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The Thermodynamic Properties of the Silver–Cadmium System

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The heats of formation of the ζ, β' and γ-phases of the Ag–Cd system have been measured by means of liquid tin solution calorimetry. These results, together with a critical evaluation of the literature, have made possible a confident thermodynamic description of the Ag–Cd system as a whole. The estimation of heats of formation from activity data (without using temperature coefficients) and the phase diagram has been described. The results are in good agreement with the experimental values, except for the γ-phase, for which an order–disorder transformation is believed to occur.

Introduction

There has been an increasing interest in the study of the thermodynamics of alloy formation and many measurements on alloy systems are being reported in the literature. Unfortunately many of these data are inaccurate and misleading. Although work has been done on many systems, the over-all thermodynamic behavior is known with confidence for only a very few. There is, therefore, a need for critical and thorough correlation work on the systems for which a large number of experimental data are available. Preliminary work indicated that the Ag–Cd system would be an excellent one to study, if reliable heats of formation of some of the intermediate phases were available.

It was therefore decided to measure the heats of formation of an alloy of one composition each of the ζ (quenched), β' and γ-phases by the method of liquid tin solution calorimetry, making possible a correlation and evaluation of the existing thermodynamic data on this system. (See the phase diagram[1–3], Fig. 1, for nomenclature of the phases.)

Experimental Procedure

The experimental apparatus and technique of measurement have been described in detail in an earlier paper.[4] It will suffice to mention here that the alloy at a temperature of 31° is dropped into a molten tin-bath (250°) until solution is complete. The heat effect is determined from the temperature change of the tin-bath, making corrections for heat flow during the process. The entire enthalpy difference between the initial and final states is measured, and it does not matter what intermediate steps are involved. (Some confusion on this point has existed in the past.) The procedure is repeated for the pure component elements. The following equations illustrate the manner in which the heat of formation is evaluated

$$\mathrm{Ag}_{1-x}\,\mathrm{Cd}_{x(\mathrm{s},\,31°)} = (1-x)\mathrm{Ag}_{(\mathrm{in\ Sn},\,250°)} + x\mathrm{Cd}_{(\mathrm{in\ Sn},\,250°)} \quad (1)$$

$$(1-x)\mathrm{Ag}_{(\mathrm{s},\,31°)} = (1-x)\mathrm{Ag}_{(\mathrm{in\ Sn},\,250°)} \quad (2)$$

$$x\mathrm{Cd}_{(\mathrm{s},\,31°)} = x\mathrm{Cd}_{(\mathrm{in\ Sn},\,250°)} \quad (3)$$

$$(1-x)\mathrm{Ag}_{(\mathrm{s},\,31°)} + x\mathrm{Cd}_{(\mathrm{s},\,31°\mathrm{C})} = \mathrm{Ag}_{1-x}\,\mathrm{Cd}_{x(\mathrm{s},\,31°)} \quad (4)$$

$$\Delta H_4 = \Delta H_2 + \Delta H_3 - \Delta H_1$$

Thus the heat of formation is evaluated at 31°, even though the solution process is carried out at 250°. Only the assumption of identical final states is involved in this method.

The alloys were prepared by melting small chunks of spectroscopically pure silver and cadmium together in evacuated Vycor tubes. The tubes were quickly quenched in water to avoid macroscopic segregation. The ingots were resealed in evacuated tubes which were then held for two weeks at a temperature about 50° below the solidus temperature of the alloy. Microscopic examination indicated the alloys to be single phases. The ingots were chemically analyzed for their Ag content by titration of an acid solution with KSCN using ferric ion as the indicator. The atomic fractions of Cd were found to be 0.500 ± 0.001 and 0.588 ± 0.002. Several samples from different portions of the ingots gave concordant results verifying homogeneity. Small cuttings of the ingots for use in the calorimeter and filings for X-ray measurements were taken. These were placed together in evacuated Vycor tubes and given the following heat treatments.

Zeta alloy, annealed at 370° for one-half hour and quenched by breaking the capsule in alcohol.

