

# Lawrence Berkeley National Laboratory

## Recent Work

### Title

THE GENERALIZED LEWIS-ACID-BASE THEORY: SURPRISING RECENT DEVELOPMENTS

### Permalink

<https://escholarship.org/uc/item/0mp2c3h2>

### Author

Brewer, L.

### Publication Date

1982-03-01

c.2



# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED  
LAWRENCE  
BERKELEY LABORATORY

## Materials & Molecular Research Division

FEB 21 1984

LIBRARY AND  
DOCUMENTS SECTION

Presented at the American Chemical Society Symposium,  
Las Vegas, NV, March 1982; and to be published in the  
Journal of Chemical Education

THE GENERALIZED LEWIS-ACID-BASE THEORY:  
SURPRISING RECENT DEVELOPMENTS

L. Brewer

March 1982

### TWO-WEEK LOAN COPY

*This is a Library Circulating Copy  
which may be borrowed for two weeks.  
For a personal retention copy, call  
Tech. Info. Division, Ext. 6782.*



LBL-14867  
c.2

## DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

THE GENERALIZED LEWIS-ACID-BASE THEORY:  
SURPRISING RECENT DEVELOPMENTS

Leo Brewer

Materials and Molecular Research Division  
Lawrence Berkeley Laboratory  
and  
Department of Chemistry  
University of California  
Berkeley, California 94720

March 1982

This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

**The Generalized Lewis-Acid-Base Theory:  
Surprising Recent Developments**

Leo Brewer

Materials and Molecular Research Division,  
Lawrence Berkeley Laboratory  
and Department of Chemistry,  
University of California, Berkeley

This symposium has been fascinating in its explorations of our roots -- the principles of the foundation of chemistry and the individuals who developed them. My roots go back to the MIT group by two paths: one through Cal Tech and the other through Berkeley. I completed my undergraduate studies at Cal Tech in 1940. I was fortunate to have the opportunity of a year of research with Professor Howard J. Lucas on reactions of unsaturated ketones. Compared to present-day students, I was rather naive about graduate schools. I went to Linus Pauling, the Chairman of the Department, to get some advice. He told me that I should go to Berkeley, which I did; I didn't even apply elsewhere.

Previous speakers have referred to Berkeley seminars chaired by G. N. Lewis and his succinct comments following each presentation. Joel Hildebrand tells a story about his first experience with the Berkeley seminars that illustrates the degree of interaction at all levels. He had just come from a university where the Professor's opinions were unquestioned. So he was terrified as to what would happen when, after Lewis expressed an opinion, a graduate student brashly disputed him. Lewis turned his head toward the student and remarked: "A very impertinent remark, young man, but very pertinent." The discussions were very valuable to the graduate students. Professor William C. Bray was particularly an aid to the students. Whenever a speaker left any point not completely clear, Bray was sure to ask for clarification.

One of the advantages of Berkeley in those days with a smaller student body, was the many opportunities for graduate students to speak at special seminars on a variety of topics not necessarily directly related to the stu-

dent's research. I think I must have given a seminar each semester. This emphasis on a broad development goes back to G. N. Lewis' definition of physical chemistry — "anything that is interesting," — and for him included economics, meteorology, anthropology, etc. William F. Giauque told a story at his retirement dinner that illustrates the emphasis on breadth of preparation. He described how he made the round of the Department each week to follow the research progress of every graduate student. This emphasis upon a broad preparation made a strong impression upon me. When students come to me for advice on which directions to pursue, I point to a mobile in my office with six hands pointing in different directions. I point out that surprises in science arise frequently enough so that one should have a broad background to be able to take advantage of new unexpected directions. Although my first research started in organic chemistry with Lucas and I did my thesis work under Professor Axel R. Olson on the effect of electrolytes upon the rates of aqueous reactions, I have since worked in the fields of ceramics, spectroscopy, astrochemistry, and metallurgy, as well as the general field of high temperature chemistry. Looking back, I realize that I could never have anticipated the directions that I would pursue, and I never regret the extra effort to prepare myself broadly.

