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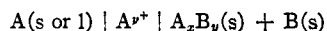
Thermodynamic Properties of the Tellurides of Zinc, Cadmium, Tin and Lead

BY J. H. McATEER¹ AND HARRY SELTZ

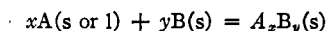
Introduction

The application of reversible galvanic cells to the study of the thermodynamic properties of compounds at higher temperatures has been made recently by Ölander,² who has studied a number of intermetallic compounds in the neighborhood of 250° using a mixture of fused acetates for an electrolyte. Seltz and DeHaven³ have studied extensively the thermodynamic properties of cadmium antimonide (CdSb) over a rather large temperature range. The use as an electrolyte of a eutectic mixture of potassium and lithium chlorides to which was added a small amount of cadmium chloride enabled them to make observations from 390 to 440°.

Their results have shown that measurements of the electromotive force at various temperatures of cells of the type



permit the calculation of the thermodynamic properties of the reaction.



It is necessary, of course, that the metal electrode A have a higher electrode potential in the fused electrolyte than that of the element B. It will be noticed also that no measurements can be taken above the eutectic temperature of the compound and pure B constituent. For any system which involves an equilibrium between the solid compound and a solid solution of A in B it would be necessary to know the activity of B in the solid solution in order to determine the free energy change for the above reaction. It is obvious that a change in concentration of the metal ions in the electrolyte or the amount of the second pure constituent in equilibrium with the solid compound will have no effect upon the electromotive force of the cell.

The results of a study of the tellurides of zinc, cadmium, tin and lead by these methods are presented in this paper. Each of the four metals

was substituted for the A constituent and tellurium formed the B constituent. The eutectic temperatures of the various tellurides and pure tellurium were obtained from the phase diagrams⁴ of these metals with tellurium.

Experimental

Purification of Materials.—Silver-free lead was purified by electrodeposition from a fluosilicic acid bath. Baker "c. p. analyzed" cadmium, tin and lead were used without further purification. Each metal was cast into sticks under a molten mixture of lithium chloride and potassium chloride. This effectively removed any oxide from the metal.

C. p. tellurium was further purified by dissolving it in concentrated nitric acid, evaporating to dryness and then adding concentrated hydrochloric acid. After diluting this solution the insoluble material was removed and the tellurium was precipitated by the addition of sodium bisulfite. The tellurium was converted into telluric acid which, after three or four crystallizations from concentrated nitric acid, was reduced to free tellurium. The purified substance was then melted in an atmosphere of hydrogen.

Baker "c. p. analyzed" zinc chloride, cadmium chloride and lead chloride were used without further purification. These salts were fused, cast into sticks and kept in an oven at 100° until used. Stannous chloride was prepared by passing dry hydrogen chloride over molten tin and then subliming the product in a stream of carbon dioxide. The sublimed stannous chloride was kept in a desiccator. C. p. lithium chloride and potassium chloride were kept dry in an oven until used. In making the electrolyte the correct quantities of lithium chloride and potassium chloride were weighed and melted. Varying amounts of zinc, cadmium, tin or lead chloride were added to this molten mixture which was then cast into sticks and kept in an oven.

Preparation of Electrodes.—The electrodes containing the telluride were formed by melting weighed amounts of the metal and tellurium in a 6-mm. Pyrex tube under a hydrogen atmosphere. Varying amounts of tellurium in excess of that required to react with the metal were used. After the compound had dissolved completely in the molten excess tellurium, a tungsten lead, which will be described below, was inserted and the material permitted to solidify. When the electrode had cooled, the glass tubing was carefully chipped away and the electrode, now firmly attached to the tungsten tip, was removed.

Cadmium, tin and lead are liquids at the temperatures employed. The pure metal electrodes were made by melting the metals in the cells under the molten electrolyte. The tungsten leads were then immersed in the liquid

(1) Abstracted from a thesis presented by J. H. McAteer to the Committee on Graduate Instruction of the Carnegie Institute of Technology, in partial fulfillment of the requirements for the degree of Doctor of Science, June, 1936.

(2) A. Ölander, *Z. physik. Chem.*, **A173**, 284 (1935).

(3) H. Seltz and J. C. DeHaven, *Am. Inst. Min. & Met. Engr., Tech. Pub.*, 622 (1935).

(4) (a) "I. C. T.," Vol. II, p. 441; (b) *ibid.*, p. 430; (c) *Tech. Pub., International Tin Research & Development Council, Series B, No. 2*; (d) "I. C. T.," Vol. II, p. 416.

metals. The pure solid zinc electrodes were made in the same manner as the telluride electrodes.

