

Chemical thermodynamics in the future development of chemistry including environmental problems

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Abstract - High-temperature science will be facing unusual challenges in the decade ahead. New technological advances are requiring new materials with unusual properties that will either be prepared by high-temperature techniques or will need to have long-term stability at high temperatures in various environments. One of the major driving forces for new materials arises from the increasing public concern about environmental pollution. Equipment using volatile fluids that can survive up to the stratosphere and destroy the ozone will have to be replaced. Processes that emit sulfur oxides will have to be modified to reduce sulfur emission to very low values. The efficiency of solar energy devices will have to be improved and nuclear power plants will have to be designed to make serious accidents extremely unlikely so that energy production by combustion to carbon dioxide is greatly reduced. Many other examples can be given of the need for new materials. The possible combinations of the elements are enormous. The problems cannot be solved by trial and error procedures. Practical predictive models must be developed to narrow down the range of materials that might have the desired products. Examples of possible models will be discussed.

As my talk will be dealing with solutions to long-term world problems, it will be a very general discussion to provide a framework for attacking the problems. I will eventually narrow down the discussion to the contributions of chemical thermodynamics to the solution of these problems. But even then, I will deal with the general problem of obtaining and compiling thermodynamic data.

The earth is headed toward a catastrophic crisis. Its finite resources cannot meet the needs of an exponentially expanding population. Even when the population growth is stopped, as it must be as soon as possible, our resources are inadequate to meet the demands to raise the standard of living of Eastern Europe, China, India, Africa, South America and the other so-called Third World nations to the level of Western Europe and the USA. Even the USA must retreat from its current standard of living. With the diversion of resources to excessive military developments over the past decade, its civilian productivity has not been adequate to provide the materials consistent with the standard of living that has been maintained by borrowing from abroad. The tremendous debt that is being passed onto the next generation will require reduction in the standard of living.

Assuming that both population and excessive military expenditures can be controlled, is it possible to increase the productivity of all countries to provide an acceptable standard of living for all, even if not at the present level of the most advanced countries?

One serious limitation to merely expanding present productive facilities world-wide to provide the food and other materials that are needed is the effect of current activities upon the environment. We have reached the point where pollution from existing facilities must be controlled. Thus, we face the problem of not only expanding productivity but of devising new materials and new procedures that will control excessive environmental damage. Equipment using volatile fluids that can survive up to the stratosphere and destroy the ozone will have to be replaced. Processes that emit sulfur oxides will have to be modified to reduce sulfur emissions to very low values. The task

seems impossible, but we must somehow succeed. The alternative would be political and economic instability and violence much beyond that of previous world wars.

Particular emphasis is needed for the problem of sources of energy. For example, we must work toward the development of economical utilization of solar energy to replace the use of petroleum which will be needed as a source for plastics and other organic materials. The use of petroleum as an energy source must be greatly reduced if it becomes clear that additional carbon dioxide in the atmosphere will substantially increase temperatures. However, the large areas of solar collectors required to generate substantial solar energy poses a problem as a large amount of energy is required for their production and it might take as long as a decade to recover the energy invested in a solar collector. Nuclear energy will undoubtedly be essential in providing the energy needed to build solar collectors. The efficiency of solar energy devices will have to be improved and nuclear power plants will have to be designed to make serious accidents extremely unlikely so that energy production by combustion to carbon dioxide is greatly reduced. A related problem is the reduction of use of energy for transportation by development of mass transportation systems that would replace individual automobiles.

There are many other changes in the technology that will be required to supply the needs of an adequate standard of living within the limitation of our resources. There are two primary steps that must be taken to provide the needed technology. The first is to provide the manpower that would be needed for expansion of new technological developments. We must improve our education systems to expand the number of young people attracted to the challenges of science and engineering, and to train them to be imaginative and innovative enough to cope with the challenge of developing new technology. The second step is to improve our ability to provide new materials with properties needed for the safer more productive processes that are needed. I wish to devote the remainder of my presentation to this problem.

High-temperature science will be facing unusual challenges in the decade ahead. New technological advances are requiring new materials with unusual properties that will either be prepared by high-temperature techniques or will need to have long-term stability at high temperatures in various environments. Many other examples can be given of the need for new materials. Materials being used today often contain a half dozen or more elements needed for the desired properties. If we started with ninety elements and wished to consider all the mixtures of 2, 3, 4, 5, and up to 6 at a time, we would be examining 4.5×10^{11} multicomponent systems. It is impractical to use an Edisonian approach of testing random selections of the elements. We must develop practical predictive models to narrow down the range of possible materials that might have the desired properties. Then the chance of finding the desired material is greatly increased.

