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CORRELATION OF MATERIALS PROPERTIES WITH THE ATOMIC DENSITY CONCEPT

Interim Final Report No. 3

FOREWORD

The work reported herein was initiated as Contract NAS8-28517 (NASA Control No. PR-M-28517) under technical monitors Daniel W. Gates S&E-SSL-TT (Principal) and Tommy C. Bannister S&E-SSL-TR (Alternate) of Marshall Space Flight Center to Nevada Engineering and Technology Corporation of Long Beach, California.

The concept,- that the atomic density, an accurate measure of the number of atoms/cc (and hence interatomic bonds/cc),- can serve as a characterizing parameter for any substance of known density and chemical combination, that together with other such parameters it can be quantitatively related to observed property values for related materials, and that if a number of different properties can be related to a common group of parameters they can then be related to each other,- has now been demonstrated to be feasible with up to ten quite different properties, with most of the solid elements and a variety of well-characterized compounds. In moving toward that demonstration several discoveries have been made of novel or previously neglected refinements which have, in most cases permitted mathematical agreement within ± one percent of observed data.

This report describes the central study and its findings, and recommends, in addition to continued study, that steps be taken to refine the method of property-comparison for immediate purposes of data screening and later purposes of critical analysis.

Appended to the report are: a discussion of the mathematical methods employed and the precautions required to minimize error, detailed examples of the generation of the mathematical expression and testing its validity, a similar example using the alkali halides and three of their different properties, and a similar example using a large number of simple and mixed oxides. The final Appendix is concerned with the solid elements and includes tabled values which have been subjected to preliminary screening on this basis.

A modest attempt to write a computer program to derive the necessary equations and perform comparative calculations has not yet been adequately debugged; the source of difficulty appears to be the interdependence of some of the parameters; expressions shown and calculations made are therefore limited to the digital and decimal capacity of the desk calculator available.

S. W. Bradstreet, Consultant

ABSTRACT

The objective of this project has been to discover whether quite different materials properties can be quantitatively related to the parameters characterizing those materials and whether, if parameters are the same for several properties, those properties can then be related to each other. This reports summarizes the major steps made toward that objective, and provides examples clarifying the rationale and techniques used.

The study was based upon the hypothesis that the number of atoms per unit volume, accurately calculable for any substance of known real density and chemical composition should be chosen as the first such characterizing parameter, other parameters being those which describe the atom and the number and energy levels of the electrons interacting among atoms of the same or different kinds. The form of equation ultimately chosen was ultimately a multiple exponential: $P = k\ N^x\ I^y\ Z^a\ W^b$, in which P is the property value, N the atomic density, I the bond intensity, Z the atomic number, and W the atomic mass.

A suitable subgroup of materials, each of which is described by such an expression, is selected, and since the equation in logarithmic form is algebraic and linear, a suitable number of these equations can be solved simultaneously to establish the values of the exponent and constant k.

The expression thus derived is tested by applying it to a material not used in the derivation. Conformance may be tested by agreement with the observed property, but since a variety of different properties are treated it was found convenient to test conformance of a parameter, in most instances the bond intensity.

For most properties studied it has been found that the value of I is also the product of exponentials describing (1) the number of electrons/atom available for bonding, (2) the number of electrons "free" for electronic conduction, and (3) a descriptor such as the ionization potential of elements or the electronegativity for compounds which describes the energy level of the bonding orbitals. For subgroups containing elements of different Periods, a descriptor called the periodicity factor is required in addition to Z. And a parameter called the mass factor is required in polyisotopic metals and compounds to modify the mass term. Techniques for reducing the requisite number of base species were developed as candidate parameters were identified and refined.

The properties thus far examined which appear relatable to these parameters include: heat of atomization, boiling point, melting point, Debye temperature, bulk and Young's elastic moduli, shear elastic modulus for cubic crystals, bulk coefficient of thermal expansion, thermal conductivity, refractive index for transparent substances, and specific heat at constant pressure.

A few of these have been tested with all or most of the following substances: the solid elements, the alkali halides, a few metal-metalloid compounds, and more than a hundred simple and mixed oxides. The majority of properties, however, have been generated from but a few materials and tested for validation with from one to a few others.

Appended to the report are: a discussion of some of the mathematical considerations involved with precautions needed for the requisite accuracy, a detailed study of the alkali metals to illustrate the treatment of elemental subgroups, a less detailed discussion of the alkaline earth metals, the results of examination of the 20 alkali halides with special attention to the refractive index and non-ideal packing, examples of the comparison using three properties of the simple and mixed oxides.

It is concluded that a number of quite different materials properties can quantitatively be described in terms of a common group of parameters and hence related to each other, at least for the solid elements and a wide variety of adequately characterized compounds. It is recommended that the study be continued with a view to discovering the limitations of the method both with respect to the variety of properties so treatable and of materials less simply described.

Because the study has already demonstrated the feasibility of choosing among conflicting data points and in some instances of forecasting missing values, it is recommended that the method of comparative property values be developed for largely automated computerized analysis of materials data for complementing the efforts of those concerned with data accession, storage, retrieval, and dissemination.

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SYMBOLS AND TERMS

Wherever possible, terms accord with the Thesaurus of engineering and Scientific Terms, and units with those of the International System. The interdisciplinary and occasionally novel aspects of the work have sometimes required new terminology which is shown below, together with such modified definitions as are needed. Symbols, where novel, are usually abbreviations suitable for the Basic computer language. Symbols and units for properties and parameters are underlined.

a	Exponent associated with Z
Av	Avogadro's Number, taken to be 60.22094 x 10^{22} a.w.u/gm
a.w.u.	Atomic mass units based on ^{12}C = 12.00000
b	Exponent associated with W
B	Bulk modulus of elasticity in GPa, reciprocal of Index of Compressibility, measured at or converted to standard conditions. Measured statically at slow loading rates it should be an isothermal property, but literature data vary enough so that the adiabatic values (variously known as "dynamic", etc.) calculated from compressional wave velocities and density have been used here. For this reason, expressions in B are suspect.
bcc	Body-centered cubic, the crystal array in which an atom at the cube center has 8 neighbors at its corners. When ideally packed its PE is 68.0184 v/o. Adopting the convention that a compound AB may be regarded as identical $A_{.5}B_{.5}$ "atoms", the CsCl structure becomes bcc .
BP	Boiling Point, the temperature, in K, at which the vapor pressure equals one torr. Where higher pressure is required to prevent decomposition this is denoted by the letter p after value.
BS	Bond Strength, in simple compounds such as the alkali halides which vaporize as diatomic molecules, the work required to separate the compound into its constituent atoms from the base state of 298K or the MP, whichever is lower. See ΔH. Kcal/gm-atom.
c	Exponent associated with C, (1+100C), etc.
C	d.c. Electrical Conductance, the reciprocal of resistance, taken at standard conditions as a measure of the relative number of valence electrons so weakly attached to an atom as to contribute nothing to cohesion. Particularly for good electronic conductors, this is perhaps the most difficult property measurement to replicate and is most sensitive to ambient conditions and impurities; the sensitivity decreases at elevated temperatures. Units are (1/microhm-cm), usually multiplied by 100 to avoid fractions.
c/a	In hcp, hex, and tetr crystals, the ratio of the c-axis to a-axis lattice dimension; for ideal hcp it is 1.63297..
ccp	Cubic close-packed, the crystal array in which the atoms occupy the corners and face-centers of the cube. When each atom is in contact with its 12 neighbors, PE = 74.04825 v/o. See fcc .
CCTE	Cubical (bulk) Coefficient of Thermal Expansion, in 10^{-6}/K . The value used is the mean of the coefficients observed over the range from just above to just below the standard temperature.

c_p	Specific Heat at constant pressure, the heat capacity of the substance as compared with that of the same mass of water.
$c_p \cdot W$	Atomic Specific Heat, in cal/gm-atom, used to eliminate the mass dimension. Unless otherwise shown, measurement is made under standard conditions. Data vary widely. (Property is the "constant" of Dulong and Petit).
CT	Curie Temperature, above which ferro-magnetism ceases. Used to estimate magnetic forces in bonding; important for c_p. In K
d	The exponent associated with n. Sometimes used for X-ray density.
DT	Debye Temperature, the threshold above which added modes of lattice vibration are denied, further heat accommodation requiring increased amplitudes. Normal symbol Θ . In K
E	Young's Modulus of Elasticity, in GPa, the ratio of applied tensile stress to observed axial elongation. For cubic crystals, equivalent to elastic constant c11. Measured under standard conditions. See Y .
f,f*	See mf .
G	Elastic Modulus in Shear, in GPa; for isotropic bodies and cubic crystals, equivalent to c_{44}. Presumed to be statically measured and isothermal, but as with other elastic moduli, may be adiabatic. The difference is important for materials with short relaxation times.
GPa	GigaPascal = 10^9 N/M^2 (1 psi = 6894.757 N/M^2) Unit of stress or pressure.
ΔH	Heat of Atomization, the work (energy) necessary to raise one gm-atom of the substance from 298K or the MP, whichever is lower, to the temperature at which it is monoatomic. Ref 1f. Kcal/gm-atom.
hcp	Hexagonal close-packed. Most elemental crystals erroneously so described, since they do not display ideal c/a ratios. Some refer to differentiation between close and closest packing; the writer prefers the simpler hcp and ideal hcp. Each atom has 12 neighbors, ideal PE identical to ccp. See p 4f .
hex	Hexagonal symmetry, such as in single crystal graphite, for which c/a criterion does not apply, the center of the hexagon being unfilled.
I	Bond Intensity The product of the number of electrons available for bonding per atom reduced by those responsible for electronic conduction, and an energy factor measuring the work necessary partly to remove those atoms. Not directly measurable; see v, C, IP .
I_m	I calculated from general expression omitting mass factor; for an element, the value of I it would exhibit if monoisotopic while retaining the same property value, N, and C, Z, and W.
I_{md}	Same procedure as I_m but contribution of C also ignored, hence the monoisotopic, dielectric bond intensity.
J	Spacing distance, in Å separating larger atoms; calculable from ratio of PE to ideal value (Ref 5').
k	General term for the "constant" of subgroup and General expressions. It is truly constant only when all parameters are included.
K	Kelvin temperature, used throughout.
l,h	Subscripts referring to lighter and heavier components, in mass factor formulae, than the mean mass W. When there are more than

component isotopes in an element, these are themselves averaged using the Law of Mixtures. See examples pp 7,8 f. In a ternary or higher compound, see mf for treatment.

mf	Mass Factor, currently: $mf = (1+2n_{le})(1+\frac{W_h-W_l}{W})$,where n_{le} is the lesser fraction. For an element or binary compound no further treatment is necessary. In ternary and higher salts, the primary mass factor is calculated as above, electron donors being combined and averaged by the LoM, electron acceptors being similarly treated. To this is added the secondary mass factor, which treats the donors as if they were isotopes in an element, and the mf thus obtained is multiplied by the factor $n_M/(n_M+n_X)$ prior to addition. The formula is quite arbitrary and not final, partial reasons for choosing it is that it be dimensionless and have a value of unity for a single isotope.
mf*	Mass Factor, differentiated from mf, which is based on mass difference, to a basis of mass ratio: $mf^* = (1+2n_{le})(\frac{W+W_h}{W+W_l})$ and treated in the same manner. Dimensionless, unity for isotope.
M	General symbol for metal
N	Atomic Density, obtained from: $N = (\rho Av)/W$, the measurement of ρ being made at or corrected to standard conditions unless otherwise shown. Units are atoms (or bonds) x $10^{22}/cm^3$; the factor of 10^{22} is customarily omitted.
N	Value of N "corrected" to correspond with a common coordination number, usually 12. Frequently tested, seldom improves conformity.
p	pressure. Used to indicate elevated pressure requirement in MP, BP
P	General Property. Units are or can be reconciled with stress or pressure.
ρ	Real density under standard conditions unless otherwise indicated. If carefully done (Ref 2b), seldom agrees with bulk density value, especially for small specimens, powders, etc. Units gm/cc .
R PE	Observed atom radius (half interatomic distance) in Å . See p 6e for calculation of R in irregular crystal structure. The value of R is required in the calculation of the packing efficiency, PE of the real material. See examples in Appendix IV.
RI	Refractive Index, the ratio of the speed of light in a vacuum to that in the material. For consistency, all property values are regarded as being zero for a vacuum, so RI-1 is normally used. It provides an example of indirect measurement of the reaction of the material to the stimulus of illumination. For consistency, all RI values thus far tested are for sodium D illumination, wavelength 5893 Å. Indices for substances having absorption bands near this wavelength are suspect.
Standard Conditions	Unless otherwise stated, 298.15K (25.00C) and 1 torr.
TT	Transition temperature, in K most often refers to the thermal threshold at which a change in lattice array spontaneously occurs, together with a change in density; it is therefore taken as the threshold for partial bond failure as in melting. The most common TT values for the elements are for transition to bcc from arrays of higher coordination number.
v	Valence, the number of electrons per atom interacting to produce lowered internal energy through formation of a condensed phase.
v_n	Nominal valence; for the first four elements of the short Periods

and the first six of the long Periods, v_n values are integers and identical with Group numbers. Continuing these to the end of the Period yields v_n values representing the maximum number of electrons/atom available. Thermal or radiation promotion of other electrons clearly occurs, however, in the heaviest and largest atoms.

v_M	valence of the electron donor in a compound. With two or more donors, their mean is used: thus for $MgAl_2O_4$ $v_M = (2+6)/3 = 2.666...$
V	Atomic Volume in Å^3 . Not needed if PE and R are used.
v/o	Volume percent
W	Atomic mass in a.w.u. units. As a parameter this appears to be of greater import than previously supposed.
x	The exponent for N. Since N appears to depend upon almost all other parameters, the order of simultaneous solution by consecutive term elimination suggests that all other terms be eliminated first.
y	The exponent for I when I is taken to be the same as v_n for the elements and halides or as $v_M(n_O/n_M)$ for oxides, etc.
y'	The exponent for IP or other measure of electron-orbital energy level. See IP below and discussion on p 16.
z	The exponent for the mf (or mf*) term. In most instances, and particularly when W and Z have been postponed, this term should be eliminated following subtraction to eliminate k.

The following terms deserve special emphasis:

10k	Thermal Conductance (or conductivity) in watt/cm-K, the multiplier is to avoid fractions. This is clearly the sum of the several conductance mechanisms, and it may be that only because its consideration has been limited to standard conditions and opaque elements and negligible radiative transfer that this transport property has been satisfactorily served here. It is probable that the form of the refined expression for it will include additive terms rather than multipliers for W and Z.
IP IP_{v_n}	Ionization Potential, the work in Kcal/gm-atom of removal of one or more electrons from the neutral atom. For some of the lower subgroups, at least, removal of the last (presumably s-) electron requires work precisely in accord with Z, W, and n, the apparent contribution of mf is vanishingly small. For this reason, and because earlier calculations of IP_{v_n} were used in calculating electronegativities for compounds (Ref 5'), IP_{v_n} appears the better candidate for solids. Note that IP_{v_n}/v_n cannot be used in the General expression because $I = v_n$ for the base species.
n	Periodicity Factor This comes from and has the same meaning in Ref 5, and is defined there as the principal quantum number of the outermost filled shell of electrons. Dimensionless.

Target Accuracy: This was self-imposed and has been adhered to as a criterion for validation; that the discrepancy between observed and calculated values for P be not more than ± one percent more than the error for P, and that where a parameter value is calculated from two or more different properties, these shall also agree within one percent or so. To avoid fortuity and increase sensitivity, extrapolation rather than interpolation has been used for validation. The target accuracy has been met in most instances and closely approached in all others tested.

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INTRODUCTION

The atomic density concept may best be defined as the hypothesis that a property value P may be mathematically correlated with values of the parameters which characterize the material being tested, and that a particularly valuable parameter of this kind is the atomic density N, given by:

$$(\rho Av) / W = N = PE / (4.1888\ R^3) \quad (1)$$

; where ρ is the real (immersion) density in gm/cc, Av is Avogadro's number, here taken as 60.22094×10^{22} a.w.u./gm, and W is the "atomic" weight in atomic mass units, N is simply and accurately the number of "atoms" per cm^3. Because the value is obtained from the real density, and the real chemical composition is used in computing the value of W, there are no weakening assumptions in regarding N as intrinsic and, under fixed conditions of temperature and pressure, as a unique descriptor of the material, having reciprocal volume as its only dimension.

The number of "atoms"/cc is also the number of bonds/cc joining them. If the bond intensity* per atom can be quantified, it follows that the restoring force within the crystal will be a function of the product of N and I, where I consists of at least two parts: v_n is the number of electrons/atom engaged in the bonding process, or for most substances simply the nominal valence, and an as yet unidentified parameter which defines the critical or average energy of those electrons, here shown simply as p_1.

For the several properties treated here, the observed value P is simply the characteristic reaction to an energetic stimulus; Le Chatelier's theorem states this as the "tendency to restore the equilibrium which existed before the stimulus was applied". In order to characterize a material adequately, then, one or more descriptors must be supplied which define the material in the free state. For the simplest example, a pure, elemental solid, two such descriptors are its atomic number Z and its atomic weight W, each of which are again characteristic of the atom. Recognizing that each of these may exert an influence both on the initial equilibrium and the restoring force which is peculiar and separable, one is led to expect that for each

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* The term "bond strength" has a meaning peculiar to compounds and, as a property, BS has been defined herein.

property value of each substance, an empirical equation of the form:

$$P = k \; f(N) \; f'(I) \; f''(Z) \; f'''(W)\ldots$$ can be written.

The nature of the several functions not being known, a number of attempts have been made to discover them. The most successful of these has been the simple exponential expression:

$$P = k \, N^x \, I^y \, Z^a \, W^b\ldots \quad \text{, or, in logarithmic} \qquad (2)$$

form: $\text{Log } P = x \text{ Log } N + y \text{ Log } I + a \text{ Log } Z + b \text{ Log } W + \text{Log } k$.

Clearly, a mathematical expression which is limited to the solid elements would have little value, and a vital part of the concept has been its application to compounds or mixtures. Pure Al_2O_3 will do as an example. Without pretending that such an "atom" exists, we can conceive of a unit having the composition $Al_{.40}O_{.60}$; for it Z is (.4x13 + .6x8) 10.0, and W is (.4x26.9815 + .6x15.9994) or 20.39224 a.w.u., or one-fifth of the commonly used molecular weight. Whether the electrons are exchanged or shared, the nominal valence of this atom is (.4x3 + .6x2) 2.40, and if the accurately measured density (at 298.15K and 1 torr) is 3.972 gm/cc, there are in one cc of it $11.729_8 \times 10^{22}$ such "atoms".

The right hand portion of equation (1) is a simple and accurate geometrical statement of the fact that in an ideally packed assemblage of identical spheres, the packing efficiency PE is determined by the packing mode and is independent of the size of the spheres given by R (half the interatomic distance). One sees either that R can be directly observed through diffractometry or calculated from the value of N. When this is done for a number of elements and compounds, one finds differences, sometimes of the order of 15% or more, even when great care has been taken to assure chemical stoichiometry and minimum porosity and strain. In this work it has been found most convenient to calculate and report the value of PE which derives from N and from the diffractometric value of R; the method for calculating it and its value for property comparisons are given in Appendices II and IV for the alkali halides and rutile as well as the I-A metals.

There is no essential difference, then, in treating the property value for any substance of known density and composition. It will be seen that the "constant" and four exponents in equation (2) can be mathematically established by the simultaneous solution of the equations of five different materials, here called base species, and the resulting expression tested for validity by using it to calculate either the value of the property or of any parameter of one or more different species.

MATHEMATICAL ACCURACY AND THE GAUSS ALGORITHM

This effort is most completely described as an attempt to coordinate mathematics with physical reality. At the risk of tutorialism it must be noted that since this effort has from the beginning had as its goal an accuracy of within one percent of the observed and calculated data points, unusual care must be taken to minimize errors in computation as well as errors in the data themselves.

DUBIOUS OR MISSING DATA

A number of property values are extremely difficult to measure for either or both of the following reasons: one or more of the measurements is so small as to make accuracy difficult (the strain in modulus measurements) or so large as to appear almost invariant (the temperature threshold of boiling and melting for refractory substances); the second kind of difficulty is involved with such observational difficulties as those involving the true onset of melting[1] or freezing, the exact point of inflection in the specific heat-vs temperature or the thermal expansion-temperature curves.

For these, one has no choice but to assume the datum is as accurate as possible and has been reported as precisely as possible.

A third source of imprecision arises from the simple fact that, like snowflakes, no two specimens are exactly alike.

It would be extremely advantageous if physical data could be critically analyzed prior to acceptance. At this time there are several organizations, the Information Analysis Centers, which perform this function; the writer is indebted to personnel of the Thermophysical and Electronic Properties Information Analysis Center (TEPIAC) both for key data supplied in its publications and for electrical conductance data for a small number of the elements. Such organizations as the National Bureau of Standards have also been kind enough to supply "recommended" values for cubical coefficient of thermal expansion, and certain melting points have been certified by private communications with individual reasearchers. The bulk of the physical data used here come from handbooks such as the Physics Handbook, the Handbook of Chemistry and Physics, Handbook of Metals, and individual publications under the auspices of a number of professional Societies here and abroad.

Let the melting point of yttrium serve as an example; it is critical because this element is necessarily one of the base species for deriving a particularly useful form of the General Expression.

Most of the handbooks list 1796K for MP_Y, the value chosen by TEPIAC is 1820K. The error involved is 1.3% (far smaller than the discrepancies of many data).

In this study, the course followed is a relatively simple one. Instead of a single expression for this element, two are separately used, and each combined with the equations for the remaining base species. Some idea of the extreme sensitivity of these expressions can be gained from the change in the value of x, the exponent for N, y, the exponent for I, and log k in the alternative expressions for MP based on the base species Rb, Sr, Y, Zr, Nb, and Mo. The small increase in MP_Y shown changes x from -0.927... to -1.3227.., y from 1.876.. to 2.5652.., and Log k from 0.35 to 2.21 .

It should be pointed out that in this series of expressions the parameters Z and W were not included; their actual influence is reflected partly in the values of N and I, the remainder being in the "constant" k, which is not a true and independent constant for a given property unless all parameters affecting it are included.

There are, then, three major sources of error, as follows:

Roundoff error While a number may be precise, a value is not. Roundoff errors are made by the researcher in reporting physical data, by the translation of these into logarithms, and by the curtailment of the number of significant figures to which multiplication and division are carried in the computation. These are more fully discussed in Appendix I.

Truncation error These arise from the fact that the equations are themselves imprecise in that at best they reflect only a part of, or a distorted part of physical reality. Examples will be found in the use of monotonically changing parameters for non-monotonic properties in Appendices II-IV.

Interdependence error A form of truncation error not generally recognized but frequently encountered here. The method of simultaneous solution of algebraic, linear equations involves the supposition that the variables are independent. When they are not, the choice of the order of their elimination may have a profound influence on the solution.

THE GAUSS ALGORITHM FOR EQUATIONS INVOLVING MULTIPLE UNKNOWNS

The method for "simultaneous" solution of linear expressions is taught in early algebra. In its simplest form, where there are two equations of the kind shown in (2) there is subtraction (which does not produce a digital error) followed by division (which does, if roundoff must occur.)

It is in the hope that others not having immediate access to extended digital capacity computers may wish to use the concept for their own purposes that these precautionary statements are made. The roundoff error can be made negligible by using a sufficient number of digits in the arithmetical steps.

In the successive steps of elimination there is a choice to be made as to which combination of equations will be used and which variables shall be eliminated first. For three equations, A, B, and C, the reduction to two by subtraction can be A-B, B-C, or A-C for the first, and one of the remaining two for the second. The choice should be made by recognizing that errors are largest when large ratios and/or small differences are used.

The problems of truncation error begin to arise with four or more equations and an equal number of unknowns. The probability that N, for example, largely depends upon other parameters is so great that the writer recommends that all other parameters be eliminated first. Examples are given in Appendix I.

A modest computer program for carrying out the Gauss algorithm for up to six equations and as many unknowns has been started. Funds needed to complete the debugging process and to refine the expressions further will be requested, but it has already proved valuable in showing that the truncation error due to interdependence can be an order of magnitude or more if the improper order of elimination is attempted; the error is magnified by the very large exponents generated.

METHODS FOR REDUCING VARIABLES: THE SUBGROUP EXPRESSION

The linear algebraic expression:

$$\text{Log } P = x \text{ Log } N + y \text{ Log } I + a \text{ Log } Z + b \text{ Log } W + \text{Log } k \qquad (2)$$

contains five unknowns, and the individual equations for five species are needed to resolve them. Among the elemental solids there is only one subgroup of five elements displaying a common crystal structure: the alkali metals.

Granted that an expression can be derived for any property, it would be merely an exercise in number-fitting unless a way can be found to test it. Fortunately, the nominal valence for these elements is one and its logarithm unity; for initial study the yLog I term can simply be omitted. When this now simplified expression was derived for MP, θ, and B the following discoveries were made: (a) Generated with four species and tested for conformity with the fifth, no expression was validated within target accuracy; either data for one or more elements are faulty or, more probable, the parameters chosen are insufficient.

(b) The exponents for Z and W are in all instances of opposite sign and dissimilar magnitude; the probability that a combination of these parameters can be used is remote.

(c) Best conformity is found when Li, Na, K, and Rb are used as base species; target accuracy would be obtained if Z_{Li} were uniformly about 3.9 and Z_{Na} about 11.4 .

