

A bonding model for strong generalized Lewis acid-base interactions in intermetallics

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Abstract - Information is needed for a wide variety of combinations of the elements to obtain new materials with the wide range of properties needed for new applications. It is not practical to carry out the multitude of experiments needed to just characterize the homogeneous phase regions, and to fix their crystal structures and temperature and composition ranges of stability. It is necessary to develop theories that will provide reliable predictions. Available bonding models have been adequate to characterize the binary systems of molybdenum. It would not be possible to provide as complete information, within the limitation of practical engineering accuracy, for many of the other transition metals with vacant d orbitals, as current bonding theories are not accurate enough in predicting interactions in which the vacant d orbitals of hafnium, for example, serve as a Lewis acid when mixed with a platinum group metal with non-bonding electron pairs that could serve as a Lewis base. These interactions can produce extraordinarily stable compounds. For example, the enthalpy of formation of HfPt_3 is $\Delta H^\circ/R = -66 \pm 5$ kilo-Kelvin. The difficulty of predicting these acid-base interactions of transition metals with sufficient accuracy is due to the partial localization of the d orbitals. The bonding capability varies markedly as different orbitals are used in bonding due to the crystal field interactions of neighbors. Titrations of palladium and rhodium by niobium have been carried out by determining the activity of niobium in alloys using high-temperature solid-electrolyte cells and by phase equilibria with oxides, carbides, and nitrides. The titration curve of niobium activity as a function of composition indicated a large crystal field effect with the two non-bonding pairs of palladium having substantially different base strengths. The non-bonding pair of rhodium is intermediate in base strength between the two pairs of palladium. At low concentrations of niobium, palladium is a stronger base, but rhodium becomes stronger at higher niobium concentrations. Additional measurements are in progress for various combinations of 3d, 4d, and 5d elements to provide the information needed for an adequate crystal field model that could provide prediction of bonding capabilities.

GENERAL CHARACTERISTICS OF HIGH TEMPERATURE SCIENCE

In characterizing high temperature science, two main features can be emphasized. One is that there are many surprises as one increases temperature. High temperature behavior cannot usually be predicted by simple extrapolation of room temperature behavior. An example is the complexity of high temperature vapors. Most people assume that only atomic or simple molecular species can exist at high temperatures. However, in vapors in equilibrium with a condensed phase, the number of gaseous species and their complexity increases as the temperature rises. A simple thermodynamic proof can be given that gaseous species that are unimportant at low temperatures will increase in importance as the temperature of the saturated vapor rises (refs. 1, 2). The stabilization of unusual oxidation states, for example, often brings about quite unexpected behavior. This complexity of high temperature behavior is a challenge to obtain a better understanding so that one can anticipate failure of materials or can utilize these unexpected chemical processes to produce new materials.

The second feature of high temperature science is the difficulty of obtaining meaningful research results that do not have serious systematic errors. The development of predictive models is essential to allow one to recognize experimental errors and, most importantly, because information is needed for many combinations of the elements to point the way to new materials with the wide range of properties needed for new applications.

Atomic Energy Review-Special Issue No. 7 on molybdenum (ref. 3) is an example of application of a bonding theory model to predict the thermodynamic properties and equilibrium phase diagrams of the binary systems of molybdenum. The International Atomic Energy Agency agreed that theoretical models could be used to predict unmeasured values, but the restriction was placed that any results presented should be of practical engineering accuracy. It was pos-

sible to meet this restriction for 101 elements combined with molybdenum even though no experimental data were available for a large fraction of the elements. Molybdenum is a special case in that all of the 4d orbitals are used in bonding in the pure metal and would not be available for generalized Lewis acid-base interactions. It would not have been possible to meet the requirement of practical engineering accuracy for so many systems of the Ti-Hf or V-Ta groups or the lanthanides and actinides as current bonding models are not accurate enough in prediction of interactions in which the vacant d orbitals of hafnium, for example, serve as a Lewis acid when mixed with a platinum group metal with non-bonding electron pairs that could serve as a Lewis base. The present paper deals with attempts to improve the accuracy of predicting these acid-base interactions.

