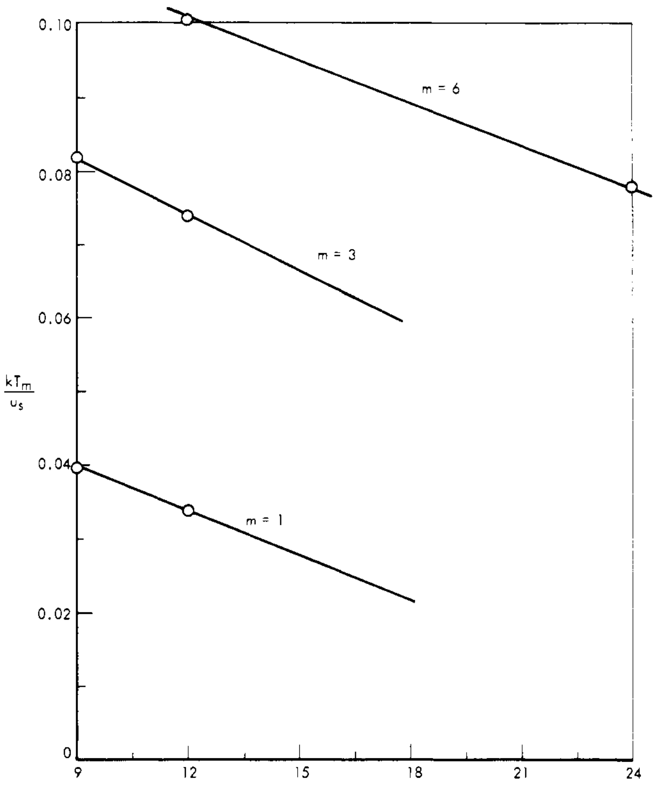

Figure 10. Theoretical relation between the generalized melting point kT_m/u_s and m,n, according to Equation 11

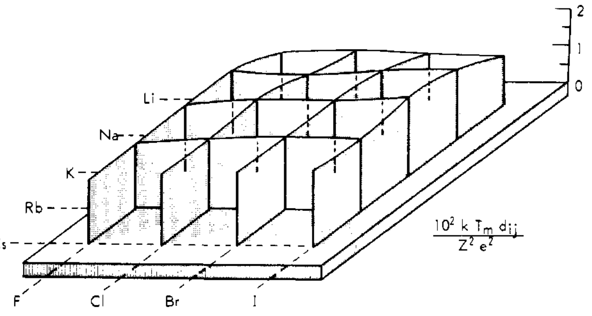

Figure 11. Generalized melting point map for alkali halides Coulombic model

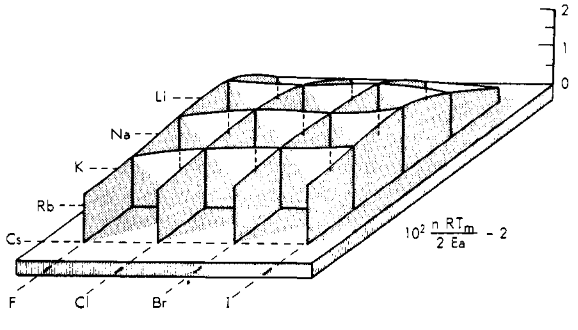

Figure 12. Generalized melting point map for alkali halides Phenomenological model

The experimentally observed generalized melting points are constant within families of compounds, except, generally, for the first member of the series, as shown by their mapping on the alkali halide field in Figures 11 and 12. Several oxide data have been assembled in Table VII, and those for the metallic elements in Table VIII. After elimination of substances undergoing solid/solid phase transitions, because their melting behavior must be formulated differently, there are still only limited family constancies. Among the metals, crystal structure seems to be a useful ordering parameter, as might have been expected, but it is obviously not the only one. Type of bonding (ionic or covalent) seems to play a major role in determining the magnitude of the generalized melting

Table VI. Ranges of Uncertainty in the Estimate[a] of Elastic Moduli at 300 K

Substance class	Uncertainty—range of modulus Zero-point modulus, %	 Due to effect of temp, %
Cubic metals	±3[b]	±15[c]
Metal oxides and sulfides	±20	±8
Alkali halides	±5[b]	±12[c]
Heavy metal carbides	±20	[d]

[a] Through use of the generalized correlations shown. [b] The data of nearly all members of these classes are known to be better than the indicated uncertainty. [c] Since the thermal expansion data are quite well known, most of this uncertainty is due to the uncertainty in B_1. [d] The few B_1 data in Ref. *6* cover such a wide range that one cannot make a meaningful generalization.