All leads consisted of tungsten wire which was welded to the copper potentiometer leads some distance from the furnace in which the measurements were made. The union at this point prevented the occurrence of thermal electromotive forces at the copper-tungsten junctions. The tungsten leads were sealed in 3-mm. Pyrex tubing in such a manner that only 2 or 3 mm. projected. This prevented contact of the leads with the electrolyte. During the process of sealing the leads in the glass a coating of oxide invariably formed on the small projecting tips. This was removed by treating with molten potassium pyrosulfate and then, after cooling, with a concentrated caustic solution. The tungsten tips were wound into the form of a small helix to ensure a tight connection with the solid electrodes.

Procedure.—The apparatus used was similar to that of Seltz and DeHaven³ with the exception that the furnace was fitted with an iron cylinder containing a low melting mixture of lead, tin and bismuth. In this were placed the cells and thermocouple. It was impossible to detect with this arrangement any temperature gradients. The thermocouple was incased in Pyrex tubing to which a small Kipp hydrogen generator was attached. This precaution prevented oxidation and subsequent deterioration of the hot junction. The temperature lag of the thermocouple was negligible.

The necessary amount of electrolyte was melted in an H-cell by means of a Meeker burner. About 2 g. of pure metal was placed in one leg. After the metal had melted, the tungsten lead was inserted and adjusted to the proper position. The gas flame was then removed, the solid telluride electrode introduced in the other leg and the cell placed in the furnace. The cell was evacuated slowly for an hour to a final pressure of 0.05 mm. of mercury. This slow evacuation prevented violent bumping caused by gas bubbles escaping from the molten electrode and electrolyte. Usually after three hours all gassing had ceased and the cell was found to have reached equilibrium. In some

series of measurements pumping was continued throughout the run while in others, after complete evacuation, carbon dioxide was admitted. The results obtained with the carbon dioxide atmosphere were concordant with those obtained under vacuum except in the cells which were used for the study of tin telluride.

In the study of tin telluride the vacuum technique had to be modified since a loss of the stannous chloride occurred owing to its volatility under reduced pressures at these temperatures. For this reason an atmosphere of carbon dioxide was used exclusively. The stannous chloride was not added to the electrolyte until the initial three-hour period of pumping had been completed. Measurements were made also with cells containing pure stannous chloride as an electrolyte. These cells functioned satisfactorily even in the presence of air.

Simultaneous readings of the electromotive force and the temperature were taken from the melting point of the electrolyte to the limiting eutectic temperature except in the case of zinc telluride where readings were carried only to the melting point of zinc. The cells responded rapidly to variations in temperature, but to ensure equilibrium the temperature was never permitted to change by more than fifteen degrees an hour.

Results and Calculations

The observed values of the electromotive force are contained in Table I. The weight per cent. of the total amount of tellurium in the telluride electrode is given together with the type of atmosphere within the cell. The results appear to be correct within ± 0.2 mv. at each temperature except for the measurements on zinc telluride where the limit of error is more nearly ± 0.3 mv. The temperature readings can be considered accurate to within $\pm 0.5^\circ$. These data are plotted in Fig. 1. From large scale reproductions of the

TABLE I

Cell	% Te and atmosphere	Temp. range, °C.	E. m. f., volts	dE/dT , volts/°C.
Zn(s)/ZnCl ₂ , LiCl, KCl(l)/Te(s) + ZnTe(s).....	95.1 vac.	355-418	0.57030	-0.0000617
	92.3 vac.			
	85.7 vac.			
	96.0 CO ₂			
Zn(s) + ZnTe(s)/ZnCl ₂ , LiCl, KCl(l)/Te(s) + ZnTe(s) ...	89.6 + electrode...	360-440	0.50282	- .0000879
	8.8 - electrode			
Cd(l)/CdCl ₂ , LiCl, KCl(l)/Te(s) + CdTe(s).....	93.5 vac.	270-395	0.31600	- .0000676
	90.4 CO ₂			
	87.6 CO ₂			
Sn(l)/SnCl ₂ , LiCl, KCl(l)/Te(s) + SnTe(s).....	76.8 CO ₂	355-408	0.34909	- .0000669
	84.9 CO ₂			
	94.7 CO ₂			
Sn(l)/SnCl ₂ (l)/Te(s) + SnTe(s).....	84.9 air	355-408	0.34909	- .0000669
	90.9 air			
Pb(l)/PbCl ₂ , LiCl, KCl(l)/Te(s) + PbTe(s).....	59.3 CO ₂	355-408	0.34909	- .0000669
	75.0 CO ₂			
	75.4 vac.			
	83.6 CO ₂			

figures the values of the electromotive force at a given temperature and dE/dT have been obtained. It will be noticed that in all cases the electromotive force-temperature curves are straight lines within the limits of experimental error.

