Title
HISTORY OF THE APPLICATION OF THE GENERALIZED LEWIS ACID-BASE THEORY TO METALS

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The history of my experiences with intermetallics has been found useful by students seeking my advice on which directions in science they should be emphasizing. In response to their question, I point to a mobile in my office consisting of seven hands pointing in different directions. Science comes up with so many unexpected developments that one's education should have a broad enough base to allow one to branch out in any direction to take advantage of unexpected opportunities. My historical presentation will be a personal account that I hope will serve as a guide to students. There have been many unexpected abrupt changes in my research.

As an undergraduate in 1936-40 at Cal Tech, I was especially stimulated in many directions by Professors Ernest Swift, Don Yost, Linus Pauling and by Howard Lucas with whom I did undergraduate organic chemical research. As a graduate student at the University of California, Berkeley, I was pointed in additional directions by Professors Ermon Eastman, Wendell Latimer, Joel Hildebrand, Gilbert Lewis, Gerhard Rollefson, and Axel Olson with whom I did my Ph.D. work on the kinetics of enolization of ketones.

Manhattan Project Challenge

In a paper presented at the ACS Gilbert Lewis Symposium [1], I have described how, after completion of my thesis, I was approached by Wendell Latimer in December 1942 to join the Manhattan Project. In contrast to my previous research on organic materials, I was asked to review the properties of all the elements and use predictive models, that Latimer had found so effective, to predict the properties of plutonium metal that was not yet available in macroscopic amounts. That is not quite correct. Latimer wanted me to predict the worst properties that plutonium might have. Then I was to devise methods of handling and processing plutonium with the worst possible properties. I was under the supervision of Professor Eastman and I had three outstanding B.S. students to work with. They were LeRoy Bromley, Paul Gilles, and Norman Lofgren. It turned out that my education had prepared me for the challenge. In addition, I had a liability that served as a bonus. My memory for specific numbers or facts is very poor and I have dealt with this problem by associating information with various models that allowed me to recover
facts by prediction. The use of such predictive models was essential to prepare for the handling of plutonium.

Our predictions did indicate difficult properties for plutonium. They were made worse by our assumption that plutonium would be high melting. This was due initially to the melting point of uranium in the literature being much too high because samples with oxide coatings were used and the liquid did not break through until well above the melting point of uranium. The work at Ames, Iowa on pure uranium provided a more reliable value. However, we did not anticipate how many different electronic configurations with varying numbers of 5f, 6d, 7s, and 7p orbitals had comparable bonding capability, taking into account promotion energies. In the liquid where the atoms are not restrained to lattice sites of fixed size, one can have a mixture of electronic configurations and sizes that yields a much better space utilization than close-packing of equal sized atoms. The high density of the liquid greatly stabilizes it and reduces the melting point.

Our assumption of the high melting point as well as the high reactivity of Pu metal led to the prediction that oxide containers could not be used for Pu as it would react to form gaseous suboxide species. Initially, there was another reason for avoiding oxides. An early bomb design required that oxygen be kept at a very low value. When one goes from an oxide to a sulfide of larger anion size, our models indicated that the higher oxidation states were destabilized relative to the divalent oxidation states and that the divalent sulfides would be stable solids in contrast to most of the refractory transition metal oxides. Thus, we initiated a project to characterize the sulfides of cerium, uranium and thorium. We also did some minor studies of Ba and Zr sulfides.

To be sure that plutonium metal could be cast and fabricated and still maintain the desired purity, we concluded that CeS, a yet undiscovered compound, could provide a crucible material that would be resistant to attack by strongly electropositive metals. We were able to prepare the compound and fabricate crucibles that were highly resistant to attack by metals.

As described in the Lewis Symposium paper [1], we met our Manhattan Project goals and we had sent 564 crucibles to Los Alamos by the end of 1944. In his review of plutonium metallurgy at Los Alamos during 1943-45, Cyril Stanley Smith [2] states, "Despite its fusibility, however, the handling of molten plutonium is rendered difficult by its extreme reactivity. No ordinary refractory was found to be satisfactory for crucibles in which to melt and cast very small pieces of the metal. Fortunately, an exotic one--cerium sulfide--had been studied by the chemistry group at Berkeley for use in vacuum at high temperatures, and they willingly gave us a supply of small crucibles. For several critical weeks these were, indeed, the only available containers in which the metal could be melted without serious contamination." One might get the impression that it was a fortunate accident that CeS crucibles were available at this critical time. Wendell Latimer's foresight in initiating the search for a plutonium container has not been adequately recognized.

