Title
THE RELEVANCE OF THERMODYNAMICS TO NATIONAL ENERGY PROBLEMS

Permalink
https://escholarship.org/uc/item/4tf555v2

Author
Brewer, Leo.

Publication Date
1974-06-01
THE RELEVANCE OF THERMODYNAMICS TO NATIONAL ENERGY PROBLEMS

Leo Brewer

June 1974

Prepared for the U. S. Atomic Energy Commission under Contract 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
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 RELEVANCE OF THERMODYNAMICS TO NATIONAL ENERGY PROBLEMS

by

Leo Brewer

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

Berkeley, California 94720

Recent events have focused attention upon the imbalance between the rate of consumption of energy in this country and the rate of utilization of domestic sources of energy. More importantly, attention has been focused upon the long-range imbalance between projected energy consumption rates and possible rates of utilization of available sources of energy. Of course, to thermodynamicists familiar with the First and Second Laws and the finiteness of the earth compared to an uncontrolled exponential function, these developments come as no surprise.

There are two questions to be considered at this conference. The first is the examination of the ways in which thermodynamics might play an important role in the development of new sources of energy and the second is the examination of the ways in which the availability of useful thermodynamic data might be enhanced. I think that we are all in agreement with respect to the first question and we are not meeting here to debate the question. Rather, I think we are here to formulate the most effective wording to explain to government administrators and to the general public the ways in which thermodynamics can be used to speed up the development of new energy processes. I would like to make just a few general remarks about the first question and I will devote most of my time to the question of accelerating compilation efforts to enhance the usefulness of thermodynamics.
One can describe two extreme approaches to the development of new processes for utilizing energy. The first would be a trial-and-error approach that would test out all conceivable procedures, whether or not they conform to the First and Second Laws. The problems of material limitations would be tackled by trying materials off the shelf until something is found to work. Such an approach has been used many times in the past and has yielded noteworthy results. However, it is a very inefficient, expensive approach that succeeds only a small fraction of the time. The limitation to materials on hand makes really novel new developments almost impossible and largely limits the usefulness of this approach to relatively small modifications of existing processes.

In contrast to the first approach, one can first use thermodynamics to clearly eliminate impractical processes. One can use thermodynamics and other basic knowledge to characterize the limitations of each possible process and to specify the design criteria that must be meet by the materials used in the process. In many instances, available materials cannot meet the design criteria, but one can predict what kinds of materials might be able to meet the criteria. This type of approach eliminates the expensive testing of large groups of materials and the effort can be concentrated on those materials most likely to succeed. Any trial-and-error developments are restricted to a few most promising materials. In particular, pilot plant or large demonstration operations, which are very expensive, are not necessary until the application of basic principles together with laboratory scale testing has demonstrated the promise of a given process.
Thermodynamics will play an important role in developing new energy sources through the prediction of reactions that might be harnessed for thermal production of hydrogen, for gasification or liquification of coal, for battery reactions, etc. Thermodynamics will play an especially important role together with models that can predict properties of materials and the composition ranges necessary for utilization of the desired properties. The thermodynamic data can predict what portions of the desired composition ranges are thermodynamically stable and can therefore be prepared and maintained in a direct way.

I think that we are all in agreement on the fullest application of basic knowledge such as thermodynamics as a prerequisite to the development of any new processes. However, we are seeing headstrong developments, pushed by political pressure for short term results, that are unlikely to contribute to any real advances in dealing with the energy problem. They are not only unlikely to make any contributions, but they will be detrimental to the sound long-term projects through diversion of money and manpower. It is especially important to emphasize to the public that any substantial developments of new energy sources are necessarily long-term objectives and that there is time for strengthening the background of fundamental knowledge to make very substantial contributions to the acceleration of these long-term developments.

I would like to examine the present status of thermodynamics and how well it is prepared to meet the demands being placed on it. There are two aspects to be considered. One is the rate of determination of new experimental data. Professor Westrum will be giving us the results
of his survey of present experimental capabilities of the country; so I will not go into great detail, but I do have some comments on the type of experimental work that I think should be encouraged. The other aspect that I wish to consider in detail is that of critical evaluation and compilation of thermodynamic data.

In regard to the types of new measurements needed, one finds many complaints about the measurements being carried out. Some of the complaints are that measurements are on materials not likely to be of any practical importance; other complaints are directed to the duplication of measurements. These complaints are sometimes valid; I would like to examine them and to describe what I would consider to be the criteria for determining whether a measurement is worth doing.