Similar studies with other elemental subgroups finally disclosed the errors of omission to be:

While W is a valid parameter in its connection with kinematic energy of the crystal it is an insufficient one except for elements which are monoisotopes; Na and Cs are, Li, K, and Rb are not. The <u>mass factor</u> is a necessary parameter.

While the nominal valence for these elements is undoubtedly the same they do not each bring one electron to the bonding mechanism because some proportion of the electrons are "free" at ordinary temperatures. Least important with MP and most important with B, the d.c. conductance C is a necessary parameter.

Through necessity it was decided simply to postpone the appearance of Z and W in the expression by regarding their (unknown) combined contribution to the subgroup as constant. This proved to be feasible during the period when early formulas for the mass factor were being studied. Appendix II provides added details for the alkali metals study and outlines and illustrates a method for forecasting certain physical properties for monoisotopes such as ^{6}Li.

Since N is itself a property of the body, the variables in equation (2) can be further reduced by so considering it.

COMBINED PROPERTY EXPRESSIONS TO REDUCE PARAMETER NUMBER

The attractive possibility had been noted that if any two properties can be mathematically related to the same set of parameters they can then be accurately related to each other. In 1910, Lindemann[2] published a semi-empirical relation between melting point and Debye temperature:

$$\theta^2 = k\ MP\ /\ W\ (V)^{.667} \qquad \text{in which}$$

V is the atomic volume and k a constant. The expression has been found valid for a number of ferrous alloys[3], and appeared worthy of testing in a manner similar to that already employed for single properties. Tested directly, the expression is in error by more than 8% for one of the alkali elements if the value of k is a least squares fit to the other four; a significant part of the error may be the better Debye temperature values now available.

For crystals of the same structure, PE is a constant, and since V = k Av / N one can restate the Lindemann expression as:

$$\Theta^2 = k\ MP\ (N)^{.666..} / W\ ,\ \text{or}$$

$$2\ \text{Log}\ \Theta - \text{Log}\ MP = \text{Log}\ k + .666..\ \text{Log}\ N - 1.0\ \text{Log}\ W$$

The five alkali metals are best fitted by the expressions:

$$\begin{array}{rcl} 2\ \text{Log}\ \Theta = & = & 5.54320 + .93616\ \text{Log}\ N - 1.0537\ \text{Log}\ W + .02818\ \text{L mf} \\ \underline{\qquad\qquad \text{Log MP}} & \underline{=} & \underline{2.52657} + \underline{.20661}\ \text{"} - \underline{\ \ .02101}\ \text{"} + \underline{.01267}\ \text{"} \\ 2\ \text{Log}\ \Theta - \text{Log MP} & = & 3.01663 + .72955\ \text{"} - 1.03269\ \text{"} + .01551\ \text{"} \end{array}$$

which does meet target accuracy. The Lindemann expression, then, can be modified to meet the finding that the exponent for N (or V) is larger than 2/3 for these elements, and W is not linearly related.

For the II-A elements, Ba departs from close packing. The relation was thus tested both with N (as determined from the real density) and ₦ (calculated from the X-ray density). The exponent for N was about 0.6, and for ₦ appreciably smaller.

If the constant is eliminated in simultaneously solving the Θ and MP expressions for the 1-A elements, one obtains:

$$\Theta^2 = (1/\ MP^{2.2})\ N^{.483}\ mf^{.0004} / W^{1.008}\ ,$$

from which it is apparent that if the exponent for MP is negative and slightly larger than that for Θ, the dependence upon N is close to its square root, very nearly linear with W, and mf can be neglected.

In a somewhat cursory search for similar bi-property relations it was found that for the six bcc transition metals, a linear relation for the MP and E values with N was achieved when the parameters are v_n, Z, and W. This mathematically restates the contention that the Young's modulus and the MP are almost identical measures of the resistance of the crystal to tension whether thermally or mechanically imposed.

THE GENERAL EXPRESSION POSTPONING Z AND W INFLUENCES

Some inaccuracy in the expression certainly results when Z and W are ignored and the accuracy is most affected in the I-A and II-A subgroups, in which W/Z not only varies widely but is non-monotonic, with a pronounced minimum at K and Ca.

It has been commonly assumed that the incremental elements

III-A - VI-A in the long periods can be regarded, in any one period, as bonded by s^2d^n hybrids, n being the group number minus two. If bonds are made equivalent by resonance, I will be most nearly proportional to v_n (provided electrical conductance C is taken into account) in that period in which the relative energy level of s- and d-orbitals is similar. This is most true in the second Long Period, as evidenced by the $4d^45s^1$ configuration of the Nb atom rather than the d^3s^2 configuration found inV and Ta.

Except for a relatively minor minimum in monoisotopic Nb, the W/Z ratios for Y, Zr, Nb, and Mo are almost identical, and it is with these elements that the widest variety of properties have been mathematically related to the widest variety of parameters. The earlier mass factor formulas were tested and found wanting in favor of those shown at the beginning of this report; the values of mf and mf* for most elements are shown in Appendix VII.

For Rb and Sr, W/Z values are nearly identical but appreciably larger than those of the elements following them. First studies used only four species, and assumed values of 3, 4, 5, and 6 for I, the d.c. conductance was introduced as (1+100C) to insure against large negative logarithms in poor conductors. The derived values for x, y, z (the exponent for the mass factor) and c (the exponent for the conductance term) need not be restated here (p 7, 2nd Interim Final) for eight properties. The expressions were tractable, exponents ranging to 4.5 or so. Best results were obtained when, after eliminating Log k, the order of elimination was mf, (1+100C), and I.

When there is no alternative, an expression derived from four species can be validated by the fifth, but there is always the possibility of fortuity (see refractive indices of alkali monofluorides and iodides in Appendix IV).

If a parameter is dimensionless it can be included or excluded from the expression without affecting dimensional compatibility. For ease in comparing data from quite different properties, the idea was seized upon of using the calculated value for I for such comparisons.

CALCULATION OF BOND INTENSITIES FOR COMPARISON PURPOSES

Prior studies of quite different properties have been difficult to evaluate in that some "effective" value of the property or a parameter must be used. Here it was realized that if the numerical values for the general expression have been derived, there is a way to compare directly other species with respect to the observed property values.

The influence of the mass factor appears to be that of increased stability (decreased energy) in the solid, presumably by adding other modes of vibration not available when all atoms have the same mass. Given the general expression used here:

$$\text{Log } P = x \text{ Log } N + y \text{ Log } I + c \text{ Log } (1+100C) + z \text{ Log } f^{*} + \text{Log } k,$$

the values of x, y, c, z, and Log k are obtained for each property of interest, and these values are now used to calculate I for other elements. If the postponed influence of Z and W is the same for each property, one can then propose, for a subgroup in which the nominal valence is a constant, a subgroup expression of the form:

$$I(\text{calc}) = \emptyset\, Z^{a}\, W^{b}$$, and

$\emptyset$ should be substantially constant for all members of that subgroup. Initial testing showed only fair conformance for the alkali metal subgroup. For the trivalent lanthanons, however, target accuracy was found for any of the monoisotopic species (Pr, Tb, Ho, and Tm) when the other three were used to establish a, b, and $\emptyset$. It was also noted that La and Lu, in each of which there is but a small proportion of a single isotope, were nearly as well served.

Accordingly, a somewhat novel parameter I_m was conceived. Calculated from the x, y, c, and Log k values established in the General Expression, I_m simply removes the influence of polyisotopy for comparative purposes ($I_m = I$ for monoisotopes).

When I_m values were used with the lanthanons, all which are clearly trivalent were in accord with the subgroup expression above; a better method involved the calculation of a, b, and Log $\emptyset$ from any three of them and using the calculated value of Z as compared to the known value as validation. For the MP expression, for example all calculated Z values agree with observed ones within ± one percent except Ce, Eu, and Yb; the majority are within estimated truncation error , ± .3 %. When similarly tested against Θ as the property, agreement was generally as good, but the exceptions now included Lu, and it was tentatively concluded that the published value of Θ for this element (116K) is too low; the "forecast" value is about 150K but depends strongly on the accuracy of C for that element.

This technique when applied to the alkali metals appears to be successful. To obtain maximum sensitivity, the subgroup expression was usually based upon calculated I and I_m values for

Cs, Rb, and K, with the then calculated values for Z_{Na} and Z_{Li} for comparison among properties. Where the I_{calc} values are not monotonic with Z this must be taken into account in the selection of the base species.

For BP, MP, Θ, B, E, CCTE, 10k, and 100 $c_p \cdot W$, the mean Z_{Na} was found to be 11.327 ± 5.2%, and Z_{Li} 4.0845 ± 9.2% when I was used. When I_m was used Z_{Na} was 11.117 ± 1.8% (omitting a very low value for E) and Z_{Li} 3.708 ± 7.7% . For the property ΔH, Z_{Na} is only 8.96 with I but rises to 9.96 for I_m.

It seems credible that still better conformity will result if, by omitting the *cLog(1+100C)* as well, the bond intensity can now be compared as if all elements, still displaying the same P and N values, are now treated as if they were both monoisotopic and dielectric. The process was repeated, and for these I_{md} values the properties except the BP and the 10k were better served: Z_{Na} is 11.144 ± 2.3% and Z_{Li} 3.763 ± 5.35% . The expected magnification of error for Z_{Na} is almost threefold and for Z_{Li} nearly eightfold, and the deviations reported meet the target accuracy.

Again, the occurrence of anomalous behavior must be used to test the expression. The great sensitivity is again shown by Z_{Na} and Z_{Li} for the boiling points; with I_m these are 10.995 and 3.74 and hence conform; for I_{md} they are 212 and 1082! The reason may lie either in the fact that the reported BP for Rb is lower than that of Cs. One would certainly expect that conductance by electron flow would be minor at elevated temperatures; that it is a *major contributor to thermal transfer at 298K is shown* both by the large exponent (an order of magnitude larger than for MP) for the conductance term in the 10k expression, but the Z_{Na} and Z_{Li} values using I_{md} are in no way remarkable.

It will be noted that the calculated I, I_m, and I_{md} for Rb represent a small extrapolation. If the bonding intensity for the four base elements involves an incremental energy/electron change which is equal to that for Rb, then I_{Rb} will be unity. For the high-temperature properties it is very nearly so: 1.0017 and 1.0067 for ΔH and BP, but for MP and E it is respectively .9641 and .9659, and the apparent equivalence of these properties is again confirmed. For CCTE, B, Θ, and 10k it lies between 1.04 and .992, but for $100c_p \cdot W$ it is .8547, and it appears that the energy difference between s-electron and d-s-hybrid bonding is appreciable. The incremental energy change per period is not the same for s- and d-orbitals, but the 5s and 4d levels being most nearly equal in energy suggests the best possibility of success in deriving an expression from all six early metals of the second long Period.

Figure 1 displays the values for four of the properties of interest: BP, MP, and Θ_{298} are measured in °K on the ordinate scale; the same scale is used for 10 ΔH, but it should be noted that this property involves exposures to temperature levels at or above boiling.

The horizontal plot is for the atomic masses, W. It is readily seen that the mass increment in successive elements varies widely and is negative for Te-I.

The uppermost curve for BP is clearly not linear from Kr to its maximum at Mo; the rise can be described as three nearly parallel steep slopes going from even- to odd-numbered elements, with slopes less steep going from odd to even numbers. The question marks show alternative BP values for Y and Zr.

The open circles represent the same plot of BP, this time with Z as abscissae. The line from Kr to Sr is nearly straight and more nearly parallel to the odd-even Y-Zr and Nb-Mo segments.

From the maximum at Mo there is the familiar drop to the 7th element, Tc, a slight rise at Ru and an almost linear decrease as the Pd subshell is filled. Plotted against W the very steep drop to Ag is accentuated, but as the open circles show, the drop is linear with Z from Pd to Cd. From this subminimum BP rises through In to Sn (again the even-odd step is the steeper rise). The overriding influence of valence on the increasingly covalent metalloid elements Sn, Sb, Te, and I is shown by the open circles; the almost parallel steeper slopes are again for even-odd steps.

As stated, the ΔH curve should perhaps be above that for BP, and it is not surprising that its trends are the same. The maximum, however, appears at Nb [3] rather than Mo. (In the preceding period there is a submaximum in this property at V, but beyond Mn the heats of atomization are highest for Co and Ni). With the subminimum at Cd and submaximum at Sn, the behavior of the later elements at the highest temperatures is quite similar.

The MP curve, shown by the solid line also, but not so clearly, shows the even-odd inflections from Sr to the maximum at Mo (in the preceding period the maximum is at V rather than Cr).

The Θ_{298} curve involves temperatures below (Kr, Rb, Sr, Y, and Zr) 298K; only Mo, Tc, Ru, Rh are reported to be below the Debye temperature under standard conditions[4]. Except for the maximum value for Tc, the Θ curve is similar to that for MP.

This similarity is particularly notable in the later elements, the subminimum occurring at In rather than Sn and the submaximum at Sb rather than Sn. The very large difference in temperature between boiling and melting for In and Sn is noteworthy.

CANDIDATE PARAMETERS AND IONIZATION POTENTIALS

Figure 2 shows, again against values of W, values of parameters to be tested. For N, the solid line of the lower plot shows values rise monotonically to a maximum at Ru and Rh and decrease monotonically thereafter.

In the upper chart, the dotted line joins mass factors, which are one for the monoisotopes Y, Nb, Tc, Rh, and I and only slightly higher for In. Largest mass factors are Ag, Cd, and Sn, all at about the same value.

The dashed, topmost curve shows (inverted scale on far left) the d.c. conductance values. Dominated by the extremely conductive Ag, the curve shows that the "free" electron population is quite high throughout the middle of the period, and that Y, Zr, Nb, and of course the metalloids Sb, Te, and I, lower than for Rb and Sr.

The IP_1 values each represent the work of removing one electron from the neutral atom. Rising sharply to Zr, the rate of rise decreases abruptly between that element and Rh. From Rh to Sn there are excursions above and below it of increasing magnitude, this time rising with odd-even and dropping with even-odd pairs. It may be fortuitous that Sb and Te values lie nearly on the line Zr-Rh, and that values for Zr, Pd, Cd, and I also increase linearly with W.

The dotted lower curve represents, for the first six elements of the period, the quantity IP_{v_n}/v_n , where IP_{v_n} is the work required to remove v_n electrons from the neutral atom, and increases from 96.3 to 1568 Kcal/gm-atom from Rb to Mo.

Despite a lack of data for valences greater than 6 for this potential parameter it is of great interest here. Granted that in the solid metals at ordinary temperatures no electrons are completely removed from the influence of the neutral atom, the fact that some are so weakly held by any single atom as to be able to drift with small electrical potential gradients suggests that for some

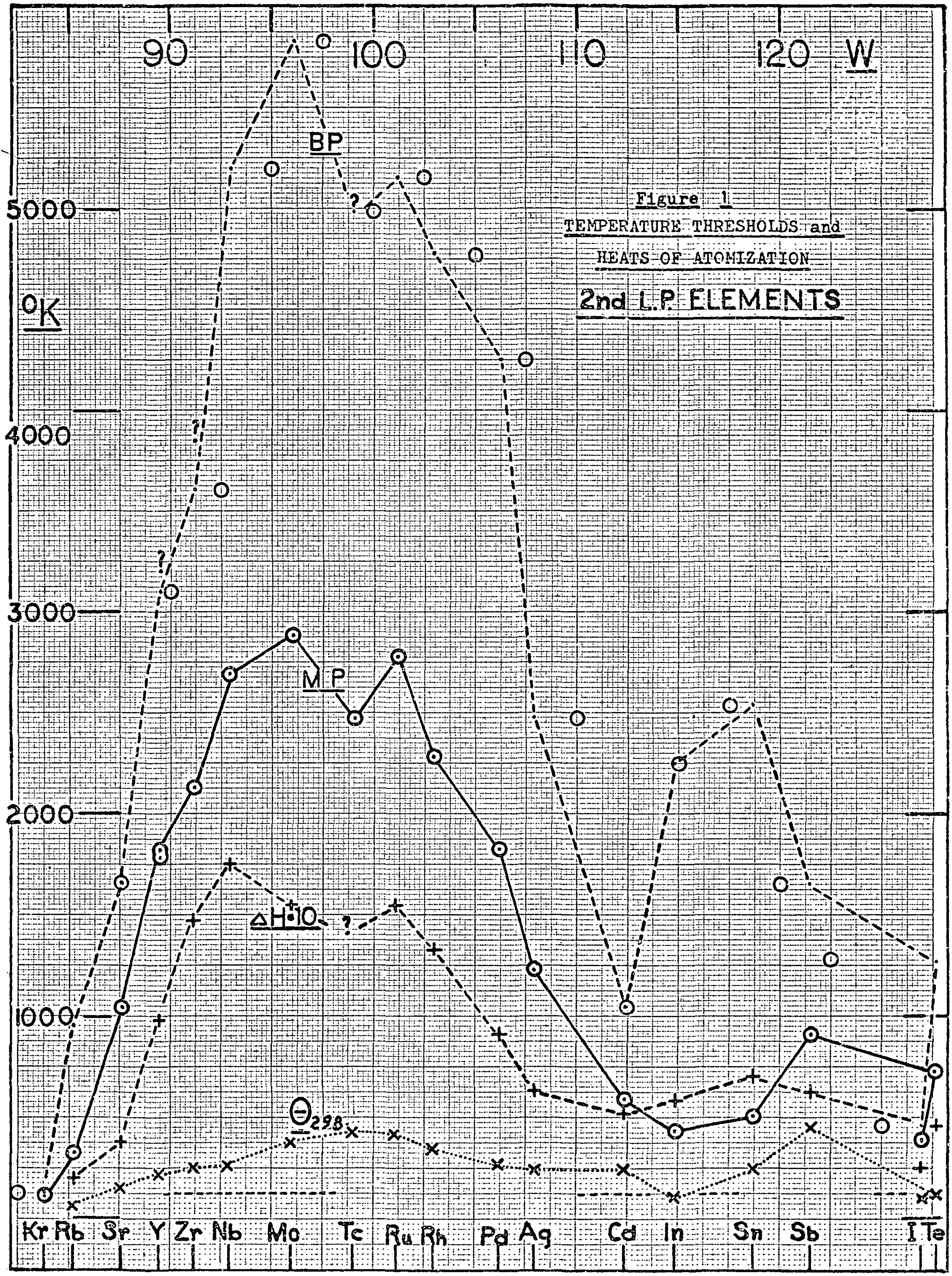

Figure 1

TEMPERATURE THRESHOLDS and HEATS OF ATOMIZATION

2nd L.P. ELEMENTS

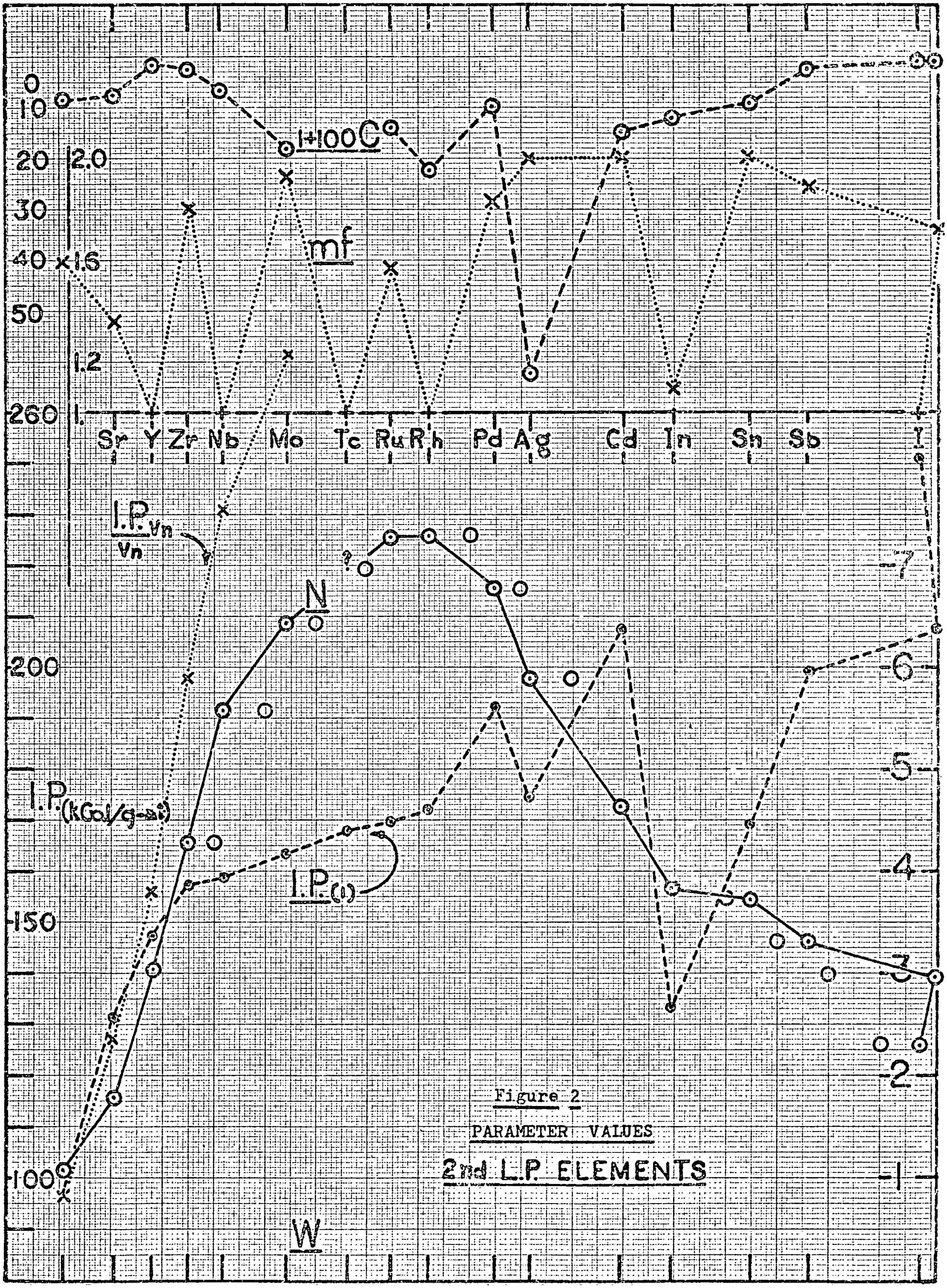

Figure 2

PARAMETER VALUES

2nd I.P. ELEMENTS

room-temperature properties there may indeed be partial ionization, so that IP_1 is a measure of it, while at high temperatures the conductance electrons are either re-engaged in covalent bonding or lost through emission.

Whether the loosely bonded electrons are orbital or form, as in the earlier descriptions of unsaturated covalency, a sort of "cloud", their mutual repulsion should always act to oppose triaxial compression involved in measuring the bulk modulus B.

Accordingly, the six-unknown expression of the form:

$$\text{Log } P = x \text{ Log } N + y \text{ Log } I + y' \text{ Log } IP + c \text{ Log}(1+100C) + z\text{Log } mf + \text{Log } k$$

was developed for eight properties as shown in Table 1 below (Young's modulus for Sr is not well documented and this property was omitted).

Table 1

<u>General Expressions Derived From Rb, Sr, Y, Zr, Nb, and Mo</u>

	x	y	y'	c	Log k	
Using IP_1,						
ΔH	1.900377	-1.131424	+1.607167	-0.163920	-1.78	
BP (TP)	-1.346423	+3.995086	-5.130036	-.220398	+13.43	
MP(Y=1820	-1.322731	+2.56522	+0.227504	-.09448	+ 2.21	
Θ	-3.783208	+6.6005	-5.624717	-.304193	+13.3	
CCTE	2.725441	-5.55074	+3.46303	+.52371	- 0.492	
B	1.882008	+2.26371	-5.174937	-.244756	+10.9	(y/x positive)
10 k	0.020529	+1.7203	-5.277798	+.736532	+10.5	" "
$c_p \cdot W$	0.446414	-0.698931	+0.343679	+.02240	+ 0.147	
Using IP_{vn}/v_n,						
ΔH	0.282802	-0.021861	+1.897262	-.303036	-2.17347	
BP (TP)	3.816826	+0.453393	-6.055993	+.223649	+14.6687	(y/x positive)
MP(Y=1820	-1.538682	+2.72187	+0.244582	-.102826	+2.20805	
MP(Y=1768	-2.079114	+2.66604	+1.35082	-.163407	+0.6980	
CCTE	-0.760029	-3.159915	+4.088134	+.223952	-5.759186	" "
B	7.09043	-1.308976	-6.108966	+.203174	+12.13047	
10 k	5.332484	-1.923407	-6.230445	+1.193369	+11.77463	
$c_p \cdot W$	0.10050	-0.461659	+0.405739	-.00735	-0.06507	
Θ	1.877937	+2.717281	-6.639987	+.182677	+14.6450	" "

Note: since Y and Nb monoisotopes, their expressions used to calculate Log k. If the above expressions are used to calculate I for other elements they will be I_m values.

With so many unknowns and the 14-digit, 6-decimal calculator used, roundoff errors are appreciable and truncation errors probably exceed ± one percent. They will be refined and tested for validity when the computer program is ready.

From them one observes that IP plays a relatively small part in ΔH but a large one in BP and Θ. The higher MP for Y appears preferable. The approximation of y to the Napierian constant for MP and Θ may be fortuitous, as may the -6+ exponents for y' with BP, Θ, B, and 10k, and the observation that the reciprocal of y'_{MP} almost exactly equals y'_{CCTE}.