Beta-prime alloy, annealed at 370° for one-half hour, then annealed at 180° for two days followed by air-cooling of the evacuated tube to room temperature.

Gamma alloy, annealed at 370° for one-half hour followed

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[1] M. Hansen, "Der Aufbau der Zweistofflegierungen," Julius Springer, Berlin, 1936.

[2] E. Owen, J. Rogers and J. Guthrie, *J. Inst. Metals*, **65**, 457 (1939).

[3] L. Muldawer, M. Amsterdam and F. Rothwarf, *J. Metals*, **5**, 1458 (1953).

[4] R. Orr, A. Goldberg and R. Hultgren, *Rev. Sci. Instr.*, **28**, 767 (1957).

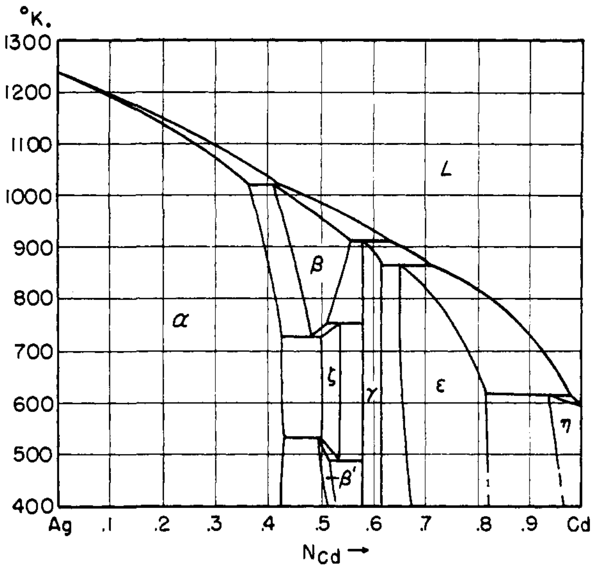

Fig. 1.—Phase diagram, Ag–Cd system.

by overnight cooling in the furnace. It was desired to develop as much long-range order in the β'- and γ-alloys as possible. Powder X-ray diffraction patterns indicated the alloys to be strain free and homogeneous. The crystal structures and approximate lattice constants were found to agree with those reported by Smithells.[5] All reflections were identifiable with the desired phase. It was not possible to ascertain the existence of long-range order due to the nearly equal atomic scattering factors of Ag and Cd.

About 0.002 g. atom of the specimen was enclosed in a weighed Au capsule, together with an additional weighed amount of Au enough to approximately balance the endothermic sensible heat and heat of solution of the specimen. (As explained in ref. 4, this is the "balanced heat effect method"; the large exothermic heat of solution of Au in liq. Sn has been accurately determined in this Laboratory for the purpose.) Two series of runs were made, the amount of the liquid Sn-bath being about two g. atoms in each case.

The experimental results are presented in Table I. Values in the fourth column are the net heat effects, after allowing for the heat effect of the Au, and expressing the results on a g. atomic basis, and are heats of reaction of eq. 1, 2 or 3, depending on whether the specimen was an alloy or one of the component elements. Values in the last column, the heats of formation of the alloys at 31°, were calculated from eq. 4 by using the average values of ΔH_2 and ΔH_3 of 4876 and 4573 cal./g. atom, respectively. An analysis[4] of the experimental apparatus and technique shows the primary source of error to be random in nature; the reliability of the selected heats of formation is estimated to be ±50 cal./g. atom.

Evaluation of the Thermodynamic Properties

The nomenclature adopted here is that of Lewis and Randall.[6] All thermodynamic quantities for the solid alloys have been referred to the solid elements, even though many of the measurements have been carried out above the melting point of Cd. For this purpose the heat of fusion was taken as 1500 cal./g. atom. The heat capacity of Cd in the hypothetical superheated solid state was assumed equal to that of liquid Cd.