Duplication of a measurement already reported in the literature may well be warranted in many circumstances. In some instances the duplication is carried out to test a new type of apparatus as a test of systematic errors. In other instances, duplication is important because of some uncertainty in the previous determinations either because of large contradictions between independent measurements or because of some theoretical basis for suspecting an error in the reported values. However, duplication of a measurement because of unfamiliarity with the literature is not warranted. If one considers the various combinations of the elements that might be studied, one finds the number of systems to be astronomical. It is important to limit the measurements to those systems which yield data of greatest significance. This requires more than a random selection of systems and, in general, it is of great
importance to have some model to which the measurements could be related. It is not possible to hope to measure properties of all the systems that might be of interest or might possibly be considered for the variety of new energy developments. It is important to develop models that allow one to predict the properties of materials that have not been studied.

The question always comes up whether certain areas or certain groups of compounds should be emphasized. It may be harmful to limit measurements to certain groups of compounds instasmuch as quite unusual compounds are often of importance for testing of models. However, there are certain areas that appear to be of special importance, at least in the near future. In spite of the fairly large amount of work that has been done in the past on the hydrocarbons, the emphasis on new methods of shale utilization, liquification, and gasification of coal, as well as the development of methods of separating impurities from the hydrocarbons makes it clear that additional information is needed on hydrocarbons in general and for large classes of organic compounds. Bonding models are well developed for organic compounds and work in this area should be related to improvement of these models. The push to high temperatures for the processing of materials and to higher temperatures to achieve better Carnot cycle efficiencies places emphasis on refractory compounds such as carbides, nitrides, borides, silicides as well as the oxides. Proposed geothermal processes would require thermodynamic data of multicomponent aqueous saline solutions as well as thermodynamic data on high pressure systems. Semiconductor materials in general are of great importance today and will certainly become increasingly important in the future and thermodynamic data for these classes of compounds would be of great value, particularly in devising different and cheaper methods of
preparation of single crystals. Of special importance for all types of processes would be the development of container materials of high-strength steels for shells of nuclear reactors or for chemical reactors. Stronger materials will be needed for carrying high-pressure gas or for extremely cold environments where normal steels tend to become brittle. The availability of thermodynamic data for metallic systems can be of very great help in the development of methods of preparing these materials and fabricating them into suitable forms.

However, in spite of my cataloguing these various groups of compounds for which thermodynamic data would be very valuable, I would not recommend an exhaustive determination of thermodynamic properties of all the members of these groups of materials. It would be too large an effort to be practical, and, in general, the examples chosen in these classes should be ones which test the reliability of applicable models in an effort to improve those models or to clearly define the areas of applicability. In some instances compounds which could be relatively easily studied would be bypassed in favour of more difficult materials that might provide crucial tests of current models.

To develop really new processes, it is not possible to restrict ourselves to commonly used materials for which properties are readily available and one must, at the first stages of examination of the possibility of a process, consider all possible materials. In many cases the amount of material required might be small enough so that even rare and expensive materials could be considered. At the first stages of examination of such processes, it is not even necessary to have highly accurate models. Even models which yield order of magnitude values
would be useful in establishing whether, in fact, any materials are capable of meeting the design criteria and if there are such possibilities, what general classes of materials should be considered. Once we have established the general classes of materials which might be useful for the particular project, then one would like to have more accurate models. When one is dealing with a limited class of compounds, it is often possible to develop models which may not be of general applicability to all kinds of materials, but could be adapted with a limited number of parameters to a given class of materials to yield useful predictions about the properties of these materials and to indicate which possible compounds might meet the requirements of the process.

There are many types of models available. For example, one can cite from the literature a large number of bonding models such as ionic bonding, covalent bonding, hybridization, electronegativity models, acid-base models, soft acids and hard acids, etc. which scientists are using to correlate properties of materials and to predict properties for materials which have not been studied. I would assert that a meaningful program of measurements of thermodynamic properties would be tied to one or more of such models in an effort to improve the models, to determine their limitations and to establish how far they may be safely used. Generally, then, this means trying to test the models under extreme conditions going to unusual conditions of temperature, pressure or composition to press each model to the limit to determine what its defects are and to determine its reliability. This often means carrying out measurements of materials that are unlikely, at least as far as we can tell today, to be of any practical importance. Nevertheless, these materials are important for testing available models and for sharpening up these models so that they
can be used for predicting the properties of a wider range of materials which could include many practical materials.

I would like to spend the bulk of my time on the topic of thermodynamic compilations. In the 1920's, a very ambitious effort was initiated which was aimed at bringing together and critically evaluating all of the available thermodynamic data. It was hoped at the time that this compilation would be a continuing effort that would keep up to date with the new experimental data. This effort was the International Critical Tables (1) and a most remarkable job was done. Unfortunately, it was not possible to maintain the effort of keeping up to date.

