small temperature coefficient, contrary to the experimental findings of this investigation. He will also show in a forthcoming publication that the addition of Br_3 to a double bond requires an energy of activation greater by 10,000 calories than that required for the addition of Br_2. Making the reasonable assumption that the calculations can be applied to cinnamic acid in carbon tetrachloride solution, it is apparent that Purkayastha and Ghosh's chain fails to explain the observed facts because it includes a step which is slower even than the thermal bromination in the dark.

Further experiments are in progress, designed to test the relative merits of the hypotheses of energy and chemical chains.

Summary

1. The photobromination of cinnamic acid in carbon tetrachloride has been measured quantitatively with a monochromator. The influence of concentration, temperature and wave length on the quantum yield has been studied.

2. The reaction is a chain reaction. The quantum yield, Φ, ranged from 1 to 15 or more, depending on the concentration of the bromine and the temperature. The reaction was studied over a range of from 2×10^{-3} to 8×10^{-3} mole of bromine per liter, and at temperatures of 0, 10, 20 and 30°.

3. The photochemical reaction has been shown to consist of two parts; first, a primary photo reaction of one molecule per quantum, and, second, a photo-excited thermal reaction which is measured by $\Phi - 1$, or Θ, and which is suppressed at great dilution of bromine or at low temperatures. Log Θ plotted against $1/T$ gives nearly straight lines whereas log Φ plotted against $1/T$ does not.

4. The experimental facts are in agreement with a theory involving activated bromine molecules and an energy chain.

MADISON, WIS. RECEIVED NOVEMBER 3, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

The Nature of the Solid Phase in the System Antimony–Bismuth[1]

BY W. F. EHRET AND M. B. ABRAMSON

Although a number of investigations have been made of the antimony–bismuth system, employing practically all of the usual physical methods, there has been no general accord on the nature of the solid phase nor on the position of the solidus in the equilibrium diagram. Studies by Hüttner and Tammann,[2] Gautier,[3] Sapossnikoff,[4] and Parravano and Viviani[5] indicated that the solidus corresponded to an isomorphous series of alloys, the curve dropping sharply from the melting point of antimony to 269° at a composition of 70% antimony and continuing horizontally from that point to the melting point of pure bismuth. Cook,[6] from a careful thermal investigation, obtained the solidus shown in Fig. 1. Ôtani[7] more recently studied the equilibrium diagram by the electrical resistance method. His solidus did not show the horizontal portion but gave the normal curve for a complete series of solid solutions (Fig. 1). After the present investigation had begun, an x-ray analysis of antimony–bismuth alloys was published by Bowen and Morris Jones.[8] They concluded that the lattice parameter varied almost linearly with the weight per cent. of the components, a slight curvature being noticed at the antimony end. There was no evidence of intermetallic phases other than the solid solution. From purely thermodynamic considerations, Yap[9] explained the horizontal solidus by assuming a peritectic reaction between a solid solution $\alpha[Sb_2\text{–}Bi_2]$ and the melt, forming solid solution $\beta[Sb_2\text{–}Bi_3]$. In this event there should be two solid solutions present between the limits of 35 and 60 mole per cent. bismuth (Fig. 1). The present x-ray investigation was undertaken to see whether any such solutions existed.

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[1] Presented in part before the Physical and Inorganic Division at the 86th meeting of the American Chemical Society, Chicago, Illinois, September 11–15, 1933.

[2] Hüttner and Tammann, *Z. anorg. Chem.*, **44**, 131 (1905).

[3] Gautier, "Contribution à l'étude des alliages," Paris, 1901, p. 114.

[4] Sapossnikoff, *J. Russ. Phys.-Chem. Soc.*, **40**, 665 (1908).

[5] Parravano and Viviani, *Rend. accad. Lincei*, **19**, 835 (1910).

[6] Cook, *J. Inst. Metals*, **28**, 421 (1922).

[7] Ôtani, *Sci. Repts. Tôhoku Imp. Univ.*, **13**, 293 (1924–5).

[8] Bowen and Morris Jones, *Phil. Mag.*, [7] **13**, 1029 (1932).

[9] Yap, Tech. Publication 397, *Trans. Am. Inst. Mining Met. Eng.*, Inst. Metals Division (1931). The authors wish to thank Mr. Yap, Chu-Phay for his interest and aid in the present work.

