Lawrence Berkeley National Laboratory
Recent Work

Title
CALCULATION OF INTEGRAL AND PARTIAL THERMODYNAMIC FUNCTIONS FOR SOLIDS FROM DISSOCIATION PRESSURE DATA

Permalink
https://escholarship.org/uc/item/1zb0f134

Authors
Meschi, David J.
Searcy, Alan W.

Publication Date
1962-04-23
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.
UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

CALCULATION OF INTEGRAL AND PARTIAL THERMODYNAMIC FUNCTIONS FOR SOLIDS FROM DISSOCIATION PRESSURE DATA

David J. Meschi and Alan W. Searcy

April 23, 1962
CALCULATION OF INTEGRAL AND PARTIAL THERMODYNAMIC FUNCTIONS FOR SOLIDS FROM DISSOCIATION PRESSURE DATA

David J. Meschi and Alan W. Searcy

Lawrence Radiation Laboratory
University of California, Berkeley, California

April 23, 1962

I. Introduction

Thermodynamic stabilities of binary inorganic solids are often determined from dissociation pressure measurements, partition function measurements, or from other measurements of the activity of one of the solid-phase components. In calculations of integral free energies $\Delta G$, integral heats of formation $\Delta H$, and integral entropies of formation $\Delta S$ from such experimental data for inorganic solids, solid-solution regions are usually assumed to be narrow and phase-boundary compositions are usually assumed not to vary with temperature.

However, many inorganic solids of high-temperature interest have wide solid-solution ranges whose boundaries vary extensively with temperature so that data obtained from use of these assumptions are of questionable exactness. Fortunately, available data make the assumption unnecessary for a number of metal hydride phases and for some metal oxide and metal nitride phases. Proper treatment of the data yields not only integral thermodynamic quantities as functions of composition, but also yields partial molal thermodynamic quantities for the second component. This additional information makes possible both more complete understanding of the bonding forces of the phases studied.
and more precise predictions of chemical behavior. The calculational methods required are familiar;\textsuperscript{[1, 2, 3]} they are frequently applied to metallic systems.\textsuperscript{[4]}

The purpose of this communication is to illustrate for the uranium-hydrogen and the zirconium-hydrogen systems the kind and consistency of thermodynamic values that can be calculated from dissociation pressures, and to discuss the chemical significance of these values.

II. Data and Calculations

Properties calculated from the data were partial molal Gibbs free energies $\bar{G}_i$, enthalpies $\bar{H}_i$, and entropies $\bar{S}_i$ for each component $i$, activities and activity coefficients, and the relative Gibbs free energy $\Delta G^M$, the relative enthalpy $\Delta H^M$, and the relative entropy $\Delta S^M$. These relative quantities correspond to the free energy, enthalpy, and entropy of formation, respectively, of a normal stoichiometric compound, except that the relative quantities refer to one g atom of total material.

The pure condensed-phase metals were chosen as standard states for uranium and zirconium. The diatomic gas at one atmosphere pressure was chosen as the standard state for hydrogen, but activities will be discussed always in terms of hydrogen atoms. Thus, the activity of hydrogen atoms is their fugacity divided by the fugacity of hydrogen atoms when the pressure of $H_2$ is one atmosphere. This activity is numerically equal to the square root of the $H_2$ pressure in atmospheres.

The solubilities of hydrogen in the various modifications of uranium are all less than $X_H = 10^{-3}$,\textsuperscript{[5]} and were neglected in our
calculations. The single known hydride phase has two known crystal modifications. Pressure data were available for the high-temperature \( \beta \)-modification only. All dissociation pressure data used in the calculations pertaining to the U-H system were taken from the paper by Libowitz and Gibb. [6]

From the dissociation pressures, the activities of the metallic components were calculated by means of a form of the Gibbs-Duhem equation:

\[
\ln a_m(B) = \ln a_m(A) - \int_A^B \frac{X_H}{X_m} \, d \ln a_H; \quad (1)
\]

where

- \( a_m, a_H \) = activity of metal and hydrogen, respectively
- \( A, B \) = two different phase compositions
- \( X_m, X_H \) = mole fraction of metal and hydrogen, respectively.

Integration was performed graphically.