PREDICTION OF GENERALIZED LEWIS ACID-BASE INTERACTIONS IN METAL FROM ENGEL'S MODEL

It has been generally believed that intermetallic phases would not have very negative enthalpies of formation. The history of the Manhattan Project experiments that led to the recognition that cerium and uranium metals could interact very strongly with platinum metal was reviewed at the American Chemical Society G. N. Lewis Symposium (ref. 4). However, it was not recognized at that time that the interaction was a generalized Lewis acid-base interaction. As described in the historical review (ref. 4), the Danish scientist Niels Engel spent a sabbatical at Berkeley in the late forties to work on a manuscript that described a bonding model for metals that has been very effective in correctly predicting the variation of properties of metals and their alloys as a function of position in the Periodic table. It is often assumed that properties will vary smoothly and consistently with change of atomic number, but there are many exceptions. For example, the enthalpies of formation of the solid alkali iodides become more negative as one goes from lithium to cesium. However, just the opposite trend is found for the fluorides. The Born-Haber model that separates the enthalpies of formation of the gaseous ions and the lattice energies of the solids shows that these two contributions vary in opposite directions with the variation of lattice energies predominating for the fluorides and the variation of enthalpies of formation of the gaseous cations predominating for the iodides. In a similar manner, the irregular variation of the stability of solid metals relative to the ground electronic state of gaseous atom as given by the enthalpy of sublimation is separated by the Engel model into (1) the enthalpy of promotion of the gaseous atom from the ground electronic configuration to the electronic configuration corresponding to that in the metal and (2) the bonding enthalpy of the promoted electronic state upon formation of the solid. As almost all atoms with two or more valence electrons have a ground electronic configuration with the outer s orbital filled with a non-bonding pair of electrons, it is necessary to promote to various excited electronic configurations to be able to make effective use of the valence electrons in bonding. Engel used the relationship between electronic configuration and crystal structure discovered by Hume-Rothery (ref. 5) in the twenties together with Lewis' electronic bonding model as used by Pauling (ref. 6) for metals to characterize the electronic configurations of the metals.

It was clear from Engel's model why platinum interacted so strongly with cerium and uranium. Platinum atoms have the ground state electronic configuration $5d^86s^2$ which has four non-bonding electron pairs and only two electrons in d orbitals that can form bonds with neighboring atoms. By promotion of one s electron and one d electron to the 6p orbitals of the $5d^66s6p^2$ configuration of the face-centered-cubic (fcc) structure, four additional electrons, or a total of six electrons, can be used in bonding. The additional bonding energy offsets the high promotion energy that must be paid. Although Pt in the fcc structure has six bonding electrons, four valence electrons are paired in non-bonding d orbitals. If one starts with lutetium with only three valence electrons and moves to the right to Hf, Ta, W, and Re, the melting and boiling points rise markedly as more electrons are available for bonding until the d^5 and d^5p configurations of W and Re that utilize all of the d orbitals in bonding. If one moves farther to the right to Os (d^6sp), Ir (d^6sp^2), Pt (d^7sp^2), and Au (d^8sp^2), the melting and boiling points drop since additional electrons going into the d orbitals will produce non-bonding pairs. However, if the platinum group metals are mixed with transition metals of the left-hand side of the Periodic table that are Lewis acids because they have vacant d and p orbitals, the platinum group metals can serve as Lewis bases and utilize their d electron pairs that are non-bonding in the pure platinum group metal to bond as a Lewis base. It has not been recognized how strong these acid-base interactions can be. It is generally expected that intermetallic phases would not have very negative enthalpies of formation. The availability of empty d and p orbitals of Hf can allow each Pt to use at least four additional electrons in bonding than can be used in pure platinum. The enthalpy of formation of $HfPt_3$ has been determined (ref. 7) to be $\Delta H^\circ/R = -66 \pm 5$ kilo-Kelvin (kK). This intermetallic phase is much more stable than the carbide, nitride, boride, silicide, or selenide of hafnium. Only the oxide and fluoride are significantly more stable. The platinum group metals are generally considered to be rather noble metals that do