Experimental

Alloys for the investigation were prepared from Kahlbaum antimony and bismuth using the usual vacuum technique. Samples 5–12 (Table I) whose melting points fall on the horizontal portion of Cook's solidus were annealed simultaneously. The furnace was kept at 300° for a short while and then lowered to 280 ± 3.0°, at which temperature it was maintained for 230 hours, then slowly brought to room temperature over an interval of 150 hours. All other samples were treated similarly, starting the annealing above the melting point in each case. In most instances microscopic examination revealed large, well-defined polygonal grains with no indication of heterogeneous structure. In a few cases a dendritic structure was coexistent with the polygonal, indicating that the process of transition to the latter form had not been completed.

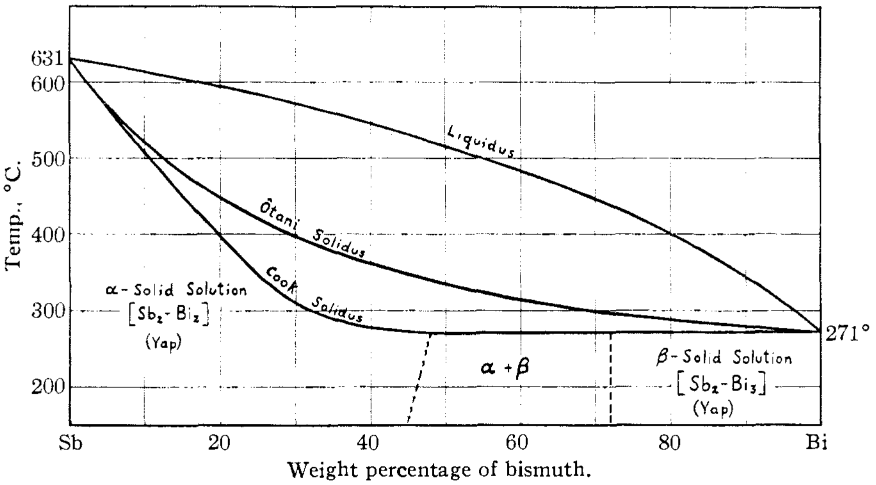

Fig. 1.—Constitutional diagrams of system Sb–Bi.

TABLE I

Sample	Weight, % Sb	Mole, % Sb	Lattice constant a_0 in Å.
Sb	100	100	4.492
1	86.0	91.6	4.519
2	66.1	78.3	4.555
3	56.1	68.7	4.577
4	52.9	65.9	4.580
5	51.0	64.1	4.582
6	47.3	60.6	4.592
7	40.8	54.2	4.607
8	35.1	48.2	4.620
9	28.8	41.0	4.643
10	25.0	36.0	4.646
11	16.3	25.0	4.713
12	6.1	10.0	4.733
Bi			4.749

The powder method and the standard type of General Electric (Davey)[10] diffraction apparatus was used for the x-ray investigation. For purposes of standardization, the diffraction pattern of pure sodium chloride (lattice constant, 2.814 Å.), was recorded at the same time and upon the same photographic film as the pattern for each alloy.

x-Ray Data.—Calculations made in the present work were for the lattice values of the small rhombohedron. In the case of bismuth and antimony the axes are mutually inclined at 57°16′ and 57°5′, respectively.[11] Since the axial angles of the two metals differ by only 11′, the angles of the intermediate alloys were assumed to vary linearly with the mole per cent. of the components; any possible error in this assumption would result in an error in the calculations which would fall well within the experimental error. The results of the calculations are given in Table I and Fig. 2. The accuracy attained in determining the lattice constant is ±0.007 Å.

Discussion of Results

The diffraction patterns obtained in all cases showed the same series of lines with similar relative intensities, all corresponding exactly with the equation for the rhombohedral unit of structure. No evidence of another pattern or "super-structure" was found. It is thus seen, both from the x-ray and microscopic investigation, that alloys of antimony and bismuth of all compositions, when properly annealed above the melting point, consist of an unbroken series of solid solutions. This is in accord with the results of Cook's and Hüttner and Tammann's analyses and is contrary to Guertler's assumption[12] of the formation of an eutectic and Yap's postulation of two solid solutions.

The parameters of the rhombohedra were found to vary linearly with the mole per cent. of the components. The value used for pure bismuth was that of Ehret and Fine[13] (a_0 = 4.749 Å.). Bowen and Morris Jones found from their x-ray investigation of this system that the lattice varied almost linearly with the percentage by *weight* of the components, with a slight curvature at the antimony end. In a solid solution of the substitution type the change in parameter should not be determined by the weight of the atoms introduced but by the number of such atoms. Consequently, when the variation of the para-

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(10) Davey, *Gen. Elec. Rev.*, **25**, 565 (1922).