Alpha Phase.—The integral heats of formation have been measured by Kleppa[7] at 450° and Orr, Goldberg and Hultgren[8] at room temperature. The two investigations agree well with each other within the experimental precision (Fig. 2). The data of Orr, *et al.*, show a little less scatter than those of Kleppa and are selected on this basis to define the integral heats of formation of the α-phase within ± 100 cal./g. atom. Four investigations of the vapor pressures of Cd over the α-phase have been made. Schneider and Schmid[9] and Birchenall and Cheng[10] determined the vapor pressures by the dew point method. Unfortunately, enough compositions were not studied in either case to permit the Gibbs–Duhem integration of the partial molar quantities. Herasymenko[11] and Scatchard and Boyd[12] have determined the vapor pressures at close composition intervals. All four investigations are in approximate agreement with respect to $\Delta\bar{F}_{Cd}$; however, Schneider and Schmid and Herasymenko find the entropies (when referred to solid Cd) to be more positive than the ideal quantities, while Birchenall and Cheng and Scatchard and Boyd found the excess entropies to be negative. Integral heats of formation were determined after performing Gibbs–Duhem integrations. Scatchard and Boyd's values agree excellently with the calorimetric data and were consequently selected. Herasymenko's values, on the other hand, are in serious disagreement. Values of $\Delta\bar{S}_{Cd}$ were selected so as to be in reasonable accord with both the vapor pressure work and the calorimetric results. Hultgren and Rao[13] measured the heat contents of the 20 and 40 atomic % Cd Alloys from about 500°K. to room temperature and found the Kopp–Neumann rule valid within the small experimental uncertainty.

Intermediate Solid Phases.—Ölander[14] has made

TABLE I

EXPERIMENTAL RESULTS

Run[a]	N_{Cd}	Phase	Heat effect, cal./g. atom	Heat of formation cal./g. atom at 31° (exp)	(selected)
42- 3	0.000	Ag	4938		
42-11			4790		
43- 3			4957		
43-12			4820		
42- 4	1.000	Cd	4610		
42-12			4541		
43- 4			4567		
42- 6	0.500	ζ	6560	−1836	−1840
42-10			6565	−1839	
42- 7	.500	β'	6889	−2165	
43- 6			6937	−2213	−2170
43- 8			6865	−2141	
42- 8	.588	γ	6657	−1959	
43- 7			6721	−2023	−1990
43-10			6664	−1966	

[a] Runs 42-1, 5, 9 and 43-1, 5, 9 were Sn calibration runs; runs 42-2 and 43-2 were checks on the heat effect of Au; run 43-11 was rejected due to an accident.

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(5) C. J. Smithells, "Metals Reference Book," Interscience Publishers, New York, N. Y., 1955.

(6) G. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., New York, N. Y., 1923.

(7) O. J. Kleppa, *J. Phys. Chem.*, **60**, 846 (1956).

(8) R. Orr, A. Goldberg and R. Hultgren, *ibid.*, **62**, 325 (1958).

(9) A. Schneider and H. Schmid, *Z. Elektrochem.*, **48**, 627 (1942).

(10) C. E. Birchenall and C. H. Cheng, *J. Metals*, **185**, 428 (1949).

(11) P. Herasymenko, *Acta Met.*, **1**, 1 (1956).

(12) G. Scatchard and R. H. Boyd, THIS JOURNAL, **78**, 3889 (1956).

(13) R. Hultgren and K. H. Rao, in *Trans. Indian Inst. Metals*, in press.

(14) A. Ölander, *Z. physik. Chem.*, **A163**, 107 (1933).

