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THERMODYNAMICS OF ALLOYS

(VAPOUR PRESSURE STUDIES)

FINAL TECHNICAL REPORT

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SYNOPSIS:

As part of a programme of studies of the thermodynamic properties of alloy systems, measurements have been made of the vapour pressures of a number of pure metals and their alloys. The torsion-effusion technique has been employed and its applicability to alloy studies has been demonstrated. New vapour pressure measurements have been made on solid cadmium (480 - 570°K), liquid bismuth (820 - 1010°K) and liquid thallium (780 - 920°K) and the results are assessed and compared with those of other workers. Bismuth vapour pressures have been measured over a wide range of liquid silver-bismuth alloys and the results used to compute the thermodynamic properties of the system at 1000°K. The rather unusual characteristics of these are discussed and it is suggested that they are attributable to the change of bonding and co-ordination of bismuth on alloying. A similar evaluation of the thermodynamic properties of liquid silver-lead alloys is also presented and discussed. Preliminary measurements on solid and liquid silver-thallium alloys are described.

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1. Introduction.

Interest in the thermodynamic properties of alloys and their relation to the character of the components has stimulated experimental work in this field. The desire to correlate experimental heats of formation with proposed theoretical models has resulted in a recent emphasis on accurate calorimetric studies, since these yield more reliable values than are normally obtainable using temperature coefficients of equilibrium measurements. However, there remains considerable scope for equilibrium studies, for the free energies of formation of few systems are thoroughly established. While these are of direct significance in relation to alloy equilibria, the entropies of formation obtainable by combining them with calorimetric data, or from their temperature coefficients, are, like heats of formation, of great fundamental interest. As part of a programme of such studies, vapour pressure measurements are being made over various alloy systems. For the derivation of the thermodynamic properties of the alloys by this means, an accurate knowledge of the absolute vapour pressures of the pure volatile components is essential. Since the vapour pressure data for many metals are sparse or contradictory, an experimental re-examination of the pure component is often a necessary preliminary to work on the alloys. The present report summarizes the results of such experimental work on four pure metals and three binary alloy systems. While a few measurements have been made using an elementary Knudsen method, the major part of the work was done using the torsion-effusion method. This method has the advantage of giving a direct, unambiguous measure of the pressure, independent of the atomicity of the vapour, which is itself a variable with some of the components studied.

2. Experimental.

A detailed description of the apparatus and a discussion of the technique has been published elsewhere [1]; a brief account will suffice here. Specimens are enclosed within a graphite effusion cell suspended, inside a vertical vacuum chamber, from a fine tungsten wire. The cell is provided with two similar orifices, which are so disposed that the effusing vapour causes a rotation of the cell about the axis of suspension. The

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vapour pressures are calculated using the relation:

$$p = \frac{2\tau\alpha}{(a_1 q_1 f_1 + a_2 q_2 f_2)} \qquad (1)$$

where p is the vapour pressure, τ the torsion constant of the suspension, α the angle of deflexion, a_1 and a_2 the orifice areas and q_1 and q_2 their respective distances from the axis of rotation. The factors f_1 and f_2 correct for the reduction in effective force of the effusing vapour caused by the finite lengths of the orifices. Freeman and Searcy[2] have shown that for orifice dimensions in the range $0 < \frac{L}{r} < 2$ (where L and r are the orifice length and radius respectively), values of f can be satisfactorily obtained from the equation:

$$1/f = 0.0147 \left(\frac{L}{r}\right)^2 + 0.349 \left(\frac{L}{r}\right) + 0.9982.$$

This relation has been used in the present calculations. Measurements were made on spectroscopical pure materials. Where solid specimens were studied these were used in a finely divided form. Alloys were prepared directly from the component metals. The appropriate amounts of the pure metals were sealed together in silica capsules under a low pressure of purified argon. They were then melted by placing the capsules in a simple resistance furnace. The alloys were maintained in the molten state for approximately one hour, shaken vigourously several times to ensure mixing and finally quenched into cold water. Small pieces were cut from the resulting homogeneous ingots and, after carefully cleaning and drying, loaded into the effusion cell. Chemical analyses were made of samples of the original ingots and also of material taken from the effusion cell after the experiment; it was found that composition changes during the run were insignificant. This was achieved by keeping the duration of individual runs short and by using alloy samples of about 10 grams.