---

The concepts of electron pair bonds, and the Generalized Lewis-Acid-Base theory were so well developed at Berkeley that it came as a surprise to me to find out later that these ideas were not immediately accepted. Particularly, the acceptance of the generalized acid-base concept was much delayed. William Jensen is discussing in his talk some of the problems that Lewis' ideas encountered, and covers in his recent book (1) the impact of the acid-base theory. My introduction to a surprising application of Lewis' acid-base concepts first arose in the Manhattan Project. When I had completed my thesis in December 1942, Professor Wendell M. Latimer approached me about working on an important secret government project. I agreed and he told me about the discovery of plutonium and the need to be prepared to handle and fabricate the metal before macroscopic amounts were available.

In this project, I worked with Professor E. D. Eastman as well as Professor Latimer, and with LeRoy Bromley, Norman Lofgren, and Paul Gilles. It was quite a jump from organic chemistry to the metallurgy of plutonium. To be sure that plutonium metal could be cast and fabricated and still maintain the desired purity, we concluded that a yet undiscovered compound CeS 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. The alkali and alkaline earth metals could be distilled from the crucibles without attack. However, one day when we wanted to calibrate our optical pyrometer against the melting point of platinum, we used a cerium sulfide crucible. The platinum chewed up the crucible. We found (2) that the platinum had reacted with the CeS crucible to form  $Ce_3S_4$  and  $CePt_2$ . We had characterized the thermodynamic stabilities of CeS and  $Ce_3S_4$ , and the  $CePt_2$  compound would need an extraordinary stability for such a reaction to proceed.

We had also been working on an apparatus for the analytical determination of oxygen impurities in actinide metals by the vacuum fusion method, which involved dropping an 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.

In the late forties, the Danish scientist Niels Engel spent a sabbatical at Berkeley and introduced me to his theory (3) of metallic bonding, which was a combination of Lewis' electron bonding model as used by Linus Pauling (4) for metals with the relationship between electronic configuration and crystal structure discovered by William Hume-Rothery (5) 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 combin-

ing  $\text{BF}_3$  and  $\text{NH}_3$ , the non-bonding pair of  $\text{NH}_3$  is shared with the vacant orbital of  $\text{BF}_3$ , 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  $d^5s$  and  $d^5sp$  configurations of W and Re are reached which utilize all of the d orbitals in bonding. If one moves toward Os, Ir, and Pt, the melting points and boiling points drop, since additional electrons going into the d orbitals will produce non-bonding pairs. For example, in going from  $d^5sp$  Re to  $d^6sp$  Os, the number of bonding electrons per atom is decreased from seven for Re to 6 for Os, with a pair of electrons left non-bonding. For Pt with a  $d^7sp^2$  configuration there are two pairs of non-bonding 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 non-bonding electrons would bond the Hf and Pt atoms together, and one could approach the effective bonding of W or Re due to matching of orbitals and electrons.

At the time, no indication was found in the literature of extraordinarily stable intermetallic phases. It was generally stated that intermetallic compounds did not have very negative enthalpies or Gibbs energies of formation. In 1962, Bronger and Klemm (6) were able to demonstrate the high stability of lanthanide platinum phases by achieving the reduction of the lanthanide oxides by hydrogen in the presence of platinum. In 1966, I was teaching an inorganic laboratory course where each student was expected to do a minor research project. I had explained to the class the possible role of generalized Lewis acid-base interactions in metallic systems, and Gerald Stowe attempted a test of the stability of Zr-Pt compounds. He heated  $\text{ZrC}$ , which is one of the most stable carbides, with platinum. He found (8) that the platinum chewed up the zirconium carbide to form  $\text{ZrPt}_3$ . One could describe the reaction as an oxidation by platinum as the carbon was displaced to form graphite. For the formation of  $\text{ZrC}$  from the elements,  $\Delta H^\circ/R$  is more negative



than -24,000 kelvin and the enthalpy of formation of  $ZrPt_3$  must be even more negative. The next year, Peter Riessenfeldt tried a more severe test. He used the method of Bronger and Klemm (6) of heating  $ZrO_2$  in hydrogen at  $1200^\circ C$  in the presence of platinum. From the Gibbs energy of formation of  $ZrO_2$ , he could calculate that the amount of water formed by reduction to zirconium metal would be infinitesimal. However, with platinum present, water streamed out of the apparatus.(9) From the weight loss and the volume of hydrogen gas, he was able to calculate that the activity of zirconium was reduced by almost a factor of  $10^{20}$  by the presence of platinum.