How do we predict the properties of yet undiscovered compounds? There are a number of models that are useful, but the most powerful one for dealing with all of the elements is the chemical bonding model. The simplest form of the chemical bonding model is that used by Mendeleev (ref. 1) that assumes that properties will show regular trends for each group of the periodic table, as well as in the horizontal direction of the table. However, there are problems with such a simple model. For many properties, the enthalpy of formation, for example, the variation is not smooth because of two or more significant contributions that vary in different directions. This is well known for the enthalpies of sublimation of the elements. There is a regular trend for most vertical groups, but the direction of increase is different for the transition metals compared to other elements and the lanthanides and actinides show quite irregular behavior. The horizontal trends are not all regular. Another illustration is given by Tables 1 and 2 that show the enthalpies for formation of the fluorides and iodides of the left-hand elements. The stability increases going down for the iodides, but the fluorides show the opposite trend.

A rather simple modification can accommodate these irregularities. One must recognize the character of the bonding and the types of electrons involved. I will use the Born-Haber cycle, that you are all familiar with, as an introductory example of how the chemical bonding models can be used. For the ionic halides and oxides, the well-known Born-Haber cycle provides a very effective

TABLE 1. $\Delta H_{298}^{\circ}/R$ for $1/x \text{MF}_x(\text{s}) = 1/x \text{M}(\text{s}) + 1/2 \text{F}_2(\text{g})$, K/g · atom F

| | | | |
|---------------|----------------------------|----------------------------|----------------------------|
| LiF 74,080 | BeF ₂ 61,740 | | |
| NaF 69,350 | MgF ₂ 67,605 | AlF ₃ 60,550 | |
| KF 68,230 | CaF ₂ 73,850 | ScF ₃ 64,610 | TiF ₄ 49,590 |
| RbF 67,080 | SrF ₂ 73,140 | YF ₃ 68,890 | ZrF ₄ 57,470 |
| CsF 66,570 | BaF ₂ 73,090 | LaF ₃ 68,130 | HfF ₄ 58,050 |

TABLE 2. $\Delta H_{298}^{\circ}/R$ for $1/x \text{MI}_x(\text{s}) = 1/x \text{M}(\text{s}) + 1/2 \text{I}_2(\text{g})$, K/g · atom F

| | | | |
|---------------|----------------------------|----------------------------|------------------------------|
| LiI 32,520 | BeI ₂ 11,300 | | |
| NaI 34,610 | MgI ₂ 22,070 | AlI ₃ 12,140 | SiI ₄ 5,700 |
| KI 39,440 | CaI ₂ 32,280 | ScI ₃ 22,800 | TiI ₄ 11,300 |
| RbI 40,120 | SrI ₂ 33,770 | YI ₃ 25,690 | ZrI ₄ 14,690 |
| CsI 41,690 | BaI ₂ 36,200 | LaI ₃ 26,740 | HfI ₄ (14,800) |

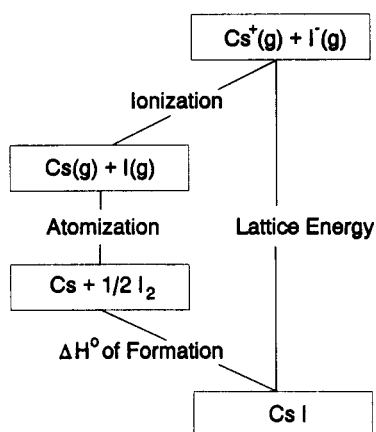


Fig. 1. Born-Haber cycle.

chemical bonding model. As illustrated in Fig. 1, the enthalpy of formation is separated into two terms. The first is the enthalpy of conversion of the elements in their standard-state forms to gaseous atomic species with the same electronic configuration as for the solid compound. For the ionic compounds, this would be the gaseous ions of the same charge as in the solid compound. The second term is then the enthalpy change upon combining the ions to form the solid, that is found to vary in a regular manner for ionic species as a function of ionic size that varies in a regular way in the periodic table.