With insufficient time and funding to test the remaining elements, it was decided to study IP_1 and IP_{v_n} using the full subgroup expression of the form:

$$\text{Log } IP = a \text{ Log } Z + b \text{ Log } W + d \text{ Log } n \ (+z \text{ Log } mf) + \text{Log } k \quad \text{(see note)}$$

For the I-A elements, $IP_1 = IP_{v_n}$ and the expression derived from Li, Na, K, and Rb:

$$\text{Log } IP = 1.104191 \text{ Log } Z - .557694 \text{ Log} W - 1.174993 \text{ Log } n + 2.036670$$

agrees on extrapolation with the observed Cs value within 0.05%. With all five elements and mf* the expression is:

$$\text{Log } IP = 1.101473 \text{ Log } Z - .555556 \text{ Log } W - 1.173815 \text{ Log } n - .000724 \text{ Log } mf + 2.036235$$

For other properties of interest, the method is repeated and discussed in Appendix II and the results used to "forecast" upper and lower bounds for Fr, for ^{6}Li, and for an equimolar mixture of the two Li isotopes.

For the II-A elements, IP_1 is the removal of one electron from the neutral atom (forming the univalent cation), IP_2 is the removal of two electrons, so $IP_2 - IP_1$ is a measure of the work of removing the 1 5s electron with which IP for the I-A metals is concerned. The expressions for these:

$L\ IP_1 = 0.984970\ L\ Z - .463911\ L\ W - 1.199965\ L\ n + .030238\ L\ mf + 2.18214,$

$L\ IP_2 = 1.257888$ " $- .615124$ " $- 1.398181$ " $+ .015513$ " $+ 2.452958,$

$L(2-1) = 1.520556$ " $- .765012$ " $- 1.583982$ " $+ .00958$ " $+ 2.126425$.

That the last of these is preferred for comparison with the I-A elements is shown not only by its minimum z and Log k values but by the value of n calculated for Ra; it is 5.857 for IP_1, 5.946 for IP_2, and 6.016 for $IP_2 - IP_1$.

Of the properties considered, only the ionization potential can be considered to be as nearly as possible that of the <u>atom</u> rather than that of the solid. It is no longer surprising to find that the parameter of mass is everywhere significant, but that the mass factor has any influence on this property may have more to do with distortions at or near the crystal surface than with a real change in the work of removal.

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n is here the periodicity factor, found with the solidified inert gas elements to have a value equal to the principal quantum number of the outermost <u>filled</u> shell: 1 for Li, Be; 2 for Na, Mg etc.[5]

The combination of "normal" parameters (such as N and I, which increase (or decrease) over the range of base species by a factor of five or so with those which embrace a far wider range ($IP_{v_n}/100$) leads to problems in calculation, particularly when there are also non-monotonic parameters of small range (mf*) and broad range (1+100C), even when the property values are normal and monotonic (θ). They are intensified when the property values are non-monotonic and broad range (CCTE). To aid in understanding both problem and solution, the raw data are shown below for the expression:

	θ	CCTE	=	N^x	• I^y	• $IP_{v_n}/100)^{y'}$	• $(1+100C)^c$	• $(mf^*)^z$	• k
Rb	59	273	=	1.0794^x	1.0^y	$0.96269^{y'}$	9.1301^c	1.57532	
Sr	148	69	=	1.7870^x	$2.^y$	$2.5420^{y'}$	8.326^c	1.30109	
Y	214	28	=	3.0191^x	$3.^y$	$4.72586^{y'}$	$\underline{2.6841}^c$	$\underline{1.0}$	
Zr	250	17	=	4.2952^x	$4.^y$	$7.91409^{y'}$	3.3593^c	1.77561	
Nb	260	$\underline{21}$	=	5.5550^x	$5.^y$	$11.5265^{y'}$	7.6262^c	$\underline{1.0}$	
Mo	377	15.0	=	6.4277^x	$6.^y$	$15.6760^{y'}$	19.648^c	1.89579	

Two orders of elimination thus far tested are (1): k, mf ,y', c and (2): k, mf, c, y . The resulting expressions for θ are:

	x	y	y'	c	z	k
(1)	3.574405	13.22301	-10.22262	0.273679	-0.676648	22.606
(2)	-3.751133	0.90197	3.37097	-.032183	0.082697	84.192

and, only partially completed, for CCTE

(1)	27.429122	-53.2197	56.38189	1.19006		.00010292
(2)	-10.71978	4.71324	5.09012	-.402762		11.857

It will be obvious that the order (2) is preferable to order (1) if only because the critical exponents are smaller. For the θ expression, calculated I values for Cs and K are both fractions with (1); with (2) they are respectively 0.7114 and 1.4773 and I_{Li} is 8.667, or Z_{Li} calculated from the subgroup expression is 3.74 and one concludes that the expression generated by order (2) may be a valid one.

PRELIMINARY STUDIES OF THE ALKALI HALIDES

The 20 alkali halides have, for a variety of reasons, been regarded as model solids. An earlier review[5'] showed that MP and G values were closely related for either the halides of each metal, or the metal salts of each halide, and that while this relation permits better understanding of structure in terms of radius ratio-dominated spatial packing, such peculiarities as the density minimum at KCl, the existence of maxima in BP and MP and minima in BS and RI in the salts for each halide could not be treated until the concept of the mass factor was applied to compounds.

Briefly examined for property relationships as the concept of a compound "atom" was being developed, these 20 salts (perhaps 25 if the hydrides can be included) reflect extraordinary care on the part of many researchers to purify, densify, and characterize them. Accurate calculation of the PE requires that both the real density and interatomic distance be observed, and the anomalously low PE values for LiI and CsF have been remarked upon, together with the comment that these are both the combination of lightest with heaviest and smallest with largest elements of the spectrum.

In Appendix IV are tables showing the currently used values for the alkali metals and their hydrides, fluorides, chlorides, bromides, and iodides for properties and for measured and calculated properties and parameters.

Current theoretical models involving additive radii and radius ratios usually ascribe the variation in the dimension of a given ion or atom entirely to changes in the electronic configuration of its environment. Because it was clear in the study of pure elements that this could hardly be important in polyisotopes and must therefore be ascribed to their different masses, it seemed reasonable to investigate the much larger influence the mass factor might have in compounds.

As stated in the Appendix, a simple subgroup expression can be derived for the refractive index of all the halides of a given metal in terms of Z, W, and mf (or mf*) but since there are only four of these the expressions cannot be validated. There are five species in each subgroup having a common halogen, however, and it was found that LiI is poorly predicted as is CsF, while no difficulty is experienced in the chlorides or bromides. When a similar expression is derived using the PE as the property, the anomalous values for CsF and LiI are of the same magnitude and sign. It appears from this that the current formulas for the mf are inadequate to explain the poor packing of these (and perhaps of RbF) adequately, but that strong deviations from ideal packing are reflected in increased refractive index. (Note that this is in accord with high refractive indices in poorly packed oxides and in anisotropic refraction in the titanias).

Note that the minima in RI for each subgroup is well served by the mass factor minimum and is observed in the equipoise compounds. Note also that the widely held opinion that ionicity-covalency relations are responsible seems not to be applicable here;

CsF is the most ionic and LiI the most covalent of these salts.

The current formulas for mf and mf* share, because of W in the denominator, the tendency to vary least as either element becomes heavier. With current interest in optical behavior related to laser reflectors and matrices and doublers, to thermal control coatings for spacecraft, and to IR windows, the possibility that ideality of packing and hence refractive index can be maximized or minimized by adjustment of the composition with regard to mass factor merits consideration for intensified study along these lines.

Among the alkali halides, three form the CsCl structure, and the remainder the familiar halite structure; the similarities of these to the elemental bcc and ccp arrangements are noted, as well as the fact that, approached from the concept of compound "atoms" of identical size, the halite structure is changed to the simple cubic array. An interesting if highly speculative interpretation of this observation in the Appendix suggests a possible rationale for the observed relation between shear modulus and interatomic distance in substances of different packing modes.

OXIDE STUDIES

As the most electronegative divalent element, oxygen forms compounds with all metals and metalloids. Unlike the halogens its valence orbitals are not saturated with the acquisition of a single electron and it can be covalently "shared" in a three-dimensional lattice. If the concept of atomic density can be applied to compounds, the simple and mixed oxides provide ample opportunities to test it, offering in addition to simple and highly ionic systems both saturated and unsaturated ones exhibiting an extreme range of properties and parameters.

Appendix V provides illustrations that show that relatively large groups of oxides can indeed be related with respect to several properties and a common group of essentially the same parameters observed with the elements and the alkali halides. These examples include the selection and testing of data points when several are reported, variations in stoichiometry and differing oxidation states for a few transition metal oxides, and the methods used for calculating PE in binary and mf in mixed oxides.

As might be expected, the simple concept of valence for the metal as being determined by the metal/oxygen ratio in the compound is not tenable here. If the metal valence is to be the number of electrons/atom available for bonding it will be immutable; quite clearly not all of these are used in the lower oxides of multivalent metals for bonding, but they are certainly present and can contribute to certain properties (electrical and thermal conduction, refractive index, bulk modulus).

If a General expression is derived using the "normal" oxides (SrO, Y_2O_3, ZrO_2, Nb_2O_5, MoO_3) for a number of properties and is then used to calculate values of I for other stoichiometries of those elements and for non-base oxides, the resultant I values strongly reflect the observed metal/oxygen ratios: all monoxides have calculated I values not far from 2 and all dioxides not far from 4, etc. In the Appendix it is shown that this can be avoided if at least one non-normal oxide is used in the general expression, the I value used reflecting both the nominal valence of the metal and the sharing capacity of the oxygen present, or $I = v_{nM} (n_O/n_M)$. Examples, I equals 2.0 for CaO, 4.5 for Sc_2O_3, 4.0 for TiO, 8.0 for TiO_2, 7.5 for V_2O_3, 12.5 for V_2O_5, 24.5 for Mn_2O_7, etc. In this way, any oxide or mixed oxide may be compared on the common basis of the total number of valence electrons of the metal(s). Generated in this way it is not perhaps surprising that v_n for Ni in NiO is very close to 8, and for Se in SeO_2 close to 16.

Doubts concerning exact stoichiometry and the achievement of maximum density (a great many researchers apparently believe the X-ray density is preferred for characterization, despite, for instance, the clear finding that stoichiometric TiO is as much as 15% below the X-ray density even under pressure and that VO is almost 5% above it) have diminished emphasis upon direct investigation of properties other than MP, G, RI, and sometmes B. In general it appears that for oxides having well-established compositions and real densities the expressions derived are less complex and more accurate than with the elements. Somewhat surprisingly, there seems to be little difference between polycrystalline bodies (if fine-grained and adequately compacted) and single crystals; indeed, the former have been used to obtain values of G for anisotropic substances.

In a few instances, the concept of atomic density has been used for data screening and for estimating small deviations in stoichiometry and packing ideality. Much remains to be done.

SUMMARY

The objective of this study has been to discover whether quite different materials properties can be quantitatively related to parameters which characterize those materials, and whether, if some of the parameters are common to several properties, the properties can then be related to each other. Target accuracy has been ± one percent of the measurement. All data used have been taken from publications and a minimum number of private communications; conflicting data points have been separately tested.

Central to this effort is the atomic density of any substance of known real density and chemical composition. If the "atom" is defined as the smallest unit which accurately reflects composition, the atomic density is simply the number of such atoms per unit volume.

With the atomic density alternatively considered as a property or as a parameter, other parameters were tested in the following way: For a single substance, an equation is written linking the observed property value to those parameters, the requisite number of equations for related materials are used to generate the numerical values for a general expression, and the expression is then validated by agreement (or invalidated by disagreement) with the observed property and/or parameter of one or more external species.

Limitations of the study have required that only a few properties have been tested for more than a hundred materials or so, and many have been tested only for the number of materials necessary to derive the mathematical expression and validate it. The materials have included the solid elements, the alkali halides and hydrides, and more than a hundred single and mixed oxides, together with a few simple organic substances, substitutional alloys, intermetallics, and metal-metalloid compounds.

Properties have included: heat of atomization, boiling point, melting point, Debye temperature, phase transformation temperature, bulk and other elastic moduli, specific heat at constant pressure, electrical and thermal conductances, bulk coefficient of thermal expansion, and where applicable, refractive index.

The standard conditions for reporting the atomic density are 298.15K and one torr and property data other than the first five above are measured at or near these conditions.

The form of the general expression which has emerged is the product of four parameter groups as follows:

The first parameter is the *atomic density N*. For purposes of test, this has sometimes been converted to achieve a common coordination number for subgroups containing species of differing crystal structure ($\overset{*}{N}$) or calculated on the basis of X-ray rather than real density (N^*). In no case thus far has improvement in conformance resulted from using X-ray densities, but refractive indices appear to require a term which depends upon deviations from ideal structure.

The second parameter has been termed the *bond intensity* I, and contains or is separately influenced by: the *valence*, defined as the number of electrons/ atom available for bonding, and modified in conductors by the electrons/atom so weakly associated with any atom as to contribute to dc *conductance*, and further modified by a measure of the energy level of the interactive electrons such as the *ionization potential* of an element or the electronegativity of a compound.

The third parameter is the *atomic number Z*, the number of electrons (and nuclear positive charges) per atom; for elemental subgroups this is augmented or replaced by n, the periodicity factor, which is currently assigned as the principal quantum number of the outermost *filled* shell of electrons.

The fourth parameter is the *atomic mass* W which appears to dominate kinematic energy storage in the solid; it is modified slightly in the elements and greatly in compounds by the *mass factor* which appears to involve additional vibrational modes and anomalous excursions from equilibrium sites of different isotopes in the elements and constituent mass species in compounds.

The fifth component of the General expression is a "constant" k. When all major contributing parameters have been included, the value of k chiefly represents the combination of units represented in them and in the property itself. Neglected parameters, then, affect the apparent value of k. Where the parameters tend to cancel each other (as is often the case with Z and W) their consideration may be postponed until other parameters have been examined.

The form of the General Expression is most conveniently generated as the linear algebraic equation of logarithmic terms:

$$\text{Log } P = x \text{ Log } N + y \text{ Log } I + a \text{ Log } Z + b \text{ Log } W + \text{Log } k.$$

Where terms for Z and W have been postponed, the expression might then become:

$$\text{Log } P = x \text{ Log } N + y \text{ Log } v_n + y' \text{ Log } IP + c \text{ Log } C + z \text{ Log } mf + \text{Log } k;$$

this expression contains six unknowns and requires the simultaneous solution of the equations of six base species for derivation.

A number of candidate parameters are provably interdependent, and the numerical values for the exponents and Log k obtained can differ when the terms are eliminated in different orders. Solutions for which numerical values are so high as to increase roundoff errors can be discarded unless extended digital capability is available; in general, the solution most often validated by external species can be resolved into from five to nine significant figures.

The careful selection of subgroups and of base species in them permits the elimination of some terms through commonality; for the alkali metals, for instance, the nominal valence is the same throughout and is eliminated with Log k through the initial subtraction, for the first few elements of a long Period the periodicity factor is constant and Z is linear and W nearly so, or for a grouping of trivalent monosisotopic elements (such as Al, Sc, Y, Pr, Tb, Ho, Tm, and Ac) v_n is common and the mass factor (as presently calculated) is one. Advantage can sometimes be taken of this commonality to reduce the number of base species required.

Not yet refined by computer calculation, a number of property-parameters have been generated. Some serve only as illustrations of such problems as order of elimination, selection of base species for non-monotonic series, etc. Others have been used for data screening (in the sense of selecting a most probable datum), for identifying important or critical substances and dubious or missing data, or for exemplifying a technique applicable to current and anticipated problems in materials science or engineering.

It is concluded that the project objective has been attained in the sense that quantitative relations with a common group of parameters have been found to apply to a number of quite different properties. While the substances tested represent a wide variety of compositions, structures, stoichiometries, and parameters, their number is too small to be confident that anomalies will not be found and additional candidate parameters included with or substituted for those now used. It appears highly improbable that properties which are highly directional or strongly influenced by local discontinuities (tensilo strength) can be so treated; the use of the atomic density concept is based upon the fictional existence of a structure which is truly homogeneous. This assumption is valid for most solids on the basis of the enormous population of atoms in even a microscopic specimen; it cannot be justified for porous or flawed substances except where even distribution of pores or inclusions can be anticipated.

Except for the periodicity factor n, the calculation of W, Z, mf, and other "atomic" parameters for compounds and homogeneous mixtures presents no serious problems. The physical reality of real systems must nevertheless be kept in mind.

RECOMMENDATIONS

For reasons which must by now be apparent, certain elements and compounds are more critically important than others in that they are best fitted as the base species from which the mathematical expressions will be derived. The great sensitivity of these expressions requires the highest possible degree of accuracy in property measurement and, of course, similar accuracy in the characterization of the material actually tested. Instances have been noted of the following:

Failure to specify density and composition,

The use of either X-ray density or bulk density values without so describing them,

Failure to report ambient conditions for property measurement (note that for a majority of metals, the change in dc conductance between 300K and 298.15K is one percent or more),

Excessive roundoff of reported data,

Smoothed data not reported as such.

Most inaccuracies are inherent in testing methods and are well appreciated by competetent technologists. It is a tribute to those who generate such information that accuracies have in most instances been so high that such relatively small parameters as the mass factor and calculated packing efficiencies could be identified and discretized.

Specific recommendations include the following:

Neglected elements: The scarcity of Sc perhaps justifies the sparsity of measurements made upon it, but this cannot be valid for Ca, Sr, and Ba. Most needed are referee-quality measurements of dc conductance, real density, bulk and Young's moduli, thermal conductance, and melting point; some have not apparently been made and conflicting values are reported for others. Slightly less critical is the need for re-measurement of these properties for the lanthanons Ho, Tm, and Tb because they are monoisotopes. The reported Debye temperature of Lu appears to be low, and its transition temperature to bcc (as well as for Er and Tm) is not known.

Preparation of the alkali metals in high purity form is not too difficult, but preventing contamination prior to or during test requires extreme care. In most instances, minor changes in chemical compositions can be tolerated because they can be accommodated in the characterizing parameters; such accommodation is impossible when the chemical composition is not remeasured.

For a few of the light elements, appreciable variations in isotope content from the "normal" can occur; this is particularly true of Li. Preparation, characterization, and quality property measurements of ^{6}Li (or alloys containing half or more of it) will be most useful in refining the formulae for the mass factor. The real density of these must of course be measured.

The stoichiometry of a large number of oxides is more often assumed than measured, and statements regarding density too often are as "percent of theoretical density" without specifying it.

The range of refractive indices given for a large number of compounds has resulted in most cases from specimens of differing real densities; the latter are not often measured and less often reported.

Compounds Doubts regarding the proper use of electronegativity and the role of hydrogen in ionic hydrides may be resolved with more and better information for the hydrides of the alkali and alkaline earth elements. On a preliminary basis, these appear to be wholly comparable with the halides.

At ordinary and high temperatures, traces of hydroxyl content in most halides have little effect on properties of interest, but heavier contaminations affect density and mass factor strongly and should be reported.

The density and MP of Sc_2O_3 have been variously reported, and refractive indices for it, for Y_2O_3, and for a number of lanthanon sesquioxides are not available. To be of value all must of course be measured for specimens of known density.

Surprisingly few measurements have been made upon SrO and BaO.

Alloys Early plans to devote a larger proportion of this study to alloys had to be modified after finding that the majority of metallurgical practice reports chemical composition only within limits of nominal tolerance and that real density measurements are seldom made. Most needed are examples, each carefully characterized, of binary substitutional alloys which appear to violate Vegard's "law" through electron interaction (copper-nickel) or radius disparity (copper-palladium).

The selection of minor alloying constituents in alloys for corrosive environments and high-temperature service has depended principally on experience coupled with metallographic examination and identifiable microstructures. The problems of identifying desirable constituents in terms of properties critically needed (and of course identifying undesirable ones) are complex. If the relations demonstrated in this study persist in alloys, the atomic density approach offers a systematic method for reducing this complexity. Preliminary inquiries among the refractory metals and some superalloys indicate that these can be so treated.

Organic Substances The large proportion of free space in most polymers leads to densities varying widely with pressure, heat treatment, and condensation and shrinkage kinetics. For thermoplastic resins, however, compaction to controlled densities is possible, and such specimens can then be measured for properties of interest in the usual way.

Non-solids To the extent that silicate glasses are supercooled liquids it has already been shown that these are amenable to treatment by these methods, the properties of interest having been fictive temperature, bulk thermal coefficient of expansion, and onset of damage by laser irradiation. For fluids whose density can be measured accurately and whose composition is adequately known the atomic density can be calculated and assigned the same meaning. In the studies already made, a fictional value for N_{Hg} was derived by extrapolating its observed thermal expansion to the standard temperature; a similar but smaller extrapolation was made with Mn_2O_7. Such studies would have most immediate value in improving casting alloys, crystals drawn from the melt, etc.

It will be clear from these recommendations that a wide variety of materials and properties appear ready and relevant to studies similar to those reported here. Of the several recommendations which can be made, however, the one which for which the atomic density concept is most fitted and for which such an approach is clearly needed is its growth and development to complement the acquisition, indexing, critical analysis, and dissemination of materials data and technical information.

Application to Information Transfer Systems

At this time the decision as to whether a physical datum is or is not true and correct must depend largely upon (a) the competence of the investigator in controlling the conditions of test, (b) the precision of the necessary testing stimulus and

and of the response of the material, and (c) the character of the material itself (defined here as the minimum number of descriptors needed uniquely to describe the material and hence replicate it).

Powerfully adding to that decision is the whole body of technical knowledge and particularly the knowledge of those deeply experienced in certain kinds of materials or in certain kinds of properties. Personnel of the several Information Analysis Centers, of information-oriented experts in facilities such as the National Bureau of Standards, the several professional Societies associated with materials research and development, with testing procedures and equipments, and with component and product design are similarly able to weigh the probable accuracy of the datum.

With the greatest respect for such experts and gratitude for some of the critically analyzed data they have compiled and provided, the writer strongly recommends that their efforts be complemented (and some of the frustrating routine work lessened) simply be setting up a largely automated system whereby:

The incoming datum for a material will be quantitatively compared with other property data for that material, and

The incoming datum for that property will be quantitatively compared to data for that property as observed with closely related materials.

In addition, the incoming datum would of course be compared to data purporting to the same property-material combination and to data obtained by somewhat different methods or equipments or under slightly different conditions of test.

In this way it is the belief that we may finally obtain the only decision which can be wholly unbiased and free from theory, that of the material itself, which merits prompt consideration.

A portion of the recent project has been devoted to beginning a modest computer program which can, by generating the empirical expression and comparing any property or parametric datum to it, test its probable validity and value. The program is not yet completed, apparently because of the choice of eliminating order not usually noted in the Gauss algorithm, perhaps because of minor inaccuracies in data now being used, and to some extent complicated by minor roundoff errors and significant truncation errors due to neglected parameters. Of these the first can be overcome simply through multiple-choice repetitive solutions, the second by using alternative base species to re-develop the expression and so isolate the incompatible datum for reexamination, and the third through continuing examination of candidate parameters and elimination of redundant ones.

Steps have been taken to consider rational rather than random indexing while retaining the speed of random access, to use a user-oriented computer language (Basic) for interrogation and reply, and to insure adequate digital enumeration in the several arithmetic steps to minimize roundoff errors.

No computer can exercise judgment, but it is strongly felt that the addition of comparative-property information can be helpful to those charged with critical analysis of such information; their recommendations will of course be used in updating and refining the values used.

The application upon which funding for this study has been provided appears to have been met. Although the limits for using the concept of atomic density need to be probed by further exploration, there is ample evidence at this time to show that even in its present state it can serve for physical data screening and for forecasting missing data, and it is strongly recommended that funding for these purposes be considered.

Acknowledgements have already been made for the contributions of persons whose advice, constructive criticism, and critically analyzed data have been most helpful. The undersigned is fully aware that neither the concept nor the demonstration of its validity could have occurred without the care, caution, and competence of the many researchers and investigators responsible for the data which have been used.

Respectfully submitted

SW Bradstreet

Consultant and Investigator

The information contained herein
covers work prior to April 15, 1975.

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3a Note Ref 1a and preliminary listing of symbols and terms.

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7a See Ref. 4, suggested values for k for II-A elements

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APPENDIX I

DIGITAL MATHEMATICS AND MATERIALS

Digital computation is the oldest mathematical technique, and one might fairly describe the growth of theoretical physics to the abilities of such men as Newton, Laplace, Helmholtz, Maxwell, Rayleigh, Einstein, and Schrödinger to coordinate mathematics with physical reality.[1a] There is always some danger that the physicist may lose contact with reality or that the materials engineer may be ignorant of the immutable principles which limit materials behavior. The writer has attempted to take a middle ground by recognizing that the actual behavior of the material is in no way affected by theory or by the aspirations of the engineer.

This behavior for any given material is presently best defined by what are known either as property values or parameter values; the general distinction being that the parameters are those characteristic and observable data which uniquely define the material and are essentially independent of surrounding conditions, while property values are characteristic of the response of the material to some change in its state. Typical parameters for the isolated atom, for example, are the atomic number Z and atomic mass W or probable cycle of nuclear decay, while among its properties might include its formal valence v_n, which for a metal diminishes at energy levels high enough to form partial or complete ionization. The ionization potential(s) IP is thus a measure of the force attracting a valence electron to the nucleus of the atom, and would be included as a potential factor in studying the strength of the bond holding atoms together.

In a simple solid, virtually all measurable characteristics change with temperature and pressure, and in the simplest cases the Equations of States are the mathematical expressions linking the observed volume of the solid with these. Unfortunately, the exact form for such an equation is not yet known, and while a few solids accord reasonably with a power series approximation for expressing the observed change in volume with changing temperature and/or pressure[2a], the solids of engineering importance are not so well served by the assumptions of continuum elasticity or the errors arising from the neglect of higher terms in the series, from relatively large changes in temperature and pressure, from structural anisotropy in the crystal, and from polycrystallinity itself.