I had mentioned these results to John Margrave of Rice University and I received a phone call from him a few weeks later about an accident that resulted from checking our results. In our experiments, we had the zirconium already tightly bonded with either carbon or oxygen. Margave's student mixed hafnium and platinum powders and started heating. Nothing happened until about  $1000^\circ C$ , when diffusion rates became significant. Then the sample detonated and destroyed the apparatus; fortunately with no injuries. For the formation of  $HfPt_3$  from the elements, a calorimetric determination (10) has fixed  $\Delta H^\circ/R = -66$  kilokelvin. If one assumes for a mole of  $HfPt_3$ ,  $C_p/R = 14$ , one can calculate that after the reaction started at  $1000^\circ C$ , the temperature would shoot up more than  $4000^\circ$ . Such high stability is not an isolated example of strong acid-base reactions among metals. Grietje Wijbenga (11) has carried out a series of calorimetric and electrochemical measurements on intermetallic phases of uranium with Ru, Rh, and Pd. For the formation of  $UPd_3$ ,  $\Delta H^\circ/R = -66 \pm 4$  kilokelvin. Other examples of strong acid-base reactions in metallic systems have been summarized.(12,13) The formation of  $ZrPt_3$  and similar intermetallic compounds is undoubtedly the cause of the so-called "hydrogen embrittlement" of Pt-Rh thermocouples in oxide protection tubes under reducing conditions.

Figure 1 illustrates the interaction of Zr with Pt showing just the d electrons and orbitals of Zr and Pt. Zr in the body-centered cubic structure (12) has the configuration  $d^3s$ , and Pt in the face-centered cubic structure has the configuration  $d^7sp^2$ . Four of the d electrons of Pt are non-bonding in pure Pt. When Zr and Pt are combined to allow the electron pairs of Pt to utilize the vacant d orbitals of Zr, all ten d electrons of Zr and Pt can be

used in bonding the nuclei together, resulting in an increase of four bonding electrons.

The strength of the interaction depends upon the degree of localization of the d orbitals. As nuclear charge is increased from Cr to W, for example, the increased nuclear charge has a greater effect upon the closed 5s,p electrons than upon the 5d electrons because of the greater penetration to the nucleus of the s and p electrons. Thus in going from Cr to W, the d orbitals become much more exposed, resulting in a much higher enthalpy of sublimation for W than for Cr. Also, as one moves from left to right in the Periodic Table, the d orbitals are at first rather expanded, but contract with increasing nuclear charge as one moves to the right.

Due to crystal field effects, the d orbitals do not remain equivalent, and some contract more than others and become quite localized. Other orbitals expand and retain reasonable bonding ability. For the 3d metals from Cr to Ni, some of the orbitals are sufficiently contracted that they can contain unpaired electrons whose interaction with adjoining atoms is so reduced that they remain unpaired and magnetic as in the free gas. Thus ferromagnetism is found for some of the 3d metals but for none of the 4d or 5d metals, for which the orbitals are sufficiently expanded to provide bonding interaction. However, the 4f orbitals are sufficiently localized to yield magnetic lanthanide metals. The 5f orbitals are sufficiently expanded so that magnetism does not occur until the heavier actinides. As the strength of acid-base interactions using the d orbitals will depend upon the degree of localization, there should be substantial changes from the 3d to 5d metals. For the right hand 3d metals, the non-bonding pairs are in the most localized orbitals and are not very basic. The base strength of metals of groups VIII to XI should increase from 4d to 5d. Figure 2 presents some early results (12) on fixing the strength of acid-base interactions using ternary phase equilibria in a system involving graphite, zirconium, and platinum group metals. The excess partial molal Gibbs energy of Zr in the platinum group metals is indicated. The base strength of the 5d metals is substantially greater than that of the 4d metals. The base strength of Re is seen to be very small, as the  $d^5sp$  configuration provides a good match of orbitals and electrons such that all are used in bonding. As one goes from Os to Ir to Pt, the number of non-bonding elec-

trons increases and the base strength increases, but eventually the increasing nuclear charge will draw the non-bonding pairs in so closely that they can not overlap efficiently into the vacant orbitals of Zr. Thus the base strength of Au is significantly lower than that of Pt or Ir.

The above discussion had emphasized the role of the inner-shell d electrons and orbitals in the acid-base interactions because they play such a large role in the transition metal interactions. However, the acid-base interactions using outer shell s and p electrons is well established. It is recognized that the tetrahedral structure of GaAs corresponds to a donation of an electron pair from As to the vacant p orbital of Ga to form the  $sp^3$  configuration corresponding to Ge.