From the activities, \( \Delta G^M \) was calculated as a function of composition for both systems at 50-degree intervals from 450° to 650°C. Figure 1 is a plot of \( \Delta G^M \) for the U-H system at 500°C. The circled points were calculated. The line drawn through them is a least-squares fit of the form:

\[
\Delta G^M = g_0 + g \, X_H + g_2 X_H^2. \quad (2)
\]

A quadratic equation is the simplest type appropriate for expressing \( \Delta G^M \) as a function of composition in single-phase regions. In two-phase regions \( \Delta G^M \) must vary linearly with composition, and the curve of \( \Delta G^M \) in a single-phase region must have a common tangent with the linear equation for \( \Delta G^M \) in the two-phase region adjacent to the boundary. Conversely, if a single straight line can be drawn tangent to each of the two curves representing \( \Delta G^M \) for two different stable phases,
then between the points of tangency lies a two-phase region for which the straight line yields values of $\Delta G^M$.

Quadratic curves fit the data for the U-H system very accurately and enabled $\Delta G^M$ to be calculated for compositions somewhat outside the observed phase region. This extrapolation is shown by the dotted line.

The straight line in Fig. 1 joins compositions of equal activities at the $\alpha$-uranium phase boundary and at the hydride phase boundary.

From the relative free energy, the relative enthalpy $\Delta H^M$ was calculated by means of the relation

$$\Delta H^M = \frac{\partial \Delta G^M}{\partial \ln T}.$$  

This calculation involved plotting $\Delta G^M/T$ against $1/T$ and drawing the best straight line through the points. The slope of this line must equal the enthalpy if the change in heat capacities is negligibly small. In this way $\Delta H^M$ was calculated for various compositions in the range $X_H = 0.738$ to $X_H = 0.750$. Figure 2 shows a plot of $\Delta H^M$ as a function of $X_H$.

The value of the heat of formation for stoichiometric $\text{UH}_3$ calculated here can be compared with that determined from the same data by Libowitz and Gibb. Under the assumption that deviations from stoichiometry could be ignored, they reported $\Delta H = -30.3 \pm 0.1$ kcal/mole, as compared with our value of $-31.4 \pm 0.3$ kcal/mole. The calorimetric value is $-30.6$ kcal/mole. [7]

On the same figure we have plotted the relative entropy $\Delta S^M$, which was calculated from $\Delta G^M$ and $\Delta H^M$ by means of the usual
relation $\Delta S^M = (\Delta H^M - \Delta G^M)/T$. Table I lists values of $\Delta S^M$ and $\Delta H^M$ for the hydride phase. Table II lists the parameters $g_0$, $g_1$, and $g_2$ used in equation (2) to calculate the relative free energy $\Delta G^M$.

Low-temperature heat capacities of $\text{UH}_3$ were measured by Flotow et al. [3]. From these Dr. Robert Altman at the Lawrence Radiation Laboratory, Livermore, very kindly estimated the high-temperature heat capacities by means of a Debye function with $\theta = 1215\,^\circ\text{K}$, and also calculated $S^\circ_T$ for this compound at various temperatures. His values of $S^\circ_T$ for $\text{UH}_3$ are: 29.59 cal/deg mole at 700$^\circ\text{K}$, 32.39 at 800$^\circ$, and 34.93 at 900$^\circ$. Ours were: 29.62 cal/deg mole at 700$^\circ\text{K}$, 32.32 at 800$^\circ$, and 34.80 at 900$^\circ$. The agreement is quite good.

Compared to the U-H system, the Zr-H system is complex. It contains at least three phases, each of which has a considerable composition range. The existence of a fourth $\epsilon$ phase has been reported, but few data are available for this phase.

The dissociation pressure data on which the calculations were based were taken from various sources. These are: Gulbransen and Andrew for the $\alpha$ phase, [8] Ells and McQuillan for the $\beta$-phase, [9] and Libowitz for the $\delta$ (or $\gamma$) phase. [10]

In the manner outlined, $\Delta G^M$ was calculated from the dissociation pressures at various values of $X_H$ and various temperatures in the range 450$^\circ$ to 650$^\circ$C. The $\beta$ phase is unstable below 540$^\circ$-550$^\circ$C, so the lowest temperature for which calculations could be made was 600$^\circ$C. Although the $\delta$ phase exists at all the temperatures considered, the lowest temperature for which data were available was 550$^\circ$C.

Some difficulty was experienced in properly positioning the phase boundaries, since the sources did not all agree. The results of
this disagreement were most severe in the case of the $\beta$ phase, but do not have any appreciable effect on the $\delta$ phase, and none at all on the $\alpha$ phase. Libowitz's values were used to locate the $\beta/\delta$ boundary, Ells and McQuillan's values for the $\alpha/\beta$ boundary, and Gulbransen and Andrew's values for the $\alpha/\delta$ boundary.

