Thermochemical Investigations of Alloys

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Received June 11, 1954

Using a recently developed high temperature calorimeter,[1] which at temperatures up to 500° permits determinations of heats of reaction with an accuracy of the order of ±1%, the author has initiated a study of the thermochemical properties of the binary alloys of Group 1B metals (copper, silver, gold) with metals of groups 2B, 3B, etc. These investigations have now reached a stage where some results can be reported for the alloys of silver with cadmium, indium, tin and antimony.

In this work the appropriate thermochemical data have been obtained at 450° by the following methods: (a) by treating pure solid silver in the calorimeter with a pure liquid metal to form a liquid alloy; (b) by dissolving pure metals and solid alloys, in separate experiments, in liquid tin.[2]

The results obtained in experiments of type (a) permit a direct calculation of the molar heat of formation of the resulting liquid alloy. The data for silver–tin alloys are of particular interest in connection with experiments of type (b) (below), and special attention was therefore given to these alloys. By extrapolation[3] of the results for alloy concentrations down to about 1 atomic per cent. silver, a value of +15,020 joule/g. atom was obtained for the limiting heat (ΔH) of solution. The estimated uncertainty in this value is about ±150 joule. For comparison, it may be pointed out that Ticknor and Bever report the somewhat higher values of 3800–3900 cal./g. atom (15,900–16,300 joule) at 240–300°, with an estimated uncertainty of 150 cal. It is quite possible that most of the discrepancy between these results may be due to the effect of temperature on the heat of solution.

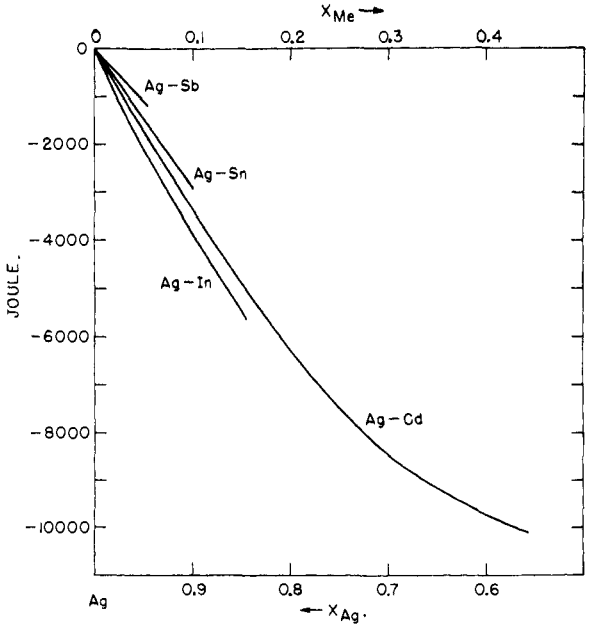

Fig. 1.—Heats of formation of silver solid solutions: $X\mathrm{Ag(s)} + (1 - X)\mathrm{Me(l)} = \mathrm{Ag}_X\mathrm{Me}_{1-X}\mathrm{(s)}$, 450°.

(1) O. J. Kleppa, "A New High-Temperature Reaction Calorimeter," to be published in *J. Phys. Chem.*

(2) L. B. Ticknor and M. B. Bever, *J. Metals*, **4**, 941 (1952).

(3) The extrapolation was based on expansion of the molar heat of formation of dilute silver alloys in powers of the atomic fraction of silver, x_{Ag}.

The liquid alloys of silver–indium and silver–cadmium were not studied as intensely as the silver–tin alloys, and the values for the limiting heats of solution are therefore associated with larger errors. For silver dissolved in indium the preferred value for the limiting heat of solution is +7200 joule/g. atom, with a possible error of as much as 2–300 joule, while for silver–cadmium the corresponding value of −13,800 joule/g. atom may similarly be in error by 2–300 joule.

By combination of these results with available data on the heat of fusion of silver, the results may be used to calculate $\overline{L}^{\circ}_{Ag}$, the limiting partial molal heat contents relative to undercooled liquid silver. If we assume, for simplicity, that the heat of fusion of silver is independent of temperature between the melting point and 450°, we have ΔH_{fusion} = 11,250 joule and get $\overline{L}^{\circ}_{Ag}$ (in Cd) ≅ −25,000 joule, $\overline{L}^{\circ}_{Ag}$ (in In) ≅ −4000 joule, and $\overline{L}^{\circ}_{Ag}$ (in Sn) ≅ +3800 joule. The positive value for $\overline{L}^{\circ}_{Ag}$ (in Sn), and the trend toward higher negative values as we go to indium and cadmium, is of special interest.

In the case of the solid alloys, the direct reaction procedure is not applicable, and the appropriate heats of formation have been calculated from the results of solution experiments (type (b) above). The heat of formation data for solid alloys are accordingly associated with a considerable error, roughly ±250 joule/g. atom, independent of alloy concentration. This error imposes a practical limit on the magnitude of the heats of formation which can profitably be studied in the present apparatus, and this limitation should be borne in mind when Fig. 1 is consulted. In this figure are plotted curves for the heats of formation from solid silver and liquid alloying elements of the silver-rich solutions in the systems Ag–Cd, Ag–In, Ag–Sn and Ag–Sb. (As antimony is solid at 450°, the data for the silver–antimony alloys have been referred to undercooled liquid antimony by adopting a value of 19,800 joule/g. atom for its heat of fusion.) It should be noted that in the case of these solid solutions the negative ΔH of formation for a particular silver concentration increases in the order Sb, Sn, Cd, In.

A detailed account of the present work will be presented in later communications.

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Refractive Indices of the Systems Uranium Hexafluoride–Bromine Trifluoride and Uranium Hexafluoride–Bromine Pentafluoride

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Received May 13, 1954

The refractive indices of bromine trifluoride and bromine pentafluoride have recently been meas-