Mixtures of metals can not only undergo acid-base reactions when one of the metals has non-bonding valence electrons and the other has low-lying empty orbitals, but metals can show amphoteric behavior as do the oxides and hydroxides. Palladium is a good example. In the ground state of the gaseous atom, the electronic configuration is  $d^{10}$ . If it stayed in that configuration, it should be a noble gas. In the pure metal, it promotes d electrons to p orbitals to reach a configuration between  $d^{7.5}sp^{1.5}$  and  $d^7sp^2$ , corresponding to the face-centered cubic structure. With  $d^7sp^2$ , only six electrons are used in bonding and four are non-bonding. The electron pairs can not concentrate between the nuclei to provide bonding because of the Pauli Exclusion Principle. If an acid with vacant orbitals such as Zr or U is present, all of the electrons can be used in bonding. Aluminum has the ground state configuration  $s^2p$  in the gas, which provides only one bonding electron. However, by promoting to  $sp^2$ , all of the electrons can be used in bonding. Although the extra bonding due to two additional electrons offsets the promotion energy, the promotion energy penalty is quite high. If aluminum is added to palladium and the palladium remains in its  $d^{10}$  ground state, the aluminum can use all of its electrons without promotion by acting as a base and donating an electron pair to the vacant s orbital of the palladium. Thus in the presence of a strong acid such as uranium, palladium is a base. In the presence of a strong base such as aluminum, palladium is an acid. It is interesting that both Al and Pd have the cubic-face-centered structure corresponding to 1.5 to 2 s,p electrons per atom according to the Engel correlation. However, the AlPd compound has

the body-centered cubic OsCl type structure corresponding to 1 to 1.5 s,p electrons per atom. With all of the palladium valence electrons in the inner shell d orbitals, the three s,p electrons of the aluminum are shared between Al and Pd for an average of 1.5 electrons per atom.

One normally considers aqueous  $H^+$  and  $OH^-$  as examples of very strong acids and bases. If one were to add 10M HCl to an excess of 10M NaOH at room temperature, the activity of  $H^+$  would be reduced by a factor of  $10^{16}$ . Dissolving Hf or U in an excess of palladium or platinum would reduce the activity of Hf or U at room temperature by a factor of more than  $10^{90}$ . The strong acid-base reactions profoundly affect the chemistry of actinides, lanthanides, and transition metals from the left side with vacant d orbitals when added to the platinum group metals. This has been a most surprising extension of the Lewis acid-base concept.

Lewis' concept of acids and bases has not been readily accepted in the past. There is considerable resistance to the extension to metallic systems. For example, Mogutnov and Shvartsman (14) remark: "Evidently, from this point of view the strongest interaction between the components of an intermetallic compound can be expected if the transition-metal components lie at opposite ends of horizontal series of the Periodic Table. These ideas, with allowance for changes in the number of d-electrons and in nuclear charge as between the different elements, have provided satisfactory qualitative explanations of the peculiarities in the heats of formation of intermetallic compounds. However we note that Brewer's model of the formation of intermetallic compounds postulates electron transfer from "right-hand" to "left-hand" elements, which is opposite to the classical electronegativity concept."

On this basis of being contrary to the classical electronegativity concept, they reject the Lewis acid-base model. However they did not carefully read Pauling's account of the role of electronegativity under such circumstances. In his discussion (4) of the interaction of Ga with As, or Al with P to form the tetrahedral structure consistent with the  $sp^3$  configuration, he remarks: "It is interesting that this effect involves the transfer of electrons to the more electropositive atoms (the stronger metals); that is, in the opposite direction to the transfer of electrons that takes place in the formation of ions in electrolytic solutions."

In the formation of  $\text{Cr}(\text{CO})_6$  from acidic Cr and basic CO, it is understood that the actual charge on the Cr does not correspond to the formal charge of minus six. The reduction of charge is described in terms of backbonding through higher orbitals. In the U-Pd interaction, the sharing of palladium electron pairs between the uranium and palladium nuclei must result in a movement of other bonding electrons away from the uranium interacting with a palladium. The important aspect of acid-base interactions in metallic systems is that electrons are not free to occupy all parts of physical space. They are primarily restricted to orbital volumes. The interaction of acids and bases makes it possible for the electrons to occupy allowed space and still interact with two or more nuclei.