Examination of the two terms of the Born-Haber cycle explains the different directions of change of enthalpies of formation for the fluorides and iodides. As the size of the atoms increases from lithium to cesium, the bonding strength of the atoms decreases and the electrons are not held as tightly; so it is much easier to produce gaseous ions from cesium metal than from lithium metal. If that were the only factor, all of the cesium compounds would be more stable than the lithium compounds. However, for the second factor, the lattice enthalpy, the strength of bonding decreases as the interionic distance increases. When the anion is large, as for iodide ion, since the cations are much smaller, the interionic distance changes by a small factor compared to the fluorides where the anion size is more comparable with that of the cations. Thus for the iodides, the first term, the enthalpy of formation of the gaseous ions predominates, and the cesium iodides are more stable than lithium iodides. While for the fluorides, the lattice enthalpy change predominates, and one has the reverse trend. There will be many instances of different contributions to the bonding enthalpy varying in different directions so that the resultant enthalpy of formation does not vary

in a smooth way across the periodic table. If one recognizes the character of the chemical bonding and separates the opposing terms, then the variation of each term can vary smoothly across the periodic table and one can make reliable predictions. The lattice enthalpies of the alkali halides have a smooth variation as a function of internuclear distance. Ladd and Lee (ref. 2) have reviewed the various equations that have been used for calculation of lattice enthalpies of a variety of structures and have tabulated lattice enthalpies of a wide variety of compounds for which the bonding is largely ionic.

However, chemical interactions can be complex and often more than two terms have to be separated to obtain a smooth predictable variation across the periodic table. Due to strong covalent bonding, the lattice energies of the silver halides are larger than one would calculate based on a purely ionic model due to the electron pair bonding between silver and the halides. The additional contribution increases from F to I as the electrons on the halide become less tightly bound. Another complication arises when transition metal compounds are considered, due to a crystal field effect upon the d electron orbitals. This illustrates a general consideration of all the bonding models in that one must treat the bonding of electrons from different main shells separately.

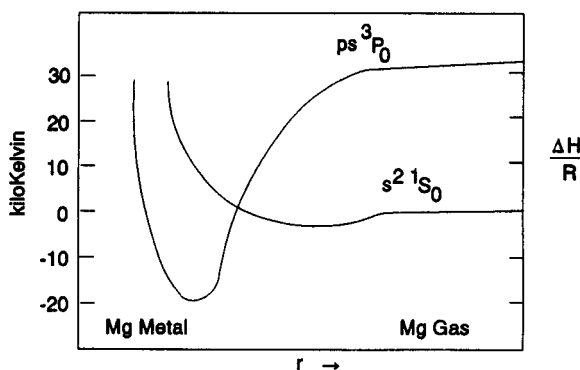


Figure 2. Energies of s^2 and ps configurations of Mg as a function of internuclear distance.

A particularly useful chemical bonding model is one that deals with metallic phases. Figure 2 illustrates the change in electronic configuration as magnesium atoms are compressed to the solid state. The gaseous ground-state configuration which has a pair of electrons in the 3s orbital behaves as a noble gas and has only weak van der Waals bonding. However, there is a small population of atoms with one of the 3s electrons promoted to the 3p orbital. With single electrons in each orbital, there can be strong bonding when the atoms come close enough for overlap of orbitals. Thus in the solid state, the electronic configuration becomes predominately 3s3p. As for the Born-Haber model for ionic solids, the enthalpy of formation of Mg metal from Mg gas is separated into two terms. The first is the enthalpy of promoting Mg gaseous atoms from the s^2 to the sp configuration, which is available from spectroscopic data (ref. 3). The second is the bonding of the s and p electrons of atoms in the sp configuration as they approach one another. As for the Born-Haber model, the bonding is described in terms of gaseous species in the same electronic configuration as in the solid state bonding together. When this is done, as will be illustrated shortly, one finds that the bonding enthalpies vary in a smooth way across the periodic table and it is possible to make predictions when data have not been measured.

