

Lawrence Berkeley National Laboratory

Recent Work

Title

RELEVANCY OF RESEARCH

Permalink

<https://escholarship.org/uc/item/3v41n9pn>

Author

Brewer, Leo.

Publication Date

1971-10-01

Presented at the Electrochemical
Medal Palladium Medal Address at
Meeting of the Electrochemical
Society, Cleveland, Ohio, Oct. 3-6, 1974;
Journal of the Electrochemical Society

LBL-195
Preprint

2

RELEVANCY OF RESEARCH

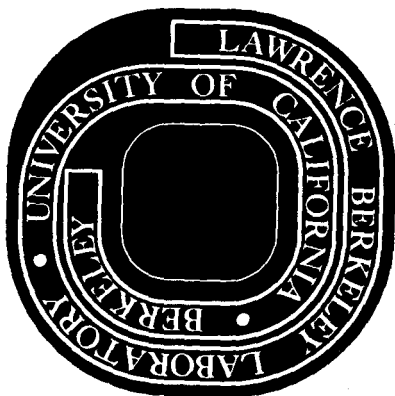
Leo Brewer

October 1971

AEC Contract No. W-7405-eng-48

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. 5545*



LBL-195

2

4

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.

RELEVANCY OF RESEARCH

Leo Brewer

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

1971 Electrochemical Medal Palladium Medal Address at meeting
of the Electrochemical Society, Cleveland, Oct. 3-6, 1971

Relevancy of Research

1971 Electrochemical Medal Palladium Medal Address

It is customary for the Palladium Medallist to present a lecture on his research work. I would like to try something a little different; I will follow the tradition, but my emphasis will not be so much on the results of this research as on the reasons for initiating the research/ and some of the consequences of the research/ I wish to use some examples of the research work of my group to examine the question of political relevancy. It is my contention that the current/pressure to orient all research toward quickly attainable practical results will be destructive of research progress and will seriously handicap the development of practical results. I wish to discuss the criteria for relevancy of fundamental research.

I think that the incident that led me to choose this topic was the remark of a colleague at the time that the announcement appeared in the Journal of the Electrochemical Society of my selection as the 1971 Palladium Medallist. He expressed surprise that I should be honored by the Electrochemical Society inasmuch as I hadn't published any research on electrode potentials. I, of course, pointed out to him that the Society was not that parochial and had a broad interest in a variety of materials and processes and that I had been a member of the Society for quite a few years and had published papers^{1,2} in the Journal. However, the question of why the Electrochemical Society should think my work of value brought up the aspect of relevancy of research along the lines that Alvin Weinberg has emphasized; namely, the extent to which the research might be of value to other disciplines.

As my emphasis will be on the reasons for doing the research and some of the consequences of the results, I will not discuss the experiments in

as much as possible detail and will try to describe them/in words rather than to use slides showing equations or equipment. I hope that I have not overestimated my ability to explain things by just waving my hands.

Much of my research work has dealt with vapor pressures and I wish to examine the relevancy of several examples of vapor pressure research. The determination of the vapor pressure of any material is a useful addition to our body of knowledge, but, in general, such an experiment would not be considered very exciting or relevant. Yet I put my first two graduate students to work on the study of the vaporization of graphite and cuprous chloride. Why would a graduate student want to devote his thesis work to the study of cuprous chloride vapor, especially since there had been several previous concordant determinations of the vapor pressure of cuprous chloride? Our work on the Manhattan Project during the war required information about the volatilities of many materials and we had developed a rather good understanding of the factors fixing the vapor pressure of a large variety of materials and ^{we} felt that we could make reasonable estimates of enthalpies and entropies of vaporization. However the reported entropy of vaporization for cuprous chloride did not conform to our expectations and it was very important for us to find out whether the data for cuprous chloride were in error or whether our model for predicting vaporization behavior was faulty. This is an important criterion for relevant research. Although the experiment is directed toward a specific substance, the results will be applicable to a better understanding of a large group of substances. (Insert *)