---

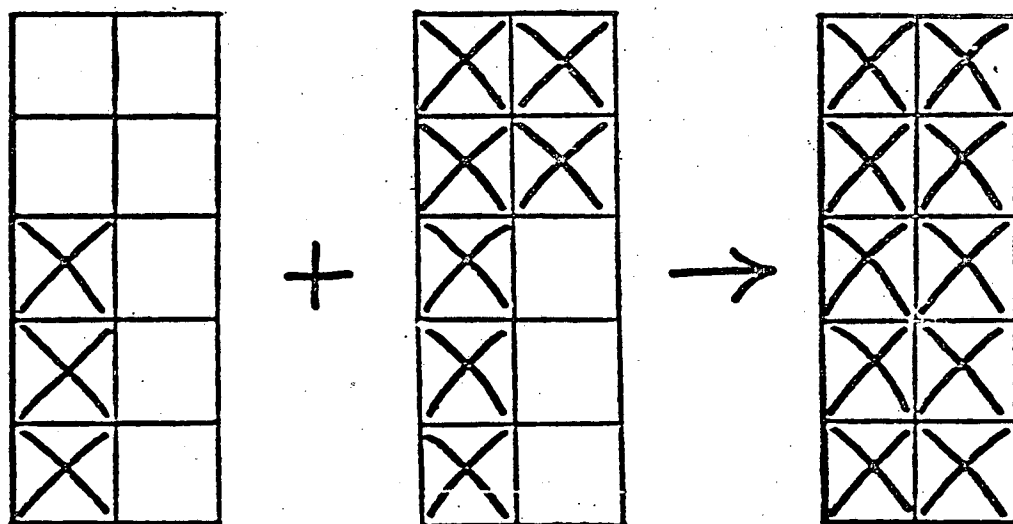
This work was supported by the Division of  
Materials Sciences, Office of Basic Energy  
Sciences, U.S. Department of Energy under  
contract No. DE-AC03-76SF00098

---

REFERENCES

- (1) William B. Jensen, The Lewis Acid-Base Concepts: An Overview, John Wiley, New York, 1980.
- (2) E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles, N. L. Lofgren, J. Am. Chem. Soc. 72, 2248-50 (1950); J. Am. Ceram. Soc. 34, 128-34 (1951).
- (3) N. Engel, Ingenioeren NiO1 1939), M1 (1940); Haandogi Metalläre (Selskabet for Metalforskning, Copenhagen, 1945); Kemisk Maandesblad 30(5), 53; (6), 75; (8), 97; (9), 105; (10), 114 (1949); Powder Met. Bull. 7, 8 (1954); Amer. Soc. Metals. Trans. Quart. 57, 610 (1964); Acta Met. 15, 557 (1967).
- (4) L. Pauling, Proc. Roy. Soc. London Ser. A 196, 343 (1949); The Nature of the Chemical Bond, p. 432 (Cornell Univ. Press, Ithaca, N. Y., ed. 3, 1960).
- (5) W. Hume-Rothery, The Metallic State (Oxford Univ. Press, Oxford, 1931); Structures of Metals and Alloys (Institute of Metals, London, 1936).
- (6) W. Bronger, W. Klemm, Z. anorg. allg. Chem. 319, 58-81 (1962).
- (7) L. Brewer, Acta Met. 15, 555 (1967).
- (8) Gerald Stowe: Report to Prof. L. Brewer for Chemistry course 106, Univ. of Calif., Berkeley, June 2, 1965.
- (9) Peter Riessenfeldt: Report to Prof. L. Brewer for Chemistry course 106, Univ. of Calif., Berkeley, 1966.
- (10) V. Srikrishnan, P. J. Ficalora, Metall. Trans. 5, 1471 (1971).
- (11) Grietje Wijbenga, Thermochemical Investigations on Intermetallic  $UMe_3$  Compounds (Me = Ru, Rh, Pd), Ph.D. Thesis, University of Amsterdam, Dec. 1981.
- (12) L. Brewer, P. R. Wengert, Metall. Trans. 4, 83-104, 2674 (1973).
- (13) P. R. Wengert, L. Spanoudis, J. Am. Ceram. Soc. 57, 94-61 (1974).
- (14) B. M. Mogutnov, L. A. Shvartsman, Russ. J. Phys. Chem. 54(3), 331 (1980).

