SELECTED VALUES OF THE THERMODYNAMIC PROPERTIES OF BINARY ALLOYS

Selected Values of the Thermodynamic Properties of Binary Alloys

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PREFACE

This volume, together with its companion, "Selected Values of Thermodynamic Properties of the Elements", represents a complete revision of the work, "Selected Values of Thermodynamic Properties of Metals and Alloys", by Hultgren, Orr, Anderson, and Kelley, published in 1963 by John Wiley and Sons, New York. The work should cover pertinent data available at the date printed on the first page of each system.

Inspection will show that many or most of the selected values differ from the 1963 edition; many of the differences are substantial. This shows progress in measurement and, at the same time, hints of uncertainties still present.

There are complexities in the thermodynamics of alloys which may surprise the incautious researcher. Solid alloys are usually berthollides; they may exist over a range of compositions. In the attempt to prepare a single, homogeneous phase, one can easily obtain highly segregated phases and even several phases in a sample. The chemical composition alone will not establish the initial state of the sample. Furthermore, phase changes may partially or completely occur during the thermodynamic measurement without change in the appearance of the sample; both the initial and final states should receive adequate metallurgical examination.

These complexities, added to the known difficulties of thermodynamic measurement, have resulted in an extraordinary number of incorrect thermodynamic data in the literature. Fortunately, the quality of papers is improving, but there are still parts of the world, including the United States, where imperfect measurements are being made.

An evaluating center needs an intimate knowledge of the processes occurring during all types of thermodynamic measurements, as well as the phase, magnetic, and other changes the alloy may experience during preparation and measurement. The staff, itself, may not have all these skills, but should at least have some and have ready access to experimentalists who have the others.

Department of Materials Science and Engineering

and the

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PERSONNEL

Each system has been assigned to the evaluator whose initials appear at the bottom of the first page of the system. He is assisted by undergraduate students or others in library work or calculations performed under his direction. He may consult with other members of the staff and, on occasion, invites another evaluator to share responsibility with him. After the evaluation is completed, it is intensively reviewed by at least one, usually several, of the authors. Suggested changes are usually minor, but frequently parts of the data are extensively restudied and reworked. The initials of the evaluators are identified in the following list:

Initials	Name
LB	Leo Brewer
JC	John Chipman
JCC	Jaime Cases-C.
PDD	Pramod D. Desai
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DTH	Donald T. Hawkins
RRH	Ralph R. Hultgren
DDJ	Dan D. Jensen
KKK	Kenneth K. Kelley
OK	Oswald Kubaschewski
SJN	Stuart J. Nelson
RLO	Raymond L. Orr
EMP	Elias M. Plaza
MCBS	M. C. Bernard Smit
MBS	Marian B. Smith
GRS	Gollakota R. Somayajulu
HIY	Hong-il Yoon

Most of the copy was typed by Rebecca Palmer on multilith masters. She was also responsible for the layout of the pages. Printing was done by the photo-offset process; the excellence of the copy owes much to the multilithing of Dorathy Brohl. We thank Gloria Pelatowski for the fine drawings.

In the course of the investigation more than 11000 carefully selected references were accumulated and properly key-worded into a Termatrex system. Most of these were microfiched to be instantly available to the evaluators.

We are much indebted to Dr. Leo Brewer for assistance and encouragement.

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Chapter 1

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METHODS OF EVALUATION

The Sample. There are special difficulties in characterizing the initial and final state of solid alloy samples. This is critical, since all thermodynamic measurements are measurements of differences between these states. The main difficulty arises from the fact that most intermetallic phases are berthollides (stable over a range of compositions) rather than daltonides (stable over a very narrow range of compositions near a formula A_xB_y with x and y small whole numbers), which are usual with nonmetallic solid phases.

Most alloy samples are prepared by freezing from a liquid of desired composition. Berthollides prepared in this manner, unless they are of a congruent melting composition, will be found to segregate. The resulting sample may be seriously inhomogeneous in composition and may even contain one or several additional phases. Generally, the desired homogeneous sample may be obtained by further treatment, especially a suitable homogenizing anneal.