Norman Lofgren, who carried out this research work, found that our model was incomplete. He was able to demonstrate³ that cuprous chloride

* An experiment should be designed not just to give a result. It should give a Yes or No answer in regard to the validity of a general model.

the
vaporized largely to/trimer, Cu_3Cl_3 , which has a puckered ring structure with alternating copper and chlorine atoms. Because of the ring structure the entropy was much lower than we had expected on the basis of either monomer or dimer models. This work required us to reexamine our ideas about the role of polymers and other complex molecular species in high temperature vaporization processes and a general theory was developed⁴ which predicted that complex species would be quite prevalent in high temperature saturated vapors. I won't go through the details of this theory as I discussed it in my Electrochemical Society Lecture last year, but the final result can be stated in this manner: For any vapor in equilibrium with a condensed phase, there will be generally one gaseous species that predominates at low temperatures. There will be a variety of minor species. From Trouton's rule, (insert *) have higher heats of vaporization than the major species and therefore their partial pressures will increase more rapidly with temperature than the partial pressure of the major species. The higher the temperature, the higher the proportion of the minor species. These minor species can be complex polymers and the saturated vapor at the very highest temperatures approaching the critical temperature, will be a complex mixture of many species.

Thus Norman Lofgren's experiments on cuprous chloride vapor did much more than clarify the behavior of cuprous chloride. They led to a much more complete understanding of the vaporization behavior of all materials. His results and the resulting vaporization theory stimulated a great deal of work on high temperature vapors. A variety of techniques, but especially the mass spectrometer, have confirmed the predicted complexity of high

* the entropy of vaporization, which is due largely to translation contribution of the gas, is known to be similar for all of the species. Thus the minor species with more positive free energies of vaporization.

temperature vapors. Without recognition of the complexity of high temperature vapors with respect to the number of different species, with respect to size and complexity of the molecules, and with respect to unusual oxidation states, quite erroneous predictions would be made about the high temperature behavior of many materials. (Insert *) / Norman Lofgren's experiments have had considerable practical results in alerting engineers in developmental work to the variety of reactions that they must take into account in their design work. These considerations have been important in the nuclear power reactor development, in the space program, in crystal growth and thin film preparation by vapor deposition, and in many other applications. Yet, under the criteria of relevant research that appear to be developing currently, an experiment of the type carried out by Norman Lofgren would probably not be funded because cuprous chloride vapor is not of practical importance.

I would maintain that the experiment that would be of greatest relevance and of great practical importance in the long run is not the one carried out with an immediate practical application in mind, but the one which offers the possibility of increasing our understanding of the properties of large groups of substances and thus the one that will be of value for many practical applications including those that lie yet/^{far}in the future. Many applications are quite impossible and could not even be considered until the background of fundamental understanding has been established to point the way to new applications. When I try to make a judgement of which of two experiments to carry out, my choice of highest relevancy is based on the question of which will increase my general understanding to the greatest extent.

* Thermodynamic calculations, no matter how precisely done, are worthless if the major species are not recognized and the correct net reactions are not considered.

From the discussion of the cuprous chloride experiments by Norman Lofgren, my second graduate student, I would like to turn to the work on the vapor pressure of graphite by Paul Gilles, my first graduate student. In contrast to cuprous chloride, we now are considering a material of considerable practical importance, but this was not the principal factor that led us to this problem. / (insert *) Several important general scientific questions were being asked in this research. The first dealt with the range of validity of the Langmuir method of determining vapor pressures by measurement of the rate of vaporization into a vacuum. The second dealt with the interpretation of observed predissociations in spectra of diatomic molecules along with other spectroscopic questions such as the validity of the Birge-Sponer method of estimating dissociation energies of diatomic molecules by extrapolation of vibrational level spacings and the proper use of promotional energies for prediction of bond energies. The generally accepted value at that time of 125 kcal/gram atom for the enthalpy of sublimation of monatomic carbon did not fit in with our models for estimating melting points, boiling points, and bonding energies. The resolution of these questions was essential if we were to maintain confidence in our ability to predict properties of materials generally.