Bichowsky and Rossini's tabulation (2) of thermochemistry followed by the Bureau of Standards' Circular 500 tabulation (3) were efforts in a more limited area to carry on the function of the International Critical Tables. The Standard Reference Data program of the Bureau of Standards has continued the effort of compilation and of coordinating thermodynamic compilations around the country. However, as the years have gone by, these compilation efforts have fallen more and more behind the accelerating accumulation of experimental data. The present level of effort is quite inadequate for the demands of the expanding energy development program. Of even more concern is the fact that support of these compilation programs has been decreasing in recent years. How to expand these programs to meet the new needs posed by the energy programs is a very serious question? The typical developmental scientist or engineer does not have the time nor the background to go through the multitudes of journal publications that might have data of interest to him and
evaluate the different determinations to arrive at a most reliable value. I have continually encountered situations in industrial laboratories where data that were very important for their operations were not being used by them because they were not aware of their existence. It is of greatest importance that every effort be made to increase the rate of critical evaluation and compilation of values judged to be the most reliable. Such an effort will help avoid dead-end developmental programs which could waste not only large amounts of money, but large numbers of valuable personnel who would be used on more fruitful endeavours.

The problem of expanding compilation efforts is not an easy one to solve. It will require not only an increase in the level of operation of funding existing compilation centers, but it will also require an active recruiting program to bring individual compilers into the program to supplement the activities of large groups such as the Bureau of Standards. The requirements for a person to engage in compilation activities are rather unique. It is important that the person have had some experience in the laboratory with a variety of thermodynamic techniques; so that he has the background for evaluating the reliability of experimental measurements. It is important that he have some understanding of the possible sources of error that have to be taken into account and, in particular, he must be able to judge the order of magnitude of systematic errors that have to be considered in judging the discrepancies between different determinations. It has been difficult to find enough people who have the qualifications and who are willing to devote the time required for a compilation program. I do
not think that it will be possible to recruit sufficient numbers of qualified people as full-time compilers. There are a number of specialists who are quite familiar with the work that has been done in a relatively narrow field and who might be willing to devote a portion of their time to the compilation effort as a side-line of their regular research program. It would be necessary to obtain funds to back up such a person with assistants who can do the literature work and some of the trivial calculations so that he can concentrate on the job of critical evaluation and the application of judgement in deciding the weighting to be given to the various data. There are hazards in such a program in that not all individuals may be qualified to carry out compilations and a system of critical review of compilation quality would have to be devised to insure that all of the in-put from the small groups would be of comparable quality. Because all areas would not be equally covered, the large compilation centers like the Bureau of Standards would have to take specific responsibility for areas that might not be of great current interests to individual research workers.

I would like to devote my remaining time to a technical aspect of compilations which is rarely discussed. That is the question about the role of models as an aid in evaluating experimental thermodynamic data. One can describe compilations in terms of two different points of view. One is the compilation in which the data are critically evaluated in terms of the experimental methods used and possible systematic errors and evaluation of other results from the same laboratory compared to laboratories with established reliability. Such compilations can
be carried out independently of any models to establish what appear to be the best experimental thermodynamic results. Another type of compilation can be carried out in the context of some model where the data are examined with respect to the expectations of the model. An example where this is now routinely done is in the treatment of aqueous electrolyte data in terms of the Debye-Hückel theory. In this instance, the model is of very great importance because its greatest validity is in the extremely dilute range where it is particularly difficult to obtain reliable experimental data.

Another example is the use of pair-interaction theory as a basis for use of a second virial-coefficient equation of state for extrapolation of gaseous thermodynamic data to the low pressure gaseous standard state. A similar pair-interaction theory is often used as the basis for a Gibbs energy of dilution equation for solutions corresponding to a linear deviation from the Henry's Law slope. In using models of these types in compilations, one must be cautious about the implications of some of the assumptions of the model. In evaluating uncertainty limits for the compiled results, one must include uncertainties introduced by the model and one must have a clear idea of the limits of applicability of the model. As example, one would not use an equation of state based on just a second virial coefficient for an ionized gas just as a linear deviation from Henry's Law is not applicable to an aqueous electrolyte. In the extrapolation of the thermodynamic data to the infinitely dilute or solute standard state, one must consider which systems might have long-range forces which would cause substantial deviations from Henry's
Law even at the most dilute concentrations which can be studied experimentally. There is also the problem that the component being assumed may be dissociated at the low concentrations such as to make Henry's Law inoperable even in the limit of infinite dilution. It is important to use bonding models as a guide that warns when difficulties can be expected and provides for reformulation of the thermodynamic data in terms of a component which is actually the major species at the lowest concentrations. These are standard thermodynamic problems, but it is very important that the role of these essential models be clearly defined by the compiler.