At a given temperature and pressure, the simple solid is most easily and frequently characterized by its density, that is, the ratio between the weight (or more properly the mass) of the atoms in a unit volume of it. The <u>atomic density</u> N is given by:

$$(\rho \cdot Av) / W = N ; \qquad (1)$$

where ρ is the observed density in gm/cc, Av is Avogadro's number (here taken to be 60.22094 x 10^{22}) which converts atomic mass units to grams, and W is the mean atomic mass in a.w.u., N is simply the <u>number</u> of atoms per cc in units of 10^{22} (customarily omitted and here chosen so that for the elemental solids the values range from slightly less than 1 for Cs and Fr to about 17 for diamond.

The value of N changes linearly with the density, of course, and standard conditions for it must be set if comparisons among substances are to be made. While N_0 values (measured at or corrected to zero temperature and pressure) appeared attractively easy to use as a base, the difficulties in measuring them accurately have become more obvious as cryogenic research matured, and the writer chose as standards 298.15K (25C) and 1 torr for this study simply because most measurements have been made at or close to these conditions.

Taking as its only assumption Le Chatelier's principle,- that a substance stimulated by any energy change will so react as to minimize the effect of that change,- it was postulated that the numerical value of N might serve as one of the several parameters defining its initial equilibrium state. For this purpose it was noted (a) that the dimension of N is simply reciprocal volume and does not include mass, and (b) that the number N also denotes the number of <u>bonds</u> between atoms, and can serve to denote electronic density, on the average, not only in an elemental solid but in any homogeneous substance of known chemical composition, if one is willing to regard that substance as composed of "atoms" each of which identically conforms to that composition.

It should be emphasized here that although no simple Equation of States, whether derived from theory or from semi-empirical thermodynamic postulates, has exactly fitted observed properties of more than a few solids, a great many materials are fitted to within ± 10 percent or so. The writer was gratified to note that in a variety of simple elements and some compounds (notably the transition body-centered cubic metals and the alkali metals and a number of halides and oxides), similar and sometimes improved conformity was observed when the atomic density was used as a parameter. Moreover, some of the properties thus related were those involving temperature levels well below or above the temperature (298K) base for the atomic densities.

In the simplest sense[3a] the property value exhibited by a substance can often be regarded as the ratio of some stimulus applied to some reaction observed. The possibility that the reaction (to energy change) is governed by or related to a relatively small number of observable or calculable parameters, of which one is the atomic density, is a challenging one.

It has been stated that the dimension of N is reciprocal volume. For properties which reflect the behavior of a unit volume of the material* one can justifiably expect some general equation:

$$P = k\ f(N)\ f'(p_1)\ f''(p_2)\ldots\ldots + k' \qquad (1a)$$

to be fitted to the observed property value P of a substance containing N atoms/cc (and N bonds/cc) and exhibiting the parameter values $p1$, p_2... . The value of k will, if all of the contributing parameters have been included, simply reflect the units used for them and the property; the value of k' can hopefully be made very small by insisting upon consistency among all properties in that the value of each property for a vacuum be zero.

The several mathematical functions f, f', f"... remain to be discovered, and the rationale for this study is based on the certainty that they can be derived more surely from empirical observations than from any theoretical model. Nevertheless, a great deal of fundamental knowledge is applicable for guidance; some of it is reviewed below. For simplicity, the discussion is limited to the elements themselves.

CANDIDATE TERMS FOR THE SOLID ELEMENTS

Little need be said regarding the property values P; the majority of these are expressed in convenient units which are, if one regards the historical development of those units, dimensionally comparable*. Those which are based simply on mass (an example is the specific heat at constant pressure) appear less so, but because the gram was originally defined on the basis of a cc of water and the heat capacity of water the comparative standard for selection of the calorie the error is small; it can be reduced

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*Note that point-defect properties such as tensile strength are not used.

by using $c_p \cdot W$, the Dulong and Petit "constant" or the atomic specific heat; like the heat of atomization and ionization potential its units are then cal/gm-atom.

Somewhat less obvious is the use of the temperature scale (as in Θ, MP, BP) on a comparable basis. Again it must be noted that the Kelvin scale derives from the phenomena of melting and boiling and agrees with the premise that these are zero for a vacuum. One might as well utilize the heats of melting or boiling, but these are less convenient and frequently are complicated by time-dependant mechanisms, and for this reason the values for Θ, MP, BP and the like are taken to mean the temperature thresholds at which some measurable physical change occurs denoting a new equilibrium condition.

In a few instances the common properties do not accord with a value of zerc for a vacuum; examples are electrical resistivity (which is infinite for a vacuum and has therefore been replaced by its reciprocal, the dc conductance), the index of compressibility (likewise replaced by its reciprocal, the bulk elastic modulus), and the index of refraction (which is unity for a vacuum and has therefore been replaced by (RI-1) or the dimensionless (RI-1)/RI.

The selection of candidate parameters is not so simply made. For the elements, one can expect them to fall into three major categories, as follows:

(1) An expression denoting the volume of space occupied in a unit volume of material; this has frequently been denoted by "atomic" radii or atomic volume but in this study utilizes the measured atomic density N,

(2) The "bond intensity" I, which necessarily includes the number of electrons/atom which interact in such a way as to produce cohesion in the solid and resist change in its dimensions, the mean energy of those electrons which determines the strength with which they are retained, and

(3) The effective mass of the atom contributing to its momentum and its kinetic energy. The discovery that in most instances the polyisotopic elements behave as if they were slightly more massive than their mean value of W may have been the most useful contribution thus far made.

The parameter I is not a simple one, and exploratory efforts showed that it cannot be directly measured. Study of the alkali halides[4a] showed that quite exact radius ratios could be deduced from melting point <u>and</u> shear modulus data only when electronegativity difference had been taken into account. It was concluded that here the rather large effects of differing masses could be discounted simply because they exerted a similar influence for both properties.

Given that the open form of (1a) above can now be written:

$$P = k\ f(N)\ f'(I)\ f''(W)$$

as an approximation which would hopefully apply to a variety of properties, it was soon recognized that at least six elemental species would be required to enumerate k, f, f', f'' and, through comparison of calculated with observed values of lighter and heavier elements, confirm or deny the validity of the expression.

Among elemental subgroups (in each a common nominal valence can be presumed) there are but five adequately characterized solid species, and in only one, the I-A metals, do these exhibit a common crystal structure. Other reasons for using them for preliminary study are given in the following Appendix. Here they will serve as examples illustrating the development of a satisfactory mathematical expression for examining and testing candidate parameters and their functions.

FUNDAMENTAL CONSIDERATIONS FOR PARAMETER SELECTION

It seems quite clear that the parameters affecting thermophysical and mechanical properties, at least, must include the atomic number Z, which reflects the number of positive charges/atom which attract both its atomic and valence electrons, and the atomic mass W. One can postulate for test purposes that the influence of each of these will oppose the other; the occasional success of W/Z ratios and 2Z-W values in relating to a number of properties is well known. For the alkali metals Li-Na-K-Rb-Cs-Fr the W/Z values are non-monotonic, decreasing to a minimum at K from either direction. The 2Z-W values increase (negatively) in a monotonic way with increasing Z but the rate of increase is far more rapid beyond K. For some time it was hoped that some regular relation between Z and W might be discovered for some property or for N itself. Largely by trial and error, linear expressions of the form: $P = xN + aZ + bW + k$, , exponential expressions of the form: $P = k\ N^x\ Z^a\ W^b$, and mixed expressions: $P = kN^x\ (aZ+W)^z$ were

were unsatisfactory (when derived from four species to agree with the fifth). The tentative conclusion was drawn that the assumption of a common value of I for these elements is untenable, that I is not adequately expressed by the nominal valence.

Results were improved when, instead of a subgroup, five of the first six elements of a long Period were used to generate the expression; the improvement was notable when Sr, Y, Zr, Nb, and Mo were used, the chosen values for I being 2, 3, 4,.. in the somewhat expanded exponential expression: $P = k\ N^x\ I^y\ Z^a\ W^b$ for the melting points, Debye temperatures, and somewhat less accurately, the bulk moduli. Numerical values for the constant and exponents were very large, and the real question of the accuracy and hence the value of such expressions arose.

ACCURACY AND PRECISION OF DATA AND MATHEMATICAL TREATMENTS

The term "scientific computing" has been used to mean "the relevant synethesis of mathematical, physical, and computing expertise" [5a]; its originator points out that there are three main sources of error: the errors in the data used which lead to inaccurate or untrue expressions, the cumulative roundoff error due to the fact that the arithmetic step is carried out only to a limited number of significant figures, and the truncation error which results from the fact that the expression itself is not exact.

In an empirical study, one can only utilize experience and a degree of common sense in the selection among data points. It is, for example, quite difficult to measure the dc electrical conductance of a highly conductive material, the MP or BP of a refractory one, the elastic constants of a porous one. Small impurity levels can be vital with regard to almost all properties, but certain impurities are tolerated even at small percentage levels. In this study, care has been taken throughout to select among the published data those property values which a) have been independently reported by several investigators, b) are accompanied by an adequate characterization of the tested material; greater credence is given to values critically analyzed by experts[6a] and to those for which the reported value comports reasonably with other property values for the same substance[7a]. Nevertheless, a number of the property data used must be considered suspect, and an important value of this study may be its potential in screening among doubtful data.

A second source of error in the data arises from the normal and understandable caution of the researcher to pretend to an accuracy unwarranted by experimental conditions and observational techniques. It is common practice, for example, to report the bulk density of most solids; the weight of the specimen is perhaps measured with extreme care, but its volume, even when properly calculated from micrometer measurements on a polished specimen, often accords only within ± 3% or so of the real value obtained using Archimedean (immersion) techniques with proper allowance for temperature, pressure, and suspension devices. The writer has referred to the latter method as the real density, and has noted often that even in dense, well-annealed single crystals, this differs appreciably from the X-ray density in an entirely characteristic way; what is sometimes judged to be a sort of porosity or an accumulation of defects is simply an intrinsic reflection of its spatial array.

Two examples may serve to illustrate this important point. The melting point can, at moderate temperatures, be most precisely judged by the onset of the endothermic melting process itself, but at higher temperatures it is most frequently noted as the threshold of formation of enough liquid to round exterior corners and edges of the specimen or observable flow. It has been pointed out[8a] that at high temperatures a specimen which can be optically observed for melting behavior is not in thermal equilibrium with its surroundings and, indeed, may not even be wholly at the same temperature. To some extent these problems have been eased by standardizing temperature scales against well-characterized elements and compounds, and by more precise techniques for temperature measurement.

The BP values for Sr, Y, and Zr, for instance, are given by a handbook as 1657, 3105, and 3851K, values recommended but not attested by TEPIAC are 1645, 3200, and 3610K. While each pair of values might be investigated separately, it suffices in this case simply to derive the expressions resulting from each set of values; the latter is more acceptable when extrapolated to derive a value of I for Rb. When this expression is compared with the two MP expressions, one of which uses the frequently given value for Y of 1768K and the other the TEPIAC value of 1820 the latter is clearly the better choice.

The second point regarding the accuracy of available data arises from the quite different sensitivity of different properties to some parameters. The density, and hence the atomic density, exerts a very strong influence on the elastic moduli and thermal expansion alike, yet the major source of error in it, the existence of gross porosity, strongly affects elastic properties without any discernible effect upon thermal expansion. Since both linear and bulk coefficients of thermal expansion can now be measured very accurately[9a] it is hoped that this comparative approach may in time be applied to the common problem of determining whether the "porosity" of a number of crystals (tungsten, bismuth) is intrinsic or extrinsic.

Although this discussion centers on the elemental solids, a few comments concerning compounds need be made, for there appears now to be little doubt that small deviations from stoichiometric proportion may and often do exist, and that these may for some properties cause considerable deviations in property values. It has been too common, particularly in physical metallurgy, to ascribe these deviations to lattice defects, dislocations, clusters of a second phase, or residual strain; the general practice of assuming textbook stoichiometry in compounds and intermetallics seems often to have been a potential source for apparent disagreement among properties.

Nevertheless, the empirical generalist has no choice other than in the selection of one among a number of different property values, and cannot ethically modify these for better fit. The writer has therefore chosen to use mathematical expressions in which the property value P is always compared directly with candidate parameters.

ARITHMETICAL ERRORS IN DIGITAL REPORTING AND COMPUTATION

Cumulative roundoff as a source of error has been mentioned; its influence in digital computation is usually dismissed on the basis that it becomes negligibly small if each arithmetic step is carried out to a large enough number of significant figures. Unfortunately, this precaution suffices only when the numerical values in the expression are exactly known. Among the property and parameter values for real materials, this assumption is valid only for Z, all others being limited in accuracy both by the indeterminacy of the measurement and the digital limitation of reporting it.

The most common real density value for pure, dense Na appears to be 0.9712 ± .00005 gm/cc at 298K and 1 torr. Noting only that values differing from this have been reported and that most real densities have been reported only to two decimals, it is instructive to observe the effect of its simple conversion to N, which involves multiplying it by Avogadro's number (60.22094 x 10^{22}) and dividing by W (22.9898). The mathematical purist will promptly round off the 2.544023 to 2.544 (the number of significant figures of the datum). It is perhaps worthy of note that doing so changes the original density value to .971191, well within the deviations suggested by the research and, while equally precise, less accurate.

The error is extremely small; the Log10 values are .4055239 or .405520 respectively. Taken, for example, in the general expression for the CCTE (in which x is 2.725441), the difference in derived Log k values is only 0.000011 and, of course, the same for Log P.

In the elements used to derive the expression itself, however, such an error can be significant. The most consistently reported density for K is 0.8606 gm/cc (note that it is lighter than Na) and N is accordingly either 1.325 or 1.325409; logarithms are .12222 or .1223509 . In the first step of simultaneous solution the logarithms are subtracted to eliminate Log k, and the xLog N term is .28330 for the rounded-off case and .283173 for the untreated value. In the next step this value is multiplied by a value determined by the ratio of the first parameter to be eliminated, and if this multiplier is large, so is the error enlarged.

Note that this kind of rounding-off error can never be eliminated completely; it can, however, be minimized even when a simple desk calculator is used by taking the following precautions:

1) Use the full significant-figure capacity of the calculator for all arithmetic steps in the derivation and subsequent check; where logarithms are used, these should be of at least the same decimal count.

2) With a six-decimal calculator, it sometimes happens that b·(a/b) is not exactly a; (1.666667/3) is .555556, which when multiplied by 3.0 is 1.666668, and the operations of division and multiplication should be checked and, where necessary, corrections made.

3) Errors are minimized when all logarithms are of a similar order of magnitude (hence 10k, 100C, etc.).

4) In selecting equations for simultaneous solution, large ratios (or very small ones) in the term to be eliminated should be avoided.

5) If the calculator possesses an adequate digital capability, the decimal capability can be artificially enlarged by multiplying

the initial expressions by 10 or 100.

6) After the solution is complete, the process of checking the numerical value should be conducted with both expressions from which it was obtained; the values of the second exponent should not differ by more than a unit in the final decimal. The process is continued with the same criterion for acceptance, each time using all of the intermediate equations.

7) In the final step of the derivation, calculated values for Log k should not deviate by more than ± .000001 and the deviation should not monotonically increase or decrease.

8) As judged by the work done this far, the 14-digit, 6-decimal capability calculator with 5/4 roundoff is adequate for most purposes, taking the precautions shown. It is marginal when differences in Log P are smaller than one percent or so of the differences in Log p; it is inadequate when exponents are larger than 8 significant figures.

Since these precautions are largely unnecessary when a computer with extended digital capability can be employed, it is strongly recommended that this be done. Based on preliminary experiences with the development of the necessary algorithms and instructions for computer operation, the following precautions have been noted.

Data should be used in raw form simply to eliminate possible errors in input by the operator. To avoid false runs, each equation should be checked prior to the sequential operation, and may then be stored for ready use and/or regression studies.

Since arithmetic solution among logarithms is simpler than multiple-approximation exponentials, the first step recommended is conversion to logarithmic form; for most purposes it appears that a 9-decimal capability for this is ample for Log_{10}. If Napierian or other logarithms on a lesser base are used, a somehat larger decimal capability is required.

Provision must be made for alternate paths of simultaneous solution; the probability that the parameters used are truly independent is remote.

Care must be taken that no automatic roundoff occurs at less than the desired number of significant figures, but techniques for artificially increasing digital capability need not be used if both memory and internal capability is of the order of 20 digits or so. Display capability of 3 digits and six decimals for exponents and Log k values appears adequate for comparison and interpretation.

TRUNCATION ERROR AND TESTS FOR VALIDATION

In most problems involving the derivation of a mathematical expression which will accord with physical reality, the factor of computability is seldom a serious obstacle, particularly when the applicable equations are linear (as the logarithmic expressions are here) and hence subject to the method of Gauss elimination taught in elementary algebra. Such expressions, however, are based upon two premises: a) that the data (in this case values of Log P) are accurately known, and b) that the several quantities with which these are equated are also accurately known and are independent. There is, of course, the well-known limitation of the Gauss algorithm that the number of equations must equal or exceed the number of unknowns.

Neither of the major requirements is met here; property values are invariably imprecise, and the parameters available to us are (with the sole exception of Z) not exactly known. It necessarily follows that any derived expression will probably be an approximation.

The approximation will trend toward accuracy, however, as more accurate property data are found and used; perhaps more importantly and certainly more sensitively it will be improved as the factors which are most important and least interdependent are discovered and applied. With modern computer capabilities, one might venture to suggest that a satisfactorily precise interrelation among properties and parameters could be generated with as few as twenty or so of the solid elements through cyclic iteration.

Unfortunately, with each added elemental species the probability of error increases unless more accurate data are available <u>in the base species</u>. (It will be obvious that the writer pleads for support of referee-quality measurements for a relatively small number of substances rather than modest improvements in all data). There is an advantage, then, in making every effort to so simplify the equations tested as to insure that the more important parameters shall be clearly identifiable. In accord with the objective of insuring that the mathematical expressions shall accord with physical reality, the preliminary selection of candidate parameters can be assisted by noting some of the trends which certainly exist, and some of the apparent exceptions to those trends.

In the not always regular filling of orbitals with incremental electrons, the interruption of filling an external shell by the formation and filling of a penultimate shell creates the most notable irregularity. The first 18 electrons do indeed successively fill the 1s, 2s, 2p, 3s, and 3p "shells" but in K and Ca the 19th and 20th electrons fill the 4s rather than the 3d shell, which begins filling with Sc.

The above statement is usually taken to explain some of the peculiarities of K and Ca with respect to their subgroups. Among these is their notable minimum in density in both solid and liquid state; this density minimum extends to their compounds. The peculiarity extends to specific heat values as well.

The concept of atomic density lends insight into this apparent anomaly. There is of course no reason to expect that because increases in atomic number are usually attended by an increase in atomic weight that occasional failure to do so is worthy of special study. Nevertheless, large deviations from strong trends often serve to identify the major factors in those trends, and one notes here that K is the first element whose atomic mass is lower than the preceding one, Ar; moreover, Ca is but a single nucleon heavier than K.

The density of the element relates simply to the ratio of its atomic mass to atomic volume. For the I-A and II-A elements there is no change in coordination number for the four lighter species, and in both subgroups the decrease in N is monotonic,- that is, the <u>size</u> of the atoms increases regularly in the two short and first two long Periods for these subgroups. This observation, together with the note that the density anomaly is <u>not</u> reflected in melting point, elastic modulus, or dc conductance leads to a suspicion that the anomaly lies not in bond energy but in mass. If this is true, then atomic mass plays a larger part in the condition of the solid state than has usually been accorded it.

Note that this suspicion is strengthened when one notes that a similar anomaly does not exist with the first two elements of the second long Period, although in these, the penultimate 5s shell is also filled before the 4d.

The electronic configurations discussed are characteristic of the isolated neutral atoms, and while one might expect that they thus exert a profound effect upon the properties of the crystal, a part of the suspected effect might be that of mass.

To test this, one can inquire mathematically into the relation between a property of the isolated atom (only slightly affected by solid aggregation) with Z, W, and some parameter which might depict the underlying electronic configuration of each element in the subgroup. In the same way, some or any of the property values for the elemental solid. Given that little is known about Fr and not much more about Ra, each subgroup still comprises five well characterized species, four of which can be used to establish the subgroup expression: $P = k\ Z^a\ W^b\ n^d$, where n represents a "periodicity factor" yet to be established, but relatable to the inert gas elements whose characteristic configurations are those underlying the monovalent I-A ions and the divalent II-A ions.

Before undertaking such a study it is of course reasonable to peruse the remaining elements with a view to identify other elements which might be affected by a mass anomaly. Clearly, two kinds of anomaly might exist: in the K and Ca case, the change in W with Z is far less than in the overwhelming majority of successive pairs, in the second it is notably greater.

The first kind of anomaly is found in Co and Ni, the second in Te and I, the third in Ba-La-Ce-Pr (successive elements increase in W, but by far smaller than normal increments) and (omitting the actinide elements) last in the series Pb, Bi, Po, and At.

As might be expected, elemental pairs in which large increases in W are noted usually precede or follow the above. Because one would expect the anomaly to exert a lesser effect as the absolute value of W increases, the following pairs are listed in decreasing order of $(W_h-W_l)/W_m$ where W_m is the arithmetic mean mass of the two: H-He, He-Li, Li-Be, Cl-Ar, Ca-Sc, Ni-Cu, Zn-Ga, Sb-Te, Pm-Sm, Eu-Gd, I-Xe, Cs-Ba, and Tm-Yb. If any property value changes unexpectedly in going from the first to the second element, the parameter of mass ought to be considered as a factor.

The subgroup expression shown above requires four base species for derivation of k, a, b, and d. Taking the alkali metals as an example, one expects that since W/Z values are (Li...Cs) 2.3130, 2.0900, 2.0580, 2.3100, and 2.4165 respectively, the expression will be more sensitive to the anomaly if the four heavier elements are used as base and Li for testing than when the four light elements are used as base and validity is tested by comparison to Cs. For properties which are non-monotonic with minimum or maximum at Rb (BP) or at Na (100C) the accuracy of the derived expression will be favored if that element is included in the base species.

SUMMARY

The highly sensitive exponential expressions which best appear to relate observed property and parameter values can, with proper precautions, be derived using Gauss elimination of the logarithms.

APPENDIX II

EXAMPLES OF TYPICAL INQUIRY AND CALCULATIONS: THE I-A METALS

In the preceding section some of the methodology of this inquiry has been introduced, together with a generalized discussion of the simple mathematical expressions derived and tested. In private communications, some have expressed concern regarding differing values obtained using identical property data, and the purpose of this section is to provide, through examples, some illumination for those who may wish to conduct similar investigations independently.

BACKGROUND: THE ALKALI METALS

For a number of reasons, the solid elements Li, Na, K, Rb, and Cs are chosen as best fitted for exploratory study. In common they display a single s-electron for bonding, the electronic substructure being in each case that of the preceding inert gas element. At ordinary pressures and temperatures all exhibit the body-centered cubic array and retain it to melting. In consequence they have been extensively studied, reasonably well characterized, and subjected to a variety of tests.

As solids they have little commercial value. The least electronegative of the metals, they form compounds with such avidity that there is some doubt that any, particularly Rb and Cs, can be regarded as pure, residual oxygen, halogen, and hydroxyl contamination being common and retained even in the molten state.

As shown in the Appendix dealing with elemental properties, the elements usually behave in a way which monotonically reflects the increasing size and mass with increasin atomic number, but note must be taken of some non-monotonic properties: Na is alone overpacked and significantly a better conductor of heat and electricity than the others, the BP for Rb is slightly lower than that for Cs, and K is lower in specific heat, lower in density, lower in Zener elastic isotropy, and lower in the ratio W/Z than the other elements of the subgroup.

A similar number of minima are observed with Ca in the II-A metals, and it is not surprising that such parameters as W/Z have been frequently employed in characterizing them. This was made simpler in this study; while the real and X-ray densities of K are lower than those of Na and Rb, values of N are monotonic and have permitted studies of a variety of properties without the obscuring influence of mass. These led to discovery of the mass factor described in the main body of this report.

For the elements, the value of the mass factor is unity for monoisotopes and larger than this for polyisotopes; the somewhat arbitrary formulae presume an increased effect when a) the constituent isotopes differ most in atomic mass, b) the differing isotopes are present in nearly equal fractions, and c) the mean atomic mass is not large. Because of its low atomic weight, the mass factor for Li is significantly affected by small differences in isotope content and if, as it presently appears, the value of mf is related to such properties as are important in mineral formation and distribution, then there may be significant differences among "natural" Li specimens[1b], and note of this has been taken by others[2b]. In the absence of mass spectroscopic data for the Li metal actually tested, however, one must at this time assume a single value for W (and mf or mf*) for this element, and this has been done here.

There is ample evidence that N_{Li} increases as the proportion of ^{6}Li is increased, and an alloy high in this isotope was observed to have an increased specific heat[3b]; unfortunately, its real density appears not to have been measured.

There appears to be some value, then, in attempting to forecast property values for the two Li isotopes and for an equimolar alloy of them which will have the highest possible mf or mf* value. In view of the use of molten lithium as a reactor coolant, one might even expect some guidance with respect to the possible use of such an alloy, or at least support experimental studies to confirm or deny the forecast values.