3. Treatment of Results.

The observed vapour pressures generally approximated to the Clausius-Clapeyron relationship and are, therefore, expressed by equations of the form

$$\log P\ (\text{mm.Hg}) = A - B/$$

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The coefficients A and B were evaluated using the method of least squares. In the case of the pure metals, as a check on their consistency, average values for the standard heat of sublimation, ΔH^{o}_{298}, have also been calculated from the various experimental results using the Third Law method, the relevant thermodynamic data being taken from Stull and Sinke.[3]

For the alloys, the results have been used to compute the thermodynamic properties of the liquid phase at 1000°K. Activities and partial free energies of solution of the volatile component have been calculated directly from the observed pressures, using values for the pure component obtained in a similar manner. Corresponding values for the silver component were evaluated by means of the α function[4]. The volatile partials were extrapolated smoothly to $N_{Ag} = 1$ for this purpose, thus the supercooled liquid is adopted as the standard state for the silver component. Similar partial free energies were calculated at 1050 and 950°K and smoothed values of these were used to estimate partial entropies at the intermediate temperature of 1000°K. Partial heats of solution were then estimated using the Gibbs-Helmholtz relationship. Integral values were obtained by the usual summation of partials.

4. Results and Discussion.

4.1. Solid Cadmium.

Measurements were made of the vapour pressure of solid cadmium between 480 and 570°K, including a few observations using the Knudsen method. The values obtained with the two independent techniques are in good agreement with each other. The coefficients of the vapour pressure-temperature equation obtained by treatment of the combined results are given below in table I; together with the standard heat of sublimation. Also tabulated are the equivalent values obtained by similarly treating the earlier results of Egerton[5] and of O'Donnell[6] and the results of Borg and Birchenall[7] and of Nesmeyanov and Il'icheva[8] reported since the present work was begun. All these workers used the Knudsen method, an isotope exchange version being employed by the Russian workers.

The results of the present investigation are in good agreement with those of Borg and Birchenall and both appear to substantiate the early work of Egerton. This group of studies gives better agreement with the

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vapour pressure of the liquid at the melting point than do the results of the other workers.

TABLE I.

Comparison of vapour pressures and standard heats of sublimation of solid cadmium.

Investigator	Temperature Range (°K)	A	B	ΔH^{o}_{298} (K.cals)
Present work	430 - 564	9.404	6146	26.90 ± 0.10
Borg and Birchenall	427 - 551	9.241	6055	26.85 ± 0.05
O'Donnell	473 - 533	9.413	6078	26.60 ± 0.10
Egerton	423 - 543	9.056	5957	26.95 ± 0.15
Nesmeyanov and Il'icheva	411 - 481	8.744	5722	26.54 ± 0.30

Computation of vapour pressures which should obtain for the solid state, from the higher liquid vapour pressures and the appropriate free energy functions, suggests that the temperature coefficient of the vapour pressure of the solid should be smaller than has generally been found experimentally. Thus while the computed values agree well with the present ones at the higher temperatures investigated, they indicated that pressures should be slightly higher than those observed at the lower temperatures; this would be in accord with the trend of the results of the Russian workers and of O'Donnell in the low-temperature range. Full details may be found in a paper[9] based on this study.