new ¶ Paul Gilles chose an experimental method that provided a clear unambiguous answer. The rate of vaporization of graphite into a vacuum had been previously well established. Evaluation of those results by the Langmuir equation yielded an enthalpy of sublimation around 170 kcal/gram atom carbon. These results were reconciled with the accepted 125 kcal/gram atom carbon by assuming an additional barrier to sublimation or condensation

* The choice of the material of study depends upon which material would put the model in question to the most severe test and not upon the practical applications of the material.

for graphite such that, at a temperature of 2600°K, carbon atoms vaporized at a rate 6,000 times smaller than would be expected from the equilibrium vapor pressure. Likewise, it required 6,000 collisions of a carbon atom with graphite surfaces before it had appreciable probability of sticking to the surface. This interpretation also could be reconciled with the spectroscopic predissociation data for carbon monoxide. Another possible interpretation would yield 141 kcal/gram atom for the enthalpy of sublimation of graphite and 300 collisions of a carbon atom with graphite for condensation. The third interpretation yielded 170 kcal/gram atom and a vaporization coefficient close to unity.

The experiment carried out by Paul Gilles was a Knudsen cell determination of the vapor pressure of graphite for which the ratio of vaporizing area of the graphite to orifice area through which the vapor could escape was 250. The logic was very simple. Each of the three models predicts distinctly different sublimation behavior for the Knudsen cell experiments compared to the Langmuir type experiment. If either 125 or 141 were the correct enthalpy of sublimation, the vapor pressure should increase as the orifice area was reduced at a rate proportional to the ratio of surface area to orifice area. At 2600°K, the observed pressure should increase from the vapor pressure of $10^{-6.2}$ atm. indicated by the Langmuir experiment to reach limiting values of $10^{-3.7}$ and $10^{-2.4}$ atm. for enthalpies of 141 and 125 kcal, respectively. With a ratio of surface area to orifice area of 250, the observed pressure should be $10^{-3.8}$ atm. for an enthalpy of sublimation of either 141 or 125 kcal. The observed values were around $10^{-6.0}$ atm. or 160-fold smaller than expected if either of the two lower

enthalpy values were correct. Thus both 141 and 125 kcal could be conclusively rejected as values of the enthalpy of sublimation of graphite.

As the spectroscopic predissociation data for carbon monoxide could be interpreted only on the basis of discrete atomic dissociation products and thus allowed only the possibility of 170, 141, or 125 kcal with no intermediate values, the Knudsen cell measurements allowed a unique evaluation of the predissociation data to yield an accurate value of the enthalpy of sublimation of graphite and dissociation energy of carbon monoxide.

These unambiguous conclusions were quite independent of any complications due to polymeric species in carbon vapor. From the results of Lofgren's experiments on cuprous chloride, which were in progress during the time that Gilles was doing the graphite studies, he was well aware and, in fact, part of his thesis was devoted to the study of Swan bands of the possibility of polymers/ However, any polymeric species must add spectrum of dimeric carbon. to the monatomic carbon partial pressures that would be attained in a Knudsen cell corresponding to each of the three enthalpies of sublimation. The fact that the observed Knudsen cell pressure did not approach the value expected for an enthalpy of sublimation of 141 kcal, even if all of the vapor were considered to be monatomic, excludes either 141 or 125 kcal as possible values. Gilles did observe a higher pressure than would be expected for 170 kcal if the vapor were entirely atomic and this higher by mass spectrometer studies pressure has since been shown/to be due to polymers. The polymeric contributions have no effect upon the conclusions of the Knudsen cell experiments since the total pressure was still more than an order of magnitude smaller than the monatomic pressure that should have been attained if 141 kcal were correct.