The free energy change, ΔF , of a cell reaction at any given temperature is related to the reversible electromotive force, E , of the cell by the equation $\Delta F = -nFE$ where n is the number of equivalents involved and F is the value of the faraday (23,074 cal. per volt equivalent). In this study all substances involved in the reactions are at their standard states (activity equal to unity) and the free energy change becomes the standard free energy change ΔF° . The value of ΔF° may be expressed as a function of the temperature if the heat of reaction, ΔH , is known. This quantity may be evaluated with the aid of the Gibbs-Helmholtz equation, $\Delta H = nF \times (T(dE/dT) - E)$. If the change in heat capacity, ΔC_p , is small the value of

ΔH will be nearly independent of the temperature and ΔF° at any temperature will be given by the equation $\Delta F^\circ = \Delta H + IT$ where I is a constant of integration. The entropy change for the reaction may be calculated from the fundamental relation $\Delta F^\circ = \Delta H - T\Delta S$.

The results of the calculations for the various tellurides are summarized in Table II. The heats of fusion used for cadmium, tin and lead were 1254, 1594 and 1228⁵ cal. per gram atom, respectively.

Discussion

The cells studied in this investigation functioned reversibly and the electromotive forces were quite reproducible. Changes in composi-

tion of the electrolyte and in the amounts of tellurium in equilibrium with the solid tellurides had no effect upon the electromotive forces of the cells. The consistent data of Table I for cells

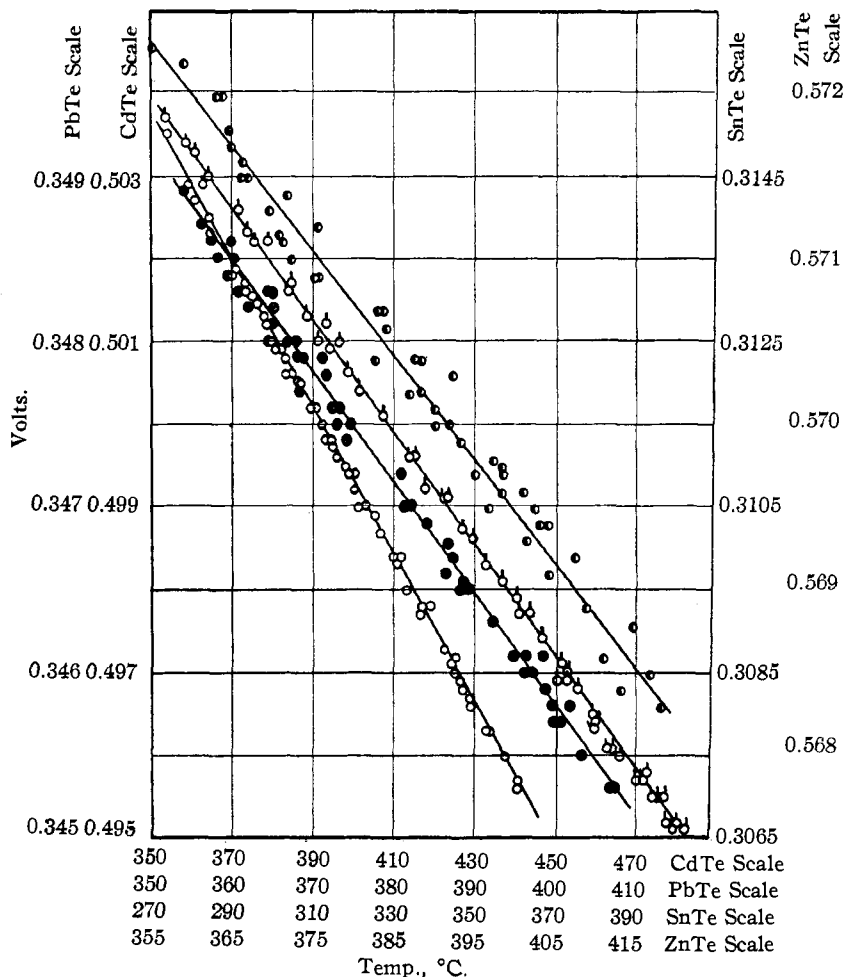


Fig. 1.—E. m. f. curves: ○, CdTe Cells; ●, PbTe Cells; ○, SnTe Cells; ●, ZnTe Cells.

in which the zinc electrode was replaced by a zinc-zinc telluride electrode also indicate the reversibility of the cell reaction.

