Thermochemical Investigations of Alloys

By O. J. Kleppa

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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.

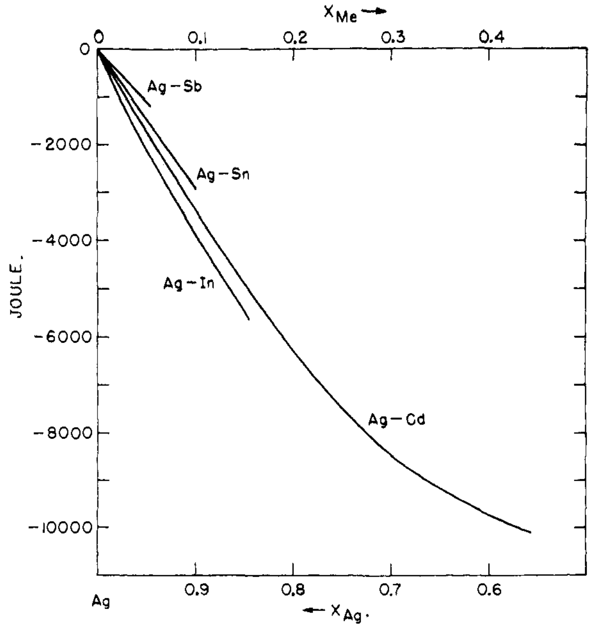

Fig. 1.—Heats of formation of silver solid solutions: $X\text{Ag(s)} + (1 - X)\text{Me(l)} = \text{Ag}_X\text{Me}_{1-X}\text{(s)}$, 450°.

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 $\bar{L}^\circ_{Ag}$, 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 $\bar{L}^\circ_{Ag}$ (in Cd) $\cong$ −25,000 joule, $\bar{L}^\circ_{Ag}$ (in In) $\cong$ −4000 joule, and $\bar{L}^\circ_{Ag}$ (in Sn) $\cong$ +3800 joule. The positive value for $\bar{L}^\circ_{Ag}$ (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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[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}.

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

By Lawrence Stein and Richard C. Vogel

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The refractive indices of bromine trifluoride and bromine pentafluoride have recently been measured[1] by the hollow prism method. The method has proved to be useful not only for examining corrosive interhalogen compounds, but for examining highly volatile substances as well. In the present instance, an electrically heated hollow prism has been used to measure the refractive indices of the systems uranium hexafluoride–bromine trifluoride and uranium hexafluoride–bromine pentafluoride. The data obtained at 70° with the sodium-D lines are given in Tables I and II. The values of $n^{70}\mathrm{D}$ for the pure components are averages of three or more determinations, whereas the values for the binary solutions are the results of single determinations.

TABLE I

REFRACTIVE INDICES OF URANIUM HEXAFLUORIDE–BROMINE TRIFLUORIDE SOLUTIONS

Mole fraction of uranium hexafluoride	$n^{70}\mathrm{D}$ Expt.	$n^{70}\mathrm{D}$ Calcd.	Mole fraction of uranium hexafluoride	$n^{70}\mathrm{D}$ Expt.	$n^{70}\mathrm{D}$ Calcd.
0.0000	1.4302	1.4302	0.5303	1.3836	1.3830
.0487	1.4248	1.4248	.6420	1.3758	1.3758
.0498	1.4247	1.4247	.8181	1.3656	1.3662
.1566	1.4131	1.4138	1.0000	1.3580	1.3580
.3484	1.3968	1.3968			

TABLE II

REFRACTIVE INDICES OF URANIUM HEXAFLUORIDE–BROMINE PENTAFLUORIDE SOLUTIONS

Mole fraction of uranium hexafluoride	$n^{70}\mathrm{D}$ Expt.	$n^{70}\mathrm{D}$ Calcd.	Mole fraction of uranium hexafluoride	$n^{70}\mathrm{D}$ Expt.	$n^{70}\mathrm{D}$ Calcd.
0.0000	1.3275	1.3275	0.5965	1.3477	1.3477
.1684	1.3338	1.3337	.7607	1.3522	1.3522
.3153	1.3388	1.3389	.9069	1.3560	1.3560
.4354	1.3428	1.3427	1.0000	1.3580	1.3580
.5134	1.3449	1.3452			