At the time of publication⁵ of these results, there was a very strong reaction/since the replacement of 125 kcal by 170 kcal for the enthalpy of sublimation of carbon caused considerable disruption in many of the current models for treatment of bond energies and spectroscopic data. It took many confirmatory experiments before the new value was completely accepted.

The questions that were posed in Gilles' Knudsen cell work and also in his spectroscopic study of the diatomic polymer C_2 have been pursued by later students in my laboratory. In particular, the question of the validity of the Langmuir method of determining vapor pressures was extended to sodium carbonate⁶ by Ketil Motzfeldt and to phosphorus and arsenic⁷ by James Kane, and several very useful generalizations have resulted. One is the expectation that vaporization or condensation coefficients for atomic solids vaporizing to gaseous atoms are expected to be close to one, probably within a factor of two. On the other hand, vaporizing of a solid which involves molecular units that must rearrange their structure considerably upon vaporization can involve very small vaporization coefficients. For the example, the vaporization of P_4 tetrahedral molecules from red phosphorus, which has almost flat planes of phosphorus atoms, requires a very substantial distortion of the lattice to produce a P_4 tetrahedron and the vaporization coefficient is of the order of 10^{-6} . / Likewise the vaporization of linear carbon dioxide molecules from a melt of sodium carbonate in which the carbonate ion has a triangular arrangement of oxygen atoms around the carbon involves a very low vaporization coefficient. The Langmuir method of vapor pressure determinations has been extremely useful for the very non-volatile refractory materials and these studies of the kinetics of

* It has also demonstrated that catalysts can bypass the barrier. Addition of liquid thallium provided a means for phosphorus to dissolve in a medium where rearrangement can take place more easily.

vaporization processes have clarified the conditions of reliable application of the Langmuir method. It has been satisfying to me to follow the progress made through extension of these earlier studies by students and colleagues of mine such as Alan Searcy, Gerd Rosenblatt, and Gabor Somorjai.

I have chosen/ the research projects of my first two graduate students because a quarter of a century provides / ^{to discuss} ^{sufficient time} to judge the relevancy of their research. In both instances, their results were important not alone for the determination of properties of cuprous chloride and graphite, but because they have had far reaching influence upon our understanding of the properties of many types of materials and they have considerably improved our ability to predict the properties of materials for which values are unknown, they have clarified the application of a number of methods of determining vapor pressures and bond energies, and more generally have tested various models that scientists have used to represent chemical processes.

In subsequent research by later graduate students, we have tried to maintain the same standard of relevancy in choice of research problems. I regret that I do not have the time to mention their work, but I would like to devote the remaining time to illustrate the interaction between apparently unrelated studies. Gilles' work on the spectroscopic study of diatomic carbon in carbon vapor started a chain of investigations using spectroscopic techniques. These have led to spectroscopic studies of various carbon species, halides, and oxides. In my Electrochemical Society Lecture last year, I mentioned some of the new results we have obtained for oxides and in particular the evidence that we have finally obtained

for triplet ground states for magnesium and calcium oxide gases that will significantly change the tabulated thermodynamic data for these molecules. As I explained at that time, the work on the oxides came directly from the earlier work on diatomic carbon and I wish today to pursue an interesting relationship between our spectroscopic studies and our work on refractory compounds of the transition metals that was initiated by our Manhattan Project work on the sulfides of barium, cerium, thorium, and uranium/ In as much as palladium metal plays a role in the connection between spectroscopic data and properties of compounds of the transition metals, this is a /appropriate topic for the Palladium Medal Address. In fact the relationship between the spectrum of C_2 and palladium metal goes back one hundred and seventy years/when the English chemist William Wollaston discovered the element palladium. He was a versatile scientist who made important contributions to the development of optics and used his equipment to discover some spectral bands in the light emitted by a candle that are now known as the Swan bands of C_2 , the same bands studied by Gilles.

(insert
separat
page)

The relationship between electronic configuration and chemical behavior is well established. The chemical behavior of each element is determined by the number of valence electrons, the electrons outside closed shells or subshells, and by the character of the valence electrons, e.g., the proportion of s, p, d, and f electrons. The spectroscopic data for the gaseous atoms provide information on the energies of electron configurations with varying proportions of s, p, d, and f electrons. I wish to emphasize this relationship for the transition metals.