A second variable common in intermetallic solids is the degree of order with which the differing atomic species are distributed over the crystalline lattice. Some intermetallic phases of suitable stoichiometric composition are, like most nonmetallic phases, completely or nearly completely ordered. However, most of them have a nearly completely random distribution with consequent increase of entropy. In a number of cases the crystal is random at high temperatures, becoming ordered at lower temperatures. The degree of order significantly affects both the heat and entropy of formation of the phase.

Phase changes of an alloy sample may not be noticed because the appearance of the sample does not change, for nonmetallic samples the change may be much more evident. Moreover, the change in phase or degree of order may not be complete, so that the final state is not in equilibrium.

The evaluator should examine each piece of research, considering whether the sample has been adequately prepared and whether the final state of the sample is that one which has been assumed by the investigator.

Heat Capacities. Few low-temperature measurements of alloys have been made, except for some at liquid helium temperatures ($T < 4.2°K$) for the purpose of determining the electronic contribution of Cp, which casts some light on the nature of the metallic chemical bond in the alloy. Above room temperature, Kopp's law of additivity of heat capacities usually supplies a reasonable approximation. Exceptions occur at temperatures where either the alloy or a standard state has an anomaly, such as near Curie or Néel temperatures, or at order-disorder changes in the alloy.

Techniques of heat capacity measurement are similar to those with elements (see "Elements" *), with due regard for phase changes as indicated by the phase diagram. Cp anomalies caused by the order-disorder reaction will be displaced depending on the rate of the reaction and the time allowed during the measurement.

Heat Contents. Techniques of drop calorimetry are the same as for the elements (see "Elements") expect that phase changes during cooling must be avoided unless they occur so fast that they go to completion and do not cause segregation or strain energy in the final sample; or are so slow they occur insignificantly.

Standard States. Values of Gibbs energy, entropy, and enthalpy (or heat) of formation require that the reference standard state of the elements be precisely defined. This is not so easy as it seems. In many papers, including some quite recent ones, the standard state is ambiguous or may even be used in error. To avoid any possible ambiguity, in all the tables in this volume in which ΔG, ΔS, ΔH, or ΔCp appear, a chemical equation is presented which shows the standard states.

It is a convention of chemical thermodynamics that the standard state be that form of the element which is stable at the temperature concerned. Where no statement of standard state is made, it is understood that this is the standard state assumed.

For reasons which seem valid to us, we have not always followed this convention. All liquid alloys (except C-Fe) have been referred to liquid elements; all solid alloys to solid elements. This makes tables more comparable with one another and avoids discontinuities with temperature of properties of the alloys at the melting point or transition points of the standard states. It does require use of the Cp of the element over the range of temperatures in which it is unstable. Only rarely are such measurements available; usually they are experimentally impossible. Extrapolations are impractical, different analysts may extrapolate very differently.

In considering any chemical reaction, it will be found that the standard states used do not influence the answer, providing they are consistently used for both reactants and products. Hence fictitious standard states may be used without error, provided their properties are well defined.

In this volume the convention has been adopted that the heat capacity of an elementary phase in a temperature region in which it is unstable, will be equal to the heat capacity of the stable form at those temperatures. As a result $\Delta Cp = 0$ between stable and unstable

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* In this and later discussion "Elements" refers to "Selected Values of the Thermodynamic Properties of the Elements", by Hultgren, Desai, Hawkins, Gleiser, Kelley, and Wagman, published 1973 by the American Society for Metals, Metals Park, Ohio 44073.

forms, and the enthalpy of melting or phase transition remains constant with temperature. The reader may then, if he wishes, very simply convert the reference states of the tables to the conventional form with a minor amount of calculation. For values, see "Elements".

Phase Diagrams. The first step in evaluating an alloy system is to adopt a phase diagram. For this purpose, great reliance has been placed on the critical compendium of Hansen (1958) with supplementary volumes by Elliott (1965) and Shunk (1969). These volumes are intended to cover all phase diagram work published before December 31, 1964. The diagrams in this volume have been altered where necessary to agree with later work, wherever the later work appears to be valid.

It must be recognized that in the best of cases many of the phase boundaries have not been determined with precision. Where liquidus and solidus have been determined by cooling curves, the solidus is commonly too low and the gap between them too wide. For diagrams containing transition metals, many conflicting results have been reported. The reason for these disagreements, probably, is the presence of N, O, H, C, and/or B in interstitial solid solution.