Figure 3 presents plots of $\Delta G^M$, $\Delta S^M$, and $\Delta H^M$ as functions of $X_H$ for the Zr-H system. For this system we did not expand $\Delta G^M$ as a quadratic function; instead we proceeded directly to calculation of $\Delta H^M$ and $\Delta S^M$ by a method different from that used with the U-H system. For each phase $\Delta G^M$ was evaluated at each of several compositions and at each of several temperatures by means of plots like that of Fig. 3. For each composition the values of $\Delta G^M$ were fitted by an equation of the form: $\Delta G^M = g_0 + g_1 T$. The parameters $g_0$ and $g_1$ corresponded to $\Delta H^M$ and $\Delta S^M$, respectively.

As with $\Delta G^M$ for the U-H system, the values of $\Delta H^M$ for the Zr-H system were easily fitted by a quadratic expression similar to equation (2). This could not be done with the entropy $\Delta S^M$ as it stood. It was possible, however, to divide $\Delta S^M$ into two components, one of which arose from the random occupation of the interstices in the Zr lattice by the H atoms, this part labeled $\Delta S^P$, and the other of which was the residue or "excess" term, labeled $\Delta S^E$. The component $\Delta S^P$ was evaluated by means of the formula,

$$\Delta S^P = R \left[ 2X_{Zr} \ln \left( \frac{2X_{Zr}}{2X_{Zr} - X_H} \right) + X_H \ln \left( \frac{2X_{Zr} - X_H}{X_H} \right) \right], \quad (4)$$

which assumes completely random mixing of vacant interstitial sites and H atoms.
The residue or excess term $\Delta S^e$ showed the same variation
with composition as $\Delta H^M$ and so could also be expressed by means of
a quadratic function. The coefficients of these equations for $\Delta H^M$
and $\Delta S^e$ are given in Table III.

As a check on the accuracy of the calculations leading to these
formulas, $S^0_T$ for the $\beta$-phase at 600°C and $X_H = 0.324$ was calculated
by use of the formulas, plus tabulated data for Zr and $H_2$. This value
was compared with one calculated from the papers of Douglas and
value for $S^0_{873} - S^0_{273}$; the necessary quantity $S^0_{273}$ was estimated from
the value given by Flotow and Osborne for stoichiometric $ZrH_2$. By
means of our formulas, $S^0_{873}$ was calculated to be -14.9 cal/deg g atom,
as compared with -15.2 cal/deg g atom obtained from the published
data.

III. Discussion

For each of these metal-hydrogen systems the composition
that shows the maximum stability per gram atom relative to the ele-
ments in their standard states shifts toward lower hydrogen content as
the temperature is raised (Fig. 4). This shift reflects the increased
importance of the entropy of random mixing of hydrogen atoms with
vacancies in the interstitial positions of the lattice.

For the uranium-hydrogen phase the composition of maximum
stability is just a few tenths of a percent poorer in hydrogen than the
composition at the phase boundary for each temperature for which data
were available, i.e., the composition of the single-phase region which
has the most negative free energy of formation lies just outside the
composition range for which the phase is thermodynamically stable at
each temperature (Fig. 1). This situation arises because the hydride phase is unstable unless the pressure of hydrogen exceeds the standard pressure of one atmosphere in the temperature range of study.

In the zirconium-hydrogen system the maximum stability per gram atom lies at each temperature in the δ-phase region. The positions of the maxima can be extrapolated in a reasonable curve to approach the ideal composition ZrH₂ at absolute zero. But low-temperature data to establish the validity or unvalidity of the extrapolation would be of interest.

The most striking feature of plots of integral free energies, heats, and entropies of formation per gram atom versus composition for the zirconium-hydrogen system (Fig. 3) is that such plots closely resemble similar plots for metal-metal systems with intermediate phases of similar solubility ranges. In metal-metal systems, the free energies change so slowly as functions of composition that the curvature that distinguishes single-phase regions from two-phase regions is scarcely perceptible. Although the magnitude of the free energy change is greater upon formation of the zirconium hydrides, the general form of stability variation is similar. The integral heats and entropies change less smoothly from phase to phase, but in the zirconium-hydrogen system as in metal-metal systems these thermodynamic quantities appear to reflect mainly the relative quantities of the components combined and only secondarily the structure and bonding characteristics of particular phases.