Insert to page 10

I have been accused of being a dilettante jumping from one field to another. I have published not only in various chemical and physical chemical journals but also in journals of metallurgy, ceramics, astronomy, optics, and geology. However, these diverse activities are closely tied together. All properties of materials depend upon the interactions of electrons with one another and with the nuclei and in that respect, all properties of materials are intimately connected and spectroscopy yields a special insight into the behavior of the electrons.

The relationship between electronic configurations and properties can be illustrated by examining the elements of the Periodic Table from Na to Cl for which the valence electrons are in the 3s and 3p subshells. The electronic configurations⁸ for the solid state of each of these elements are as follows:

Na	Mg	Al	Si	P	S	Cl
s	sp	sp ²	sp ³	s ² p ³	s ² p ⁴	s ² p ⁵

Both the melting and boiling point steadily rise from Na to a maximum at Si as the number of bonding electrons per atom increases from one to four. Beyond Si additional electrons must be paired internally and the number of electrons available for bonding between the atoms decreases to two for sulfur and one for chlorine.

Let us now consider the sequence from Rb to Pd for which valence electrons in the 4d, 5s, and 5p subshells do not differ much in energy. The low-lying electronic configurations^{8,9} for the solid states of each of these elements are as follows:

Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
s	ds	d ² s	d ³ s	d ⁴ s	d ⁵ s	d ⁵ sp	d ⁶ sp	d ⁶ sp ²	d ⁷ sp ²
	sp	dsp	d ² sp						

The melting and boiling points rise with increasing number of bonding electrons to maxima at Nb and Mo and then decrease as the number of bonding electrons decreases as d electrons must be paired internally rather than between the atoms.

For the Na to Cl sequence, each element has a different proportion of s and p electrons and each of these seven elements has a different crystal structure. For the Rb to Pd sequence, the electrons of the inner 4d orbital do not extend out far enough to control long range order. The electrons of the 4s and 4p orbitals are found only as s, sp, or sp^2 and only the body-centered cubic, hexagonal close-packed, and cubic close-packed structures of Na, Mg and Al, respectively, are found for the ten metals Rb to Pd. Sr, Y, and Zr have / ^{electronic} configurations so close in energy that more than _{is observed} one stable crystal structure/ depending upon the temperature.

Two decisive experiments can be proposed to test the role of electronic configurations upon the chemical behavior of elements. One experiment can take advantage of the two structures of Zr: the body-centered cubic structure at high temperatures with electronic configuration d^3s and the hexagonal close-packed structure at low temperatures with configuration d^2sp . In contrast to the 5s and 5p electrons, the electrons of the inner 4d orbital are largely localized between nearest neighbors and d electron bonding resulting largely from overlap of the d orbitals. To make best use of the d electron bonding in alloys, the d electrons available for bonding for the alloy constituents should match as closely as possible. If Pd with three bonding d electrons were added to Zr, which of the two structures of Zr would be stabilized? We would predict that the body-centered cubic phase with 3 bonding d electrons would be stabilized relative to the phase with d^2sp configuration. This is found to be true not only for Pd and Pt but for all of the transition metals to the right of Zr since all have three or more bonding d electrons.

An alternative confirmation of the role of electronic configurations is provided by the phase transformations of Ti, Zr, Hf, Mn, Fe, and Co. Because of the poor overlap of the d orbitals, increase of pressure will improve d bonding and enhance the stability of the phase with the largest number of bonding d electrons. The body-centered cubic structure always has an electronic configuration with more d electrons than for the close-packed structures. For the elements on the left hand side of the transition series such as Ti, Zr, and Hf, all of the d electrons are used in bonding and the bcc structure with the greatest number of bonding d electrons should be stabilized by pressure relative to the close-packed structures. For transition metals to the right, the bcc structure with the greatest total number of d electrons has the most paired d electrons and therefore the fewest bonding d electrons. For those metals, pressure should stabilize the close packed structures. All of these predictions have been confirmed.

