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Additional Data Needed to Establish the Thermodynamic
Properties of Alloying Systems

UCRL - 17122

by Ralph Hultgren

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Conference on Applications of Fundamental Thermodynamics to Metallurgical
Processes-----University of Pittsburgh

It would be much easier to describe the data we have than what we need because we have so little and need so much. The data can be discussed under three categories:

- (1) Elements (unary systems)
- (2) Alloys (binary, polynary systems)
- (3) Interstitial alloys (B, C, O, H, N, with transition metals)

With your indulgence, the statistics on the first two categories will be derived from the book, "Selected Values of Thermodynamic Properties of Metals and Alloys." This book contains substantially all thermodynamic data for unary and binary metallic systems up to the closing dates which are, on the average, about 1961. Systems were included only if they had thermodynamic measurements. Systems for which there were phase diagrams alone, for example, were not evaluated, although phase diagrams were used to evaluate and expand measured data.

Metallic systems were defined as those which conducted electricity by motion of electrons; about 80 elements including 11 trans-uranic elements were included. Metallic and semi metallic phases formed by C, H, O, N, B in interstitial compounds or solid solutions were not included in the first edition.

Of the 80 elements 64 were included. Those omitted were 10 trans-uranic elements (all except Pu), and Tc, Po, Fr, Ra, Ac, Pa, and Pm. The omissions, as can be seen, are very natural in view of the difficulty of obtaining samples of the rarer elements.

Pertinent measurements of elements are the low- and high-temperature heat capacities and enthalpies and heat capacities of gases calculated from spectroscopic data. From these measurements can be calculated the enthalpies, entropies, and Gibbs energy functions of the elements.

In most cases the necessary measurements have been made with reasonable accuracy for the solid up to the melting point or, for higher melting metals, to temperatures well over 1000°C. Techniques for heat content measurements at truly high temperatures need to be developed.

The paucity of liquid data for the elements is, however, astonishing. It would seem that these measurements went out of fashion forty or more years ago. Data on even simple and important metals dates mainly from that time and are

often seriously in error. It is probably true that liquid heat capacities decline with temperature increase; the measurements are sufficiently accurate to show this in only a few cases. As an example, our laboratory had occasion to measure liquid tin and liquid silver recently and found notably different latent heats of fusion and heat contents than the best values found in the literature. The state of affairs is shown in Slide 1.

Sl 1.

Binary alloys are much more inadequately studied. Of 3160 possible combinations, only 166 are listed. When it is remembered that the data on some of the listed systems is very sketchy indeed, the magnitude of the work to be done can be appreciated. Trans uranic metals and rare ones (Tc, Po, Fr, Ra, Ac, Pa) are not represented at all and only five systems involving lanthanides were found. Of the remaining 49 metals less than 6% of the systems are covered. This distribution of the systems is shown in Slide 3.

Sl 2.

Sl 3.

Most of the systems are between the more common, low-melting metals. The transition metals, except for iron, are a vast wasteland. The intensity of coverage of the 12 systems involving iron is usually low. It would seem that in this area data badly needed for modern technology is almost entirely lacking.

The reasons for the neglect are technical. Transition metals are high-melting and easily contaminated especially by elements difficult to detect as C, H, N, O, etc. Acid solution calorimetry is inaccurate and most of the metals will not dissolve with sufficient rapidity in solvents such as tin. The product of combustion bomb calorimetry may be complex and difficult to quantitatively identify. Equilibrium emf measurements have to be carried out at high temperatures where techniques have not been well developed; moreover, electrode potentials may not differ enough for easy measurements. Vapor pressure measurements look the most promising, but techniques are difficult. The problem of concentration depletion of the more volatile component on the surface has not been adequately handled.

Interstitial solid solutions and compounds are becoming enormously important to our technology and have been scarcely touched, except for the iron-carbon system. These systems occur between B, C, O, H, and N with the transition metals. (The columns of the periodic table headed by Sc to Ni which contain incompletely filled d-shells of electrons.)

Many phases in these systems may vary in composition over wide limits; a fact which is incompletely recognized. Two investigators may study the same carbide phase, for example, but get widely different results because their samples differed in composition. Chemical analyses are difficult and, because of the widely different atomic weights of the components, small differences of weight percentages may reflect large differences in the more significant atomic percentages. Techniques of measurement are even more inadequate than in the case of the transition metal alloys with one another.

Even the method of calculating and recording the results is often, in my opinion, unnecessarily complex and confusing, though I think I could get arguments here. Usually the attempt is made to characterize a phase by a composition A_xB_y where x and y are small integers. This composition may be included in the range of existence of the phase, or may be merely near compositions which are stable. Composition variance of the phase is then treated as solid solubility with, perhaps, assumptions made as to the ideality of the solution.

It would take too much time to show how this leads to confusion in some cases. In my opinion, these phases could be treated as are alloy phases of variable composition. Partial and integral quantities should then be tabulated as functions of composition.

The amount of data in this field is small but rapidly increasing. I have at present no way of citing statistics of coverage, but it is certainly small. We hope at my laboratory to develop these fragmentary ideas I have mentioned within the next few years.