not react strongly. At high temperatures where diffusion rates become large enough to provide significant contact between the platinum group metals and compounds of left-hand side transition metals, many unexpected reactions take place. For example, the oxides of the lanthanides are very difficult to reduce. However, if platinum is present to reduce the thermodynamic activity of the lanthanide metal through formation of an extremely stable intermetallic phase, the oxide can be readily reduced by hydrogen (ref. 8). Mixtures of the pure metals can be very dangerous. Once the temperature of a mixture of hafnium and platinum metal powders gets to around 1000 °C where diffusion rates become significant, the formation of the intermetallic phase will increase the temperature by more than 5000°. The reaction can become so rapid that the sample can detonate and destroy the apparatus (refs. 4, 7). Many unexpected reactions will take place because of the strong Lewis acid-base interactions of platinum group metals with transition metals with vacant d orbitals. The platinum group metals are amphoteric and can also serve as Lewis acids when combined with metals like aluminum or gallium for which the gaseous atoms have the ground state configurations s^2p and a large promotion energy to sp^2 is required to make all three valence electrons available for bonding in the pure metals. Gaseous palladium has the ground state configuration d^{10} and would be a noble gas if it did not promote d electrons to s and p orbitals to achieve the fcc configuration f^7sp^2 . For each electron promoted, two bonding electrons are obtained, one d electron remaining in the d orbital and one electron in the outer-shell s or p orbital. The promotion energy is very high and significant bonding by the d electron is required to offset the promotion energy. Because the d orbitals are somewhat localized, their overlap with outer-shell s and p orbitals is much poorer than their overlap with d orbitals of adjoining atoms. Pd atoms surrounded by aluminum or gallium atoms will not be able to achieve sufficient d electron bonding to offset the high promotion energy and the configuration remains d^{10} . The d^{10} configuration with an empty s orbital offers aluminum the opportunity to use its s electron pair in bonding without having to pay a promotion energy. Thus, the three electrons from the aluminum provide an average of 1.5 bonding electrons per atom and the fcc coordination of twelve for the pure metals changes to eight in AlPd, with CsCl structure, as one would predict from the Hume-Rothery correlation of s,p electron concentration and crystal structure.

VARIATION OF BONDING CAPABILITIES OF THE d ORBITALS OF THE PURE METALS

For the pure metals, the variation in bonding capabilities of the various atomic orbitals across the Periodic table is well-characterized (ref. 9). The bonding capability of an electron in the extended outer-shell s and p orbitals decreases as one goes down in a given group because of increasing size of the atomic core and greater distance from the nucleus to the region of maximum density of the bonding electrons. As one moves horizontally, the bonding increases at first more rapidly, and then more slowly as the atomic core is compressed by the increasing nuclear charge. When one considers the inner-shell d and f orbitals, the behavior is much different. These orbitals can vary from complete localization within the atomic core bounded by filled s and p shells and thus minimal overlap bonding with adjacent atoms to partially delocalized orbitals that can contribute significantly to bonding, depending upon the degree of overlap with neighboring orbitals. As one moves from left to right in the Periodic table, the d orbitals are quite extended at the beginning of the transition series but become more localized on the average as the nuclear charge increases, particularly far to the right where the s,p core does not compress rapidly. However, if one goes down in a group, e.g., Cr-Mo-W, the d orbitals become much more extended relative to the filled core. The increased nuclear charge is largely shielded from the 4d orbitals by the filled 4s and 4p shells as one goes from Cr to Mo, as the s and p electrons have appreciable probability near the nucleus. This effect is enhanced in going from Mo to W by the filling of the 4f shell. The 5d orbitals are quite extended and strongly bonding. As one increases the order of s,p electron bonding or the number of electron pairs per bond, there is some decrease in bonding contribution per electron although the effect is small for metals where the order of s,p electron pairs per bond to nearest neighbors varies between 0.15 to 0.25 compared to 1 for Sn or Ge in the diamond structure. The effect of increasing the order of d bonding which can exceed 0.6 for Mo and W is twofold. There is the usual effect of electron repulsion as the order of bonding is increased. However, a much more important effect is the crystal-field effect upon the spatial distribution of the d orbitals. Some orbitals become more extended and better bonding while some become more contracted and contribute less to bonding. The crystal field splitting results in five overlapping bands of levels of which a considerable fraction can be so localized for 3d metals from Cr to the right that some orbitals can contain unpaired electrons that cannot bond with neighboring unpaired electrons and result in ferromagnetism. The fraction of localized orbitals or the average per atom increases from 0.5 at Cr to 1.5 for bcc Mn to 3.7 for bcc Fe. In the instance of bcc Fe, 1.5 of the localized orbitals are filled with non-bonding paired electrons and 2.2 are filled with unpaired magnetic electrons. For the fcc