Much thermodynamic information can be obtained from phase diagrams, after making suitable allowance for their possible inaccuracy, because the activity of each component in a phase is precisely equal to the activity of that component in any phase in equilibrium. Available resources did not permit the extensive calculations possible from phase diagrams; tables were checked however, and in some cases refined, to agree with the selected phase diagram.

Gibbs Energy Measurements. The relative partial molar Gibbs energy, $\Delta\overline{G}_B$, of one of the components is frequently measured by the emf or one of the equilibrium measurements described below. If $\Delta\overline{G}_B$ is measured over a range of compositions which includes one composition where $\Delta\overline{G}_A$ is independently known (for example, in pure A, $\Delta\overline{G}_A = 0$), then, by Gibbs-Duhem integration, $\Delta\overline{G}_A$ and ΔG can be calculated over the whole range of compositions.

Furthermore, if $\Delta\overline{G}_B$ is measured over a range of temperature, entropies can be calculated: $\Delta\overline{S}_B = -(\partial\Delta\overline{G}_B/\partial T)_x$, at constant $x = x_B$, the atomic fraction of B in the alloy. Thus entropies and enthalpies of formation can also be found. The drawback here is that errors in measuring $\Delta\overline{G}_B$ are multiplied when temperature coefficients are taken. It can happen that satisfactory precision in $\Delta\overline{G}_B$ measurements will produce unacceptable errors in $\Delta\overline{S}_B$. In such cases the Gibbs energies may be accepted and combined with calorimetric ΔH values.

Caution should be taken in considering the temperature coefficient of $\Delta\overline{G}_B$ measured in a two-phase region lest the composition of the phase change with temperature. The quantity measured in this case,

$$d\Delta\overline{G}_B/dT = (\partial\Delta\overline{G}_B/\partial T)_x + (\partial\overline{G}_B/\partial x)_T(dx/dT)$$

equals $-\Delta\overline{S}_B$ only if the last term is negligible.

Electromotive Force Measurements. The free energy can be determined from a measured potential, as $\Delta\bar{G}_B = -n\mathcal{F}\mathcal{E}_B$ where $\mathcal{E}_B$ is the voltage between an electrode composed of pure B and one composed of the alloy $A_{1-x}B_x$. The electrolyte must contain B ions, usually with the charge B^{+n}, and it must not react appreciably with A in the alloy electrode. Success normally is to be expected only when the two components of the alloy differ considerably in electropositivity. In some cases, it is possible to alter the relative electropositivity by a suitable choice of electrolyte. Electropositivities have even been reversed, so that the potential of each component could be measured independently. However, it is so difficult to set up a correctly functioning reversible cell that the experimenter usually confines himself to systems in which one component is much more electropositive than the other.

The rate of diffusion must be sufficient to maintain the surface of the alloy electrode in equilibrium with the interior. Temperatures of measurement for most alloys must therefore be high. Aqueous electrolytes, for which techniques are best developed, are practical only for amalgams and similarly low-melting alloys. Fused salt electrolytes are the most common for high temperature measurements; problems are greater and accuracy less than with aqueous electrolytes. Considerable success has been attained recently in the use of high-temperature solid electrolytes.

Vapor Pressure Measurements. This technique has been applied to the determination of the free energies of alloys with increasing success as the methods improve. The difficulties encountered in measuring vapor pressures of elements are ameliorated to some extent by the fact that the significant quantity, $a_B = P_B(\text{in alloy})/P_B(\text{in element})$, is a ratio of vapor pressures. If both are measured in the same apparatus, systematic errors tend to cancel.

A source of considerable difficulty is depletion of the alloy of its more volatile component. This may lead to serious errors, if depletion of the surface is not replaced by diffusion from the interior; the rate of diffusion should be more rapid than the rate of evaporation.

In some alloys significant amounts of both components are vaporized, in which case there should be a chemical analysis of the vapor. Then the Gibbs energies of both components are independently measured, and should obey the Gibbs-Duhem relationship.

Chemical Equilibria. In some cases reaction equilibria can be set up and the equilibrium constant measured. For example, for the reaction

$$x\text{Fe(in alloy)}_{(s)} + H_2O_{(g)} = Fe_xO_{(\text{wüstite})} + H_2(g) ,$$

a_{Fe} can be determined from the partial pressures of the gases in equilibrium with the alloy sample and with pure Fe. Some experimenters neglect to prove, however, that their oxide phase is really pure wüstite, Fe_xO of known composition and is not contaminated with oxides of the other metal component, or with Fe_3O_4. Not many equilibria involving alloys have been measured.