An empirical equation has been fitted to the data in each table, representing $n^{70}\mathrm{D}$ as a function of N, the mole fraction of uranium hexafluoride. Equation 1, below, applies to the uranium hexafluoride–bromine trifluoride solutions, and equation 2 applies to the uranium hexafluoride–bromine pentafluoride solutions. The equations have been made to yield the experimental values of $n^{70}\mathrm{D}$ at $N = 0$ and $N = 1$, since the data are most reliable at these points. The calculated values of $n^{70}\mathrm{D}$ are listed in column 3 of Tables I and II.

$$n^{70}\mathrm{D} = 1.4302 - 0.1123N + 0.0484N^2 - 0.0083N^3 \quad (1)$$

$$n^{70}\mathrm{D} = 1.3275 + 0.0380N - 0.0065N^2 - 0.0010N^3 \quad (2)$$

The statistical probable error of $n^{70}\mathrm{D}$ computed from equation 1 is ±0.0004, and that computed from equation 2 is ±0.0001. The smaller value is believed to be fortuitous, and a single measurement is believed to have a precision of approximately ±0.0004. Since $n^{70}\mathrm{D}$ of bromine trifluoride differs from that of uranium hexafluoride by 0.0722, it should be possible to analyze the binary solutions to within ±0.6% by refractive index measurements. Analysis of uranium hexafluoride–bromine pentafluoride solutions within ±1.3% should be possible, since the difference in $n^{70}\mathrm{D}$ is 0.0305.

In the present investigation, $n^{70}\mathrm{D}$ for uranium hexafluoride was found to be 1.3580 ± 0.0004, whereas the value 1.367 has been previously reported in the literature.[2,3] The earlier value, which was obtained by measuring the critical angle of reflection at the surface of liquid uranium hexafluoride, is believed to be in error.

Experimental

The apparatus used in making these measurements and the method of purification of the bromine fluorides have been previously described.[1] In the present work, the original hollow prism was modified by the addition of electric heating coils to the top and bottom jackets, so that a temperature of 70.0 ± 0.5° could be maintained. This temperature was chosen in order to keep the uranium hexafluoride in the liquid state over the entire range of composition. The temperature was measured to ±0.1° by means of a calibrated copper–constantan thermocouple and a Leeds and Northrup model K potentiometer.

The uranium hexafluoride was obtained from Carbide and Carbon Chemicals Company. Its freezing point was found to be 64.0°, in good agreement with the value of Oliver and Grisard.[4]

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[1] L. Stein, R. C. Vogel and W. H. Ludewig, THIS JOURNAL, **76**, 4287 (1954).

[2] J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," National Nuclear Energy Series, Div. VIII, Vol. 5, McGraw-Hill Book Co., New York, N. Y., 1951, p. 432.

[3] D. R. Llewellyn, *J. Chem. Soc.*, 28 (1953).

[4] G. D. Oliver and J. Grisard, THIS JOURNAL, **75**, 2827 (1953).

Yttrium Chromium Oxide, a New Compound of the Perowskite Type

BY JOHN T. LOOBY AND LEWIS KATZ

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The search for suitable systems in which to study the distribution of trace ions between a molten salt and a solid led us to consider the possibility of the replacement of lanthanum in $LaCrO_3$ with yttrium using sodium chloride as the liquid phase. This appeared to be a convenient system since suitable radioactive isotopes of both yttrium and lanthanum are available. In the course of this work a finely divided green solid was prepared from the oxides Cr_2O_3 and Y_2O_3. Casual inspection of the X-ray diffraction pattern suggested that the structure was similar to that of perowskite. This result is perhaps not surprising in view of the fact that the tolerance factor t in the Goldschmidt relationship $R_A + R_O = t\sqrt{2}(R_B + R_O)$ has the value of 0.86. According to Náray-Szabó,[1] this would lead one to expect a monoclinic distortion of the perowskite structure or according to Megaw[2] an orthorhombic distortion.

Experimental

Chromic oxide was prepared by ignition of reagent grade chromic nitrate until there was no further loss of weight. The yttrium oxide was obtained from Fisher Scientific Company and was labeled 99% pure. Mixtures of the two oxides, with the yttrium oxide to chromic oxide molar ratio always greater than one, were heated in a sodium chloride flux at 900° in a hydrogen atmosphere. The flux was removed from the water-insoluble product by leaching with water; excess yttrium oxide was removed by leaching with very dilute hydrochloric acid. In all cases the X-ray diffraction patterns appeared the same. The density of the com-

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[1] I. Náray-Szabó, *Muegyetemi Közlemenyek*, **1**, 30 (1947).

[2] H. D. Megaw, *Proc. Phys. Soc.*, **58**, 133 (1946).