In addition to our work on the development of the CeS crucible, we also devised a procedure for the analysis of the O, N, and H content of metals such as Pu and U. The unanticipated event that ultimately lead me to the study of intermetallics could be described as an accident. The CeS crucibles that we had developed were found to be so
highly resistant to attack by metals such as alkali and alkaline earth metals that could be boiled out of the crucible without attack and metals such as lanthanide and actinide metals that we thought that the "Impervium" crucibles could contain any molten metals. Thus, when we wished to calibrate our optical pyrometer using the melting point of platinum, we melted the platinum in a CeS crucible. To our dismay, the platinum ate through the crucible. X-ray diffraction indicated that the reaction $3\text{Pt} + 4\text{CeS} = \text{Ce}_3\text{S}_4 + \text{CePt}_3$ had taken place. From our thermodynamic data for CeS and Ce$_3$S$_4$, it was clear that CePt$_3$ must be extraordinarily stable.

Our apparatus for the analytical determination of oxygen impurities in actinide metals by the vacuum fusion method involved dropping a uranium sample into a molten iron bath in a graphite crucible and measuring the evolved carbon monoxide. We had difficulty due to the volatility of uranium, which acted as a getter for the carbon monoxide. In recognition of the capacity of platinum to reduce the thermodynamic activity of lanthanides and actinides, we replaced the iron by platinum. The vapor pressure of uranium was so greatly reduced that we had no more trouble.

After the war, the values of the thermodynamic properties of actinides and their compounds that had been evaluated together with the data for all of the elements were published in volumes of the National Nuclear Energy Series, Division IV--Plutonium Project Record and in Chemistry of Uranium. Updated revisions of most of these compilations have been published every decade or two. However, the main direction of our research was aimed at improving the predictive models that had been used on the Manhattan Project. In some instances such as the enthalpies of atomization of carbon and nitrogen, the accepted experimental data did not agree with our models. We were able to carry out new measurements that eventually convinced people that the older accepted values were in error. In some instances such as the data for the vaporization of halides such as cuprous chloride, we found that our model was inadequate. We had assumed that gaseous molecules would remain simple in high temperature vapors. Our work with cuprous chloride stimulated a broader examination of high temperature vaporization. We were able to prove that saturated vapors would become more complicated both in respect to the number of different species and the complexity of the high temperature species. Thus our vaporization model had to be modified to include gaseous polymers and a variety of unusual species [3]. Aside from some work on refractory borides and silicides, the main effort of our research was directed to characterization of high temperature vaporization that could be classified as astrochemistry as the species we were studying were also found in atmospheres of comets and stars. My return to the problem of the unusually stable intermetallics of cerium and uranium came about in an unexpected way.

Engel Theory of Metallic Bonding

In the late forties, the Danish scientist Niels Engel spent a sabbatical at Berkeley and introduced me to his theory of metallic bonding, that was a combination of G. N. Lewis' electron bonding model, as used by Linus Pauling for metals, with the relationship between electronic configuration and crystal structure discovered by William Hume-Rothery in the late twenties. It was clear from Engel's model why platinum interacted so strongly with cerium and uranium. The classical example of a generalized
Lewis acid-base reaction is the reaction of BF$_3$ and NH$_3$. BF$_3$ does not have enough electrons to use all of the 2p orbitals of boron, and one orbital is vacant. NH$_3$ has enough electrons to fill all of its valence orbitals, but only three pairs of electrons can be used to bond the three hydrogens and one pair is left nonbonding. By combining BF$_3$ and NH$_3$, the nonbonding pair of NH$_3$ is shared with the vacant orbital of BF$_3$, and all of the electrons and all of the valence orbitals are used in bonding. Exactly the same description can be given for the reaction of cerium with platinum or, in general, for the reaction of transition metals from the left-hand side of the periodic table with platinum group metals from the right-hand side of the periodic table.

If one starts with lutetium with only three valence electrons, and moves to the right toward Hf, Ta, W, and Re, the melting points and boiling points rise markedly as more electrons are available for bonding until the d$^5$s and d$^6$sp configurations of W and Re, that utilize all of the d orbitals in bonding, are reached. If one moves on toward Pt, the melting points and boiling points drop, since additional electrons going into the d orbitals will produce nonbonding pairs. For example, in going from d$^5$sp Re to d$^6$sp Os, the number of bonding electrons per atom is decreased from seven for Re to six for Os, with a pair of electrons left nonbonding. For Pt with a d$^7$sp$^2$ configuration there are two pairs of nonbonding electrons, and only six of the ten valence electrons are used in bonding. However, if the platinum atoms had Ce or Hf neighbors, for example, with vacant 5d orbitals, the nonbonding electrons would bond the Hf and Pt atoms together, and one could approach the bonding effectiveness of W or Re because both the orbitals and electrons could be fully used.