In the exercise described here, the first property to be considered shall be one which ought to be most independent of possible interaction between differing masses; this is the ionization potential, which is the work necessary to convert a gram-atom of these elements from the neutral atoms to unipositive ions, and excludes cohesive forces in the solid. It is usually taken as improbable that mass will exert an appreciable effect, and equally agreed that both the number of electrons per atom (Z) and the size of the atom (or more exactly, the distance from the nucleus to the electron being removed) will be important. One therefore suggests an expression of the form IP= aZ + bW + k (for which size is absent) and a companion expression N = aZ + bW + k for comparison. Were so simple a relation to exist it would long ago have been noted.

The exponential expression ($IP_1 = k Z^a W^b$) is almost as unacceptable. Clearly, another parameter is required for test, and on the basis of an earlier empirical study relating the reported atomic diameters of the elements to their atomic numbers[3b'] the periodicity factor ,n, was chosen.

Hume-Rothery had deduced the expression (symbols modified):

$\text{Log } R = a \text{ Log } Z + \text{Log } n + \text{Log } k$, in which R is half the observed interatomic distance, a has a value of about -1/3 for the solidified halogens, inert gas elements, and I-A and II-A metals, while the value of k is specific to each of these subgroupings. The values for n are the principal quantum numbers of the outermost filled electron shell, 1 for He and Li, 2 for Ne and Na, 3 for K and Ca, etc. The measurement of R was taken at half the critical temperature for the element, and all values had been corrected (using Goldschmidt's method) to conform to the coordination number 12 typical of closest packing of identical spheres.

With somewhat better data the writer reevaluated this argument[4b] and found: (a) that while no subgroup expression applied exactly to all members, deviations (in R or k) seldom exceeded ± two percent, (b) the value for a was more nearly -0.368, or the negative reciprocal of the Napierian constant, and (c) an equally precise expression for the solidified inert gas elements could be developed using a modified Z and observed W value for each, omitting n. (On the advice of physicists these findings were not published on the basis that the influence of mass on cohesive bonding must be negligibly small).

Since $N = PE/(4.1888\ R_N^3)$, the Hume-Rothery expression can be written: $\text{Log } N = 1.10364 \text{ Log } Z - 3 \text{ Log } N + \text{Log } k'$ for an elemental subgroup in which the packing efficiency is identical for all members (as it is assumed to be in calculating X-ray density), and this expression, for which a and k can be determined from any pair of elements, serves admirably to provide guidance here. If the deviations are principally due to dissimilarities in PE (not given for most elements and not too precisely known yet, PE for Li....Cs are: 67.97, 68.24, 65.70, 63.43, and 66.71 percent respectively, the ideal for bcc packing being 68.045 percent), then correction of the N values to accord with ideality will improve conformity. It does so, although calculated values of k' agree only fairly when Li and Rb are used as the base species (1.38, 1.44, 1.34, 1.38, and 1.31; all other pairings result in poorer conformance, the worst being K-Cs and Na-Cs. The last pairing is of monoisotopes, and one concludes that the mass factor contribution will be small.

From the Hume-Rothery findings one expects, in the expression

$$N = k\ Z^a\ W^b\ n^d$$

that the value of a will be of the order of ± 3; if the value of b is numerically similar and of opposite sign, then Li and Rb represent an additional commonality, since their W/Z ratios are almost identical.

SUBGROUP EXPRESSIONS FOR CANDIDATE PARAMETERS IN TERMS OF ATOMIC NUMBER, ATOMIC MASS, PERIODICITY FACTOR AND MASS FACTOR: I-A METALS

The Hume-Rothery relation provides a tenuous basis for forecasting the subgroup expression for N when the mass factor is neglected, no such background is available for the ionization potential. It appears credible that the mass of the neutral atom will be a weaker determinant in the work of electron removal than in the kinetic energy of the coherent solid. In an earlier study of candidate formulae relating Z and W it was noted that for Li...Cs the values for $Z/n{\cdot}W^{\frac{1}{2}}$ are1.139, 1.147, 1.013, 1.000, and 0.954 . These are, with the exception of Na, curiously similar to IP/100 values, and it was decided to test the above relation for N, IP_1, and (because its dimensions are work/gm-atom) ΔH.

This will be done as follows: neglecting mf, the expressions will first be developed using Na, K, Rb, and Cs; if the forecasts are correct, the extrapolated values for Li will not agree with those observed. From the expressions and the observed Li values, one can then calculate Z_{eff} for Li; if these are nearly the same for the N and IP_1 expressions, then n is not unity for the short Period.

Because n is clearly related to Z for the elements from Cl to La ($Z = 18(n-2) + v_n$, v_n being unity for these metals) one would expect an interdependence between n and Z as parameters. A "balanced" relation is: $Z = 2n^2 + (n+c)$, where c is zero for Li and Cs, 1 for Na and Rb, and -2 for K. In neither case is there a relation between Z and n common to more than three elements.

For those who may wish to test the computational accuracy of their calculators, the following page will reproduce the values obtained using a 14-place, 6-decimal calculator with six-place Log_{10} input as shown. Values have been checked as described in the preceding section of this report and where necessary refined so that Log k does not vary more than ± .000001 .

Table 1b

Pertinent Data and Calculations for I-A Subgroup Based on $P = k\, Z^a\, W^b\, n^d (mf)^z$

	Log ΔH	Log N	Log IP_1	a Log Z	b Log W	d Log n	z Log mf	or z Log mf'
Li	1.58433	0.66494	2.094315	=0.477121a	+0.84130 b	+0.0 d	+0.118613z	0.09241z'+L k
Na	1.41330	0.405538	2.073535	=1.04139 a	+1.361536	+0.30103 d	+0.0 z	0.0 z' "
K	1.33244	0.122348	2.00009	=1.27875 a	+1.59182b	+0.477121d	+0.077842z	0.077077z'"
Rb	1.29003	0.033182	1.983487	=1.56820 a	+1.93181 b	+0.60206 d	+0.20236 z	0.197372z'"
Cs	1.27184	-.07145	1.95299	=1.74036 a	+2.123536b	+0.69897 d	+0.0 z	0.0 z'"
(Na-K)	.8086	2.83190	.73445	=-2.3736 a	-2.30646 b	-1.76091 d	-0.77842 z	-0.77077 z'
(Rb-Cs)	.1819	1.04632	.30497	=-1.7216 a	-1.91726 b	-0.96910 d	+2.0236 z	1.97372 z'
A-1	.404587	1.00769	.227735	= 0	.244358b	-0.308108d	-	-
A-2	.490254	1.307716	.305547	=-.251471a	0	-0.494668d	-	-
A-3	.263105	.512190	.099227	= .415312a	+.647922b	0	-	-
(Na-Rb)	1.2327	3.72356	.90048	=-5.2681 a	-5.70274 b	-3.0103 d	-2.0236 z	-1.97372 z'
(K-Cs)	.6060	1.93798	.4710	=-4.6161 a	-5.31354 b	-2.21849 d	0.77842 z	0.77077 z'
B-1	.474136	1.324738	.318033	= 0	.316593b	-0.419244d	-	-
B-2	.542571	1.531455	.368024	=-.292464a	0	-0.586364d	-	-
B-3	.302458	0.806158	.192623	= .733687a	1.110813b	0	-	-
10·1	-.386317	.146907	.177344	= 0	0	-0.154797d		
" 2	-.237321	.090836	.108932	= 0	0	-0.095087d		
" 3	-.866854	-.419690	.131274	= .126377 a	0	0		

						calculated		corrected
a_1	-6.858699	-3.320723	1.038578					
a_2	-6.859086	-3.321112	1.038474					
a_3	-6.85927	-3.321007	1.038749					
b_1	4.802431	2.919062	-.512570					
b_2	4.802683	2.919315	-.512502					
b_3	4.802802	2,919247	-.512682					
d_1	2.495636	-.955490	-1.145655					
d_2	2.495830	-.955293	-1.145603		Log ΔH	Log N	Log IP_1	Log N
d_3	2.495925	-.955346	-1.145739	Li				
Log k_1	1.265936	-.176929	2.034730		2.033792	.694491	2.099032	.694491
" k_2	1.265938	-.176931	2.034730		2.033821	.694517	2.098983	.694519
" k_3	1.265939	-.176933	2.034730		2.033834	.694507	2.099011	.694511

Note: Values in (Na-K) etc. expressions multiplied by ten
Values in A-1, etc. expressions multiplied by ten

Subscript 1 denotes first cancellation of a Log Z term
2 " " " " b Log W "
3 " " " " d Log n "

mf and mf' values not used in this derivation.

- -

As expected, the expressions for ΔH are not valid; calculated values are of the order of 108+ (while the observed value is 38.4) KCal/gm-atom. Parameters tested are insufficient to relate to this property.

Also as expected, the expression for N is not valid; calculated values are of the order of 4.95 x10^{22} atoms/cc while the highest credible experimental value is 4.6257. While the parameters tested are certainly significantly related to N they certainly do not validate the expression. As with the ΔH series, conformance is slightly improved when Z is eliminated first.

If all operating parameters have been included, mathematical precision requires that Log k be a constant for any given property. Small imprecisions such as that shown in the N series can be accounted for by setting Log k to its lowest value and recomputing Log P; as the tabled values show, this slightly increases the advantage of first eliminating the Z term.

The IP_1 expressions are far better fitted by the observed value of IP_{Li} (error = $100\ (P_{calc}-P_{obs})/\ P_{obs} = 1.08\%$), and the relative exactitude of this measurement provides a reason for extending the inquiry to a similar series in which Li, Na, K, and Rb are the base species and Cs the validating species. Were Log k values here the same as those for the heavier metals, the errors would be of the same magnitude and opposite sign, and (since Na,K,and Rb are common in both) the net result is that the ideal expression would exhibit exponents intermediate in magnitude.

Accordingly, this series of calculations was carried out in the same way as that illustrated on the previous page. Because ΔH had been so poorly fitted, the MP was also tested. As before, it was found that conformance was improved when Z was eliminated first, and that Log k values were indeed different. With the exception of (1+100C) all errors judged by P_{Cs} were appreciably smaller (and as expected opposite in sign).

Since values of Log k differ in all cases, the supposition is confirmed by these expressions that a significant parameter has been neglected, and because the substitution of Li for Cs results in this difference, the parameter must have a different value in these elements. For reasons already stated, the obvious candidate among parameters is the mass factor, which ought to have a minimal influence on IP_1.

The principal objection to deriving any expression utilizing <u>all</u> subgroup species is that its validity cannot be directly disproved or proved; granted that it fits the observed data, it may be a mere exercise in mathematical agreement. In this case, however, it appears that if the expression thus derived yields exponents lying between those based on the four heavier metals and on the four lighter ones, some consistency in this intermediacy might be shown.

It is not yet known whether the mass factor should be introduced as mf or mf*; both will be tested, as will the alternative 100C and 1+100C. Table 2b shows the derived exponents and Log k values for easy comparison. The uppermost for each property is derived from Na..Cs from Table 1b; the error is that of the calculated property value for Li.

The second expression is calculated from all five elements using mf as the mass factor and the third using mf*; for these there is no error value. Below this is the expression derived using Li..Rb, the error being that for the calculated value of the property for Cs. The remainder of the tabled data will be described later.

Table 2b

Subgroup Expressions in Terms of Z^a, W^b, n^d Alone or With mf^z

	a	b	d	z	Log k	error
ΔH (Na-Cs	-6.858699	4.802431	2.495636		1.265936	181.5%
"	-0.885793	0.720611	-0.179482	-0.066918	1.408658	(mf)
"	-0.865103	0.705709	-0.187287	-0.068872	1.409741	(mf*)
" (Li-Rb	-0.605300	0.501340	-0.299948		1.451354	-53.4%
MP	-3.317928	2.262355	1.270991		2.561673	68.6%
"	-0.315296	0.210006	-0.073081	-0.034504	2.633715	(mf*)
"	-0.185134	0.107617	-0.129524		2.654562	-2.16%
N	-3.320723	2.919062	-0.955490		-0.176929	7.13%
"	1.774420	-0.562892	-3.23750	-0.057078	0.298657	(mf)
"	1.792050	-0.575596	-3.244141	-0.058748	0.299594	(mf*)
"	2.013691	-0.749931	-3.340276		0.335083	-3.83%
IP_1	1.038474	-0.512502	-1.145603		2.034730	1.08%
"	1.101258	-0.555402	-1.173733	-0.000701	2.036225	(mf)
"	1.101473	-0.555556	-1.173815	-0.000724	2.036235	(mf*)
"	1.104191	-0.557694	-1.174993		2.036670	-0.05%
1+100C	86.594265	-60.18530	-38.688621		4.72276	-0.0%
"	11.519231	-8.87974	-5.064517	0.841164	2.928915	(mf)
"	11.259070	-8.69238	-4.96632	0.86570	2.915986	(mf*)
"	7.993408	-6.123524	-3.550195		2.392128	73.1%
100C	195.13418	-131.75445	-92.08509		NC	NC
"	13.15997	-10.18500	-5.725359	1.089973	3.174557	(mf)
"	12.82286	-9.942221	-5.59812	1.121776	3.156765	(mf*)
"	8.591215	-6.613488	-3.763120		2.478978	64.6%
ΔH	95.845	95.248	95.970		77.55	(mf*)
"	95.514	94.902	95.691		76.97	(mf)
MP	95.845	95.248	95.970		77.56	(mf*)
"	95.514	94.902	95.691			
N	95.845	95.248	95.969		93.069	(mf*)
"	95.514	94.902	95.690		92.886	(mf)
IP	95.864	95.269	95.992		77.58	(mf*)
"	95.537	94.928	95.713		77.06	(mf)

The tabled values warrant discussion. It will first be noted that the values for a, b, d, and Log k obtained from the full expressions are invariably intermediate and approximate more closely to those derived with Li,Na,K, and Rb than with Na,K,Rb, and Cs. The unidentified values in the lower portion of the table are based on linear interpolation: = 100 $(a_{Na-Cs}-a_{all})/(a_{Na-Cs}-a_{Li-Rb})$ etc.

For ΔH, MP, N, and 1+100C these are 95.845 for a, 95.248 for b, and 95.970±.001 for d. For the same properties when mf is used they are 95.514 for a, 94.902, and 95.690 ±.001 for d.

In empirical analyses, such exact agreement sometimes indicates that the independent variable (in this instance the property value) no longer influences the numerical values, but if this were true all of these expressions would also exhibit a fixed value for interpolating in Log k. Using mf* these are 77.55, 77.56, 77.58, and 77.52 for ΔH, MP, IP, and 1+100C respectively; the mf-derived values are 76.97, NC, 77.06, and 76.97 . For N, the values approximate 97% of the usual a, b, and d values.

The IP expressions, however, do not agree with these for a, b, and d interpolation, yet agree well with respect to Log k. It may be that this is simply a result of the extremely small z values.

Not shown are these values for 100C; here the exponents are too large for accuracy of their differences, and values with a, b, and d are 97.7, 97.3, and 97.9 . On this basis, the term 1+100C appears to be preferable.

The tabled data do not provide unequivocal selection between mf and mf*, but past inquiries of this sort have generally shown that the form leading to the lower exponents for the dominating factors (here Z and W) is to be preferred.

Note is taken of the absolute value obtained for Log k, particularly when a multiplier is used (as with C), or where the property values are large but fairly constant (IP).

One can place some confidence in these expressions insofar as they indicate interdependence with Z and W and demonstrate its regularity. Since Z, W, n, and mf* are known or can be calculated for other species of the alkali metals (for which there are no available data regarding any of these properties) the exercise can best be concluded by forecasting those properties.

FORECAST VALUES FOR ΔH, MP, IP$_1$, N, AND 100C FOR Li ISOTOPES & Fr

Table 3b gives the necessary data and calculated values for the property values of ^{6}Li, ^{7}Li, an equimolar alloy of these isotopes, and Fr. For easy comparison, observed values for Li and Cs are included.

Table 3b

	^{6}Li	^{6}Li·^{7}Li	Li	Li*	^{7}Li	Fr	Cs
Z	3	3	3	3	3	87	55
W	6.01512	6.51556	6.9390	6.94173	7.0160	223.0198	132.905
n	1.0	1.0	1.0	1.0	1.0	6.0	5.0
mf*	1.0	2.15448	1.23713	1.23710	1.0	1.0	1.0
IP_1	134.54	128.63	124.26	124.23	123.52	90.06	89.74
ΔH	35.23	35.35	38.40	38.41	39.27	17.51	18.7
BP	1456	1437	1590		1636	906.1	963
MP	443.5	439.26	453.70	453.73	458.1	287.5+	301.9
Θ_{298}	440.8	445.72	448		448.2	29.8	43
N	5.0826	4.6401	4.6232	4.6222	4.6517	0.7928	0.84833
ρ	.50767	.50203	.5327	.5328	.5419	2.9362	1.8722
CCTE	149.6	143.44	141		140.79	324.28	300 (@ 293K)
10 k	21.527	14.562	8.47		7.5355	2.8547	3.590
100C	32.63	31.63	11.33		8.562	2.106	2.8027
B	12.77	12.86	11.88		11.64	0.457	2.23
E	13.36	13.73	13.42		13.31	1.862	2.180

Note: W for Li* based on ^{6}Li and ^{7}Li fractions of .0742 and .9258 .
Li data used in generating subgroup expressions

Because the expressions cannot be validated internally it is hoped that data exist for ^{6}Li and perhaps Fr for comparison with the above calculated extrapolations, which deserve some comment.

The forecast ionization potentials for both Li isotopes and Fr are somewhat surprising; the apparent influence of absolute mass on this atomic property can be most easily checked with Li alloys moderately high in ^{6}Li (note that mf has little effect). The much higher W/Z ratio for Fr than Cs is responsible for the increased IP.

Heats of atomization, boiling points, melting points, and Debye temperatures appear to be decreasingly affected by the mass factor and increasingly affected by mass itself. That the MP of pure ^{7}Li should be more than two percent higher than that of ^{6}Li is susceptible to observation at this temperature. The equimolar alloy value shows the mass factor influence; if there were none it would be 448.6 . That the forecast Debye temperature is higher than the forecast MP for this alloy seems improbable, and again it should be noted that in none of the texts are observed Li properties supported with observed atomic weights. The strong influence of Li values on all expressions thus makes all of them suspect at this time.

The forecast temperature thresholds for Fr will probably not be observed; it has been assumed here that the Fr is monoisotopic, but in view of its 22-minute half life it is probable that all Fr observed thus far is heavily contaminated with daughter isotopes, and the mf values and W values accordingly different. Based on an early estimate of the equilibrium content at 1.5 times the half life, one calculates a MP of about 300K and BP about 880K. Despite the rarity and strong radioactivity of this element, these measurements can be made.

The expression for N is the first to exhibit a strong dependence on the periodicity factor n; since the real density is directly calculable from N and W, values for this property are shown, and a difference of almost 7 percent forecast for the pure Li isotopes.

Coefficients of thermal expansion can now be measured accurately^{5b} enough to refine the derived expression. Again it should be noted that the alloy expands less than would be expected with no mass factor at room temperature, but since the Debye temperature is close to the MP in both cases the instantaneous CCTE values will probably deviate less at elevated temperatures. As expected, the CCTE forecast for Cs is the highest possible for a pure element.

The bulk and Young's elastic moduli expressions are strongly suspect because published data vary so widely; the strong influence of periodicity in both suggests a reason for the success of the atomic density in correlating among elastic properties. As might be expected the resistance to triaxial compression measured by B depends mostly on the total electron/atom ratio and the mass factor; note that the forecast value for B in the equimolar Li alloy is larger than that for either isotope, correlating with the suggestion in the MP and BP that a sort of eutectic may occur.

The thermal and electrical conductances are most interesting, and may in this series prove of some practical value as discussed below.

THERMOPHYSICAL PROPERTIES: LITHIUM AS A COOLANT

These expressions and the forecast values may, in addition to serving in refining the available property data base, be used to approach the optimization of liquid metal cooling of atomic reactors. It should be noted, however, that all but the temperature threshold data refer to the solid state.

The specific heat at constant pressure for the alkali metals is increasing almost linearly with temperature at 298K except for Li, for which the Debye temperature considerably exceeds the standard for measurement of N and the electrical and thermal conductances C and k.

From Table 3b it is apparent that both transport phenomena seem to be more strongly influenced by Z and W than any other properties and in much the same way; the expressions (and that for N) are:

Log P =	a (Log Z)	+ b (Log W)	+ d (Log n)	+z (Log mf*)	+ Log k
100C	12.82285	-9.942221	-5.59812	+1.121776	+3.156765
10 k	8.606140	-6.828733	-3.533367	+0.201641	+2.548087
N	1.79205	-0.575596	-3.244141	-0.058748	+0.299594

Because the specific heat is germane to coolant purposes, its expression was also derived; it is:

$c_p \cdot W$ 1.397949 +0.177695 -2.69068 +0.049925 -0.05863 ,

and it is noted that this is the only subgroup expression thus far for which the exponents a and b have the same sign. From it and the W values, the calculated specific heats for ^{6}Li, ^{6}Li·^{7}Li, and ^{7}Li are found to be .9274, .9030, and .8178 watt/ cm K respectively, and if similar values persist into the liquid state the higher specific heat of the lighter isotope is desirable. That it will persist is indicated by the higher ratio for c_p (1.134) than for N (1.093) for the two isotopes, and of greater interest is the observation that most of this gain is obtained in the equimolar alloy.

The mechanism of electron transport as a major part of the conduction of heat in the crystal is obvious from the above expressions. Duly noting that the 100C expression is suspect because only the Rb and K values are those recommended by TEPIAC, it is interesting to note that when the C and k expressions are combined by eliminating the n term one obtains:

$1.58436\ L\ 10k - L\ 100C = .81076\ L\ Z - .87694\ L\ W - .8023\ L\ mf^* + .88032$;

the near-constancy of all exponents suggests an almost linear relation.

One can in the same way combine the 10 k and N relations:

$L\ 10k - 1.08915\ L\ N = 6.6546\ L\ Z - 6.21182\ L\ W + .26563\ L\ mf^* + 2.221783$,

and if desired these combined expressions can be joined, losing mf*:

$1.52455\ L\ 10k = .33108\ L\ 100C + 1.08915\ L\ N + 6.9230\ L\ Z - 6.50216\ L\ W + 2.51324$, and the approximate exponents 3/2, 1/3, and unity will be familiar to heat transfer theorists.

Granting that the electronic conduction will diminish with increasing temperature, the advantage of the lighter isotope and alloys containing an appreciable proportion of it should continue through all of the solid and into the molten state. Soret separation will not be damaging, since the heavier isotope will tend to concentrate at the hotter surface; the alloy will become slightly less conductive but its vapor pressure will be slightly lowered.

CRITIQUE AND SUMMARY

As stated in the first Appendix, it is highly improbable that such simple expressions as those shown here can be adequate for confident predictions, and the forecast values in Table 3b should, with one exception, be taken as indications of probable bounds. On the basis of experience it seems improbable that the differences between ^{6}Li and ^{7}Li can be so large, that the MP of Fr can be so low or the BP so high.

The exception is the first ionization potential, for which the value for z is so small as to question the existence of any mass factor influence. That target accuracy is almost attained with the expression based on the four heavy elements, and is easily met when the light ones are used suggests that this property of the isolated atom be considered as a parameter in future study; its inclusion may reduce the need to consider Z and W normalizing procedures.

Shown herein in some detail are the numerical values obtained in a typical Gauss elimination of several arithmetic equations relating the observed property values with the parameters Z and W and finally either expression for the mass factor for the I-A metals. They illustrate most of the mathematical-physical interactions discussed earlier, and provide for preliminary interpretation, for the cautious forecasting of values for the pure isotopes of Li and for Fr.

Where no alternatives exist, such forecast values must serve until measurements have been made. Here, however, the possibility of <u>external</u> testing,- the comparison of these expressions and of similar forecasts using other elements,- is worthy of consideration. Most closely associated with the alkali metals in a wide variety of properties but with twice the nominal valence, the II-A metals will be similarly treated in lesser detail.

APPENDIX III

EXAMPLES OF TYPICAL INQUIRY AND CALCULATIONS: THE II-A METALS

The II-A metals are in many respects what one might expect of the I-A elements with doubled bond strength, but a cursory look at the ratio of property values (P_{II-A}/ P_{I-A}) shows that the effect is variable both with the property and with atomic number (and weight):

	IP_1	ΔH	BP	Θ	k	C	N	IP/v_n	B	MP
Be/Li	1.73	2.03	2.04	2.30	2.36	2.42	2.688	3.38	10.1	3.43
Sr/Rb	1.36	2.00	1.72	2.51	0.57	0.90	1.617	2.64	2.53	3.34

from which there is ample reason to expect mathematical expressions to differ from those for the alkali metals. Some of the reasons for difference can be anticipated, and can serve to illustrate the methodology involved in using data from different properties for a material or data from a given property for several materials.

As with the I-A metals, the alkaline earth elements show a monotonic increase (or decrease) in N, IP_1, IP_2, Θ, and of course Z and W. But Mg is significantly lower in _H, BP, and MP than Be and Ca, and is slightly less conductive electrically and thermally as well. It is customary to describe this relative lowering in bond strength in the second short period to promotion of s-electrons to occupancy of d-orbitals[1c]. Here one notes that there is a serious minimum in the ratio W/Z at Ca, the value for Mg being nearly as low. In the I-A series one notes that the exponents a and b are not of similar magnitude; for the least doubtful property, IP_1, the relation is close to $Z/W^{\frac{1}{2}}$, and for the six elements Be....Ra this ratio is monotonic: 1.332, 2.434, 3.139, 4.060, 4.779, and 5.854 .