The second decisive experiment tests the prediction of extremely stable intermetallic compounds.

(no new para.) When the sequence Na-Cl is compared to the Rb-Pd sequence, we note that the d orbital acts as a sink for electrons and thus extends the occurrence of the metallic structures of Na, Mg, and Al over the entire transition metal sequence. Elements such as Zr, with unused d orbitals, should act as acids in the generalized Lewis acid sense while elements such as Pd, with so many d electrons that they are paired internally and are not used in bonding, should act as bases. A combination of the two elements should result in electrons from Pd using the unoccupied orbitals of Zr with an increase in the number of electrons contributing to bonding. A decisive test of this concept was carried out by Paul Wengert as part of his thesis work. He heated palladium with zirconium carbide, one of the most stable carbides known. The palladium displaced the carbon forming $ZrPd_3$ and graphite. He found that other platinum group metals such as Rh, Ir, and Pt behaved similarly. In confirmation of the model described above, experiments have demonstrated that these intermetallic compounds are among the most stable compounds known.

I would like to finish with one more demonstration of the value of interaction of atomic spectroscopy and metallurgy by extending the comparison of the Na-Cl and Rb-Pd sequences to the next sequence containing the lanthanides for which the 4f electrons must be considered along with 5d, 6s, and 6p electrons. The availability of d and f orbitals acting as electron sinks extends the occurrence of the body-centered cubic, hexagonal close packed, and cubic close-packed structures of Na, Mg, and Al by an additional fourteen elements. Palladium is again found to favor the body-centered cubic forms ($f^n d^2 s$ configuration) of the lanthanides just as for

the example of Zr considered above. Also extremely stable compounds are formed between the lanthanides and Pd.

We can use our understanding of the relationship between the electronic configuration and the properties of these metals to make an unusual contribution. The spectroscopic data for the ^{transition} elements discussed previously are rather well established. The availability made it possible to develop the concepts that have proven so useful in predicting alloy behavior of transition metals. For the lanthanides and actinides the spectroscopic data are rather incomplete and it is fruitful to reverse the process whereby we predicted metallurgical behavior of the transition metals from spectroscopic data. From the properties of the lanthanide metals, I have been able to evaluate sufficient information on energies of electronic configurations of the lanthanide atoms to establish the variations with change of atomic number of the relative shielding of the nucleus by s, p, d, and f electrons. This has made it possible to predict the yet unobserved energies of the electronic configurations of the lanthanide and actinide elements.¹⁰ The spectra of these elements are extremely complex because of the large number of levels. The availability of these predictions should greatly accelerate the characterization of the many unidentified lines and levels of the lanthanide and actinide spectra.

For a series of substances we are accustomed to melting points and boiling points increasing together. The values for the lanthanide metals shown in Fig. 1 present the dilemma of melting points increasing from cerium to samarium while the boiling points or heats of sublimation decrease. As expected, divalent europium has a low melting and boiling point with an increase for gadolinium, but beyond Gd the boiling points and melting points again go in opposite directions.