Although the Engel theory of metallic bonding opened up the possibility of very effective predictive models for metallic systems, I was so involved with high temperature gaseous species that I might not have ventured into metallurgy if it were not for another unexpected development. In 1962, Professor Paul Beck of the University of Illinois asked me if I would give a presentation of the chemist’s view of metallic bonding at a meeting at which similar presentations would be made by metallurgists and physicists. Niels Engel had been unable to have his papers accepted by metallurgical journals in this country and I thought this meeting would provide the opportunity to call attention to the value of Engel’s theory. I did present a summary of his theory, referring to Engel’s Danish publications, and mentioned that he had not been able to publish his English manuscripts. I noted that they were rejected because they were considered too original and novel [4]. Professor Pol Duwez of Cal Tech wrote a book review of the proceedings of Beck’s conference. He particularly emphasized the rejection of Engel’s novel ideas by the journals. As a result, Engel received invitations from these journals to resubmit his manuscripts and they were published. This experience entrapped me in the field of intermetallics. Many years later, I met Beck at a meeting and asked him why he would have invited me when my research was rather far removed from metals. His response was that he was not familiar with my current work but he recalled my work in the Manhattan Project and had assumed that I was still working with lanthanide and actinide metals.

Following my first publication on Engel’s theory, I received many requests to give seminars on metals and I prepared an extensive review [5]. I still had not put any graduate students to work on metals. However, in 1966, I was teaching an undergraduate
inorganic laboratory course in which the students undertook minor research projects. In the Lewis symposium paper [1], I have described how Gerald Stowe and Peter Riessenfeldt were able to establish very high stability for ZrPt$_3$ by the demonstration of the reaction of Pt with ZrC to form carbon and ZrPt$_3$ and by the extension of the Bronger and Klemm method [6] for reduction of lanthanide oxides by hydrogen in the presence of platinum to the reduction of ZrO$_2$ by hydrogen in the presence of platinum. At 1200 °C, the presence of platinum was found to lower the activity of zirconium by almost a factor of $10^{20}$. Although I published additional papers [7-9], my graduate student research still dealt with gases of importance for high temperature systems. Again an unexpected development changed the direction of my research. In 1969, I received a letter from Paul Wengert, an undergraduate student in metallurgy, who had read my papers and wanted to do Ph.D. research with me even though he was not a chemist. He was most productive and the results of his work [10] clearly established the strength of the acid-base interactions between a metal such as zirconium and the various platinum group metals.

Although I did not put any more graduate students to work on the intermetallics, I did work on extending the theory more quantitatively to the lanthanides and actinides by developing models for predicting their electronic configurations [11-14]. This work on lanthanides and actinides has been extended in later publications [15-17]. However, the main direction in application of the models for predicting properties of the intermetallics was in the demonstration that reliable predictions could be made for many metallic systems for which no experimental data were available. The power of the Engel theory of bonding in predicting properties of metals has been confirmed in many respects. For example, the theory predicted [5] that additions of all transition metals from the fifth group of V, Nb, and Ta through the eleventh group of Cu, Ag, and Au will stabilize the bcc structures of Ti, Zr, and Hf relative to the hcp structures even though many of these additives have close-packed structures. In the recent ASM compilation of phase diagrams [18], the predictions have been confirmed for all twenty-one of these transition metals. Many other examples can be given to verify the reliability of the predictions of the Engel theory. As one example of the ability to predict values for systems for which no experimental data exist, the thermodynamic properties and phase diagrams were provided for 101 of the binary systems of molybdenum [19,20]. With that job out of the way, my research program has been largely focused on the intermetallics and the improvement of the theoretical models. The use of atomic spectroscopic data to characterize the electronic configurations in metallic systems has been a most powerful tool. It provides prediction of the occurrence of various crystal structures and their variation of stability with temperature, pressure, and composition as illustrated in the molybdenum compilation. In addition to the references given above, there have been fifteen additional publications dealing with metallic systems in recent years. I could never have possibly anticipated that I would have become so deeply involved with the challenging intermetallics. I hope that the history of my experience will convince students that they should prepare themselves broadly so that they will be able to take advantage of all the unexpected developments that they will encounter in their careers.
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References


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A02, H02, P02, P03, T01, U01