This equation fits the data fairly well. The value for the heat of dissociation is 41,200 cal. The entropy of $^1/_2Br_2$ (liquid) at 298°K. is found by Latimer and Hoenshel[14] to be 18.4. Lewis and Randall[15] find the entropy of vaporization of $^1/_2Br_2$ to be 11.3. From Equations 9 and 11 we calculate the entropy of dissociation to be 8.5. This gives as the entropy of monatomic bromine at 298°K. and 1 atmosphere 38.2. The Tetrode equation predicts 39.0. No significance can be attributed to the close agreement with the predicted value since we have neglected terms for ΔC_p in our equation for log K_p.

Summary

A new method has been developed for the measurement of the thermal dissociation of diatomic gases.

Satisfactory values have been obtained for iodine, and the entropy of monatomic iodine appears to agree with the value predicted by the Tetrode equation.

Results have been obtained for bromine which, while not entirely satisfactory, are believed to be better than any previous data.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 121]

AN X-RAY STUDY OF THE ALLOYS OF LEAD AND THALLIUM

BY EDWIN MCMILLAN AND LINUS PAULING[1]

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Review of Previous Work

The system lead-thallium gives, on investigation by the methods of thermal analysis, an unusual type of phase diagram, whose interpretation has raised some interesting questions. Four significant reports of previous work on this system exist. Lewkonja[2] and Kurnakow and Puschin[3] investigated it by the method of thermal analysis, while Kurnakow and Zemczuzny[4] and Guertler and Schulze[5] used the method of electrical conductivity.

The phase diagram of the system is shown in Fig. 1. The upper part (above 300°) was taken from the work of Kurnakow and Puschin, and the lower part from that of Guertler and Schulze. Lewkonja deter-

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[14] Latimer and Hoenshel, THIS JOURNAL, **48**, 19 (1926).

[15] Ref. 6, p. 513.

[1] National Research Fellow in Chemistry.

[2] Lewkonja, *Z. anorg. Chem.*, **52**, 452 (1907).

[3] Kurnakow and Puschin, *ibid.*, **52**, 430 (1907).

[4] Kurnakow and Zemczuzny, *ibid.*, **64**, 149 (1909).

[5] Guertler and Schulze, *Z. physik. Chem.*, **104**, 269 (1923).

mined the positions of the lines above 260° in good agreement with those determined by Kurnakow and Puschin. According to him, however, the maximum in the freezing-point curve lies at 33.5 atomic % of lead, and corresponds to a compound $PbTl_2$. All later evidence, however, including that of this paper, is against the existence of the compound. Kurnakow and Puschin found the maximum to lie between 35.7 and 37.5 atomic % of lead; this agrees with no simple rational formula, and hence

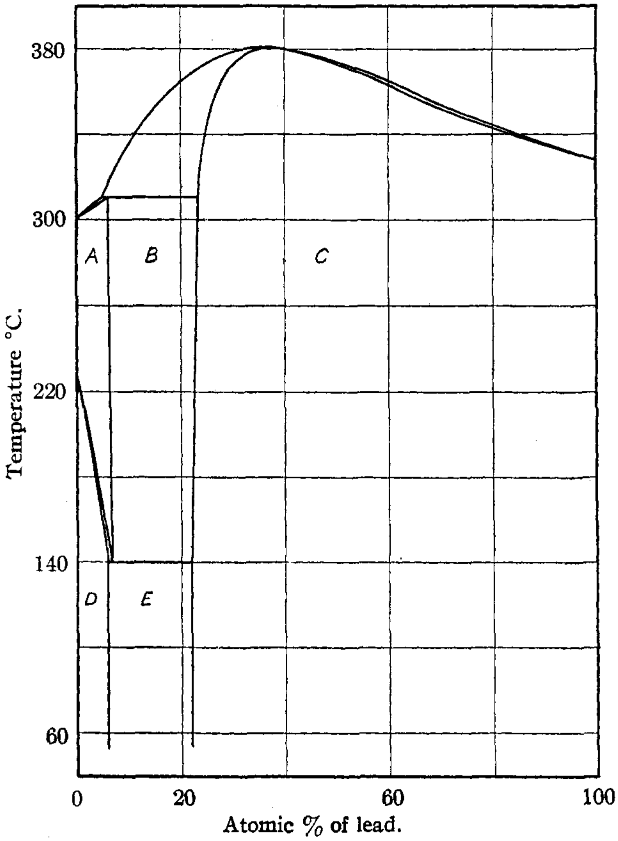

Fig. 1.

they concluded that no such compound as $PbTl_2$ exists. Kurnakow and Zemczuzny measured the electrical conductivities of a series of lead-thallium alloys at room temperature, and found no evidence for the existence of a compound. Guertler and Schulze went a step further, and investigated the electrical conductivities over a temperature range of 20–250°, obtaining the curves given in the lower part of the figure. The field marked A in the figure appears to correspond to a solid solution of lead in thallium, having the crystal structure of thallium at high temperatures. This undergoes a transformation at lower temperatures, giving a similar solid solution having the low-temperature thallium structure in the field marked D. The fields B and E are regions in which two phases exist together. The constitution of the field C appears from the consensus of evidence to be homogeneous, representing a single solid solution having the structure of metallic lead. It was to test these conclusions as to the structure of the system, particularly the final one, that this x-ray investigation was undertaken.