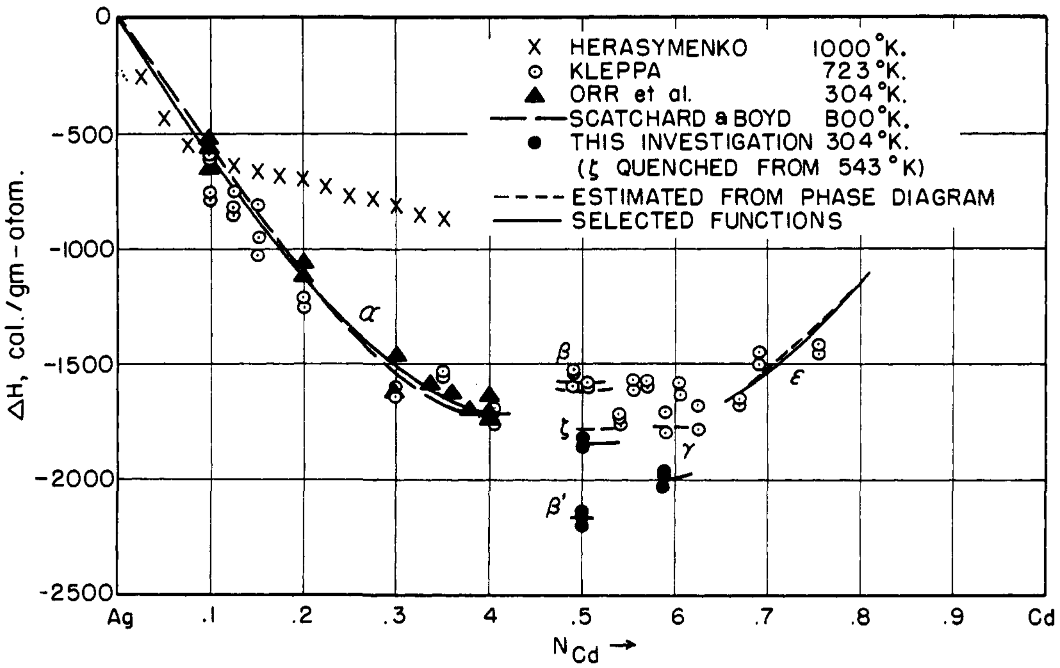

Fig. 2.—Experimental, calculated and selected heats of formation of solid Ag–Cd alloys.

extensive e.m.f. studies of the ζ, β, γ and ϵ-phases. Integral heat of formation data are available from the experimental portion of this investigation and the measurements of Kleppa. In addition, the phase diagram can be used to estimate the entropies of most of the intermediate solid phases. Ölander's partial free energy results are in good accord with the phase diagram for temperatures near 700°K., and his value of $\Delta\bar{F}_{\mathrm{Cd}}$ at the $\zeta(\alpha)$-phase boundary is within 200 cal./g. atom of the value obtained by extrapolating Scatchard and Boyd's results to the $\alpha(\zeta)$ boundary. If, however, the e.m.f. temperature coefficients are used to extrapolate $\Delta\bar{F}_{\mathrm{Cd}}$ to higher temperatures, the agreement with the phase diagram becomes quite poor. Ölander has studied the Cu–Zn system by similar methods; his value for the heat of the $\beta \rightarrow \beta'$ reaction obtained from the e.m.f. temperature coefficients was found to be less than half that yielded by direct calorimetric measurements. On these bases the entropy results of Ölander are rejected, and only the free energies accepted. The integration of Ölander's values for $\Delta\bar{F}_{\mathrm{Cd}}$ was accomplished by the use of the condition that the values of $\Delta\bar{F}_{\mathrm{Ag}}$ at adjoining phase boundaries are equal; Scatchard and Boyd's integrated results for the α-phase were used to obtain $\Delta\bar{F}_{\mathrm{Ag}}$ at the $\alpha(\beta)$- and $\alpha(\zeta)$-boundaries. It should be mentioned here that Ölander found the e.m.f. temperature coefficients to change discontinuously with temperature for the γ-phase at about 723°K.; he interpreted this as an order–disorder reaction.