One consequence of insensitivity of integral thermodynamic functions to phase changes is that values of such functions, and especially of free energies, are poor data from which to fix phase
boundaries or even to decide the existence or non-existence of an intermediate phase such as solid SiO, whose free energy of formation must be close to one-half that of SiO₂. Values of activities or related partial molar quantities, on the other hand, are much more sensitive to phase changes (Fig. 5).

Examination of Fig. 3 demonstrates that the free energy of formation and especially the heat of formation of a hydride phase may be changed significantly by small composition changes within the single-phase region. In general, the heat of formation for a phase at some composition for which all the interstitial hydrogen positions are filled will be significantly more exothermic than will the heats of formation for the same phase at compositions that require vacancies to be present.

Transition metal carbides of ideal formulas MC appear to resemble these hydrides in that the carbides are usually stable, always with less than the stoichiometric concentrations of carbon, and the maximum carbon content that can be achieved in the single-phase region decreases with increased temperature. [13] These carbide phases and related MN and MO phases can also be expected to have heats of formation per gram atom that become increasingly negative with increased content of the nonmetal.

Comparisons of values of the entropy of mixing, not per gram atom of total material, but per gram atom of hydrogen, are of interest because entropies of formation per gram atom of oxygen, nitrogen, or halogen have been shown to be nearly constant independent of the metallic reactant for a variety of compounds. [14] However, this generalization was made for solids of relatively narrow composition ranges.
No similar constancy is found for these hydrides. The entropy of formation per gram atom of hydrogen changes from -13.2 when $X_H = 0.738$ to -14.9 when $X_H = 0.750$. Entropies of formation per gram atom of hydrogen range from approximately -5 for the saturated $\alpha$-phase to -16 cal/deg for the highest hydrogen content observed. If the entropy of mixing of hydrogen atoms with vacancies in the hydrogen lattice is subtracted, the corresponding range in values becomes -10 to -17 — still a much wider range than found for stoichiometric compounds of different metal oxidation states. Investigations of entropies of additional similar phases as functions of composition are certainly to be desired.

Partial molal functions for hydrogen and the metal atoms can best be discussed, probably, in terms of activities and activity coefficients. The activities for zirconium and hydrogen have been presented in Fig. 5 and of uranium and hydrogen.

The point at which activities of the two components are equal occurs necessarily at the composition of minimum free energy of formation from the elements in their standard states. Since all compositions of the uranium hydride phase are unstable at 500°C relative to the standard states, the uranium and hydrogen activity curves do not cross.

The sharp change in activities of each component in the $\delta$-zirconium hydride phase reflects the much greater sensitivity of the nature of the bonds to composition in the $\delta$-phase than in the $\alpha$- or $\beta$-phase.

Examination of activity coefficients reveals the, at first surprising, fact that Henry's law is a better approximation to describe
the activity of hydrogen for the \( \beta \) phase than for the \( \alpha \) phase. In the \( \alpha \) phase the activity coefficient \( \gamma_H \) varies from 0.25 to 0.36 at 600°C and \( \gamma_{Zr} \) varies from 1 to 0.98. In the \( \beta \) phase over a composition range more than 4 times as wide, \( \gamma_H \) varies from \( 7.2 \times 10^{-2} \) to \( 6.4 \times 10^{-2} \) and \( \gamma_{Zr} \) varies from 1.23 to 1.30.

From the heat and entropy of transition of \( \alpha-Zr \) to \( \beta-Zr \), the activity coefficient of zirconium in \( \beta \)-solid solution with hydrogen at 600°C can be calculated to vary from 1.08 to 1.13 relative to pure \( \beta \)-zirconium as a standard state. Zirconium in the \( \beta \) phase thus approximates Raoult's law behavior from \( X_{Zr} = 1 \) to \( X_{Zr} = 0.6 \). The much lower activity coefficient of hydrogen in the \( \beta \) phase reflects the more open packing of zirconium in that form and consequent reduction in repulsive interactions.

The practical utility of activity data such as obtained in this study is illustrated by the recent work of Rudy and Benesovsky, who calculated the free energy of formation of UC\(_2\) from knowledge of the uranium and carbon activities in ternary \((M, U)C\) phases with which UC\(_2\) was in equilibrium.