Unlike the I-A metals, the II-A elements are not isostructures; Be and Mg are cph, Ca is normally ccp but cph and mixed stacking have been observed. Sr is ccp at ordinary temperatures, cph above about 510K, and bcc above 810K. Ba, on the other hand, is bcc at all temperatures to melting, and this structure is also reported for Ra. There is some question, therefore, as to whether an expression for N in which no account is taken of differing coordination numbers can be accepted. In planning this study, therefore, two expressions will be derived, one for N as measured and the other in which the same N values are used for Be, Mg, Ca, and Sr, but the value N* for Ba is recalculated by increasing R_N using Goldschmidt's[2c] correction for a change in coordination number and by using the PE for the close-packed array ($N^*_{Ba} = 1.4393$, $N \approx 1.5391$).

While some of the properties of Ra have been measured (IP_1 and

IP_2, BP, and MP) but its real and X-ray densities are not accurately known. Most texts show 5? gm/cc, and with available radiochemical techniques this should be within ± 0.2 gm/cc of the real value. Fortunately, Ra is much longer-lived than Fr, and a realistic assessment can be made by assuming a one percent contamination with lead, so that W becomes 225.81 and mf* is 1.0634 . The expressions derived are found to be as shown in the table below, together with the calculated values for the periodicity factor n for Ra.

Table 1c

Selected Values for Subgroup Expressions of the II-A Metals

Expression: Log P = a Log Z + b Log W + d Log n + z Log mf* + Log k

	a	b	d	z	Log k	n_{Ra}
IP_1	0.984970	-.463911	-1.199965	+0.030238	+ 2.18214	5.857
IP_2	1.257888	-.615124	-1.398181	+0.015513	+ 2.452958	5.946
MP	-3.370598	+2.06981	+1.874404	-0.43837	+ 3.243405	5.856
IP_2-IP_1	1.520556	-.765012	-1.583982	+0.00958	+ 2.126425	6.016_4
N_h	-3.016809	+1.978020	+.174508	+0.478591	+ 1.015741	70+
N_1	"	"	"	"	"	45.2
N^*_1	-1.481976	+1.206643	-0.999883	+0.202409	+ 0.828214	1.476

The value for n, the periodicity factor, should be 6.0 if it is indeed expressible as the principal quantum number of the outermost filled shell, and that IP_1 and MP expressions yield a calculated value only two percent lower, and IP_2 and IP_2-IP_1 well within the target accuracy of ± one percent would seem to indicate that this value can be used by those elements for which the Rn configuration forms the shell of the ion; this certainly includes Fr, Ra, and perhaps most of the actinons, and may also include At and perhaps Po and Bi.

It is obvious from the above, however, that the atomic density cannot be treated in this way. As suggested in the main body of this report, the realities of both material physics and dimensional compatibility must be considered; the latter is violated when the expression attempts to relate reciprocal volume to the dimensionless Z, n, and mf* and mass alone; if the "constant" contains the missing parameter its dimension must be $m^{-1} \ell^{-3}$. Nevertheless, the expressions for N and N* are useful here for indicating the tremendous sensitivity inherent in the method. Note that since the N expressions overstate the value of n_{Ra} and the N* understates it, a lesser modification in the value of N for Ba and Ra would result in conformity

COMPARISON AMONG EXPRESSIONS FOR THE IONIZATION POTENTIAL

It has been stated that of the properties tested, all but one are expressions of the behavior of the solid: the exception is the ionization potential (note that this has been chosen rather than the work function, either thermionic or photoelectric, largely because the latter are highly sensitive to surface conditions and entrapped gases. Nevertheless, it may be notable that the ratio IP_1/wf increases from 2.23 in Li to 2.25 in Na, drops to 1.94 in K, thereafter rising to 2.05 in Cs, while in the II-A elements this ratio is lower in Mg and Sr than in the other three elements).

It is, of course, the lone s-electron which is removed in measuring the ion potential of the I-A elements. For the II-A elements it is the second s-electron removal which is designated IP_1 and both in IP_2; for comparison between I-A and II-A elements the values for IP_2-IP_1 in the latter designate more nearly the same initial and final conditions. One observes that in its expression, a, b, d are numerically greater than for IP_1 and IP_2, while z and Log k are reduced.

It has been reiterated that k is not truly a constant unless all parameters are considered. In the selection of suitable subgroups, the expectation that the value of some parameter is common to all forms the basis for selection; in elemental subgroups the common factor is the nominal valence v_n, which is unity for the I-A metals and hence zero in the logarithmic expression regardless of y, the exponent commonly associated with valence number and charge.

But in the II-A elements, v_n is 2.0, and if no other parameters are considered, $\text{Log } k_{(II-A)} - \text{Log } k_{(I-A)} = y \text{ Log } 2$. For the admittedly non-comparable IP_2 expression the value of y is thus -1.3843, while for IP_1 and (IP_2-IP_1), in each of which only one electron is removed, y is respectively -0.1459 or -0.09019 .

For the MP expressions, similar treatment yields $y = -2.0253$, for N and N* $y = -2.379$ or -1.756; such values are reasonable, but to assume that v_n is the <u>only</u> neglected parameter is untenable at this time. So large a change in the derived expression for so small a change in N for but one base element serves only to illustrate the sensitivity of the method; it cannot in itself show that a correction for coordination is unnecessary, but does show that the value of N responds strongly to it.

In sum, it appears that the ionization potential is a valuable parameter for characterizing the atom-electron relation in at least the first several elements of a subgroup or Period. That they can so precisely related to Z, W, and n for the transition and later elements was tested and foun wanting.

The III-B elements begin supposedly with Sc and Y; in them there is the presumption of s^2d hybrid bonding. This description also fits the majority of the lanthanons (and perhaps the actinons). If the periodicity factor n has been properly described, its value will be 5.0 in all trivalent lanthanons and 6.0 in Ac.

So large a subgroup is in itself attractive. Preliminary studies of it (see Interim Final Report No. 1, pp 11-17) resulted in the first unequivocal delineation of the mass factor as a necessary parameter. Table 2 of that report shows exponents and k values for the relation of N itself to Z, W, and mf as parameters. This was applied to all elemental subgroups having enough solid species. For the first four metal subgroups the ratio of the Z to the W contribution changes from -1.5 to -1.1, and one concludes that the assumption of bond energy equalization through resonance is insufficiently precise for this study.

Four species are needed to derive the expression. The III-B subgroup using Ac, La, Y, and Sc fits B quite well and Al not at all (but the high electronic conductivity of Al may be responsible; on the whole these elements are indifferent conductors. But C (as graphite) is observed to fit the subgroup based on Hf, Zr, and Ti while Si does not. Expressions were therefore derived for Au, Ag, Cu, and Na, and for Hg, Cd, Zn, and Mg, and for Tl, In, Ga, and Al, and for Pb, Sn, Ge, and Si. In that order the contribution of Z appears to decrease and the contribution of W to increase 300 times. It was concluded that the overwhelming influence of these parameters may have obscured the existence of the smaller ones and prevented a higher degree of accuracy in theory.

The study was also carried out for the oxides of the divalent metals and the halides of the univalent ones. In no instance was the contribution of Z and W equal, and it was regretfully decided that formulae such as W/Z or 2Z-W cannot serve in property expressions.

SUMMARY

Except for the III-B subgroup, populations in the transition metals and their simple compounds are not large enough to permit the derivation of expressions testing other candidate parameters. It was therefore decided to delve more deeply into compounds of the early elements. Of these, the alkali halides provide a satisfactory number of species (among which a number of properties and parameters are surprisingly non-monotonic) and can be grouped either according to the halogen or the metal.

APPENDIX IV

EXAMPLES OF TYPICAL INQUIRY AND CALCULATIONS: THE ALKALI HALIDES

The alkali halides are attractive as models for study as a group and a wide variety of optical, electrical, thermophysical, and mechanical properties have been measured and reported. All are here presumed to be exactly equimolecular and fully dense.

The term "fully dense" deserves comment; here it means only that there is negligible porosity or residual dislocations and strain, and in most instances researchers have taken care to obtain high-purity, annealed specimens. Nevertheless, traces of impurities[1d] such as hydroxyl substitution for halogen or hydrogen for metal are encountered.

The concept of atomic density when applied to a compound is that of treating it precisely as if it were an element; the "element" NaCl consists of "atoms" of mass $W = (\frac{1}{2}W_{Na}+\frac{1}{2}W_{Cl}) = 29.2214$, and of "radius" $R = \frac{1}{2}\,AD_c$, the distance separating adjacent atoms (or ions) of the two species.

STRUCTURAL CONSIDERATIONS AND PACKING EFFICIENCIES

The measured real density of pure NaCl is most frequently reported as 2.1650 gm/cc under standard conditions, and from the atomic density equation $(\rho\,Av)/W = N = PE / 4.1888\,R^3$ one finds $N_{NaCl} = 4.4617_4$ (x 10^{22}) "atoms" of $Na_{.5}Cl_{.5}$ per cm^3.

Like all but three of these salts, NaCl crystallizes in the rock-salt or halite structure, usually described as a face-centered cubic array of the larger "host" species; each octahedral void in the array contains the atom of the smaller species.

The structure can as well be described as two interpenetrating fcc lattices. In the real crystal, only the host spheres are in contact (along the face diagonals), but as we imagine all of the constituent atoms to be of a single size a simple cubic unit cell can be visualized.

From quite exact geometrical requirements, the closest packing of identical spheres displays, whether cubic or hexagonal, a common ratio of the cell volume / sphere volume; expressed in percent, this is 74.04825 for ideal closest packing, and the packing efficiency PE for the simple cubic structure is ideally given by dividing the above value by $\sqrt{2}$, or 52.3600%, and one would expect that when half the observed interatomic distance in the salt is introduced as R in the atomic density expression, the calculated value for PE would conform to this within experimental error. From X-ray diffraction data R_{NaCl} is 1.41005Å and PE is calculated as 52.396%. For very compliant substances a small correction ought to be made for the difference between atmospheric and the reduced pressure at which most X-ray examinations are performed (and which is seldom given), but NaCl is sufficiently rigid so as to make such a correction negligible, and it would, in any case, be toward an increased N and PE.

Table 1b shows pertinent current data both for the alkali metals and the alkali halides and hydrides. Scanning PE values for the 20 alkali halides one observes that five are so highly discrepant from the ideal as to require comment.

Three of these, CsCl, CsBr, and CsCl, crystallize in the CsCl structure, describable as two interpenetrating simple cubic lattices. If the atoms of both are identical in size, the bcc structure is obtained, and its ideal PE is related to the ideal PE for cph crystals by: $PE_{bcc} = 3\ PE_{cph} / 2\ (c/a)_{id}$, where c/a_{id} is the ratio of the c-lattice dimension to the a-lattice dimensions in the ideal case (it the ratio of the altitude of a regular tetrahedron to its edge) or 1.63297, and PE_{bcc} is found to be 68.0184% .

The alkali metals are all bcc; note that only Na exceeds the ideal packing efficiency, Li most closely approaches it, and Rb is lowest.

The three Cs halides exhibiting this structure are all slightly underpacked. If one presumes the causes of underpacking to be independent of coordination number, these can be converted for comparison with the remainder by multiplying the PE values by the ratio of ideal PE_{sc} to ideal PE_{bcc} (52.360/68.018 = 0.769 . For CsCl, CsBr, and CsI the comparison values are 51.88, 51.84, and 51.96 for a mean of 51.89%, the observed PE for CsF is clearly anomalous.

It is also clear that PE for LiI is also far lower than either the iodides as a whole or the remaining Li salts. The value of RbF is also somewhat low.

One thus observes CsF (and perhaps RbF) exhibiting serious underpacking comparable to that of LiI. On the other end of the spectrum, NaF and NaCl are slightly overpacked.

The first three anomalous salts are combinations of heaviest (and largest) metal atoms with the lightest (smallest) halogen and the combination of lightest (smallest) metal atom with the heaviest (largest) halogen; one therefore expects a relation with Z and W

Table 1d

Data Relevant to the Behavior of Alkali Halides

Metal	Li	Na	K	Rb	Cs	Units
ΔH	38.4	25.9	21.5	19.5	18.7	Kcal/gm-atom
BP	1590	1165	1047	961	963	K
MP	453.7	371.0	336.8	312.0	301.9	K
Θ	448	155	100	59	43	K
B	11.883	6.63	3.35	2.996	(2.06)	GPa
E	13.42	6.24	3.71	2.86	2.18	GPa
G	8.89	4.19	1.88	1.65	1.48	GPa
CCTE	141	207	246	273	300	10^{-6}/K
c_pW	5.787	6.609	5.395	7.359	7.384	cal/atom
100C	10.33	20.43	14.889	9.130	3.803	100/microhm-cm
IP/100	1.24256	1.18446	1.00027	.962693	.897453	Kcal/gm-atom
10 k	8.47	14.10	10.24	5.82	3.59	W/cm K
ρ	0.533	0.970	0.858	1.532	1.8756	gm/cc
Z	3	11	19	37	55	-
W	6.939	22.9898	39.102	85.47	132.905	a.w.u.
mf	1.31404	1.0	1.19631	1.59352	1.0	-
mf*	1.23713	1.0	1.16702	1.57532	1.0	-
N	4.6232	2.5409	1.3214	1.0794	0.84986	10^{22} atoms/cc
PE	67.948	68.239	65.699	63.43	66.71	v/o
Hydrides						
BS	56.91	48	43.8	40	42	Kcal/gm-atom
MP	953	1073d	d	573d	d	K
ρ	0.82	0.92	1.47	2.60	3.41	gm/cc
Z	2	6	10	19	28	-
W	3.97348	11.9989	20.05498	43.2390	66.9565	a.w.u.
mf	2.9853	3.6640	3.7990	3.9065	3.9398	-
mf*	4.38124	5.38004	5.61716	5.81774	5.88134	-
N	12.4277	4.6174	4.4141	3.6211	3.067	10^{22} atoms/cc
Fluorides						
BS	137.5	114	118.9	116.1	119.6	Kcal/gm-atom
BP	1949	1968	1778	1683	1524	K
MP	1121.3	1235	1119	1032	957	K
G	70.35	26.93	12.90	8.90		GPa
RI	1.3915	1.336	1.363	1.398	1.478	-
ρ	2.634	2.750	2.48	3.557	4.115	gm/cc
Z	6	10	14	23	32	-
W	12.9687	20.9941	29.0502	52.2342	75.9517	a.w.u.
mf	1.85977	0.38024	1.38406	2.54514	2.99945	-
mf*	3.21153	2.19961	2.8386	2.86632	4.39929	-
N	12.2311	7.8883	5.1410	4.1009	3.2627	10^{22} atoms/cc
PE	51.77	52.72	51.29	49.13	47.57	v/o
IP*/100	3.56781	3.62591	3.8101	3.84768	3.91292	Kcal/gm-atom

Note: IP* $=-IP_M + IP_X$, where IP_X 3.306 (estimated) for H, 4.8104 for F, 3.8322 for Cl, 3.5045 for Br, and 3.1160 for I. The quantity is in rough correspondence with electronegativity, but electron affinity is not included.

Table 1d, (cont.)

Chlorides	Li	Na	K	Rb	Cs	units
BS	111.9	97.5	101.3	100.7	106.2	Kcal/gm-atom
BP	1633	1686	1775s	1663	1563	K
MP	887	1074	1049	988	919	K
G	26.46	12.81	6.36	4.51		GPa
RI	1.662	1.5442	1.490	1.493	1.6418	-
ρ	2.068	2.1650	1.9840#	2.80	3.988	gm/cc
Z	10	14	18	27	36	-
W	21.1960	29.2214	37.2775	60.4615	84.1790	a.w.u.
mf	2.69051	.85302	.195774	1.6545	2.31535	-
mf*	4.02694	2.47741	2.10034	3.04295	3.6292	-
N	5.9755	4.46174	3.2051	2.7889	2.85298	10^{22}atoms/cc
PE	51.98	52.396	51.91	51.06	67.40	v/o
IP*/100	2.58964	2.64774	2.83193	2.86951	2.93475	Kcal/gm-atom
Bromides						
BS	100.2	86.7	90.9	90.4	96.5	Kcal/gm-atom
BP	1538	1663	1708	1613	1573	K
MP	820	1028	1003	955	909	K
G	20.05	10.17	5.16	3.43		GPa
RI	1.784	1.6412	1.559	1.553	1.6984	-
ρ	3.464	3.203	2.750	3.350	4.440	gm/cc
Z	19	23	27	36	45	-
W	43.4240	51.4494	59.5055	82.6895	106.407	a.w.u.
mf	3.36081	2.21263	1.37154	.13450	.99610	-
mf*	4.89776	3.5293	2.8277	2.0684	2.60705	-
N	4.8039	3.7491	2.7831	2.4397	2.5128	10^{22}atoms/cc
PE	52.14	52.0	52.04	51.414	67.35	v/o
IP*/100	2.26194	2.32004	2.50423	2.54181	2.60705	Kcal/gm-atom
Iodides						
BS	84.6	72.7	76.8	76.7	82.4	Kcal/gm-atom
BP	1453	1577	1603	1573	1553	K
MP	719	924	959	915	894	K
G	13.69	7.37	3.79	2.70		GPa
RI	1.955	1.7745	1.677	1.6474	1.7876	-
ρ	3.494	3.667	3.130	3.55	4.510	gm/cc
Z	28	32	36	45	54	-
W	66.9217	74.9471	83.0032	106.1872	129.9045	a.w.u.
mf	3.58525	2.77301	2.11564	.78042	.092384	-
mf*	5.2484	4.12207	3.43814	2.43238	2.04673	-
N	3.19416	2.9465	2.2709	2.0133	2.0907_5	10^{22}atoms/cc
PE	46.80	52.04	52.125	51.81	67.50	v/o
IP*/100	1.87340	1.93150	2.11569	2.15327	2.21851	Kcal/gm-atom

Note: *Significant non-monotonic values underlined.*
Density of KCl lower than all salts except LiH, NaH, KH.
Data herein supersede values shown earlier.

and perhaps mf. In itial trials tested the possibility that the relation: PE = a X + b W + k exists. Tested when Z and W are either for the metal or for the salt, agreement was poor in all cases.

Any attempt to relate properties to parameters must involve some speculation regarding possible causality. That most substances differ slightly and some differ greatly from ideal packing can no longer be ignored, and in view of the supposedly non-directioned electronic configurations of monovalent cations and anions alike, together with the extremely rapid increase in repulsion as atoms are brought more closely together, there is perhaps more than usual justification in considering the alkali halides as consisting of aggregates of incompressible spheres. While early hopes that ionic radii might be almost constant and additive are no longer held, semiquantitative evidence indicates that where radius ratios are used to agree with observed interatomic distances, both MP and G are in fair accord with radii which have been sized according to the calculated electronegativity of each salt[2d].

It was shown earlier that to a first approximation the IP, on which electronegativity depends, is given for the I-A metals by their Z and W values, mf having an almost negligible effect. No such statement can be made about the halogens, since all but I are not solid under standard conditions. But if the IP (with or without the electron affinity) for each halogen is also fixed by Z and W, it follows that the alkali salts of each halogen make a potentially useful subgroup.

This possibility was tested in the following way. The "equipoise" salts (those for which W_M is nearly equal to W_X, and for which mf is smallest) are NaF, KCl, RbBr, and CsI, and if mf exerts little influence, the expression $PE = k\,Z^a\,W^b$ should very nearly apply if the values of a, b, and k are derived using the average of Na, K, and Rb salts of the lighter halogens. Validation would be tested by testing this expression with the Na, K, and Rb iodide average. When this is done, one finds a - .411154, b = - .365686, and k = 59.859; the calculated PE value for the iodide group is 51.653%, well below the 51.992% observed. The systematic error can be slightly reduced when the Li salts are also used in determining the average; the calculated PE becomes 51.13% for KI (51.125 obs.).

There is thus a closely approximate relation between these PE values and Z and W values, and it should therefore be possible to derive a similarly valid expression from average values of PE, Z, and W for all or some of the halides of each metal. The attempt to do so provides a good illustration of the difficulties related to non-monotonic series.

PROBLEMS IN BASE SPECIES SELECTION: THE POLYTONIC SERIES

The foregoing example shows the following:

Among the properties of the alkali halides, the observed PE may be related to Z and W in a rather simple way for a limited number of them. Since there are but four available halogens, only two exponents and the constant can be derived if the expression is to be tested by a virgin member of the subgroup.

Where the property values change monotonically among chosen members of a subgroup, the principal problem is that their number be sufficient to delineate the values of major parameter candidates. Clearly, the alkali halides can be broken down in a way which provides five subgroups rather than four, each being one or more salts of a given metal.

For LiX...CsX the undisturbed PE means (values for CsCl, CsBr, and CsI having been "corrected" to 51.883, 51.845, and 51.961% by a novel and hence suspect method), are: 50.672, 52.289, 51.841, 50.853, and 50.814% respectively. The parameters increase monotonically (if Z, W, N, or IP* are considered) not only for the means but for each MX series. The PE values, together with such properties as bond strength, BP, MP, and RI, clearly do not. With few exceptions, the underlined values are for NaX and/or KX, but it must surely be noted that, for example, the maxima in BP shift from NaX to KX in the chlorides and in MP only in the iodides, while the minimum in RI shifts to a heavier metal with each successive halogen.

For the PE NaX is maximum for fluorides and chlorides but in bromides and iodides is lower than KX. In the series of average PE values shown above the maximum for NaX is clear. The secondary maximum at RbX is, in view of the treatment of the CsCl-structure species, less certain. The anomalously low CsF and LiI values, if incorrect, contribute slightly to the magnitude of the NaX maximum and may be at the root of the apparent RbX submaximum.

Mathematics are incapable of perceiving numerical trends; it is quite clear that an expression derived from RbX, KX, and NaX can only extend the probability that PE increases in both directions from the minimum at KX; extrapolation to LiX yields the clearly false value of 52.83%, but the calculated value for CsX is 50.24, appreciably lower than that observed. Nevertheless, the derived expression is greatly different from that from the halogen subgroups, (a=.00402..,b=-.05585, k = 63.84%), suggesting an extreme distortion of the relative significances of Z and W usually observed.

In the same fashion expressions were derived using Li-Na-Rb and Li-K-Rb salts; the first yields a maximum rather than a minimum for KX, but the second, while predicting a moderately higher NaX (52.37%) than observed, suggests that the PE mean for the Cs salts might be still lower (50.22%).

In this last expression, a = .473742, b = -.466599, and k = 73.11%. This is the closest equivalence to the simple ratio W/Z thus far noted, and the speculation that when the PE expression is finally evolved the value of the constant will be comparable to the ideal condition of closest packing as both Z and W approach unity is commensurate with the "metallic" hydrogen concept.

In summary, it appears that of the parameters considered, Z and W are most strongly related to the ideality of observed packing in these salts, at least, but that at least one other parameter must be included in the ultimate expression. In view of the sensitivity of PE values and of the fact that there are virtually no records in which AD_c and real density have been measured on the same specimen under the same conditions of temperature and pressure, the study need not be carried farther until such measurements have been made.

SELECTION OF BASE SPECIES AND CANDIDATE PARAMETERS

The observed packing efficiency is, since no stimulus is involved in measuring it, more nearly a parameter than a property. It will be observed from direct observation of the underlined data in the Table that the minimum in refractive index invariably occurs in the metal-halide combination exhibiting the smallest mf (and mf*); it will further be observed that for a given metal, the change in RI values is monotonic with the Z (or W) of the halogen.

Only among the fluorides does the Cs salt exhibit the halite structure. According to its PE value, CsF is seriously underpacked, and if it were not its atomic density would be greater.

It is quite clear from the data that RI is not dominated by density (which is least in K salts and chlorides). One initiates the exploration on the basis of the subgroup expression in linear form:

$$RI = x\ N + z\ mf\ (\text{or } z\ mf^*) + k$$

, using for maximum sensitivity LiF, NaF, and KF as base species. Using RI as given, the values of x and z are so small as to introduce inaccuracies, so 100 RI and, so that its value will be zero in a vacuum, 100(RI-1). The latter is preferable, but no expression is acceptable; using mf x = .187138, z = 3.201894, k = 30.906311, and the calculated RI values for RbF and CsF are 1.3982 and 1.4359 . The observed values are 1.398 and 1.478, and were RbF the criterion for acceptance, one might mistakenly accept the relation as valid.

Using mf*, calculated values for RbF and CsF are 1.380 and 1.436; both are unacceptable.

When IP is substituted for N, concordance is poor with mf (1.4026 and 1.4157) but slightly improved with mf* (1.3814 and 1.4418). It appears, however, that the relation is probably non-linear.

The large increase in RI in going from RbF to CsF simply does not accord with any combination of listed parameters and either mf or mf*; concordance is slightly improved for the logarithmic expressions when mf* is used.

Time and funding limitations prevent further study at this time. The possibility that some variety of formula for the mass factor will be found which does not become less sensitive with increasing mass ought to be examined, but it seems unlikely that this is a mass effect, and more probable that, in the most ionic of salts, the crowding of electrons in the Cs ion increases its effective radius (and hence lowers the packing efficiency as observed). A more conventional explanation is that in CsF the radius ratio has become equal to or smaller than the .414 for octahedral filling of voids so that the repulsion between Cs ions becomes dominant.

If either explanation can be accepted, a similar situation must exist in RbF but to a lesser degree, and this is observed in that RbF is also significantly underpacked.