## METALLIC LEWIS-ACID-BASE INTERACTIONS



d orbitals of

Zr  
*acid*Pt  
*base*

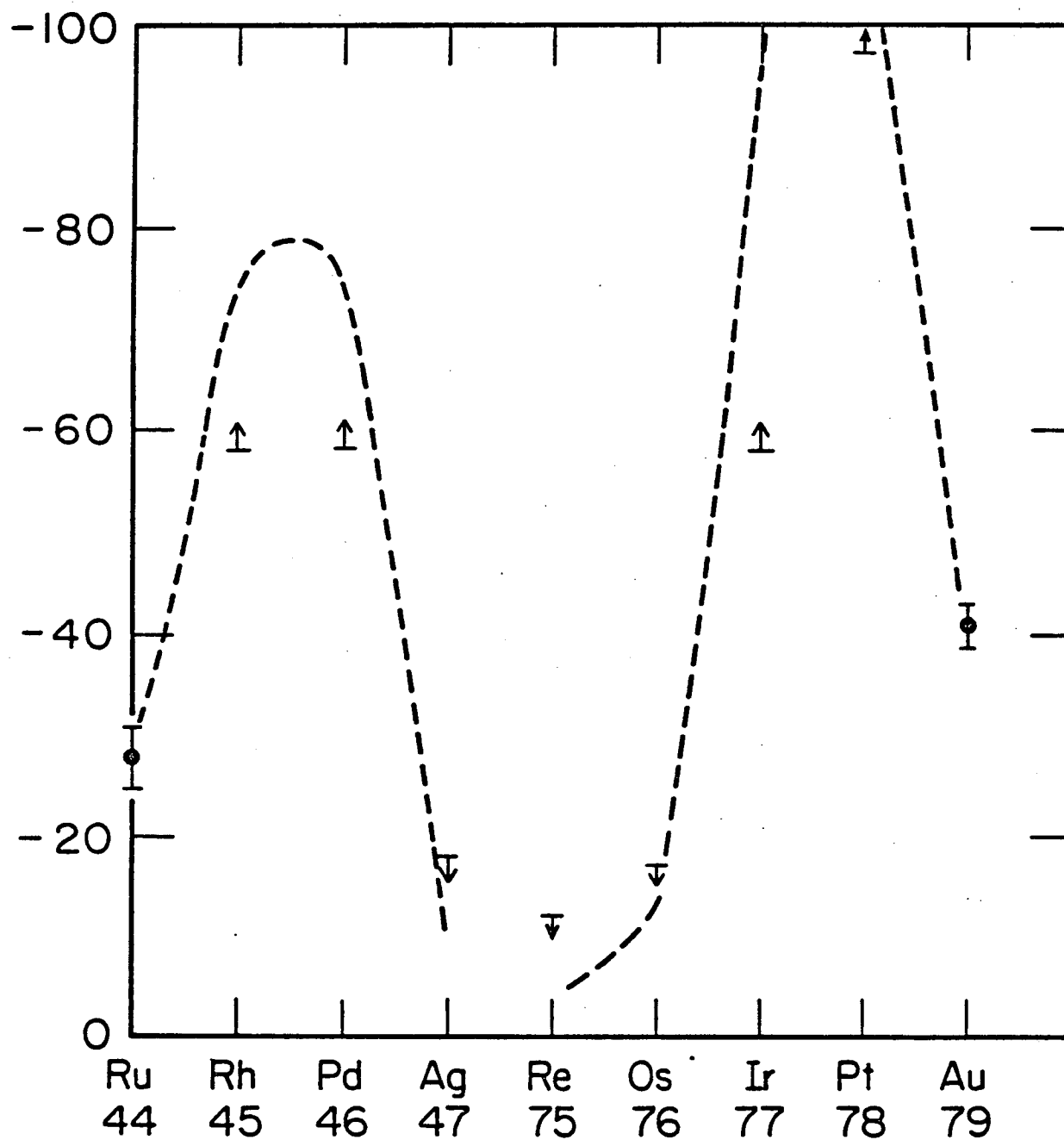
ZrPt

6 bonding e

4 non-bonding e

10 bonding e  
*d electrons*

Fig. 1



XBL722-2471A

Fig. 2 Excess partial molal Gibbs energy of Zr in kcal/gram atom at low concentrations in Ru, Rh, Pd, Ag, Re, Os, Ir, Pt, and Au at 1800 K.



This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT  
LAWRENCE BERKELEY LABORATORY  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA 94720