The value of partial molal thermodynamic data in studies of diffusion rates must also be mentioned.\(^{[15]}\)

IV. Conclusion

We have attempted to demonstrate by examples that experimental data which have already been collected and reported for certain inorganic systems can be made to yield considerably more thermodynamic information than is usually calculated from the initial data. We have further attempted to demonstrate some of the insight into the
nature of solid-state chemical interactions that can be obtained by analysis of the thermodynamic information.

The compilation and analysis of data such as presented here will inevitably become one of the most fruitful areas of high-temperature solid-state studies during the next few years.
Bibliography


Table I. Thermodynamic values pertaining to β hydride phase of U-H system

<table>
<thead>
<tr>
<th>$X_H$</th>
<th>$\Delta H^M_{\text{kcal/g atom}}$</th>
<th>$\Delta S^M_{\text{cal/deg g atom}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.738</td>
<td>-6.707</td>
<td>9.75</td>
</tr>
<tr>
<td>0.740</td>
<td>-6.989</td>
<td>10.07</td>
</tr>
<tr>
<td>0.742</td>
<td>-7.232</td>
<td>10.35</td>
</tr>
<tr>
<td>0.744</td>
<td>-7.333</td>
<td>10.59</td>
</tr>
<tr>
<td>0.746</td>
<td>-7.565</td>
<td>10.75</td>
</tr>
<tr>
<td>0.748</td>
<td>-7.726</td>
<td>10.96</td>
</tr>
<tr>
<td>0.750</td>
<td>-7.862</td>
<td>11.14</td>
</tr>
</tbody>
</table>
Table II. Coefficients for integral relative free energy equation

\[ G^M = g_0 + g_1 X_H + g_2 X_H^2 \]

<table>
<thead>
<tr>
<th></th>
<th>450°C</th>
<th>500°C</th>
<th>550°C</th>
<th>600°C</th>
<th>650°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( g_0 )</td>
<td>+1457.78491</td>
<td>802.51334</td>
<td>542.57554</td>
<td>433.85042</td>
<td>432.62857</td>
</tr>
<tr>
<td>( g_1 )</td>
<td>-3895.694</td>
<td>-2148.496</td>
<td>-1454.788</td>
<td>-1166.238</td>
<td>-1166.788</td>
</tr>
<tr>
<td>( g_2 )</td>
<td>2603</td>
<td>1439.3</td>
<td>977.5</td>
<td>787.0</td>
<td>790.9</td>
</tr>
</tbody>
</table>
Table III. Coefficients for $\Delta H^M$ and $\Delta S^e$, Zr-H system

$$\Delta H^M = h_0 + h_1 X_H + h_2 X_H^2; \quad \Delta S^e = s_0 + s_1 X_H + s_2 X_H^2$$

<table>
<thead>
<tr>
<th>Coeff.</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h_0$</td>
<td>0</td>
<td>-547.3</td>
<td>29,573.0</td>
</tr>
<tr>
<td>$h_1$</td>
<td>-14,600</td>
<td>-2,244.4</td>
<td>-111,532.5</td>
</tr>
<tr>
<td>$h_2$</td>
<td>24,000</td>
<td>-28,304</td>
<td>70,471.1</td>
</tr>
<tr>
<td>$s_0$</td>
<td>0</td>
<td>0.936</td>
<td>11.416</td>
</tr>
<tr>
<td>$s_1$</td>
<td>-15.32</td>
<td>0.68</td>
<td>-51.930</td>
</tr>
<tr>
<td>$s_2$</td>
<td>29</td>
<td>-28.0</td>
<td>26.76</td>
</tr>
</tbody>
</table>
List of Figures

Fig. 1. Integral relative Gibbs free energy $G^M$ of U-H system at 500°C.

Fig. 2. Integral relative enthalpy $\Delta H^M$ and entropy $\Delta S^M$ of U-H system.

Fig. 3. $\Delta G^M (600^\circ C)$, $\Delta S^M$, and $\Delta H^M$ for Zr-H system.

Fig. 4. Comparison of maximum stability of hydride phase, U-H system.

Fig. 5. Activities of H and Zr in Zr-H system at 600°C.
Fig. 1. Integral relative Gibbs free energy $G^M$ of U-H system at 500°C.
Fig. 2. Integral relative enthalpy $\Delta H^M$ and entropy $\Delta S^M$ of U-H system.
Fig. 3. $\Delta G^M(600^\circ C)$, $\Delta S^M$, and $\Delta H^M$ for the Zr-H system.
Fig. 4. Comparison of maximum stability of hydride phase, U-H system.
Fig. 5. Activities of H and Zr in Zr-H system at 600°C.
This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.