More important, a similar situation should exist at the other end of the alkali halide spectrum; with the LiI also exhibiting both a spectacularly high refractive index and an anomalously low packing efficiency, there is here the challenging possibility that the elusive radius ratio effect can be directly approached. Since LiF is the least ionic of these salts, the probability of electron crowding in the I anions is more remote.

Unfortunately, additional property data needed to separate the mass factor effect from the radius ratio effect have not yet been acquired. It is hoped that they will be, and that the parameter or parameters which relate to this anomaly can be identified when computer studies can begin. In view of the similarity of these compounds with a number of important interstitial compounds in metal alloys, such a study is of great practical importance.

SUMMARY AND RECOMMENDATIONS

In view of current and future requirements for optical materials (laser matrices, reflectors, doublers, IR windows, coatings for passive thermal control) these findings appear to represent an unrecognized potential both for improved understanding of optical behavior and for improving upon it.

For the IR window one wants minimal absorption and refraction in the critical spectral region; this combination is largely achieved in KCl not only because of its minimal density but because, apparently, of its near-ideal packing, which seems to reflect minimal populations of electrons at energy levels critical to photon interaction. If a minimum mf is a criterion for this, the judicious admixture of a small proportion of KBr in solid solution may further improve the transparency.

Where higher refraction is desired the high mf values and poorer packing idealities can almost certainly be achieved; it seems probable that the influence of Pb, Ba and the like in glasses is one way of doing it, while compounds such as the dihydrogen phosphates perform the same purpose at the other end of the mass-ratio spectrum.

Gilman[3d] reported a strong and reasonably consistent relation between the observed shear modulus and the observed interatomic distance both in elements, the alkali halides, and a few other compounds of known crystal types. For bcc elements and the halide and simple oxides having the halite structure the moduli were proportional to the inverse 4th power of the "diameter" of the atom, or, if PE is constant one obtains from eq (1): $G = k(N)^{\frac{4}{3}}$. PE is not, however, the same for these quite different structures, being ideally 68.018 for bcc and 52.36% for s.c. For a fixed interatomic distance, then, N would be .7698 as large in the s.c array. But in this array each atom has 6 neighbors as compared to 8 in bcc, and in terms of a mean atom-to-atom strength there is a small net gain (2.6%) in the s.c configuration. This may to some extent explain why the halite structure appears even when radius ratios argue against its spatial stability.

For elements the radius ratio problem does not exist. If a given interatomic distance represents a fixed unit of modulus then N for an fcc lattice will be 74.058/68.018=1.0887 times as many atoms as in the equivalent bcc lattice. These bonds are, however, shared with 12 neighbors rather than with 8 so that 3/2 as many would be required for the same stress field; rather than an $(N)^{4/3}$ relation with G one expects about $(N)^{1.38}$. The value of N, then, becomes more or less self-adjusting with respect to packing efficiency and coordination number. This is simply a restatement of the adoption by any material of the structural arrangement which will minimize its internal energy. It appears that for this reason one can directly compare the property relations for compounds with those for elements.

Alternative expressions have been derived using both mf and mf* values. For the refractive indices there appears to be a preference for mf*, but for the remaining properties thus far tested no preference has been noted. It is recommended that when a study can be made of a sufficiently large population the mass factors be replaced by a mass difference and a mass ratio. This can most easily be done if in all members of the test population there is an equal number of two species of differing mass. The alkali halides and hydrides best fit this description.

APPENDIX V

EXAMPLES OF TYPICAL INQUIRY AND CALCULATIONS: SIMPLE AND MIXED OXIDES

Because the halogens are monovalent, there is little internal bonding between halogen atoms in halides. With divalent oxygen, however, the "sharing" of oxygen atoms between adjacent cells is very common, and it is more difficult to regard a number of them as bonding solely through interaction between metal and oxygen.

Nowhere is the difference between halides and oxides more apparent than in their observed elastic properties[1e]. The sharing of adjacent oxygen ions (or the edge of an M-O unit) frequently leads to a distortion of the cell and to the formation of highly anisotropic crystals.

It was decided to begin the study by utilizing a subgroup of well-characterized oxides having (in common with oxygen) the neon substructure in the ion: thus oxides of Na, Mg, Al, and perhaps Si were included. The Na oxides (Na_2O, NaO) have seldom been adequately characterized and are usually of doubtful purity; MP values for the former range from 1020 to 1590K, and the latter decomposes at about 730K. In the initial study, NaF was used as a prototype of the oxide of a monovalent element.

Table 1e shows the data pertinent to the brief study. Except for the base species, oxides for validating purposes were selected at random. The properties chosen for test were MP, G, and RI, the subgroup expression being in this case a shortened form of the general expression: $\text{Log } P \doteq x \text{ Log } N + y \text{ Log } I + z \text{ Log } f + \text{Log } k$

Many of the now routinely observed precautions in calculation were developed during this study; the exponents and "constant" are very large:

$$\text{Log MP} = -39.61767 \text{ Log N} + 42.25994 \text{ Log I} - 55.70962 \text{ Log f} + 70.51541$$
$$\text{Log G} = -57.89831 \text{ Log N} + 61.80848 \text{ Log I} - 80.85435 \text{ Log f} + 99.78921$$
$$\text{Log RI}^* = -15.32438 \text{ Log N} + 16.62685 \text{ Log I} - 21.77802 \text{ Log f} + 25.64271 .$$

It must be noted that f, an early variant of the mass factor, possesses the dimension of mass (unlike the later f* and current mf and mf* which are dimensionless); the very small differences in mass of the base species is responsible for large derived values.

Given these expressions, for any oxide for which P and N are known and f can be calculated, a value for I can be obtained, and if that value is the same for two or more of the properties. It was of course hoped that the value might bear some visible relation to the valence of the metal as given by the stoichiometry and modified by the sharing of oxygen atoms.

Table 1e

Data and Calculated Intensities for Oxides of Second Short Period

	MP	G	RI	N	f	W	v_{MP}	v_G	v_{RI}
Base species									
NaF	1235	26.93	1.336	8.004#	2.1858	20.994	1.0	1.0	1.0
MgO	2852	156.0	1.736	10.697	5.0135	20.155	2.0	2.0	2.0
Spinel	2378	157.6	1.723	10.667	7.7880	20.324	8/3	8/3	8/3
Al_2O_3	2318	161.4	1.763	11.730	8.7184	20.392	3.0	3.0	3.0
Test species									
Na_2O	1548?			6.617	2.5930	20.659	1.054		
NaO	735			8.665	4.1218	19.495	1.228		
SiO	1975?			5.819	7.6993	22.043	1.972		
SiO_2a	1480t		1.416	5.893	11.2995	20.0283	1.644		
" b			1.422	5.713	"	"			1.661
" c	1244	31.17	1.4588	6.585	"	"	1.825	1.798	1.849
" d			1.470	6.795	"	"			1.876
" e	1996		1.4855	6.976	"	"	1.938		1.936
" f			1.520	7.517	"	"			2.070
" g			1.547	7.962	"	"			2.184
" h			1.600	9.050	"	"			2.467
" i			1.812	13.079	"	"			3.500
BeO	2803		1.724	14.496	4.4698	12.5050	2.236		2.227
Chrysoberyl, $BeAl_2O_4$									
	2143		1.7507	12.483	6.6045	18.13897	2.476		2.483
Beryl, $Be_3Al_2Si_6O_{18}$									
	1683	68.6	1.5690	8.7427	8.1841	18.5346	1.886	1.875	1.869
Lithium metaaluminate, $Li_2Al_2O_4$									
	2175		1.609	9.318	8.4656	16.4798	2.612		2.606
Clinoenstatite, $MgSiO_3$									
	1830d		1.655	9.573	8.7941	20.0792	2.495d		2.503
Mullite, $Al_6Si_2O_{13}$									
	2193		1.6463	9.868	9.6886	20.2882	2.5741		2.5694
Cordierite, $Mg_2Al_4Si_5O_{18}$									
	1745		1.5243	7.5534	9.5983	20.1713	1.517	1.521	1.521

Note: # Note N value now taken as 7.8883; if used, all calculated values of v would be increased about 1½ percent.
In expressions, RI* = (RI-1)/RI

Silicas: (a) silica-W, MP is transition to (e); (b) bleached melanophlogite, (c) in vitreous silicas, MP is observed transition to cristobalite; (d), a-tridymite, (e), a-cristobalite MP is disappearance of long-range ordering; (f), keatite, (g), a-quartz, (h), coesite, (i), stishovite.

Some of the tabled values deserve comment. The values of v are for the base elements, the nominal valence of the <u>metal</u>; since spinel is $MgAl_2O_4$ $v = (2+6)/3$. Supposing oxygen always is divalent, I in the expressions is given by: $I = v\ (n_O/n_M)$, or for the base species, 0.5, 2.0, 3.5555.., and 4.50 .

Were a calculated value for v to agree exactly with the nominal it would be surprising. Crysoberyl is the beryllium analog of spinel, and its nominal valence is thus 2.5, but since the expected valence in BeO is 2.0 and is calculated near 2.48, one suspects that oxides of the lighter metals in ternary systems cannot be so simply judged. This is confirmed in $Li_2Al_2O_4$, for which nominal v is also 2.0.

In selecting the test oxides, priority was given to those deviating considerably from the base species with respect to W. Most, however, are of comparable atomic mass, and it may be that this contributed to commonality of the subgroup.

The silicas are, with the exception of vitreous silica and a-cristobalite, mostly indicative of the frequently cited linear change in RI with density. Note, however, that while the RI expression is certainly not linear, the calculated value of v for stishovite is reasonably in accord with a valence approaching 4 for Si; the observed RI for this compound (which approaches diamond in bulk modulus) is less than half the value "predicted" by a linear relation.

In some instances, at least, it appears that the temperature of thermally-induced transition or decomposition can be taken as the melting point.

Fortunately, it has become common for ceramic researchers to measure and report real density (frequently as a percentage of the theoretical density), melting point, and refractive index. The use of the shear modulus here is entirely fortuitous and resulted largely from the disappointing large number of discrepant bulk moduli found.

No rigorous conclusions can be drawn from so small a sample, but it encourages the possibility that expressions of this kind will be more tractable if the base species can be taken from a population in which a larger number of binary oxides exist, and one among which such obvious complexities as deviations from stoichiometry and full density will be encountered.

BINARY OXIDES OF THE ELEMENTS OF THE FIRST LONG PERIOD

There are at least 40 binary oxides in this group. While the majority of them appear to deviate little from stoichiometry, some (nominal FeO, ZnO, the oxides of Ti, V) certainly do so. The range of melting points lies between Mn_2O_7, a liquid under the standard conditions, to CaO as the most refractory monoxide known, and RI values (unfortunately not known in a number of them) from 1.8+ to 3+.

As with oxides of the short periods there are here problems in selecting the base species. As shown in Table 2e, there are four potassium oxides, an unknown number of titanium oxides as well as three varieties of TiO_2, etc. For reasons similar to those used in choosing base species among the elements, the preliminary study reported here utilized CaO, rutile TiO_2, V_2O_5, and NiO. A brief resumé of the potassium oxides will suffice to illustrate some of the considerations used.

In most cases (note that FeO is an exception), the lowest oxide is more refractory than the metal. Among the I-A oxides, the M_2O variety all crystalize in the antifluorite structure, and (unlike the monohalides) Li_2O is the most refractory of them, its MP being 1421K higher than that of the metal. Supposing the size of the oxygen ion to be nearly constant[2e], stability diminishes with increasing cation radius and increasing ionicity, the difference in MP between metal and this oxide is 1277K for Na and a less stable monoxide with the more tolerant halite structure is observed. As expected from earlier discussion of the larger increase in size going from Na to K, K_2O is only 286K more refractory than K, and the most refractory oxide is KO (316K higher). The situation persists with Rb and Cs, the ions of which are so large as to make the antifluorite structure unstable, and RbO is 395K above, and CsO 371K above, the MP of the metal.

The existence of K_2O_3 seems well established but its real density has not been reported and its exact stoichiometry not known; it has been suggested on the basis of its intermediate MP that it may be a variety of solid solution of K_2O and KO.

As is commonly observed, oxidation beyond some optimum state reduces refractoriness, and KO_2 is no exception. If the "effective valence" of the metal is argued from the divalence of oxygen and the formula for the oxygen, K in KO is divalent. At such moderate temperatures as its MP it is improbable that electrons have been promoted from the Ar subshell, and the second electron must be assigned to sharing of oxygen atoms between adjacent cells.

One sees that when the donor atom is limited to fewer available electrons than demanded by the acceptor, the simple concepts of ionic transfer must be greatly modified or abandoned, and it is now commonly agreed that virtually all bonding in true compounds lies somewhere on a spectrum between electron transfer (ionic) and sharing (covalent). Moreover, the point on that spectrum is not necessarily fixed, being influenced by temperature and certain impurities.

Among the oxides, the most prevalent and persistent impurity is water, which may take the form of substituting hydroxyl for oxygen ions and even hydrogen for metal ions. As might be expected, this tendency is enhanced in oxides where the cation is too large for spatial stability, and it has been suggested that true oxide stoichiometry has yet to be achieved in any alkali metal oxide other than Li_2O.

These, and the lack of RI values, deny acceptance of any potassium oxide as base species.

Divalent Ca is very close to the optimum radius for occupation of octahedral voids in a closest packing of oxygen atoms. That metal-metal repulsion is important in defining stability is clear from the following: in BeO (in which Be is smaller than optimum), PE = 49.46% and MP = 2805+K, while in MgO PE = 52.316% and MP = 2852K; for these the comparison is analagous in both respects to the early halides of Li and Na. But in CaO, PE is almost ideal (51.96%) and MP = 2887K. In SrO, PE and MP begin to decrease (49.12% and 2703K). Thus CaO makes a very satisfactory base species.

Sc_2O_3 is less satisfactory. Rarity of the element caused a lack of commercial interest; among the few attempts to purify and densify it densities deviate only slightly from 3.864 gm/cc . As with all very refractory substances there are doubts about its MP, and RI appears never to have been measured for publication. Its position among the oxides for both treatment by period and by subgroup make it perhaps the most critical of compounds deserving refree-quality study.

The choice of rutile TiO_2 as a base species is open to criticism, not only because measured densities vary between 4.18 to 4.26 for oxygen-annealed crystals but because its color, sensitivity to u.v. damage, and electronic (dielectric) behavior suggests the presence of some small proportion of trivalent Ti. Nevertheless, it is densest of the polymorphs of TiO_2 and, despite occasional references to other phases prior to melting, appears to melt without decomposition in an oxygen atmosphere at close to 2112K.

Optically rutile is highly anisotropic, with refractive indices of 2.616(a) and 2.903(c), a fact reflected in its elastic constants (c_{11}=266, c_{33}=470, c_{44}=125, c_{66}=189, c_{12}=176, c_{13}=149 GPa).

The crystal structure of rutile is less easily understood in terms of the atomic density concept than are the isotropic crystals of equimolar compounds. In the real crystal, the Ti atoms form a structure quite analagous to bcc, except that the cube is considerably foreshortened in the c-direction (c/a = 0.6441). The oxygen atoms occupy positions about the central Ti atom which roughly conform to an octahedron similarly distorted; of the six Ti-O bonds, two are 1.988 and four 1.944 Å. The O-O distances are similarly nonequivalent: 8 at 2.780, 2 at 5.20, and 2 at 2.959 Å in the unit cell, which contains two molecules of TiO_2 in a volume of 62.4200 $Å^3$. In the atomic density notation the $Ti_{.333..}O_{.666..}$ "atom" is a sphere in a body-centered array which is not cubic, its packing efficiency in the ideal case being 68.0184 x .6441 = 43.8104%. From the Ti-O and O-O interatomic distances shown one obtains an average for the 18 bonds of 2.4972 Å and this is the diameter of the "atom"; its volume is thus 8.15399 $Å^3$ and it occupies 1/6 of the original unit cell, 20.807 $Å^3$, and PE = 39.19%. Note that these "atoms" are still in contact along the body diagonals as in the bcc structure, but these diagonals no longer are orthotropically directed.

Note that this simplified structure is quite sumilar to that of body-centered tetragonal tin, in which the c-axis foreshortening is even more pronounced (c/a = 0.5455). It may be of interest to note that the least dense, low-temperature anatase form of TiO_2 is also body-centered tetragonal but the c-axis is greatly lengthened; as might be expected anatase is optically negative while rutile is positive. The third form of TiO_2, brookite, is rhombohedral, and its RI value simply the mean of the three axial values.

The concept of treating the relatively complicated structures of compounds as if they were elemental is not new; the similarity of the halite structure to ccp, of the wurtzite structure to diamond, and of the CsCl structure to bcc has frequently been used in describing similarities such as in elastic behavior. It is suggested here that it can be carried considerably farther, and comparing some of the properties of rutile with those of tin will, if proper attention be paid to the other parameters which prevail, contribute to improved understanding of materials behavior; the writer has found, in studies involving the elastic behavior of certain micas, the similarity of the graphite crystal to be helpful.

For a third base species, the compound V_2O_5 was chosen; in it the valence of the metal is certainly 5, and its RI has been well established. The MP shown is most commonly used, some texts show a value about 20K lower.

Because V_2O_3 has been well documented with respect to MP and most parameters to be tested, the General expression of the form:
Log MP = x Log N + y Log I + z Log f + Log k was based upon this oxide, together with CaO, TiO_2(r), and V_2O_5; the calculated values for I and v_M obtained for other oxides in the Period were simply compared to the nominal values. That the calculated effective valences of the potassium oxides approximated 2+ confirmed the expectation that O-O linkages play a large part in cohesive bonding of the oxides of electron-poor elements.

Calculated v_M values approximated 6 for the Fe oxides, 7 for CoO, and 8 for NiO. Since the last of these is clearly the most stable (if not the only) oxide formed by Ni, it was chosen as having v_M = I = 8.0 to replace V_2O_3 as base species (note that in V_2O_3 if v_M = 5.0, I = 7.50) simply because bunsenite has been characterized with respect to a fairly large number of properties, exhibits slight underpacking (PE=51.29%) together with a small increase in Young's modulus with increasing temperature, and has been subjected to frequent analyses which show deviations from stoichiometry to be small in oxidizing atmospheres. Nevertheless, its slight electronic conduction and concomitant thermal conduction at moderately elevated temperatures suggest free electron population large enough to render its refractive index suspect, and it must be emphasized here that the derived expressions below and the calculated v_M values in Table 2e are preliminary only.

Again the now outmoded mass factor f was used; it possesses the dimension of mass, and is based on the <u>difference</u> in atomic mass between metal and oxide. The expressions are:

Log MP = 2.098934 Log N - 2.809990 Log I + 3.701982 Log f - 2.05914
Log RI*= 1.775415 Log N - 4.450636 Log I + 7.451324 Log f - 9.72514

Alternative expressions based on f* (dimensionless and calculated from the <u>ratio</u> of atomic masses) and f*·W were derived; in them the magnitude of one or more exponents was so large as to exceed accurate calculation requirements, and it was decided that attempts must be made to derive comparable factor formulae in dimensionless forms.

Again it is less the agreement of calculated v_M values with accepted nominal valences than with agreement between v_M(MP) and v_M(RI) which is needed for validation.

That v_M(MP) for Sc_2O_3 is so close to 3.0 appears to support the TEPIAC-suggested MP shown and increases the importance of obtaining

Table 2e

Data and Calculated v_M Values: Oxides of the First Long Pericd Elements

	MP	RI	N	f	W	v_M(MP)	v_M(RI)	
(KF)	1119	1.363	5.141	13.130	29.050	1.5066	1.2274	
K_2O	623d		4.494	9.5895	31.401	2.255d		
KO#	763		4.411 ?	16.394	27.551	2.104		(# most refractory
K_2O_3	703			21.474	25.2404			oxide of the metal)
KO_2	653		5.438	25.411	23.700	2.3161		
CaO#	2887	1.838	7.1304	17.210	28.040	(2.0)	(2.0)	(base species)
CaO_2	548d	1.895	7.319	26.7804	24.0263	3.298d	2.1007	
Sc_2O_3	2680	(2.38)	8.4366	28.318	27.582	2.9992		(assumed 3 for RI_{calc},)
TiO	2023d		9.3039	23.913	31.950	4.2708d		(assumed stoichiometric)
Ti_2O_3#	2350d		9.241	30.585	28.7596	3.714 d		
Ti_3O_5			8.1317		27.962			
TiO_{2a}	2100	2.513	8.683	38.2494	26.6329	3.8680	3.8678	(see text)
TiO_{2b}	2112	2.637	9.497	37.6325	26.825	3.9655	3.9668	" "
TiO_{2r}	2112	2.807	9.610	38.2494	26.6329	(4.0)	(4.0)	(base species)
VO#	2322		10.360?	26.592	33.470	5.0679		
V_2O_3	2273		9.7835	35.628	29.9764	4.796		
VO_2	2240		9.4511	38.249	27.648	3.869		
V_2O_5	963	1.580	7.7807	48.934	25.983	(5.0)	(5.0)	(base species)
CrO					34.00			
Cr_2O_3#	2708	2.551	10.3216	36.943	30.398	4.9191	5.202	
CrO_2	570d							
CrO_3	469		6.5042	56.153	24.999	5.644		
MnO#	2057	2.16	9.27	30.156	35.469	5.746	5.472	
Mn_3O_4	1978?		8.9465	37.397	32.6872	6.288		
MnO_2	808d		10.444	49.211	28.980	8.336		(see text)
Mn_2O_7	279	liq.	5.853?	67.490	24.653	6.87		" "
$Fe_{.85}O$	1693	2.32	9.685	32.148	35.4437	6.644	5.852	
(FeO)	"		"	30.972	35.925	5.916		
Fe_3O_4	1811d	2.42	9.4312	39.121	33.0765	6.272d	6.0583	
Fe_2O_3#	1827	3.127_{Li}	9.8805	41.806	31.938	6.445	6.152	(see text)
CoO#	2208		10.368	33.7676	37.465	7.072		
Co_3O_4	1175d		10.6265	42.0306	34.3995	9.020d		(see text)
Co_2O_3	1168d		9.404	45.764	33.173	8.206		
NiO#	2263	2.1818	10.753	33.5636	37.355	(8.0)	(8.0)	(base species)
Cu_2O	1508	2.705	7.5762	21.112	47.693	6.906	5.365	
CuO#	1599	2.63	9.827 ?	37.9775	39.770	8.805	7.934	
Ga_2O	933		5.5441	24.0956	51.813	7.719		
Ga_2O_3#	2061	1.930	10.345	59.9456	37.488	10.275	12.33	
ZnO#	2248	2.015	8.2980	39.6627	40.685	7.355	8.402	
GeO	980s	1.607		46.370	44.295			
GeO_2#	1388	1.650	7.4313	79.929	34.263	10.121	13.733	(sol. "low" form)
"	1360+		10.966	"	"	13.633		
As_2O_3#	588p	1.755	5.6892	66.942	39.568	11.88p	11.81	
As_2O_5	588d		7.9235	96.037	32.834	14.68d		
SeO_2#	618s	1.76+	6.4315	89.606	36.987	14.1 s	15.3+	
SeO_3	391		6.8305	117.47	31.740	16.5		

Note: ? doubtful value d decomposes s sublimes p MP under pressure

In both calcium oxides, the source of electrons for electron-photron interaction is presumably Ca; there are 3.5652 Ca atoms/cc ($x10^{22}$) in CaO and only 2.4397 Ca atoms/cc in CaO_2, and the latter must be considerably more covalent to account for the RI value. The high v_m(MP) value for the peroxide indicates that decomposition occurs through the loss of a weakly bonded oxygen atom. Note that similar behavior occurs with MnO_2 and the higher oxides of cobalt, all recognized as good oxidizing agents.

The calculated RI value for Sc_2O_3 is to be taken as an estimate only. Exact agreement in v_M values would occur only if melting destroys only the long range ordering of the crystal.

Stoichiometric TiO contains about 15 percent of Schottky defects; if the N value were increased to compensate for this "atomic porosity", v_M would be 4.82 . From this one concludes that TiO can be regarded as metallic titanium with oxygen atoms in octahedral voids. Thus Ti_2O_3 is the first compound of the series[3e] Ti_nO_{2n-1}. If one presumes exact stoichiometry for rutile (n=infinity) then: n=2 in Ti_2O_3 with the MP decreasing to some value representing a eutectic between n = 1 and n = 2 and again decreasing as n approaches zero (MP for Ti is 1955K). This accords with qualitative observations and with the electronic conductivity observed in the whole range $TiO_{.7}$ to $TiO_{1.2}$ (comparable to that of the metal but somewhat reduced on annealing, presumably due to ordering). On the basis of the agreement shown between v_M(MP) and v_M(RI), a first-order approximation for brookite suggests the selection of the N value shown from among the several densities published, and that it is non-stoichiometric, roughly corresponding to $Ti_{19}O_{39}$. It should be noted that a deviation from stoichiometry requires recalculation of W, mass factor, and the n_O/n_M ratio used to convert I to v_M.

VO is a good electronic conductor; the value of N is much higher than that calculated from X-ray, and its formula must therefore approximate V_3O_2. As judged by the MP, however, the calculated v_M value is surprisingly close to five. That this represents an optimum in thermal stability is suggested by diminishing MP values without decomposition in the higher oxides of this element.

It will be recalled that the calculated v_M value for metallic Mn is close to 5, at least one electron/atom being unused in bonding because of the great stability of the octet $3d^6 4s^2$. Apparently even the highly electronegative oxygen atom is unable to ionize it fully until Mn_2O_7 is formed. This is an explosive liquid under the standard conditions; the doubtful N value was calculated by extrapolating the value obtained at the MP for the solid to standard conditions, as was done for Hg in the solid elements.