Hume-Rothery (ref. 4) was able to demonstrate that the crystal structures of pure metals as well as multicomponent metallic phases could be related to the electron concentration. With less than 1.5 electrons per atom (e/a), the crystal structure was body-centered cubic (bcc). With 1.7 to 2.1 e/a, the crystal structure was hexagonal close-packed (hcp). With 2.5 to 3 e/a, the structure was cubic close-packed (ccp), and with 4 e/a the diamond structure is formed. Hume-Rothery used the total number of valence electrons and encountered difficulties with the transition metals. Engel (ref. 5) was able to resolve this problem by recognizing that the inner-shell d and f electrons were

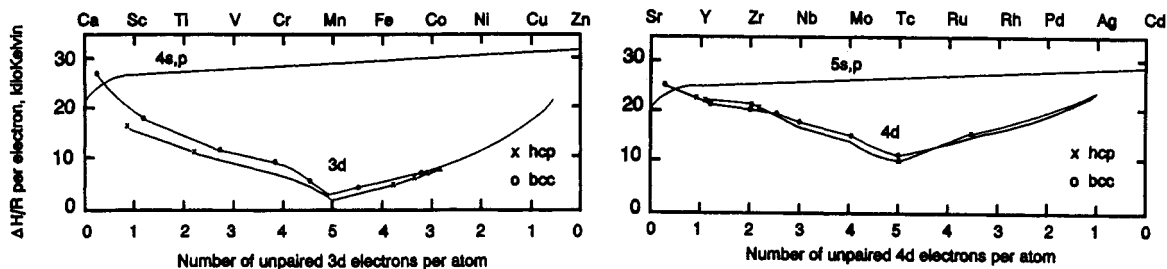


Fig. 3. Valence-state bonding enthalpies per unpaired electron for 3d and 4d transition metals.

in contracted orbitals that could bond only with nearest neighbors and that it was only the outer-shell s and p electrons that would fix the long-range order. This made it possible to develop a model that could accommodate all mixtures of metals. When one examines the bonding enthalpies of formation of metals from gaseous atoms in the same electronic configuration as the metal, one finds that for systems with only outer-shell s and p electrons used in bonding, the bonding enthalpy per electron decreases as the size increase as one goes down a given group in the periodic table, and increases as one goes horizontally as the size decreases with increasing nuclear charge. From the regular pattern of the s,p bonding, one can subtract the contribution of s,p bonding from the total bonding of transition metals to obtain the bonding due to the d electrons. This is illustrated in Fig. 3 for the transition metals using 5s,p and 4 d electrons and for those using 4s,p and 3d electrons. Due to the crystal field effect that expands some d orbitals, thus increasing their overlap and bonding ability with neighbors and contracts other d orbitals with reduction of their bonding ability, the average bonding enthalpy per d electron decreases as more of the d orbitals are used. When the number of d electrons is increased above five, then pairing of d electrons makes them nonbonding in the pure metals, and the average calculated by dividing by the number of unpaired d electrons in the valence state increases as one moves to the right in the periodic table. Similar curves are obtained for the metals using 6s,p and 5d electrons. As the nuclear charge is increased for a given transition metal group, the d orbitals do not respond to the increased nuclear charge as strongly as the s and p orbitals, and they become more expanded relative to the filled s,p core. Thus the bonding ability increases from 3d to 4d to 5d. The minimum is particularly low for the 3d electrons as some of the orbitals are so contracted that unpaired d electrons remain unpaired and do not bond with electrons of neighboring atoms. They are responsible for the ferromagnetism of Cr to Ni.

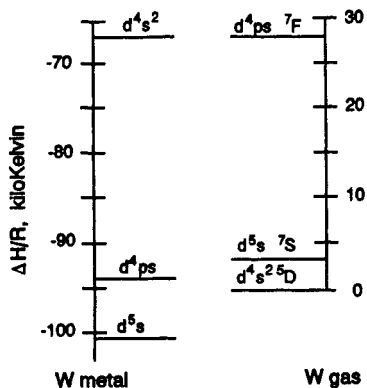


Fig. 4. Energies of d^4s^2 , d^5s , and d^4sp configurations of tungsten for the gaseous atom and for the solid.

The use of the curves of bonding enthalpies of the s, p, and d electrons across the periodic table provide the ability to predict the stability of phases for which data are not available. Figure 4 is an example of a simple case. For tungsten gas, the energies of the lowest levels of the three configurations, d^4s^2 , d^5s , and d^4ps , from spectroscopic data, are given on the right-hand side. Then using the bonding enthalpies of the 6s,p and 5d electrons, the enthalpies of solids with the three electronic configurations are calculated. The d^4s^2 configuration with only four electrons available for bonding is seen to be very unstable relative to the solids with d^4ps and d^5s configurations. Although the d^4ps configuration with two outer-shell bonding electrons is the most strongly bonding configuration, its high promotion energy leaves the hcp d^4ps solid unstable, relative to the bcc d^5s solid, by about seven kiloKelvin. Table 3 illustrates the results of a more detailed calculation for eight configurations for yttrium. The bcc and hcp structures are much more stable than the ccp structure or solids using any of the other configurations. The most stable hcp structure is the phase found at low temperatures. The bcc phase with a higher entropy becomes stable at high temperatures.