metals the number of localized orbitals is only 1.5 for Mn with all filled with unpaired magnetic electrons. For Fe to Cu, the number of localized orbitals is in the range of 3 to 3.5 with the number of unpaired magnetic electrons decreasing as more of the localized orbitals are occupied by non-bonding electron pairs. The number of magnetic electrons in localized orbitals decreases from 2.8 for Fe to 1.8 for Co to 0.5 for Ni to 0 for Cu. For the 4d and 5d metals, the degree of localization is reduced and the most localized orbitals are occupied by non-bonding electron pairs with no localized orbitals available for unpaired magnetic electrons. However, the strength of bonding varies with the orbitals used. For example, for the 4d metals (ref. 9), as one moves from left to right using more and more of the d orbitals in bonding, the average bonding enthalpy, $\Delta H/R$ in kilo-Kelvin (kK), per d electron starts at 22.3 kK, with only the most delocalized d orbital of Y being used, and drops to 21 kK with two orbitals being used. With three orbitals, the average is 18 kK. With Nb using four d orbitals, the average bonding $\Delta H/R$ per electron is only 15 kK and for Mo and Tc, which use all five orbitals, the average has dropped to 10.5 kK. As more electrons are added, the non-bonding electron pairs formed will occupy the most localized orbitals leaving the more extended orbitals available for effective bonding. Ru, that only uses four d orbitals in bonding, has an average $\Delta H/R$ of 27 kK. With another electron added, leaving only the three most extended orbitals available for bonding, the average $\Delta H/R$ per bonding electron would be expected to rise to 16 kK. This is lower than the 18 kK value when only three orbitals were used with no non-bonding electron pairs because of the higher nuclear charge on the right side of the Periodic table that contracts the average of all d orbitals.

ACID-BASE BONDING

The fact that electrons are being transferred from platinum to the more electropositive hafnium or cerium disturbs some people (ref. 4). They do not realize the primary factor that determines the direction of transfer is the availability of orbitals and non-bonding electrons pairs and the electronegativity difference determines the distribution of electrons in the bond after the electron pair has been transferred. It is well established that the more electro-negative arsenic (s^2p^3) transfers a non-bonding electron pair to the empty orbital of gallium metal (sp^2) so that each has the electronic configuration (sp^3) with tetrahedral coordination (refs. 4, 6). However, the distribution of electrons in the gallium-arsenic bond is shifted toward the arsenic to reduce the negative charge on the gallium. Another example is the formation of triple-bonded CO from carbon with four valence electrons and oxygen with six valence electrons. The oxygen contributes more electrons to the bond than does carbon and the carbon formal charge is -1. Dipole measurements on CO indicate that the carbon is negative relative to the oxygen, but the negative charge is greatly reduced due to distortion of the electrons in the bond toward the oxygen because of its greater electronegativity. Yet another example is $Cr(CO)_6$ where the CO molecules contribute six electron pairs to the very electropositive chromium to give it a formal charge of -6. However, it is understood that backbonding from the chromium occurs to reduce the negative charge. Thus it is not surprising that in the examples given earlier, the more electro-negative palladium can accept electrons from aluminum but can also transfer electrons to niobium or zirconium.

If we add to the complication of the crystal field effect on the bonding capability of d orbitals the effect of electron transfer, one can see that the accurate prediction of the acid-base interactions becomes difficult. One factor to consider is that the bonds formed in the acid-base reaction through sharing of a pair of electrons from one atom with the vacant orbital of another atom are not as strong as bonds formed by contribution of one electron from each of the interacting atoms. If the bonding enthalpies found for d orbitals of the pure metals were used to calculate the enthalpy of formation of an intermetallic like $NbRh_3$, for example, one would calculate $\Delta H/R = -42$ kK, compared to the experimental (ref. 10) $\Delta H/R = -25$ kK. If the electrons were evenly distributed as in the pure metal, the Nb would have a formal charge of -3. This charge must be reduced by backbonding with movement of other bonding electrons away from the niobium. To be able to accurately predict the acid-base interactions, one must have a more quantitative model for the acidity of vacant orbitals and the basicity of filled orbitals.