Table VII. Generalized Melting Points $n_c RT_m/2\,E_a$ of Various Metal Oxides

Cubic Lattice	
MgO: 0.078	
CaO: 0.069	
SrO: 0.067	
BaO: 0.056	
Y_2O_3: 0.0126	Al_2O_3: 0.0127 (rhombic)
HfO_2: 0.0113	TiO_2: 0.0093 (tetragonal)
ThO_2: 0.0128	ZrO_2: 0.0116 (monoclinic)
UO_2: 0.0128	

Table VIII. Generalized Melting Points $RT_m/\Delta H_s$ of Metallic Solids

bcc				hcp	fcc	
Li: 0.0248				Mg: 0.0513	Cu: 0.0329	Al: 0.0246
Na: 0.0259				Ca: 0.047	Ag: 0.0355	Ga: 0.0093!
K: 0.0297				Sr: 0.0505	Au: 0.0253	Pb: 0.0247
Rb: 0.0291				Ba: 0.0455		Bi: 0.0222
Cs: 0.0318						
Ti: 0.0435	V: 0.0332	Cr: 0.0510	Fe: 0.0374	Zn: 0.044	Co: 0.0333	Ni: 0.0336
Zr: 0.0319	Nb: 0.0312	Mo: 0.0365		Cd: 0.044	Rh: 0.0320	Pd: 0.0390
Hf:	Ta: 0.0328	W: 0.0360			Ir: 0.0327	Pt: 0.0298
		Re: 0.0362			Os: 0.0339	

temperature of the salt crystals. This is particularly evident from the comparison of the greater constancy, in a given group, of the phenomenological form $n_c kT_m/E_a$ than that of the form $kT_m d_{ij}/(Ze)^2$ which assumes ionic bonding to be dominant.

Considering the comparative ease with which one can generally determine the melting temperature, but not E_a or d_{ij}, of a substance, the value of the correlation is restricted to the following items:

Likelihood of a particular combination of elements to yield an extremely high or low melting compound is estimated; the reasonableness of an experimentally determined melting temperature is assessed in light of the requirement of external consistency; and if the observed melting point is reliable and the compound fits into a particular correlation family, E_a can be roughly estimated from the observed T_m.

Conclusions

The primary purpose of this investigation, the estimation of unknown equilibrium properties of a given substance from the known properties of another substance through a physically acceptable scaling procedure, has been accomplished with varying degrees of success. Better than order-of-magnitude estimates are possible in all cases. The Debye temperature can be estimated to within ±15%, the elastic moduli of nonmetals to within ±30%, and the thermal expansion coefficient at $T > \theta_D$ to within ±30%. The melting point appears to be predictable for some classes of ionic crystals but not for others. This predictability sequence reflects the state of basic understanding of the underlying theory.

The extension of the method to other properties, such as critical temperature, surface free energy, etc., appeared too obvious to include with the examples presented. Its utility depended largely on the general availability of the basic scaling parameters such as the energy of atomization E_a (*11*), the zero-point volume V_o (*4*), or the appropriate atomic and ionic radii. When E_a is not available from experiment, it can be estimated by the Sanderson method (*11*). Similarly, V_o can often be estimated by group increments developed by Biltz (*4*). Practically every elementary text book on solids contains atomic and ionic radii; one must just be careful to use self-consistent sets of such radii.

Nomenclature (SI system of units)

a = lattice parameter, m
A, B = constants in pair potential Equation 1
B_o = bulk modulus at zero pressure, Nm^{-2}
B_1 = pressure coefficient of bulk modulus, –
C_v = heat capacity at constant volume, Nm K^{-1} mol^{-1}
$C_v{}^s$ = lattice heat capacity at constant volume, Nm K^{-1} mol^{-1}
d_{ij} = distance between centers of ions on a lattice, m
e = Elementary charge, $(Nm^2\,mol^{-1}\,N_A{}^{-1})^{1/2}$
E = tensile modulus, Nm^{-2}
E_o = tensile modulus at 0K, Nm^{-2}
f = number of external degrees of freedom per atom, ion, or molecule on a lattice site, –
h = Planck's constant, Nm s mol^{-1} $N_A{}^{-1}$
ΔH_m = heat of fusion per mole, Nm mol^{-1}
ΔH_s = heat of sublimation per mole (or per kg-atom) at 0K, Nm mol^{-1}
K_o = bulk modulus at zero pressure, Nm^{-2}
k = Boltzmann constant, Nm K^{-1} mol^{-1} $N_A{}^{-1}$
m = mass per atom or ion, kg $atom^{-1}$ $N_A{}^{-1}$
$\bar{m}$ = reduced mass per atom or ion, kg $atom^{-1}$ $N_A{}^{-1}$
m,n = exponents in pair potential Equation 1, –
M = weight per mole or per kg-atom, kg mol^{-1}
N_A = Avogadro's number, mol^{-1}