4.2. Liquid Bismuth.

Existing vapour pressures for liquid bismuth were particularly contradictory and, as a preliminary to work on silver-bismuth alloys, new measurements were made over the temperature range 820 - 1010°K using the torsion effusion method. Coefficients for the vapour pressure equation, yielded by the present investigation, are given in table 2, together with those obtained by new least square treatments of the results of other workers. For the purpose of comparison, formal values of the latent heat of vaporization, calculated simply from the temperature coefficients of each set of results are also included. However, no simple significance attaches to these values in view of the varying atomicity of the bismuth vapour.

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TABLE 2.

Comparison of the vapour pressures of liquid bismuth.

Investigator.	Temperature range (°K)	A	B	ΔH° (K.cal)
Present work	822 - 1011	8.579	10,108	46.2
Ko[10]	1100 - 1220	8.582	10,230	46.81
Weber and Kirsch[11]	876 - 911	7.919	9,709	44.4
Yosiyama[12]	913 - 971	8.514	10,122	46.3
Granovskaya and Lyubimov[13]	743 - 978	7.709	8,522	39.0
O'Donnell[14]	682 - 771	9.390	10,500	48.0

The present results extrapolate to give good agreement with those reported by Ko, Barus[15], and Ruff and Bergdahl[16], they are slightly higher than those obtained by Yosiyama, using the same technique, but remain lower than the values of O'Donnell and do not substantiate the extremely high values reported by Granovskaya and Lyubimov.

By combining the torsion-effusion results with the results of Knudsen measurements at similar temperatures, an estimate was made of the proportions of the two species Bi and Bi_2 present in the vapour. Application of the third law treatment yields the following heats of vaporization.

$$Bi\ (liq.) = Bi\ (vap) \qquad \Delta H^{\circ}_{298} = 50.13 \pm 0.92\ K.cal/g.atom$$

$$Bi\ (liq.) = \tfrac{1}{2}\ Bi_2\ (vap) \qquad \Delta H^{\circ}_{298} = 26.36 \pm 0.35\ K.cal/g.atom$$

These values, and the implied dissociation energy for Bi_2 of 47.5 K.cal., are in good agreement with values selected by Brackett and Brewer[17] on the basis of a similar re-evaluation of the data of Ko, and Yosiyama.

4.3. Liquid Silver-Bismuth Alloys

Measurements were made on 14 alloys ranging in composition from 100 - 24 atomic per cent bismuth and at temperatures between 900 and 1070°K. The vapour pressure equation coefficients for each of these alloys, obtained from the experimental results in the usual way, are summarized below in table 4. These results have been evaluated in the manner outlined in section 1 and partial and integral thermodynamic quantities obtained are assembled in table 4.

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TABLE 1.

Vapour pressures of bismuth over silver-bismuth alloys.

Mole fraction bismuth	A	B	Temperature range (°K)
0.886	8.085	9,66[illegible]	954 - 1009
0.868	9.44[illegible]	11,0[illegible]0	940 - 1009
0.809	8.646	11,444	952 - 1017
0.805	7.773	[illegible]76	987 - 1025
0.753	9.67[illegible]	10,394	958 - 1023
0.670	8.260	9,942	975 - 1046
0.516	8.240	10,049	958 - 1037
0.497	8.607	10,436	948 - 1016
0.440	9.045	10,954	972 - 1031
0.393	8.075	10,990	894 - 1048
0.285	8.4[illegible]3	10,518	967 - 1050
0.235	8.211	10,218	1020 - 107[illegible]
0.233	7.915	10,106	971 - 1073
0.141	7.884	10,275	994 - 1078

Rather unusual characteristics are indicated. The activities of bismuth deviate positively from ideal behaviour in the bismuth-rich alloys, the deviation gradually decreasing to zero at approximately the equiatomic composition and becoming negative in bismuth-dilute alloys. Gibbs Duhem integration yields silver activities showing negative deviations from ideality over the whole composition range. The corresponding deviations appear in the excess partial free energies and these give rise to integral excess free energies which are negative throughout and which are asymmetric in form, with the trough displaced to ca. $N_{Bi} = 0.35$.