EXPERIMENTAL ACID-BASE TITRATIONS

To obtain enough data to characterize accurately the basicity and acidity of the transition metals, three types of experiments have been carried out. A variety of systems with fixed metal activity have been equilibrated with platinum group metals. For example, a mixture of zirconium carbide and graphite has a fixed zirconium thermodynamic activity or partial molal Gibbs energy that can be calculated from the thermodynamic data of the carbide. By equilibrating platinum metal with the mixture of zirconium carbide and graphite and analyzing the platinum for its equilibrium zirconium content, one can calculate the excess partial

molal Gibbs energy of zirconium or its activity coefficient. Similar experiments were done for nitrides in equilibrium with a fixed nitrogen pressure (refs. 11, 12). For elements such as titanium, vanadium, and niobium that have a large number of oxide phases, pairs of oxides can be equilibrated with platinum group metals and activity coefficients can be determined for a variety of compositions (ref. 13). Vapor pressure measurements of metal alloys can also yield activity coefficient data (ref. 12). It is difficult to obtain highly accurate data because the vapor pressure are greatly reduced in the system with strong acid-base interactions, but they are valuable in providing checks of the activity coefficients obtained by other methods. The third type of experiment uses a galvanic cell measurement with solid electrolytes such as yttria-doped thoria where one electrode consists of a mixture of a metal and its oxide or a mixture of two oxides for which the oxygen activity is known. The other electrode, for example, would contain a mixture of a niobium-palladium alloy with NbO_2 . The potential measurements yields the activity of niobium in the alloy. Although these measurements are readily made, careful control of the materials and the apparatus is necessary to avoid serious systematic errors (ref. 13).

From the measurements made to date, it has been possible to characterize the interactions of zirconium, at low concentrations, with transition metals of the right-hand side of the Periodic table (refs. 11, 12, 14). In the previous discussion, the electronic configurations have been discussed in terms of simple integral electron assignments, e.g., $5d^6 6s 6p^2$ for Ir. The Hume-Rothery correlation assigns the fcc structure to s,p electron concentrations between 2.5 and 3. Thus Ir could have a configuration between $d^{6.5} sp^{1.5}$ and $d^6 sp^2$. Because of the high promotion energy, the actual configuration will be closer to $d^{6.5} sp^{1.5}$; $sp^{1.5}$ will be used for the fcc configurations of Ir to Au in the following assignment of non-bonding electron pairs. If Zr is added to the 5d metals from Re to Au, there is no acid-base interaction with $\text{Re}(d^5 sp)$ as it uses all seven valence electrons in bonding. $\text{Os}(d^{5.9} sp^{1.1})$ with approximately one nonbonding electron pair reduces the excess partial molal Gibbs energy of Zr by less than 9 kK. $\text{Ir}(d^{6.5} sp^{1.5})$ with 1.5 non-bonding electron pairs and $\text{Pt}(d^{7.5} sp^{1.5})$ with 2.5 non-bonding electron pairs reduce the excess partial molal Gibbs energy of zirconium by more than 50 kK, whereas $\text{Au}(d^{8.5} sp^{1.5})$ with 3.5 non-bonding pairs reduces the excess partial molal Gibbs energy of zirconium by 20 kK. As these data were obtained by extrapolation to infinitely dilute Zr (ref. 11), these values are a measure of the base strength of the electron pairs in the most extended orbit containing non-bonding pairs. There is a competition between two trends. As the nuclear charge is increased, the average extension of the d orbitals beyond the filled 5s5p shell is reduced. On the other hand, as the number of non-bonding electron pairs increases, higher orbitals with greater extension and better bonding relative to the average will be used. The maximum base strength is reached at two or slightly more non-bonding electron pairs between Pt and Ir. Although Au has a substantial acid-base interaction with Zr, it is greatly reduced due to the greater degree of localization of the 5d orbitals. The 3d metals from Fe to Cu show no indications of an acid-base interaction as not only the non-bonding electron pairs but some of the unpaired electrons are in orbitals so localized that bonding overlap with orbitals of nearest neighbors is negligible.