In actual situations, simple electron configurations with integer numbers for each type of electron are not found because there will be configuration mixing. One can calculate the most stable mixture (ref. 6), as illustrated in Table 4, for the 5d metals. For a number of multicomponent systems, one can do similar calculations to calculate the structures of different compositions. This is illustrated by Fig. 5 for binary systems of Mo with W, Re, Os, Ir, and Pt, and for higher order mixtures up to the six component system. Each horizontal line at the integral e/a value, say, 7, or rhenium-molybdenum, represents a binary diagram. A horizontal line halfway between Re and Os would be the portion of the ternary Mo-Re-Os, with equal Re and Os. For a six-component system, one calculates the average e/a for the combination of right-hand metals and draws a horizontal line at the average e/a to predict the phases of the six-component diagram. The sum of the binary up to the six-component diagram adds up to 57 phase diagrams. The figure shows the maximum composition range of each structure at the optimum temperatures. Similar diagrams are available for many other transition metal combinations (ref. 7). To obtain the thermodynamic values needed to calculate the composition ranges as a function of temperature, one must consider not only the bonding capabilities of the various electronic configurations, but one must consider internal pressure differences and size differences (refs. 7, 8, 10).

There are more complications that one must consider when desiring to predict the properties of multicomponent systems. One modification of the bonding calculations that must be made is to consider generalized Lewis acid-base interactions when one is combining left-hand transition metals with vacant d orbitals with right-hand transition metals with nonbonding electron pairs in d orbitals (refs. 10-15). Phases of extraordinary stability are formed when the nonbonding electrons are partially transferred to a vacant orbital of a neighboring atom. However, the bonding will not be as strong as when an unpaired electron is provided by each neighbor.

TABLE 3. Electronic configuration of yttrium.

| $\Delta H^\circ/R$ kK | Y(g) | Y(s) | |
|-----------------------|------|------|---------|
| dp^3 | 65 | - 8 | |
| sp^3 | 49 | -26 | ccp III |
| d^2p | 43 | -22 | |
| d^3 | 43 | -12 | |
| dsp | 22 | -51 | hcp II |
| d^2s | 16 | -50 | bcc I |
| s^2p | 15 | -10 | |
| ds^2 | 0 | -22 | |

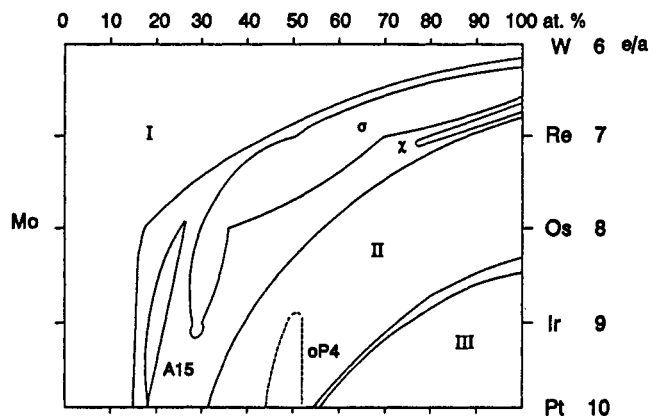


Fig. 5. Multicomponent phase diagrams projected along the temperature axis for Mo with 5d metals.

TABLE 4. Electronic configurations of 5d metals.

| | Lu | Hf | Ta | W | Re | Os | Ir | Pt | Au |
|---|--------------------------|--------------------------|--------------------------|--------------------------|----------------|----------------|--------------------------|--------------------------|--------------------------|
| melting point, K | 1936 | 2504 | 3293 | 3695 | 3459 | 3306 | 2720 | 2042 | 1338 |
| boiling point, K | 3675 | 4970 | 5790 | 5960 | 5885 | 5300 | 4712 | 4109 | 3136 |
| electronic configuration, gaseous ground state | ds^2 | d^2s^2 | d^3s^2 | d^4s^2 | d^5s^2 | d^6s^2 | d^7s^2 | d^9s | $d^{10}s$ |
| electronic configuration of metal | $d^{1.5}sp^{0.5}$ bcc | $d^{2.5}sp^{0.5}$ bcc | $d^{3.5}sp^{0.5}$ bcc | $d^{4.5}sp^{0.5}$ bcc | d^5sp hcp | d^6sp hcp | $d^{6.5}sp^{1.5}$ ccp | $d^{7.5}sp^{1.5}$ ccp | $d^{8.5}sp^{1.5}$ ccp |
| or | dsp hcp | $d^{2.3}sp^{0.7}$ hcp | | | | | | | |
| number of bonding valence electrons | 3 | 4 | 5 | 6 | 7 | 6 | 6 | 5 | 4 |
| number of nonbonding valence electrons | 0 | 0 | 0 | 0 | 0 | 2 | 3 | 5 | 7 |
| number of vacant d orbitals | 3.5 | 2.5 | 1.5 | 0.5 | 0 | 0 | 0 | 0 | 0 |
| or | 4 | 2.7 | | | | | | | |