The entropies are also unusual. The partial excess entropies of solution of each component are positive where it is present in high concentration and show minima at ca. 30 atomic per cent in each case. The minimum is [illegible] . 5 atomic per cent for bismuth and since the values for this component are the one obtained directly from experiment they are likely to be the more significant. The resulting excess integral entropies of formation are positive at either end of the system, but exhibit a negative minimum in the central regions.

The heat values are of similar form to the entropies, but these are likely to be the least accurate quantities obtained by the present method. The partial heats of solution of bismuth are positive at high bismuth concentrations,

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TABLE 4.

Thermodynamic properties of liquid silver- bismuth alloys at 1000°K.

N_{Bi}	N_{Ag}	a_{Ag}	$\Delta\bar{G}_{Bi}$ (cal./g.atom)	$\Delta\bar{G}_{Ag}$ (cal./g.atom)	$\Delta\bar{S}_{Bi}$ (cal./deg.g.atom)	$\Delta\bar{S}_{Ag}$ (cal./deg.g.atom)	$\Delta\bar{H}_{Bi}$ (cal./g.atom)	$\Delta\bar{H}_{Ag}$ (cal./g.atom)	ΔG (cal./g.at)	ΔS (cal/deg.g.at)	ΔH (cal./g.at)
.9	.91	0.[illegible]	- 180	- 5210	0.29	5.10	+ 110	- 110	-685	0.77	+ [illegible]
.8	.88	0.13	- 370	- 4115	0.75	2.69	+ [illegible]	-1420	-1130	1.14	+ 20
.7	.74	0.18	- 610	-3385	1.01	1.75	+ [illegible]	-1640	-1140	1.34	-210
.6	.63	0.21	- 920	- 2850	1.30	1.60	+ [illegible]80	-1250	-1690	1.[illegible]2	-370
.5	.52	0.32	-1[illegible]75	- 2265	1.11	1.39	- 260	- 870	-1820	1.26	-365
.4	[illegible]	0.42	-2125	- 1650	0.86	1.59	-1270	- 60	-1840	1.29	-540
.3	.2[illegible]	[illegible]	-3160	- 1035	1.20	1.19	-1360	+ 90	-1715	1.37	-345
.2	[illegible]	0.73	-4575	- 625	[illegible].40	0.59	-1180	- 30	-1415	1.15	-260
.1	[illegible]	0.8[illegible]	-6718	- 250	5.55	0.23	-117[illegible]	- 20	-[illegible]00	0.77	-135

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but rapidly become negative as more silver is added. The values pass through a minimum at N_{Ag} = 0.3, but rise in negative sense at infinite dilution. For silver the partial heats of solution are approximately zero at high silver concentrations, they become negative as the bismuth content increases, passing through a minimum at ca. 30 atomic per cent silver and finally show positive values in the bismuth-rich alloys. The resulting integral heats of formation have slightly positive values in bismuth-rich alloys but are negative over the majority of the composition range with a minimum value of ca. - 500 cal./g. atom ca. 45 atomic per cent bismuth.

Little thermodynamic work has been previously done on this system and none is directly comparable with the present results. Two calorimetric studies have been made of the liquid alloys and the results of these are not in accord with the present values, since they show only positive heats of formations. Direct mixing calorimetry at 1323°K by Kawakami[18] gives values rising to a maximum of ca. 1 K.cal at the equiatomic composition, but his values have in the past often been shown to be inaccurate. Unfortunately, the generally more reliable tin-solution calorimetry of Kleppa[19] has only been applied to alloys between 0 - 30% silver and at 723°K. While this indicates more positive values in this range than found in the present work, it is noteworthy that, if the reported values are converted to the present standard state of supercooled liquid silver, constant values are obtained for the three alloys richest in silver, which suggests the existence of a maximum and a fall to less positive values at higher silver concentration. Since the heat values obtained calorimetrically should be the more accurate, it would appear that the present heats are too negative, nevertheless it is considered that the observed trends are qualitatively substantiated. The forms of the observed thermodynamic properties are characteristic of systems involving opposing factors. They are consistent with the existence of positive excess contributions throughout the system, but partially counterbal nced over a range of intermediate compositions by negative contributions. A system, such as this, with a large size and valency difference between the components generally exhibits positive heats of mixing attributable to misfit energies. Also the mixing of such atoms will be expected to reduce the mean vibrational frequency and so give positive entropy coefficients. These in turn will make positive contributions to