Models are of value to the compiler aside from the problem of extrapolating to the infinitely dilute standard state or for carrying out the Gibbs-Duhem integration to infinite dilution. For example, it is sometimes convenient to express solution data in terms of the solubility parameter of the regular solution theory as a valuable means of tabulating the data more compactly. However, one must consider the implications of entropy assumptions that are implicit in the model. All of these models are useful in compilation efforts, but the possible influence of the model upon the resulting values must be clearly spelled out.

I would like to discuss specific examples to present my views on how to handle the role of the model in compilations. There are many instances where a straightforward thermodynamic treatment of the data is not possible and some extra-thermodynamic treatment is necessary. One of the most troublesome examples is that of determination of Third Law entropies of magnetic compounds of the transition metals, the lanthanides, or actinides. It is difficult to determine from the
available data, in many instances, whether magnetic ordering has removed contributions to the entropy at low temperatures or whether additional amounts of entropy will be extracted at lower temperatures. Thus some of the tabulated entropies must be considered as lower limits until the magnetic contributions are fully elucidated. It is important to attempt to estimate the magnitude of this uncertainty and to clearly include the uncertainty prominently displayed with the tabulated entropy value.

A common example of use of an implicit model without warning to the user of the thermodynamic data is that of compilations of entropies and other thermodynamic data for high temperature gases. In many instances, one finds tabulated thermodynamic data based on just the spectroscopic levels tabulated by Herzberg (4) or in other spectroscopic compilations as if no other levels would be expected. For many molecules at high temperatures, and particularly for compounds of the transition metals, the lanthanides, and the actinides, the available models clearly indicate that there should be many yet-unobserved low-lying levels that can have a very marked influence on the thermodynamic properties at high temperatures. For many of these molecules, the ground electronic state has not yet been established. In part, the problem is a matter of education to convince scientists who publish their thermodynamic calculations based on spectroscopic data that their values are merely limits and the fact that these are limits should be clearly pointed out and reflected in the uncertainty cited.

An example of two contrasting but equally appropriate treatments can be cited for the gaseous diatomic oxides. Gerd Rosenblatt and I have compiled (5) the thermodynamic data for all of the gaseous diatomic oxides...
of the elements using a model based on the spectroscopic data for the free gaseous ions to approximate the electronic contribution to the entropy of the diatomic oxides over a range of temperatures. The electronic contributions to the entropy were tabulated separately so that their magnitude is clearly evident. The uncertainty due to use of the model was reflected in the uncertainties cited for the derived thermodynamic data. It was shown that the model would generally be expected to give somewhat higher entropies than the actual value by comparison with examples for which rather complete spectroscopic data were available. However, the model was expected to give consistently more correct results for all molecules as a group compared to values based only on observed spectroscopic data. The JANAF Tables (6) have recently reviewed the data for some of these oxides. The choice was made to calculate the entropies using only the observed spectroscopic data, but it was clearly pointed out that the values were lower limits and a comparison was made with the values that Rosenblatt and I had tabulated to indicate the range of possible values and the tabulated probable errors reflected that range of uncertainty. There should be no ambiguity in the reader's mind about the magnitude of the uncertainty and the role of models in arriving at the values tabulated. In contrast to those two examples, one must admonish the Bureau of Standards for a complete lack of indication of uncertainties in the NBS Technical Note 270 series (7) aside from the lack of any discussion of the role of models or references to sources of data. This is due in part to lack of funds. The Bureau of Standards' Standard Reference Data Program is the keystone to the compilation
effort and it is most important that adequate funds be obtained not only to bring the NBS Technical Note 270 series to a successful completion but to carry on a continuing program of updating these compilations and providing extensions to higher temperatures. The expansion of the number of compiling programs under the supervision of the Standard Reference Data Program is especially important for insuring sufficient manpower to maintain an adequate compiling rate.

The availability of up-to-date critically evaluated compilations of thermodynamic data together with the availability of models that can predict the missing data can have a very large impact upon the solution of our energy problems. With such data, it should be possible to select the most promising processes at any early stage before large investments of money and manpower have been made. Such compilations will be indispensable for surmounting the materials problems which are usually the main obstacles to development of economical, practical processes.

This work was done under the auspices of the U. S. Atomic Energy Commission.
BIBLIOGRAPHY


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.