$r_{i,j}$ = radius of ion *i* or *j*, m
R = gas constant, Nm K^{-1} mol^{-1}
ΔS_m = entropy of fusion, Nm K^{-1} mol^{-1}
T_m = melting point in absolute temperature scale, K
u_o = pair potential at equilibrium distance r_o, Nm mol^{-1} $N_A{}^{-1}$
u_s = energy of sublimation per atom or molecule at 0K, Nm mol^{-1} $N_A{}^{-1}$
V_o = volume per mole or kg-atom at 0K, m^3 mol^{-1}
Z = number of charges per ion active in electrostatic interaction between adjacent ions, –

Greek Letters

α_s = cubic thermal expansion coefficient, K^{-1}
ρ^* = packing density, –
θ_D = Debye temperature = $\omega_D h/k$, K
ω_D = Debye frequency, s^{-1}

Basic Units

N = Newton
m = meter
K = Kelvin
kg = kilogram
mol = kg mole or atom
s = second

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Received for review February 28, 1972. Accepted October 11, 1972.

Thermochemistry of *N,N*-Dimethyl-*p*-nitrosoaniline Complexes

Salvatore Gurrieri,[1] Rosario Cali, and Giuseppe Siracusa
Istituto di Chimica Generale ed Inorganica, Università di Catania, 95125 Italia

Enthalpies of formation of crystalline, oxygen-bonded $MnLCl_2$, CoL_2Cl_2, and $NiLCl_2$ (L = *N,N*-dimethyl-*p*-nitrosoaniline) from crystalline anhydrous metal chlorides and ligand have been obtained by reaction calorimetry. The values found at 25° ± 0.001°C are, respectively, −8.85 ± 0.15; −10.12 ± 0.24; −11.71 ± 0.16 kcal/mol. The enthalpies of formation of gaseous complexes cannot be measured, since these decompose without any phase transition when heated, as indicated by thermal analysis.

N,N-dimethyl-*p*-nitrosoaniline complexes with some transition metals were previously investigated; the ligand behaves as a monodentate and coordinates through the nitroso oxygen (*2*). Successively Popp and Ragsdale (*5*) came to the same conclusion; Batten and Johnson do not preclude that, in the Pd-*N,N*-dialkyl-*p*-nitrosoaniline complexes, the ligands coordinate through the nitroso oxygen. Other papers (*1, 2. 5*) deal with the use of *N,N*-dialkyl-*p*-nitrosoanilines as reagents in the spectrophotometric determination of Pt group metals and in the preparation of several complexes having fungicidal properties.

Continuing our studies on nitroso derivative ligands we report now the calorimetric determination of the enthalpies of formation of crystalline complexes $MnLCl_2$, CoL_2Cl_2, and $NiLCl_2$ (L = *N,N*-dimethyl-*p*-nitrosoaniline) from crystalline anhydrous metal chlorides and crystalline ligands.

Experimental

Materials. $MnCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, and *N,N*-dimethyl-*p*-nitrosoaniline (C. Erba RP) were employed. $Mn(C_8H_{10}N_2O)Cl_2$, $Co(C_8H_{10}N_2O)_2Cl_2$, and $Ni(C_8H_{10}N_2O)Cl_2$ were prepared as previously described (*2*). All salts and complexes are completely soluble in 1.00*M* aqueous HCl.

Calorimetric measurements. A calorimetric equipment LKB Model 8700-1 was employed. The measurements were performed at 25° ± 0.001°C.

The calorimetric cell was charged with 100 ml of aqueous 1.00*M* HCl. After equilibration the reaction was started by breaking a thin-walled glass ampul containing 2–3 mmoles of solid reactant; the reaction periods for all experiments were short and the rates of heat evolution were exponential with time.

The expression $(R_i - R_f)/(R_i + R_f)$ was considered proportional to the temperature change.

The mean temperature of the reaction period was calculated to the time for 0.632 of total heat evolution (*6*).

In each experiment two electrical calibrations of the system were performed before and after reaction. Since the heat evolution is linear with time, the mean temperature corresponds to the time for half the temperature rise (*6*). The reproducibility of the electrical equivalent was usually better than ±0.2%. The enthalpies of reaction were calculated by using a Hewlett-Packard 9100 B calculator and an appropriate program.

Thermal analysis. Simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) were performed using a Mettler thermoanalyzer, at different heating rates, in vacuum and dynamic nitrogen atmosphere.

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[1] To whom correspondence should be addressed.