TABLE II
THERMODYNAMIC PROPERTIES OF THE TELLURIDES
AT 25°

Reaction	ΔF° , cal.	ΔS , cal./°C.	ΔH , cal.	ΔH , cal. (Fabre)
Zn(s) + Te(s) = ZnTe(s)	-27,360	-2.9	-28,210	-33,200
Cd(s) + Te(s) = CdTe(s)	-23,950	-2.0	-24,530	-15,800
Sn(γ) + Te(s) = SnTe(s)	-14,660	0.0	-14,650
Pb(s) + Te(s) = PbTe(s)	-16,590	-1.0	-16,810	- 5500

The limits of error for the values tabulated in Table II depend somewhat on the calorimetric data which have been employed. The deviations in the values of the electromotive force of the cells and of dE/dT lead to an uncertainty of

(5) "I. C. T.," Vol. II, p. 468.

about ± 50 cal. The probable errors in the heats of fusion amount to about ± 40 cal. and the assumption that Kopp's law can be applied to these tellurides might introduce an error of not more than ± 30 cal.

The calculations at 25° for tin telluride have been made using the γ form of the metal. Apparently this form is stable above 161° and consequently is not stable at 25° . Unfortunately no data on the heat of transition exist so that it is impossible to make calculations for the compound using the allotropic modification which is stable at 25° . The question of the existence of tellurium in two allotropic forms has been raised by S. Umino,⁶ who in measuring the specific heat of tellurium up to 550° reported a transition at 348° accompanied by the absorption of 630 cal. per gram atom. However, no other investigator has mentioned this behavior and Simek and Stehlek⁷ were unable to confirm his results. For this reason it has been assumed that no transition occurs. No data are available for the entropy of tellurium. Consequently the entropies of the tellurides have not been calculated.

(6) S. Umino, *Kinzoku no Kenyaku*, [10] 3, 498 (1928).

(7) A. Simek and B. Stehlek, *Coll. Trav. Chim. Tchechosl.*, 2, 304 (1930).

No other measurements of the thermodynamic properties of the tellurides have been reported except those of Fabre⁸ on the heats of formation. His results which were obtained by a calorimetric method are tabulated in Table VII. They are not, as will be seen, in agreement with the present values. A review of his work, however, indicates that his results may be unreliable owing to the uncertainty of some of the thermal values he used to calculate the heats of formation. Lack of data prevents recalculation of these values.

Summary

1. A potentiometric study of the tellurides of zinc, cadmium, tin and lead has been made at higher temperatures using fused salt electrolytes.
2. The method has been shown to give results which are reliable and accurate when applied to the proper substances.
3. The data thus obtained have been employed in calculating the free energies of formation, heats of formation and entropies of formation at 25° .

(8) Fabre, *Ann. chim. phys.*, 14, 110 (1888).

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RECEIVED JUNE 22, 1936

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A Thermodynamic Study of the Lead-Bismuth System

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Although the properties of the alloys of lead and bismuth have been investigated extensively, the phase diagram of the system is not well established. In the "International Critical Tables"² diagram, two series (α and β) of solid solutions forming a eutectic at 58 weight per cent. bismuth are shown. The limits of solubility are 18 and 99% bismuth at 0° and 37 and 97.3% bismuth at 125° , the eutectic temperature. References cited for this are Guertler³ and Herold,⁴ from whose critical reviews it is evident that the limits of solubility and the solidus curves are not too well defined. Furthermore, Solomon and

Jones,⁵ studying alloys of this system by means of x-rays, have found recently a new solid solution phase existing from 25 to 33% bismuth.

In the present work, thermodynamic data obtained from measurements of galvanic cells of the general form Pb/Pb⁺⁺/Pb (in Pb-Bi solution) have been used to calculate a considerable portion of the phase diagram, making use of the methods previously proposed by Seltz.⁶

Experimental

The cells used were of the three types:

- I. Pb(l)/PbCl₂ in LiCl-KCl(l)/Pb(in Pb-Bi liquid solution)
- IIa. Pb(s)/Pb(OAc)₂-NaOAc(l)/Pb(in Pb-Bi liquid solution)
- IIb. Pb(s)/Pb(OAc)₂-NaOAc(l)/Pb(in Pb-Bi equilib. liquid and solid solutions)
- III. Pb(s)/Pb(OAc)₂-NaOAc(l)/Pb(in Pb-Bi solid solution)

(5) Solomon and Jones, *Phil. Mag.*, 11, 1090 (1931).

(6) Seltz, *This Journal*, 56, 307 (1934); 57, 391 (1935).

(1) Abstracted from a thesis presented by H. S. Strickler to the Committee on Graduate Instruction of the Carnegie Institute of Technology, in partial fulfillment of the requirements for the Degree of Doctor of Science, June, 1936.

(2) "International Critical Tables," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., pp. 414-417.

(3) Guertler, "Metallographie," Vol. I, Gebrüder Borntraeger, Berlin, p. 548.

(4) Herold, *Z. anorg. allgem. Chem.*, 112, 131 (1920).