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[illegible] responsible for positive excess entropies. A specific positive contribution in the silver-bismuth alloys may be expected to arise from the [illegible] of bismuth. It is considered, by Kuo [illegible] [illegible] in pure liquid bismuth until quite high [illegible] silver should [illegible] association of [illegible] the [illegible] will [illegible] contribution to the [illegible] of bismuth and therefore to the integral [illegible] contribution to the entropy will [illegible] of such partially ordered clusters.

[illegible] of the opposing negative influences may lie in the [illegible] co-ordination likely to be involved on mixing bismuth and silver. Liquid silver and silver-rich alloys would be expected to exhibit close packing with co-ordination numbers probably approaching the value 12 of solid silver, while liquid bismuth approximates to the NaCl structure with a very low co-ordination number (6 - 6)[21]. Thus it might be expected that the addition of silver would result in the dispersion of bismuth into more closely packed environments accompanied by negative contributions to the excess entropy and heat. Examination of the partial excess entropies of bismuth suggests that the covalent cluster dissociation (positive) dominates in bismuth-rich alloys while the co-ordination effect (negative) becomes dominant as the silver content increases. The negative contribution is particularly marked in the region N_{Bi} = 0.3 - 0.4. Frequently such minima in liquid alloys reflect the existence of intermediate phases in the solid state, but the silver-bismuth system is a simple eutectic case with no such phases. This composition range does, however, approximate to the atom ratio Ag_2Bi and the sizes of silver and bismuth are appropriate for the formation of a Laves phase of this form.[22] Such phases are of high co-ordination and thus one may speculate that negative contributions to the excess entropies and heats of the silver-bismuth liquids arise in this region from a partially ordered packing effect associated with Laves phase packing conditions. The non existence of such a phase in the solid state is due to the lack of any stabilising electrochemical factor to prevent unmixing at lower temperatures. In the gold-bismuth system, where the atomic size relationship is identical with present case, a Laves phase (Au_2Bi) is formed, [illegible] stabilized by the electronegativity difference between the components.

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4.4. Liquid Silver-Lead Alloys.

Similar experimental studies to those described above were made earlier on eight silver-lead alloys. Simultaneously new measurements were also made of the vapour pressure of liquid lead between 880 and 1050°K. These results have now been evaluated and details may be found in a recent publication[23]. The thermodynamic properties obtained for the silver-lead alloys are summarized in table 5 of the present report for comparison with those of silver-bismuth.

It will be seen that they are of much simpler form than those of the latter system. Both components show positive deviations from Raoultian behaviour at all compositions and the system is characterised throughout by positive heats and excess entropies of formation. Comparison of the present enthalpy values with those for other temperatures obtained by other workers suggests that these liquid alloys must exhibit anomalously large positive deviations from Neumann-Kopp behaviour. The observed positive heats of formation may again be partly due to a misfit energy arising from the large atom size disparity of the components. Also, as before, the mixing of atoms of differing size and valency may be expected, through the influence on the vibrational frequency, to result in positive excess specific heats, positive contributions to the enthalpies and the excess entropies. Since the bonding of lead is also probably somewhat covalent in character, it is possible that as with bismuth, positive contributions could again partly arise from the dissociation on alloying of any covalent clusters persisting in liquid lead; results for other lead alloys support this idea and the partial properties of lead as a solvent are, in many cases, consistent with the view that such dissociation is accelerated as the valency and ionic size of the solute become increasingly different from those of the solvent. The negative influences proposed in previous system would not be expected in the silver lead alloys; lead, f.c.c. in solid state, will exhibit a similar close-packing in the liquid form, so that co-ordination changes on mixing are likely to be of minor significance.