The contradiction between the trends of melting and boiling points is resolved by Fig. 2 which shows the energies of the lowest electronic levels of some of the configurations of the lanthanides. As the 4f electrons do not contribute significantly to bonding, the divalent or trivalent character of a given configuration is determined by the number of non-f electrons. In contrast to the trivalent character of the lanthanide metals other than Eu and Yb, the ground electronic states of almost all of the gaseous lanthanides are divalent. Between La and Eu, the energy of the divalent ground state drops steadily, relative to the trivalent configurations followed by a jump at Gd and then resumption of the stabilization of the divalent configuration. The abnormality of the trend of boiling points is not due to the metallic phase, but is due to the gaseous atom. The vapor consists predominantly of atoms of different valence character than in the metal. The correct measure of the cohesive energy to which the melting point should be related is the enthalpy of sublimation to a gaseous atom with the same electronic configuration as in the metal. Fig. 3 shows the melting-point trend again, compared now with the cohesive energy of the body-centered cubic trivalent metals subliming to the gaseous atom in a trivalent state. The cohesive energies of the trivalent metals are seen to vary in a smooth manner consistent with the melting points. With the ability to estimate cohesive energies of the metals in various structures, it is possible to calculate the energy difference between gaseous electronic configurations. Then by considering the effect of shielding of the nucleus by f, d, s, and p electrons one can ultimately estimate the energies of the lowest states of each of the electronic configurations. Energies were estimated for the lowest levels of over 150 lanthanide configurations for which values were missing and for many more actinide

configurations. Since these first estimations were made, almost fifty experimental values have become available with the average deviation well within the assigned uncertainties. The availability¹⁰ of these results now allows widespread predictions of the chemistry and metallurgy of these elements. For example, just as for Zr, we can predict very stable intermetallic compounds of Pd with the lanthanides and actinides.

I hope that these examples have illustrated how experiments in rather distant disciplines cannot only be closely related, but how they can supplement one another to yield much more than their sum. I would contend that the relevance of an experiment can be measured in terms of how widely the result of the experiment will be felt. The significance of the experiment should not be judged by the practical value of the immediate results, but by the contribution to improved understanding of the behavior of all materials. The most fruitful design of an experiment to test a model of bonding, for example, might require measurements on a rare material that might have little prospects of practical use; nevertheless, the measurements on this useless material could help develop an understanding that could point the way to the design of extremely practical materials. Developmental research aimed at information required for an immediate practical goal can be very costly without the fundamental understanding that can pinpoint the fruitful directions. A small advance in understanding can repay its cost many fold in redirection of numerous developmental projects. I hope that my remarks today may serve to counter the narrow-sighted pressure that tends to redirect all research toward immediate practical results in very limited areas.¹¹

1. Leo Brewer and Haakon Haraldsen, The thermodynamic stability of refractory borides, J. Electrochem. Soc. 102, 399 (1955).
2. Leo Brewer and Oscar Krikorian, Reactions of silicides with carbon and nitrogen, J. Electrochem. Soc. 103, 38, 701 (1956).
3. Leo Brewer and Norman L. Lofgren, The thermodynamics of gaseous cuprous chloride, monomer and trimer, J. Am. Chem. Soc. 72, 3038 (1950).
4. Leo Brewer, The fusion and vaporization data of the halides, National Nuclear Energy Series, Plutonium Project Record, Vol. 19B, paper 7, pp. 193-275 (1950).
5. Leo Brewer, Paul W. Gilles, and F. A. Jenkins, The vapor pressure and heat of sublimation of graphite, J. Chem. Phys. 16, 797 (1948).
6. Ketil Motzfeldt, The thermal decomposition of sodium carbonate by the effusion method, J. Phys. Chem. 59, 139 (1955).
7. Leo Brewer and James S. Kane, The importance of complex gaseous molecules in high temperature systems, J. Phys. Chem. 59, 105 (1955).
8. Leo Brewer, Bonding and structures of transition metals, Science 161, 115 (1968).
9. Leo Brewer, in Phase Stability in Metals and Alloys, P. Rudman, J. Stringer, R. I. Jaffee, Eds., McGraw-Hill, New York, 1967; pp. 39-61, 241-9, 344-6 and 560-8.
10. Leo Brewer, Energies of the Electronic Configurations of the Lanthanide and Actinide Neutral Atoms, J. Opt. Soc. Am. 61, 1101 (1971); and Energies of the Electronic Configurations of the Singly, Doubly, Triply Ionized Lanthanides and Actinides, J. Opt. Soc. Am. 61, No. 11 (1971).
11. All of my research during the last twenty eight years has been supported by the Manhattan District Project or the U.S. Atomic Energy Commission.

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or 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.

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