Distribution Coefficients. Another equilibrium method sometimes used involves measurement of the distribution coefficient of a solute metal between two immiscible liquid metal solvents. Since, at equilibrium, the activity of the solute metal is the same in both phases, knowledge of its activity in one phase gives that in the other. The method does not have wide applicability and is infrequently used.

Heats of Formation. These may be measured from direct reaction of the metallic components in the calorimeter. For liquid alloys, this presents no particular difficulty if the required temperature of operation is not too high. For solid alloys the problem is much more difficult because a long period of time may be required to form a homogeneous solid phase, too long for measurement of the heat of reaction. For some solid alloys with highly exothermic heats of formation, reasonable success has been attained in a few cases of direct reaction of the elements, though adequate testing of the completeness of the reaction and homogeneity of the resultant solid phase has not always been done. Attempts are being made to extend these methods to endothermically formed alloys.

More promising are those methods where the homogeneous alloy is decomposed into a state in which the enthalpy with respect to the components in their pure, standard states is known or can be determined. Liquid metal solution calorimetry has had great success. The accuracy of acid solution calorimetry has been disappointing, while combustion calorimetry has not been tried successfully, though it is obvious that it presents formidable difficulties.

Evaluation of Data

Comparison of values of the same property measured at different temperatures requires that the temperature dependence of the property be known or estimated. Heats and entropies may often be transferred over moderate temperature ranges assuming Kopp's law without great uncertainty. Free energy data measured at different temperatures and from different sources are much more difficult to compare in the absence of data from which reliable entropies may be obtained.

All experimental measurements of the same property which can be reduced to a single evaluating temperature are plotted, if possible, as a function of composition on a single graph. Best results are secured if the data are expressed in the form of functions which vary comparatively slowly with composition. For partial molar free energies the α-function has proved especially useful:

$$\alpha_B = \Delta\bar{G}^{xs}_B/(1 - x)^2 , \quad \text{where } x = x_B .$$

α_B is finite at all concentrations and can be extrapolated to x = 0 and x = 1. For regular solutions α_B is constant with composition; for others it can be frequently selected as a linear function of x or as a smoothly varying curve, making interpolations easy. It also has advantages in Gibbs-Duhem integration.

If $\Delta\bar{G}_B$ (or α_B) is known over a range of concentrations, including one concentration, x_0, where $\Delta\bar{G}_A$ is independently known, then $\Delta\bar{G}_A$ can be calculated over the entire range of concentration by the following equation derived from the Gibbs-Duhem relation:

$$\Delta\bar{G}^{xs}_{A,x} = \Delta\bar{G}^{xs}_{A,x_0} + x_0(1-x_0)\alpha_{B,x_0} - x(1-x)\alpha_{B,x} + \int_{x_0}^{x} \alpha_B dx .$$

When it is appropriate to extrapolate α_B to x = 0, where $\Delta\bar{G}^{xs}_A = 0$, the above equation can be written with $x_0 = 0$, giving:

$$\Delta\bar{G}^{xs}_{A,x} = - x(1-x)\,\alpha_{B,x} + \int_{0}^{x} \alpha_B dx .$$

For entropies the β-function has similar advantages:

$$\beta_B = \Delta\bar{S}^{xs}_B/(1 - x)^2 ,$$

with similar Gibbs-Duhem equations substituting β_B for α_B. From $\Delta\bar{G}$ and $\Delta\bar{S}$ of the two components, it is easy to calculate the partial enthalpies, and the integral free energies, enthalpies, and entropies.

For selecting integral enthalpies measured by calorimetry, the Q-function has similar advantages:

$$Q = \Delta H/x(1 - x) .$$

Sometimes Q is constant with composition; for regular solutions $Q = \text{constant} = \alpha_A = \alpha_B$. When Q is expressible as a straight line or an analytic curve, values of $\Delta\bar{H}_B$ and $\Delta\bar{H}_A$ are readily derived. From these $\Delta\bar{H}_B$ values and the $\Delta\bar{G}_B$ values from equilibrium measurements, $\Delta\bar{S}_B$ values can be calculated which normally are more accurate than those derived from temperature coefficients.