When transition metals are mixed with non-transition metals, additional factors must be considered (ref. 16). The transition metals have to pay considerable promotion energy penalties to be able to utilize their d electrons in bonding to neighboring atoms. The additional bonding due to the d electrons can offset the promotion energy penalty. The d orbitals cannot overlap with the very extended s and p orbitals as well as with the d orbitals. Thus when transition atom neighbors are replaced by non-transition atoms, the amount of promotion of the transition metal will decrease. The mixture of Pd with Al can be taken as an example. In pure Pd, promotion has taken place from d^{10} to d^7sp^2 yielding ccp Pd. For pure Al, promotion has taken place from s^2p to sp^2 yielding ccp Al. When Al is added to Pd, depromotion occurs. For the 50 atomic percent mixture, Pd has dropped to its gaseous ground state configuration d^{10} leaving its 5s orbital vacant. With Pd neighbors with vacant s orbitals, Al does not have to pay a promotion energy to use all of its valence electrons. It can serve as a Lewis base providing a pair of electrons to the vacant s orbital of the Lewis acid Pd. The resulting solid has three bonding electrons per pair of atoms, or 1.5 e/a. According to the Hume-Rothery rules, the two ccp metals should form a bcc alloy. This is what is found (ref. 16). An ordered bcc structure is produced; AlPd has the CsCl structure. As small amounts of a non-transition metal such as Al or Ga are added to a transition metal such as Cu or Pd, there is a gradual reduction in the amount of promotion of d electrons to p orbitals. Pd will depromote from d^7sp^2 to d^8sp to d^9s or d^9p and finally to d^{10} . Thus it can behave as several different elements as its structure changes from ccp to hcp to bcc. In addition, there will be regions where two configurations are of comparable importance. Then even more structures can form like the β -Mn and other structures that require a range of sizes of atoms that can be provided if there is a range of electronic configurations. When the internal pressures of the transition and non-transition metals are not too greatly different, one can obtain a large number of intermetallic phases. For example, in the Al-Cu system, thirteen stable intermetallic phases have been reported (ref 16).

It is clear that chemical models cannot be used in a mechanical manner without taking the types of chemical interactions into account. However, it is possible to develop models that can predict the enthalpies of formation of virtually all combinations of metals. One starts with the spectroscopic data for the various electronic configurations. When spectroscopic data are lacking,

it is possible to predict them with reasonable accuracy for most purposes (refs. 17-20). Then one selects the appropriate electronic configurations for the crystal structures of interest. Contributions of internal pressure and size differences have to be considered, but the major job is of assigning bonding enthalpies to the various types of electrons, taking into account the bond order or number of bonds per atom. One must first assign bonding enthalpy contributions for the outer-shell s,p electron bonding. Then one must consider the bonding due to inner-shell d or f electrons, taking into account the crystal field effect that produces a marked change in bonding depending upon which d or f orbitals are used. One must take into account generalized Lewis acid-base interactions with a reduced bonding contribution per electron when an electron pair is transferred to a neighbor, compared to bonding with an electron coming from each neighbor. Finally, in mixtures of non-transition metals with transition metals, one must correct for the reduction in bonding by inner-shell electrons as the transition metal is surrounded by non-transition metals. In the time available, I have not been able to examine these procedures in detail, but the cited references will provide detailed information.

This is not a trivial procedure when one is dealing with multicomponent mixtures of different types of metals, but we have reached a stage where such models can be developed to yield useful information for the astronomical number of combinations of the elements. This process must be developed to be able to meet the demands for new materials with a wide range of properties that have not been available in the past.

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