Experimental Methods

Various x-ray powder photographs were taken in the usual manner at room temperature, with samples having the compositions given in Table II. Samples were prepared by melting thallium and lead together in Pyrex test-tubes, filing the resulting reguli, and putting the filings in thin-walled glass tubes about 1 mm. in diameter. The operations of preparing the sample were all carried on in an atmosphere of carbon dioxide.

The x-radiation was obtained from a tube with a molybdenum anticathode operating at 15 milliamp. and 40 kv. peak, there being a zirconia filter in front of the film. Twenty-four hours' exposure was found necessary. The reflections obtained from sodium chloride, with $d_{100} = 5.628$ Å., were used for standardization.

To obtain measurements of d_{100} for Samples 5 to 9, the samples were mixed with the sodium chloride, making considerable accuracy possible, since all influences produce equal errors in the positions of both the lines due to the samples and due to the standard. The error in the measurements given in Table I is estimated to be about 0.1%.

Experimental Results and Discussion

Eleven lines were obtained from pure lead in good agreement with the cubic, face-centered structure, with four atoms in the unit, previously assigned to the metal. Twelve lines, which do not permit the deduction of the structure of the substance, were obtained from pure thallium. No lines not belonging to one of these two patterns were observed in any alloy.

In Table I are given the compositions of the alloys, the patterns observed (with the number of lines where only a few are present) and the sides of the unit cubes of the solid solutions from 20 to 100 atomic % of lead.

TABLE I

PHASES PRESENT IN VARIOUS ALLOYS AS SHOWN BY X-RAY LINES

Alloy no.	1	2	3	4	5	6	7	8	9	10
Atomic % of lead	0	4	7	10	20	25	33.3	45	75	100
Pattern shown	Tl	Tl	4 Tl lines	3 Tl lines	Pb	Pb	Pb	Pb	Pb	Pb
		4 Pb lines	5 Pb lines	Pb						
d_{100} for Pb phase, Å. U.					4.858	4.864	4.879	4.892	4.920	4.948

It is obvious from these results that only two phases exist in this system at room temperature and that these are solid solutions with two different structures, the lead and low-temperature thallium types, respectively. This can be seen to agree fairly well with the phase diagram reproduced in Fig. 1.

The atomic spacing in the alloys having the lead structure varies with the composition, being decreased by the addition of thallium nearly linearly up to 80% of thallium, which is about the limit of its solubility.

Summary

Powder photographs of the system lead-thallium have been taken at room temperature. These give no evidence whatever of the existence of a compound $PbTl_2$, but agree with the assumption that at this temperature two solid solutions exist, one having the low-temperature structure of thallium and the other the structure of lead.

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TERNARY SYSTEMS. IV. POTASSIUM CARBONATE, SODIUM CARBONATE AND WATER

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Introduction

Aqueous solutions of sodium and potassium carbonate have naturally received attention over a considerable period of time, and the composition of solid phases obtained at room temperature has been frequently the subject of discussion. The greater part of such work was done prior to the enunciation of the phase rule or, when later, without its use; as a consequence the evidence assembled is contradictory and unconvincing. Mellor[1] cites a large number of papers on the topic in which claims are made that the solid phase obtained from mixed solutions of the two carbonates is a solid solution or that it is a hydrated double salt, for which varying formulas are proposed; the one point of general agreement is that the solid obtained at room temperatures is hydrated and that it is intermediate in composition between the two carbonates. Two investigations have been made according to phase-rule methods, but in both cases, as will be shown, with erroneous result; Kremann and Zitek[2] show on the basis of analysis that the solid phase at 24.8° is a compound of the formula $K_2CO_3.Na_2CO_3.12H_2O$,[3] and Osaka,[4] working at 25°, decides that the solid is without doubt

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[1] Mellor, "Comprehensive Treatise," Longmans, Green and Co., London, **1922**, vol. 2, p. 768.

[2] Kremann and Zitek, *Monatsh.*, 30, 323 (1909).

[3] The formula given is $K_2CO_3.Na_2CO_3.6H_2O$, but the analysis indicates that it is a typographical error for $K_2CO_3.Na_2CO_3.12H_2O$.

[4] Osaka, *Mem. Coll. Sci. Eng. Kyoto*, 3, 51 (1911).