The phase diagram, together with the free energy data of Ölander, can be utilized to calculate the difference in the partial molar entropies of two phases in equilibrium. The condition that $\Delta\bar{F}_{\mathrm{Cd}}^{\alpha(\beta)}$ equals $\Delta\bar{F}_{\mathrm{Cd}}^{\beta(\alpha)}$ at all temperatures, where $\alpha(\beta)$ and $\beta(\alpha)$ refer to the limits of the α- and β-phases, respectively, requires that

$$\frac{\mathrm{d}\Delta\bar{F}_{\mathrm{Cd}}^{\alpha(\beta)}}{\mathrm{d}T} = \frac{\mathrm{d}\Delta\bar{F}_{\mathrm{Cd}}^{\beta(\alpha)}}{\mathrm{d}T} \tag{5}$$

Note that $\Delta\bar{F}_{\mathrm{Cd}}^{\alpha(\beta)}$ and $\Delta\bar{F}_{\mathrm{Cd}}^{\beta(\alpha)}$ are functions of both temperature and composition, since $N_{\mathrm{Cd}}^{\alpha(\beta)}$ and $N_{\mathrm{Cd}}^{\beta(\alpha)}$ change with temperature. Expressing the total derivatives in terms of the appropriate partial derivatives, and substituting $-\Delta\bar{S}_{\mathrm{Cd}}$ for $\partial\Delta\bar{F}_{\mathrm{Cd}}/\partial T$, eq. 5 becomes

$$\left[\frac{\partial\Delta\bar{F}_{\mathrm{Cd}}}{\partial N_{\mathrm{Cd}}}\frac{\mathrm{d}N_{\mathrm{Cd}}}{\mathrm{d}T} - \Delta\bar{S}_{\mathrm{Cd}}\right]^{\alpha(\beta)} = \left[\frac{\partial\Delta\bar{F}_{\mathrm{Cd}}}{\partial N_{\mathrm{Cd}}}\frac{\mathrm{d}N_{\mathrm{Cd}}}{\mathrm{d}T} - \Delta S_{\mathrm{Cd}}\right]^{\beta(\alpha)} \tag{6}$$

$\partial\Delta\bar{F}_{\mathrm{Cd}}/\partial N_{\mathrm{Cd}}$ is obtained from activity data (Ölander's data in this case) and $\mathrm{d}N_{\mathrm{Cd}}/\mathrm{d}T$ is the reciprocal of the slope of the phase boundary. $\Delta\bar{S}_{\mathrm{Cd}}$ and $\Delta\bar{S}_{\mathrm{Ag}}$ were calculated for the ζ- and β-phases at their Ag-rich limits by this method, using the selected values for the α phase; eq. 6 is of course valid for the Ag component if all of the subscripts are replaced by Ag. Since the concentration dependence of the partial entropies is unknown in the ζ- and γ-phases, this equation cannot be applied to the Cd-rich phases. However, the integral entropy would be expected to vary less rapidly with N_{Cd}, and thus an assumption regarding its concentration dependence would not cause appreciable error.

Representing the compositions $N_{\mathrm{Cd}}^{\alpha(\beta)}$ and $N_{\mathrm{Cd}}^{\beta(\alpha)}$ by a and b, respectively, and using the relation

$$\Delta S = N_{\mathrm{Cd}}\,\Delta\bar{S}_{\mathrm{Cd}} + (1 - N_{\mathrm{Cd}})\Delta\bar{S}_{\mathrm{Ag}} \tag{7}$$

the following expression is easily verified

$$\Delta S^{\alpha(\beta)} - \Delta S^{\beta(\alpha)} = {}^1/_2\{(a + b)(\Delta\bar{S}_{\mathrm{Cd}}^{\alpha(\beta)} - \Delta\bar{S}_{\mathrm{Cd}}^{\beta(\alpha)}) + (2 - a - b)(\Delta\bar{S}_{\mathrm{Ag}}^{\alpha(\beta)} - \Delta\bar{S}_{\mathrm{Ag}}^{\beta(\alpha)}) + (a - b)(\Delta\bar{S}_{\mathrm{Cd}}^{\alpha(\beta)} - \Delta\bar{S}_{\mathrm{Ag}}^{\alpha(\beta)} + \Delta\bar{S}_{\mathrm{Cd}}^{\beta(\alpha)} - \Delta\bar{S}_{\mathrm{Ag}}^{\beta(\alpha)})\} \tag{8}$$