The above discussion dealt with very dilute solutions of Zr and required consideration of the base strength only in the most extended orbitals containing non-bonding pairs. To characterize the variation of base strength as a function of concentration requires a quantitative measure of the bonding capability of all of the orbitals containing non-bonding pairs. This requires a titration of the base with the acid with measurements of the excess partial molal Gibbs energy or activity coefficient as a function of concentration. This has been done for the Nb-Pd system using equilibration of pairs of niobium oxides with palladium metal with analysis of the palladium to determine the equilibrium niobium concentration and by high-temperature solid-electrolyte galvanic cell measurements (ref. 13). At low concentrations, niobium will be a very effective acid using not only its one vacant d orbital but also its vacant p orbitals to receive electron pairs. Palladium will be a very effective base as it will be providing electron pairs from its most extended d orbitals containing non-bonding pairs. At high niobium concentrations, the average s,p concentration decreases. The niobium will be using less of its p orbitals and the fractional share of d orbital activity will increase. This will cause some reduction of the acid strength of the niobium. A much larger effect will be the reduction in palladium basicity as electron pairs in more localized orbitals are used.

At 1000 °C, the niobium activity coefficient at low concentrations is $10^{-9.5}$. As the niobium concentration in palladium is increased the activity coefficient rises rapidly, going above 10^{-7} before a mole fraction of $x_{\text{Nb}} = 0.1$ is reached. At $x_{\text{Nb}} = 0.2$, the activity coefficient has risen above 10^{-4} and is up to $10^{-1.5}$ around $x_{\text{Nb}} = 0.3$. There is clearly a large crystal field effect and the basicity of the more localized d orbitals of palladium is greatly

reduced. This large crystal field effect can be illustrated with additional data. The measurements of niobium activity coefficients in rhodium by Kleykamp (ref. 15) have been extended to x_{Nb} greater than 0.3 using oxide equilibration (ref. 13). At low niobium concentration, the activity coefficient of niobium at 1000 °C is above 10^{-8} compared with the activity coefficient in palladium of $10^{-9.5}$. As the niobium content in rhodium is increased, the activity coefficient does not rise as rapidly as in palladium. At $x_{\text{Nb}} = 0.2$, the activity coefficient in rhodium of $10^{-5.5}$ is much below the value of $10^{-3.8}$ in palladium. There are two factors to consider in comparing the basicities of $\text{Rh}(d^{6.5}sp^{1.5})$ and $\text{Pd}(d^{7.5}sp^{1.5})$. Because of the higher nuclear charge of palladium, a d orbital would be more localized than the comparable orbital of rhodium. On the other hand, with an additional non-bonding electron pair, palladium would be offering its first electron pairs from a higher orbital that would be less localized. When palladium has used up these more exposed electrons and would be using an orbital comparable to the one used by rhodium, then its basicity would drop below that of rhodium. Since rhodium has fewer non-bonding pairs than does palladium, the palladium will have greater base capacity and around $x_{\text{Nb}} = 0.4$, the activity coefficient of niobium is close to 10^{-1} in both rhodium and palladium. Consideration of these factors indicate the complexity of the acid-base bonding. Although in a mole of gas, there are not many electronic levels corresponding to a given electronic configuration because of the high degeneracy of many of the levels and the equivalence of levels of all the atoms in the gas. When the atoms are condensed to the solid metal, there are the same total number of levels in the mole of solid as in the mole of gas, but the degeneracies have been removed, including the equivalence of the different atoms, so that there are several times Avogadro's number of levels that form the metallic bands. The variation of the bonding contributions of the electrons in these must be characterized.

The data discussed above have calibrated the bonding for the acid-base intermetallics of the 4d transition metals. Experiments are now in progress combining Ti and V with Pd and Rh and also Ir and Pt to characterize the bonding when d orbitals from different main shells are combined. With these calibrations, it should be possible to make accurate predictions of the acid-base interactions of the transition metals. It may then be possible to provide complete compilations of thermodynamic properties and phase diagrams for all of the transition metals as was done for molybdenum. The intermetallic phases formed by generalized Lewis acid-base interactions have interesting properties. The recent paper of Jaksic (ref. 16) indicates unusual variations of electrocatalytic behavior through a sequence of acid-base titrations.

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