4.5. Thallium and Silver-Thallium Alloys.

Work has begun on a comparable study of the similar system, silver-thallium. As a preliminary to work on these alloys, the vapour pressure of pure liquid thallium has first been measured. Observations have been made at temperatures between 780 and 920°K. The results have been fitted by the method of least squares and may be expressed satisfactorily by

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TABLE 5.

Thermodynamic properties of liquid silver-lead alloys at 1000°K.

N_{Pb}	a_{Pb}	a_{Ag}	$\overline{\Delta G}_{Pb}$ cal/g.	$\overline{\Delta G}_{Ag}$ atom	$\overline{\Delta S}_{Pb}$ cal/deg.g.	$\overline{\Delta S}_{Ag}$ atom	$\overline{\Delta H}_{Pb}$ cal./g.	$\overline{\Delta H}_{Ag}$ atom	ΔG cal./g. atom	ΔH atom	ΔS cal./deg.g. atom
0.9	0.91	0.18	-190	-3450	0.30	6.96	11[illegible]	3510	- 5[illegible]	45[illegible]	.97
0.8	0.86	0.31	-300	-2345	0.60	4.89	200	2545	- 710	75[illegible]	1.66
0.7	0.80	0.41	-445	-1780	0.90	3.68	455	1900	- 845	880	1.73
0.6	0.73	0.49	-630	-1440	1.35	2.84	720	1400	- 955	9[illegible]	1.95
0.5	0.65	0.56	-370	-1140	2.04	1.99	1170	350	- 1005	1010	2.02
0.4	0.55	0.64	-1200	-875	2.83	1.40	1630	525	- 1[illegible]05	97[illegible]	1.97
0.3	0.44	0.72	-1650	-640	3.63	0.88	2030	240	- 385	775	1.72
0.2	0.31	0.81	-2335	-415	4.45	0.57	2115	155	- 30[illegible]	54[illegible]	1.35
0.1	0.17	0.90	-3565	-205	6.35	0.23	2785	25	- 5[illegible]	[illegible]	0.84

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the equation:

$$\log_{10} P\ (\text{mm. Hg.}) = 8.536 - \frac{9,247}{T}$$

Using the third law method and thermodynamic data taken from Stull and Sinke, the present results yield a standard heat of vapourization, $\Delta H^{\circ}_{[illegible]}$ = [illegible] ± [illegible] cal./mole. This compares satisfactorily with the value, $\Delta H^{\circ}_{[illegible]}$ = [illegible],500 ± 100, chosen by Hultgren[24] on the basis of earlier studies.

Only seven alloys have been studied so far; the compositions include two in the silver rich solid solution, while the remainder were again mainly in the liquid state in the temperature range of the investigation, 850 - [illegible]°K. The vapour pressures observed have been treated in the usual way and the equation coefficients are collected in table 6; activities and activity coefficients of thallium at 900°K are also included.

TABLE 6.

Silver-Thallium Alloys.

N_{Tl}	A	B	a_{Tl}(900°K)	γ_{Tl}(900°K)
0.88	8.522	9,258	0.940	1.07
0.74	8.544	9,282	0.931	1.26
0.67	8.607	9,341	0.925	1.38
0.57	8.043	8,883	0.815	1.43
0.31	8.062	8,940	0.736	2.37
0.044	6.506	7,765	0.413	9.39
0.02	5.463	7,034	0.243	12.15

The results show marked positive deviations from ideality in both the solid and liquid phases. The indicated partial entropies of thallium are also non-ideal, but the values are extremely scattered and no significance can be attached to them at present; this uncertainty is similarly reflected in the partial heats. Further work is necessary before a full thermodynamic evaluation of the results is justified.

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