TABLE II

SELECTED FUNCTIONS FOR SOLID Ag–Cd ALLOYS

(Referred to the solid elements)

N_{Cd}	Phase	a_{Cd}	$\Delta\bar{S}_{Cd}$, e.u.	a_{Ag}	$\Delta\bar{S}_{Ag}$, e.u.	ΔH, cal./g. atom	ΔS, e.u.
	673°K.						
0.100	α	0.0023	3.48	0.869	0.26	− 590	0.58
.200		.011	1.70	.664	.56	−1130	.79
.300		.039	1.04	.431	.77	−1520	.85
.400		.127	1.04	.243	.71	−1710	.88
.426		.150	1.12	.198	.71	−1710	.90
		(± .010)	(±0.50)	(± .015)	(± .50)	(± 70)	(± .15)
.501	ζ	.150		.198		−1840	.76
.520		.170		.175		(−1840)	(.76)
.540		.193		.153		(−1840)	(.76)
.580	γ^a	.193		.153		−1990	.49
.600		.269		.094		−1990	.49
.617		.352		.061		(−1970)	(.49)
.654	ϵ	.352		.061		−1660	.80
.690		.489		.040		−1570	.79
.750		.628		.016		−1360	.74
.792		.832		.006		−1180	.73
	773°K.						
.474	β	.171		.242		−1570	1.11
.500		.203		.206		−1580	1.11
.522		.233		.178		−1570	1.11
	453°K.						
.500	β'					−2170	0.10
	573°K.						
.940	η	.922		.002			

[a] Ordered modification.

The first two terms on the right can be evaluated from eq. 6 and the appropriate values of a and b, but the third term cannot be determined. However $a - b$ is only about 0.04 for both the $\zeta - \gamma$ and $\gamma - \epsilon$ cases in the Ag–Cd system; therefore if it is assumed that all of the partial entropies involved differ by less than ± 3.0 e.u. from the ideal quantities, the corresponding error in the calculated ΔS would be less than 0. 24 e.u. if the ideal entropies were used in the third term. ΔS was thus estimated for the γ- and ϵ-phases, assuming it to be proportional to the product $N_{Ag}N_{Cd}$ within each phase. (Almost identical results were obtained from the two independent calculations for the γ-phase, one using the ζ and the other the β-phase.) These results, together with the integrated free energies from Ölander's data, were used to estimate the integral heats of formation of these phases, which are shown in Fig. 2 by the dashed line.

Unfortunately Kleppa's measurements were performed at 723°K. This is approximately the temperature of both the $\zeta \rightarrow \beta$ transition and the suspected ordering reaction in the γ-phase. The agreement of Kleppa's results with the phase diagram calculation must be considered to be quite good in view of the amount of his scatter (due mainly to the poor choice of temperature for the β- and γ-compositions) and the uncertainty of the phase diagram calculation. The experimental results of the present investigation were quite reproducible and, as mentioned before, are believed to be correct within ± 50 cal./g. atom at 304°K. Comparison of these results with Kleppa's definitely supports the view that the γ-phase undergoes an ordering reaction. The phase diagram result (independent of temperature) lies intermediate between the two experimental determinations; hence the shapes of the γ-phase boundaries as reported in the literature probably are incorrect.

Liquid Alloys.—The properties of the liquid are not nearly so well-defined as those of the solid. Schneider and Schmid[9] have measured the vapor pressures and their temperature coefficients for $N_{Cd} = 0.27$–0.68 at 1100°K. The free energy results agree approximately with those calculated from the selected properties of α-alloys and the phase diagram. $\Delta\bar{S}_{Cd}$ was found to be more positive than the ideal entropy of mixing; however, their entropy results on other systems have often proved incorrect. Kleppa[7] has measured the heats of formation of Cd-rich alloys at 723°K. His data yield $\Delta\bar{H}_{Ag}$ at infinite dilution to be -6000 ± 200 cal./g. atom. Kubaschewski and Schneider[15] have measured the heat contents of solid and liquid alloys at $N_{Cd} = 0.675$ from temperatures near the melting point to room temperature. A heat of fusion about equal to the additive heats of fusion of the component elements was found. This result, together with the selected ΔH for the ϵ-phase, can be used to calculate ΔH for the liquid at this composition. The three investigations described above can be compared to each other by defining $Q = \Delta H/N_{Cd}N_{Ag}$ and assuming that $\Delta C_p = 0$. The values of Q compare as follows: Schneider and Schmid, −1500; Kleppa, −6000; and Kubaschewski and Schneider, −7200. The two latter results can be fitted with the equation: $\Delta H = -6000N_{Cd}N_{Ag} - 5500N_{Cd}^2N_{Ag}^2$. This equation