For Fe, Co, and Ni the MP data suggest effective nominal valences of roughly 6, 7, and 8. Note that in wüstite, a metal-deficient, halite structured salt, the MP is lower than that of the metal (1810K) and no appreciable thermal stability develops through oxide formation until Fe_2O_3 is reached. The values for FeO are indicated for information only, stoichiometry is never achieved.

The remaining oxides show the familiar effects of "inert pair" formation (presumably of s^2 electrons) once the intermediate Ni core has been completed. Thus CuO and Ga_2O_3 and ZnO are more refractory than Cu_2O, Ga_2O, or a lower oxide of Zn. With the rapid increase in electronegativity as completion of the Kr core is approached, the lower oxides As_2O_3 and SeO_2 are the more refractory. That v_M values for the higher oxides of Ga, Ge, As, and Se are about 12, 14, 15, and 16 for at least one of the expressions may be fortuitous, the extrapolation has been very large.

SUMMARY AND RECOMMENDATIONS

When one considers the apparent complexity of the compounds as compared to the solid elements, the relations which have been observed suggest that some of the complications may have been self-imposed. The major problems actually encountered arise from some doubtful property values and from deviations from maximum density and nominal stoichiometry. There is reason for some confidence in the probability that, when these and similar oxide data have been subjected to regression analysis with these and with respect to properties such as specific heat, bulk modulus, and thermal and electrical conductances, they will serve in data screening to identify dubious values and point to the more important missing ones.

The selection of defect semiconductor NiO as a base species cannot be justified in retrospect. RI and other property values for the dielectric oxides Ti_2O_3, V_2O_3, and particularly Sc_2O_3 are needed.

The problem of interdependent variables in the derivation of the General expression is clearly apparent here; if one chooses the "normal" oxides CaO, Sc_2O_3, TiO_2, V_2O_5, CrO_3 as base species, the exponent y will so dominate the expression that v_m for all oxides will closely reflect the formula value, and details of behavior be lost.

APPENDIX VI

SOME PROPERTY AND PARAMETER RELATIONS FOR THE SOLID ELEMENTS

Central to the concept of atomic density is the possibility that those parameters which can be related to materials behavior can be used to characterize a wide variety of substances, and need not be different whether the elements or compounds are considered. This view is not particularly unconventional. The molecular weight of a compound differs in no important respect from the atomic weight of an element and is used similarly. Nevertheless, there is a conventional usage here which bars easy comparison of one with the other; the mol differs from the gram-atom, and while normal usage in thermodynamics reduces molecular weight according to one or more constituent atoms, the comparisons then drawn are limited to groupings which contain those atoms.

That a number of elemental solids can be semiquantitatively compared to compounds has long been known. To test the converse it appeared necessary to find a convenient yet accurate way of treating compounds as if they were elemental. In the previous sections it has been shown how one obtains from the chemical formulation an adequate description of the fictional "atom" of a compound. Once this has been done, the values of its parameters are as easily understood.

It must be re-emphasized that there is no pretense that such "atoms" exist in the real world of materials; the purpose of creating them is so that they may be used in the man-made world of measurement units and mathematics.

In the elements, however, they do exist, and the best opportunity to learn to coordinate mathematics with physical reality lies in learning more about this (fortunately) limited number of substances. In this wholly empirical study, one is necessarily limited to the elements which have been prepared and tested by countless researchers. To the purist, none of these are absolutely pure nor wholly dense in the solid state and no crystal perfect, but to the engineer these are real materials exemplifying what must be chosen and used.

THE PERIODIC TABLE AND DESCRIPTORS FOR THE SOLID ELEMENTS

While the Periodic Table is extremely important to early understanding of chemical behavior it may not always so serve for describing physical behavior. Its present form is somewhat different from that suggested by Mendeleev; one example of his highly perceptive work was his prediction that an element he called "eka-boron" would underlie that element in the Table, and like the crude boron then made, be rigid and a poor conductor of heat. It is impossible to accept Al as such a solid.

The early chemists quickly adopted the precepts of valence, and the current Table is simply a listing according to subgroups having identical nominal valence values. Unfortunately, there is little evidence for and much evidence against a belief that nominal valence is an overriding influence in elemental bonding; one cannot, for instance, explain the high electrical conductance of Cu, Ag, and Au on the basis of one-electron/atom, far less their large heats of atomization. Nevertheless, the knowledge that to some extent the common-valence convention in elemental subgroups is useful, and it can be employed here if limited to understanding that it represents, in nearly all instances, the <u>maximum</u> <u>number</u> of outermost electrons/atom under normal conditions in the neutral atom. There is no guarantee that all are involved in bonding, and given certain environments the number can be decreased by the formation of inert pairs or increased by energetic promotion.

For the purposes of this study it was simply decided that one could be too strongly influenced by knowledge of electronic configuration of the free and neutral atom, from which very large deviations can occur when the atomic environment becomes that of the crystal. The deviation must be least in the I-A metals, and Appendix II provides examples of the treatment of these elements as a subgroup.

Now if Al does not properly underlie B in a Periodic Table devoted to physical properties of the solid, perhaps Mg should not underlie Be, nor Na underlie Li! It soon became obvious that such treatment is, like the familiar devices of screening constants, polarizing distortions, assumptions of equivalence through resonance, etc. a method for reconciling fact to partially but not wholly correct theory.

Reverting to the I-A metals for illustration, many if not all of the properties of the solids show, if not anomalous, certainly non-monotonic relations at Na, which is more conductive, less refractory, etc. than would be expected by interpolation between Li and K. Note, however, that most of these can be as well considered anomalies in K, and that when this is done for the elements, similar treatment serves to show a like effect in the halide salts of these metals. To the extent that a single s-electron overlying an inert-gas electronic configuration characterizes all five elements (and Fr) they form a valid subgroup in the solid state.

Regarding the Periodic Table as a matrix, one immediately sees that the rows are as informative as the columns, and a contain a larger number of elemental species. Unfortunately, the commonality of parameters in a given Period can not be stated so simply. The first few elements of each Period, however, exhibit a number of points of similarity. Incrementally increasing values of Z are of course exact, but while these are accurate counts of the <u>total</u> number of electrons/atom (or protons) for the neutral atom they cannot all enter into any descriptor (except perhaps size) or property on an equivalent basis. W increases (usually), but not evenly. Early studies showed that no simple formula for Z <u>and</u> W together could be applied for any property, and that when used separately, the relative influence of each differed with each kind of property.

ELEMENTAL CRYSTAL STRUCTURES AND THE PERIODIC TABLE

Since crystal structures were first delineated it has been noted that most of the metallic subgroups exhibit some commonality among them. Taking as theme the view that elemental bonding is covalent in nature, Brewer[1f] conceives that an orbital can be simply regarded as a region of space capable of being occupied by electrons. Where orbitals of adjacent atoms overlap and are occupied by one electron from each atom, an electron-pair bond is formed between them. In the inert gas elements all four outer orbitals are already occupied by two electrons and a covalent bond cannot be formed. In the halogens one of the four orbitals is only half filled, and two of these can overlap to form an electron-pair bond. Once this bond has formed, however, there are no additional orbitals available, and in the three-dimensional solid these elements consist of weak bonds between diatomic molecules.

At the other end of the period in the I-A metals, none of the four outer orbitals contains a pair of electrons, all are therefore available for covalent bonding, and the remaining availability of unsaturated orbitals permits formation of similar bonds to other atoms. One need not presume that all such bonds are equivalated through resonance to agree that this simple picture roughly represents bonding in the solid elements. Taking ΔH, the heat of atomization, as an indicator of the strength of the electron-pair bond, Brewer points out that: (a) for elements in which atoms are of similar size, ΔH is about the same for the I-A metals and the halogens, about twice this for the II-A elements and the chalcogens, etc.,

(b) that, counting from the inert gas element, there is a roughly linear increase with nominal negative valence in every period, and (c) there is a similar increase with positive nominal valence in the first three metals of the short Periods, the first five metals of the first long Period, and the first six metals of the later long Periods. He then introduces the concept of s-p hybrid bonds and suggests a reasonable basis for comparing these to the added strengths conferred by d-electrons and orbitals in the transition elements.

While there is no doubt that the general tenor of observed crystal structure accords with the number and kind of electrons available for bonding, it is hoped that this study may permit a fuller view of such structures. Of the elemental subgroups, for example, not only I-A metals exhibit bcc packing from ordinary temperatures to melting, this being also observed in V, Nb, and Ta and in Mo and W. That Cr and Fe adopt this structure at low temperatures to transform to close packing at higher ones has yet to be explained.

No less than 28 of the solid elements adopt hexagonal symmetry, and the writer suggests that this popularity reflects the greater degree of freedom from internal strain this permits; the atoms in the hexagonal plane can be closer together or farther apart than those of the plane above or below. Indeed, the c/a ratio is the sole direct evidence of ideal packing (in which it is 1.330) and of large deviations from ideality (for Zn and Cd c/a values are 1.861 and 1.890, for Hg, Be, and Mg the observed values are 1.51, 1.585, and 1.625. Of the elements, only Co can be regarded as ideally packed at low and ordinary temperatures; it transforms to ccp at high temperatures.

Judged indirectly on the basis of agreement between X-ray and real density, a number of ccp elements are very nearly ideal; this group includes Al, Ni, Cu, Rh, Pd, Ag, Ir, Pt, and Au. This structure is also adopted at low and ordinary temperatures by Ca, Ce, Yb, and Th and at intermediate temperatures by Mn and Fe.

It has been suggested[2f] that the structure of each element is, at a given temperature, that array which leads to the smallest internal energy. The orbitals for s-electrons are spherically symmetrical and were there no other considerations one might expect close-packing for the I-A and II-A metals. The observation that the heavier species do transform to the close-packed structure under pressure and at low temperatures, together with the fact that Ba and Ra are also bcc, seems to confirm the probability that this structure, with fewer but shorter and hence stronger bonds, is thermally considerably more stable than close packing of any kind. In the metals which seem to exhibit a preference for ccp rather than hcp, it may be useful to note that the former is favored by 180° orbital angles.

Detailed discussion of crystal structure is beyond the scope of this report. The atomic density of the solid is, by reason of the formula for it, quite clearly related to the characteristic PE of the real structure. Since for many of the elements this may change with temperature and/or pressure, a major obstacle to the acceptance of N as a characterizing parameter was the improbability of relating it to properties at other than the standard conditions for measuring it. Fortunately, the solid elements have been frequent candidates for measurement of MP, Θ, and ΔH measurements, and these were used to demonstrate the following:

That a rather simple mathematical relation could be drawn between observed property values and such characterizing parameters as Z, W, and v_n from a few base species properly selected;

That when such a relation was extended to non-base species, the calculated values for v accorded best with species which were poor electronic conductors, and when a term treating C as a parameter was added a wider variety of properties could be thus interrelated;

That when the relation was based principally or wholly upon species which are natural monoisotopes or contain only small proportions of a second isotope, conformity was improved with those elements which are least polyisotopic, and that when a formula based on isotope proportion was used as an added term in the relation, conformity which often met target accuracy was achieved;

That a General expression based upon early elements in the first or second long Period for MP and Θ could be extrapolated to calculate the "monoisotopic bond intensity" I_m for the lanthanons, all the trivalent members of which conformed within measurement accuracy to a linear equation: $I_m = bW + k$;

That when alternative derivations of either Subgroup or General expressions were performed using (a) either N values "corrected" to a common coordination number, (b) N values "corrected" to agree with X-ray densities, or (c) both of these were used, conformity was not improved for elements which crystallize in the simple diamond, bcc, cph, and bcc structures and was appreciably reduced for elements of complex structure (B, Mn, Ga, etc.; and

That for a few properties, at least, B appears to be a member of the III-B subgroup, and carbon in the form of graphite a member of the IV-B subgroup, and that when I_m values were calculated for each of the long periods, earlier anomalous values disappeared or were greatly lessened.

SUMMARY AND RECOMMENDATIONS

The study has necessarily been confined to (a) correlation of a very few properties, principally MP, Θ, and B, with virtually all the solid elements, and (b) the subsequent correlation of ten properties with the I-A , usually II-A, and early elements from other Periods. Until these restrictions can be lifted it cannot be stated that the atomic density concept has been demonstrated as valid. The slow and laborious computation of the mathematical expressions, together with the limited digital capability of the calculator used to derive them, renders the expressions shown in this report somewhat suspect as to both precision and accuracy. That some of the data used may be marginally accurate is quite probable, and that data errors will be magnified by roundoff and truncation is certain. Fortunately, errors of the former kind are sometimes identifiable through comparison of calculated I values derived from quite different properties, and this has to some extent already been capitalized upon in data screening. Roundoff errors can of course be greatly reduced by using calculators with extended digital capability, and truncation errors involved in the Gauss algorithm are to some extent alleviated in reversing the elimination process.

It is strongly recommended that the modest computer program already started be completed and debugged, that it then be used to derive alternative General expressions based not only on early elements of the several Periods but later ones as well, and that these expressions then be compared in such a way as to identify uncertain or missing data points and to forecast their probable values. Only by comparing such values with those obtained by referee-quality experiment can further refinement be made.

2/20/75

The Elements: Mass Factors and Data to Compute Them

	$1 + 2n_{le}$	W_h	W_l	W	mf	mf'
H	1.0003	2.01400	1.007825	1.00797	1.99882	1.49960
He	1.000003	4.00260	3.01603	4.0026	1.24649	1.14057
Li	1.14840	7.01600	6.01512	6.939	1.31404	1.23713
Be*				9.0122	1.0	1.0
B	1.39560	11.00931	10.0129	10.811	1.52423	1.46238
C	1.0222	13.00335	12.00000	12.01115	1.10759	1.06491
N	1.0074	15.00011	14.00307	14.0067	1.07911	1.04326
O	1.00482	17.84357*	15.99491	15.9994	1.12092	1.06288
F*				18.9984	1.0	1.0
Ne	1.18154	21.96314*	19.99244	20.183	1.29688	1.23950
Na*			22.9898	22.9898	1.0	1.0
Mg	1.4260	25.50855*	23.98504	24.312	1.51536	1.47098
Al*			26.9815	26.9815	1.0	1.0
Si	1.1558	29.37207*	27.97693	28.086	1.21321	1.18456
P*				30.9738	1.0	1.0
S	1.09988	33.82183*	31.97207	32.064	1.16333	1.13165
Cl	1.4894	36.9474	34.96885	35.453	1.57252	1.53124
Ar	1.0080	39.9627	36.59678*	39.944	1.09294	1.05233
K	1.137624	40.98082*	38.96371	39.102	1.19631	1.16702
Ca	1.060566	43.67540*	39.96259	40.080	1.15881	1.10976
Sc*				44.956	1.0	1.0
Ti	1.95640	48.28770*	47.5072*	47.90	1.98828	1.97240
V	1.0048	50.9440	49.9472	50.942	1.02446	1.01478
Cr	1.2386	53.1398*	51.7841*	51.996	1.27089	1.25478
Mn*				54.938	1.0	1.0
Fe	1.1164	55.96517*	53.9396	55.847	1.15689	1.13700
Co*				58.9332	1.0	1.0
Ni	1.6432	59.5157*	57.9353	58.710	1.68743	1.66546
Cu	1.6182	64.9278	62.9298	63.54	1.66908	1.64376
Zn	1.9778	66.70087*	63.9291	65.37	2.06166	2.02020
Ga	1.7920	70.9249	68.9257	69.72	1.84339	1.81784
Ge	1.9592	74.07111*	71.0667*	72.59	2.04029	2.00017
As*				74.9216	1.0	1.0
Se	1.8198	80.2280*	77.2084*	78.96	1.88939	1.85499
Br	1.9892	80.9163	78.9183	79.909	2.03894	2.01422
Kr	1.5146	84.37875*	82.13076	83.80	1.55523	1.53511
Rb	1.5570	86.91636	84.9117	85.47	1.59352	1.57532
Sr	1.2888	87.9056	86.2476*	87.62	1.31319	1.30109
Y*				88.905	1.0	1.0
Zr	1.7462	93.13848*	90.08361*	91.22	1.80468	1.77561
Nb*				92.906	1.0	1.0
Mo	1.8574	98.13464*	94.2044*	95.94	1.93349	1.89579
Tc*				(97)	1.0	1.0
Ru	1.8251	102.3916*	99.17841*	101.07	1.88312	1.85437
Rh*				102.905	1.0	1.0
Pd	1.7704	108.5162*	105.12303*	106.40	1.82686	1.79880

Note: *Starred elements are natural monoisotopes*

Starred W_h, W_l values indicate two or more isotopes in fraction; value shown obtained by Law of Mixtures

In underlined $1+2n_{le}$ fractions nearly equal.

$$mf = (1+ 2n_{le})(1+ (\frac{W_h-W_l}{W})$$

$$mf' = (1+ 2n_{le}) (\frac{W_h+ W}{W_l+ W})$$

The Elements: Mass Factors and Data to Compute Them (cont.)

	$1+2n_{le}$	W_h	W_l	W	mf	mf'
Ag	1.9636	108.9047	106.9041	107.868	2.0002	1.98189
Cd	1.9740	113.96362*	110.96061*	112.40	2.02674	2.00053
In	1.0856	114.9041	112.9043	114.82	1.10451	1.09513
Sn	1.9582	120.3760*	116.9491*	118.69	2.01474	1.98668
Sb	1.8550	122.9041	120.9038	121.75	1.88548	1.87029
Te	1.6746	128.9463*	125.0340*	127.60	1.72594	1.70053
I*				126.9044	1.0	1.0
Xe	1.92388	133.14225*	129.71825*	131.30	1.97405	1.94910
Cs*				132.905	1.0	1.0
Ba	1.56676	137.905	135.8660*	137.34	1.59002	1.57845
La	1.00178	138.9061	137.9068	138.91	1.00899	1.00539
Ce	1.22154	141.909	139.8901*	140.12	1.23914	1.23035
Pr*				140.907	1.0	1.0
Nd	1.7454	146.6023*	142.8572*	144.24	1.79072	1.76817
Sm	1.9886	152.8395*	147.9427*	150.35	2.05337	2.02124
Eu	1.9564	152.9209	150.9160	151.96	1.98221	1.96935
Gd	1.9354	158.85264*	155.8477*	157.25	1.97238	1.95357
Tb*				158.924	1.0	1.0
Dy	1.42624	163.6106*	160.7940*	162.50	1.45096	1.43866
Ho*				164.93	1.0	1.0
Er	1.8390	168.6429*	166.2631*	167.26	1.86516	1.85212
Tm*				168.934	1.0	1.0
Yb	1.8915	174.5113*	171.8507*	173.04	1.92058	1.90609
Lu	1.0518	175.9419	174.9409	174.97	1.05782	1.05481
Hf	1.9798	179.6659*	177.36314*	178.49	2.00534	1.99261
Ta	1.00025	180.948	179.9415	180.948	1.00581	1.00304
W	1.8190	184.9148*	182.2938*	183.85	1.84493	1.83202
Re	1.7414	186.956	184.9530	186.2	1.76013	1.75080
Os	1.81904	191.86999	189.0418*	190.2	1.84609	1.83260
Ir	1.7460	192.9633	190.9609	192.2	1.76419	1.75512
Pt	1.6502	196.4091*	194.4407*	195.09	1.66685	1.65854
Au*				196.967	1.0	1.0
Hg	1.9974	201.9808*	199.2207*	200.59	2.02488	2.01119
Tl	1.5900	204.9745	202.9723	204.37	1.60558	1.59781
Pb	1.9536	207.9766	206.387*	207.19	1.96859	1.96111
Bi*				208.980	1.0	1.0
Po*				208.983*		
At				(210)		
Rn				210.991*		
Fr				233.02*		
Ra				226.025*		
Ac				227.028*		
Th				232.038*		
Pa				231.036*		
U				238.04		

The remaining elements do not exist in nature.
Starred values of W indicate atomic mass of longest-lived isotope.

ID	Z	NAME	BP	MP	DT	CT	TT	10k	N
1	1	H	20.28	14.01	105				
68	2	He	4.215	?					
2	3	Li	1590	452.0	448			8.47	4.6232
7	4	Be	3142	1556	1031			10.0[illegible]	12.429
42	5	B	2823s	2583	1362			2.70[illegible]	13.03
48	6	C	5100s	3825	1874			12.9	17.648
53	7	N	77.35	63.29	70				
58	8	O	90.19	54.75	500				
63	9	F	85.01	53.53					
69	10	Ne	27.07	24.48	30				
3	11	Na	1165	371.0	155		35	14.1	2.54407
8	12	Mg	1380	924	330			15.6	4.305
43	13	Al	2740	933.5	390			23.7	6.0308
49	14	Si	2628s	1685	692			14.8	4.9960
54	15	P	553	317.2	576			12.1	5.2301
59	16	S	717.82	392	527			.0269	3.888
64	17	Cl	238.55	172.17	115				
70	18	Ar	87.27	83.95	90				
4	19	K	1047	336.8	100			10.24	1.3225
9	20	Ca	1760	1118	230		464	20	2.3244
12	21	Sc	3105	1812	476		1608	1.58	4.004
14	22	Ti	3535	1953	380		1165	2.19	5.708
18	23	V	3655	2161	390			3.07	7.223
21	24	Cr	2755	2125	424			9.37	8.293
24	25	Mn	2370	1525	363		1000	.782	8.155
27	26	Fe	3025	1810	373		1660	8.02	8.4908
30	27	Co	3145	1768	386			10.0	8.9801
33*	28	Ni	3005	1726	345			9.07	9.131
36	29	Cu	2868	1356	310			40.10	8.4853
39	30	Zn	1180	692.7	237			11.6	6.5713
44	31	Ga	2676	302.9	240			4.06	5.097
50	32	Ge	3105	1210.6	403			5.99	4.4171
55	33	As	886s	1080p	275			5.00	4.6034
60	34	Se	958	490.2	150			.204	3.6533
65	35	Br	331.93	265.95					
71	36	Kr	119.8	116.55	60				
5	37	Rb	961	312.04	59			5.82	1.0794
10	38	Sr	1645	1042	148		875+	3.53	1.7870
13	39	Y	3200	1820	214		1752	1.72	3.028
15	40	Zr	3610	2125+	250			2.27	4.2952
19	41	Nb	5200	2741	260			5.37	5.555
22	42	Mo	5835	2883	377			13.8	6.428
25	43	Tc	5305	2475	422			5.06	6.97
28	44	Ru	4175	2675	415			11.7	7.2693
31	45	Rh	4000	2239	350			15.0	7.2626
34	46	Pd	3415	1827	275			7.18	6.8033
37	47	Ag	2485	1234	221			42.9	5.862
40	48	Cd	1038	594.1	221			9.68	4.634
45	49	In	2355	429.75	129			8.16	3.834
51	50	Sn	2545	505.04	254			6.66	3.7090
56	51	Sb	2025	903.9	200			2.43	3.3096
61	52	Te	1263	722.6	141			.235	2.945
66	53	I	457.5s	386.6	105			.045	2.3395
72	54	Xe	166.05	161.25	76.1				

Note : For computer storage: DT = Debye Temperature, Θ_{298}
CT = Curie Temperature
TT = Principal Transition Temperature
For expected data, see I-A elements, Table 1b

ID	Z	NAME	BP	MP	DT	CT	TT	10k	N
6	55	Cs	963.1	301.7	43			3.59	.84833
11	56	Ba	1913	998.2	116			1.35	1.5391
74	57	La	3727	1159	135		1134	1.35	2.6732
75	58	Ce	3972	1068.2	138		999	1.14	2.9101
76	59	Pr	3485	1192	148		1068	1.25	2.8985
77	60	Nd	3400	1283	148		1128	1.65	2.9238
78	61	Pm	3003	1305				1.79	
79	62	Sm	2170	1345	184		1197	1.33	3.0185
80	63	Eu	1870	1095	127			1.39	2.0818
81	64	Gd	3506	1585	155	289	1531	1.06	3.0247
82	65	Tb	3810	1633	158		1560	1.11	3.1202
83	66	Dy	2610	1682	158		1657	1.07	3.1649
84	67	Ho	2990	1740	161		1701	1.62	3.2063
85	68	Er	2785	1795	163	56	?	1.43	3.2566
86	69	Tm	2000?	1818	167		?	1.68	3.3217
87	70	Yb	1466	1097	118		1065	3.49	2.4264
88	71	Lu	3588	1929	?		?	1.64	3.3851
16	72	Hf	5675	2423	213		1585	2.30	4.4806
20	73	Ta	5698	3269	225			5.75	5.5427
23	74	W	6200	3685	312			17.4	6.3317
26	75	Re	5900	3455	275			4.79	6.798
29	76	Os	5300	3320	400			8.76	7.1462
32	77	Ir	4800	2716	228			14.7	7.025
35	78	Pt	4100	2045	225			7.16	6.6214
38	79	Au	3213	1337.6	178			31.7	5.9070
41	80	Hg	629.73	234.28	92			.834 l	liq
46	81	Tl	1730	576.6	96			4.61	3.4919
52	82	Pb	2013	600.65	87			3.53	3.2988
57	83	Bi	1833	544.5	116			.787	2.8088
62	84	Po	1235	527	?			2.0	2.673
67	85	At							
73	86	Rn	211.35	202.15	400				
17	87	Fr	879	300.2					
47	88	Ra	2000?	973	87			1.86	1.33
89	89	Ac	3470	1323	100			1.2	2.6715
90	90	Th	4070	1980	100		1670	5.4	3.0428
91	91	Pa		1870+	262			4.7	4.0
92	92	U	4090	1406	300		1050	2.76	4.7944
93	93	Np	4175	913	163		825	.63	5.1456