When the original data have been plotted as α-, β-, and Q-functions, or other functions, for each evaluating temperature, the evaluation process can begin. Inspection of each plot gives an indication of probable scatter of data and the agreement or disagreement between different experimenters. Where there is agreement, or where only one set of data is available, a preliminary selection of values for that function can be made. Where there is disagreement, the previously known reliability or unreliability of the method, the experimenter, and the laboratory concerned are taken into account. A preliminary set of selected values is then chosen.

There follows what may be a lengthy process in which the internal consistency of the data and the consistency with the phase diagram and with the data of other phases are examined. An attempt is made to construct tables of values which are consistent with each other and with all pertinent experimental work. Values which are not founded on experimental work usually are omitted from the tables. In those cases where estimated data, or data of uncertain validity are tabulated, the values are presented in parentheses. Where convenient and possible, uncertainties also are tabulated.

Contradictory data are not permitted in the tables. Where it is uncertain as to which set of contradictory data should be excluded, the sitaution is described in the discussion. Some tables are labelled "(according to -----)" where the data seemed of uncertain validity and could not be checked with other data by the criteria outlined above.

Very Dilute Solutions (Amalgams). Data for very dilute amalgams are treated somewhat differently. Most of the reliable data found on highly dilute solutions are in the form of emf measurements on amalgams using aqueous electrolytes. This technique was brought to high precision some twenty years before the successful use of nonaqueous electrolytes for higher melting alloys. The accuracy attained in these earlier works has never been equalled with the nonaqueous electrolytes. A number of such studies of very dilute solutions with mercury as the solvent are available.

In many cases potentials were measured between electrodes, each of which was an amalgam of different concentration of the solute. Such results cannot be referred to a standard state of the pure solute in the absence of other data. However, $\Delta\bar{G}_{Hg}$ can be calculated. If there exists a measurement that can be referred to the pure solute, M, $\Delta\bar{G}_M$ values can also be found.

Consider the composition $Hg_{1-x}M_{x(\ell)}$. Let

$$\Delta\bar{G}^{xs}_{M,x} = \Delta\bar{G}^{xs}_{M,x=0} + G' x$$

where G' is the limit of the first derivative of $\Delta\bar{G}^{xs}_{M}$ with respect to x as $x \rightarrow 0$. Henry's law predicts a zero value of G' as well as for the higher derivatives. A value for G' is therefore a measure of the deviation from Henry's law. A regular solution may have a nonzero value for G', but the higher derivatives are zero. In some cases the experimental values show a sharp change in the value of G' as $x \rightarrow 0$. These were ascribed to the difficulties in obtaining equilibrium concentrations in very dilute solutions and were discarded.

It is easily verified that Gibbs-Duhem integration yields

$$\lim_{x\to 0} \alpha_{Hg} = -1/2\, G', \text{ and } \lim_{x\to 0} d\alpha_{Hg}/dx = -1/3\, G',$$

giving values of $\Delta\bar{G}_{Hg}$ which may be compared with Hg vapor pressure data, for example.

Uncertainty Estimates. Proper interpretation of the significance of tabular thermodynamic data requires that the reliability of listed values be defined as well as possible. Precise numerical estimates of probable error or uncertainty are difficult to make. Statistical measures of precision such as the standard deviation are only significant when calculated from a sufficiently large sample of data, and at most can reveal only the precision or reproducibility of the data without regard to systematic errors.

What is really desired is an estimate of the accuracy which includes the uncertainty due to systematic experimental error. Such estimates are aided by comparisons of data obtained either by different laboratories or by two or more methods which differ in principle. The degree of consistency of data with other measurements, with thermodynamic relationships, and with the phase diagram help greatly in assessing the uncertainty to be assigned to the selected values. General experience gained from examining data for many systems and from many sources also enables improved evaluation.

Inevitably, however, the uncertainty or probable error attached to the selected values in the tables is to a considerable extent arrived at subjectively, with the aid of the criteria mentioned above. The tabulated uncertainties may be taken to represent, roughly, the 95% confidence limit of the associated values. Those data which have been obtained from estimates or from extensive extrapolations of measured values are placed in parentheses throughout the tables. The user of the tables also can gain an impression of the validity of the data by reading the discussions preceding the tables for each system.