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(15) O. Kubaschewski and A. Schneider, *Z. Elektrochem.*, **49**, 261 (1943).

might be expected to hold fairly well in the Cd-rich region, but extrapolation to Ag-rich alloys is probably unjustified. The free energy results obtained from the α-phase and those of Schneider and Schmid can be fitted at 1100°K. with the function

$$\Delta\bar{F}_{\mathrm{Cd}} = (-5480 + 2340N_{\mathrm{Cd}})N^2_{\mathrm{Ag}} + RT \ln N_{\mathrm{Cd}}$$

which integrates to

$$\Delta\bar{F}_{\mathrm{Ag}} = (-6650 + 2340N_{\mathrm{Cd}})N^2_{\mathrm{Cd}} + RT \ln N_{\mathrm{Ag}}.$$

Discussion

The agreement of ΔH as calculated from the phase diagram and Ölander's activity data for the β, ζ- and ϵ-phases with the directly measured quantities is surprisingly good. It appears that this method may well be applied to other systems for which activity data, but not reliable entropies or heats of formation, are available. The incorrect calculated result for the γ-phase illustrates the necessity of an accurate phase diagram. The viewpoint that this phase is ordered at low temperatures is supported by the small integral entropy calculated from the measured ΔH and ΔF. The ζ- and ϵ-phases have similar crystal structures. If the tabulated values of $\Delta\bar{F}_{\mathrm{Cd}}$ are plotted for all of the solid phases, it will be noticed that the curves for these two phases could be extended smoothly into each other. The measured values of ΔH could similarly be fitted with one curve. In light of this, it seems probable that the two phases would become one phase were it not for the interjection of the γ-phase.

Summary and Conclusions

1. The heats of formation of the ζ, β' and γ-phases of the Ag–Cd system have been measured for one composition of each by the method of liquid tin solution calorimetry.
2. A literature survey and critical evaluation has been made of all of the important thermodynamic work on the system.
3. Experimental information on the α-phase is sufficient to allow the complete determination of all of the thermodynamic properties with confidence.
4. The partial free energies of Cd in the β, ζ, γ- and ϵ-phases appear to be approximately defined by the measurements of Ölander. Information is sufficient to permit the Gibbs–Duhem integration for $\Delta\bar{F}_{\mathrm{Ag}}$. The partial entropy results of Ölander were not accepted.
5. The heats of formation of all of the intermediate solid phases are established well enough by the measurements of Kleppa and the experimental results of this investigation to distinguish the integral energy and entropy characteristics of these phases relative to each other. Phase diagram calculations support the above results. The variation of ΔH with composition within the individual phases is not well enough established to permit evaluation of the partial heats or entropies of formation.
6. The difference of 400 cal./g. atom between Kleppa's measurements of ΔH of the γ-phase at 450° and the experimental results of this investigation at 31° supports Ölander's observation of an order–disorder transition in the γ-phase.
7. The ζ-phase is regarded as an isolated portion of the ϵ-phase; the two are separated by the distinctly different γ-phase.
8. Five different investigations of the Ag–Cd system have been made by equilibrium (vapor pressure, e.m.f., chem. equil.) methods. All five have yielded free energies of at least fair reliability; only one has produced acceptable values for the partial entropies of formation. Thus the danger of placing confidence in unconfirmed values of ΔH and ΔS obtained from these methods has been illustrated.

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