(11) Neuburger, *Z. Krist.*, **80**, 103 (1931).

(12) Guertler, "Metallographie," Vol. I, p. 798.

(13) Ehret and Fine, *Phil. Mag.*, [7] **10**, 551 (1930).

meter is plotted against the mole per cent. of the components, the resulting curve can be more accurately interpreted as the true effect on the crystal units produced by alloying the two metals. The value for the edge of the face-centered rhombohedral lattice for bismuth as given by Bowen and Morris Jones (a_0 = 6.540 Å.) is lower than previous values, and differs considerably from that accepted by Neuburger[14] (a_0 = 6.578 Å.) in his critical résumé of lattice constants of the elements. If the values of the intermediate alloys as given by Bowen and Morris Jones are replotted against the molar percentage, and the last mentioned value for bismuth is used, a linear relation is evident similar to that found in this investigation (Fig. 2). Because of this simple relationship between lattice dimensions and molecular percentage, the equilibrium diagram of this system when obtained from annealed alloys is believed to be of the normal type as found by Ôtani. The horizontal solidus obtained by Cook cannot be considered part of the true equilibrium diagram and may be explained, as he suggested, by assuming that there is only a small amount of diffusion in the crystals separating from the melt during the cooling process. If the crystals so obtained are properly annealed, diffusion is increased and equilibrium is attained; the melting points of such annealed alloys will then lie on the normal solidus as obtained by Ôtani. That it is difficult to establish the true solidus using thermal methods will be seen from the following experiment in which the authors attempted to establish the melting point of a 40 weight per cent. Bi alloy. The latter was cooled from the molten state to 400° and kept at this temperature for 300 hours, after which it was slowly cooled, over a period of three days, to 280°, at which temperature (±2°) it was annealed for 300 hours. Slow cooling, over a period of ten days, then brought the alloy to room temperature. This procedure had been shown by Cook to be the most rapid way to attain homogeneity. The sample thus obtained was practically homogeneous and consisted of large polygonal grains. When heated at an average rate of 1.6° per minute to 465°, there were no perceptible halts in the time-heating curve even though the alloy had been partially melted as shown by the microscope. Such behavior can be understood for a solid solution since the melting point rises gradually but it seems to rule out definitely the existence of a compound, eutectic, or peritectic reaction in this alloy.

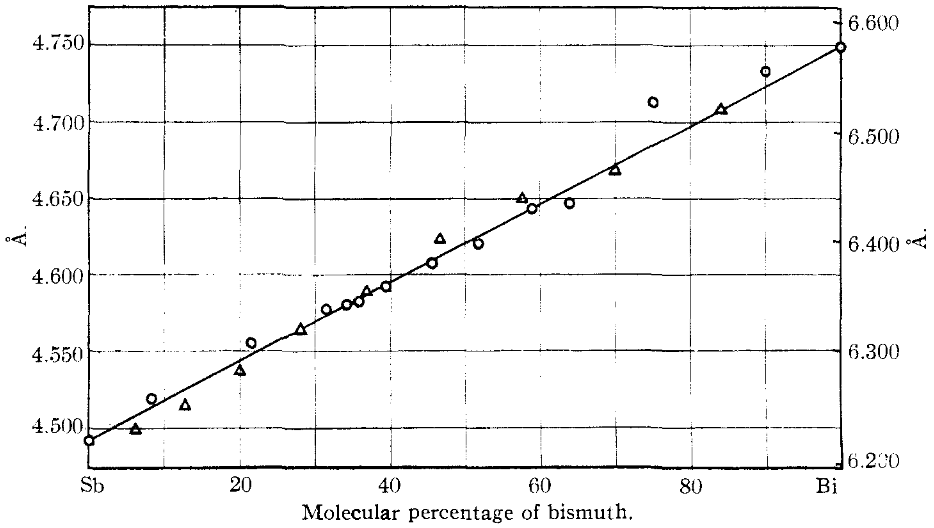

Fig. 2.—Variation in lattice parameter in Sb–Bi alloys: ordinates at left permit plotting of the edge-length of the unit rhombohedra (present work), small circles; ordinates at right permit plotting of edge-length of face-centered rhombohedra against molecular per cent. (recalculated from work of Bowen and Morris Jones), small triangles.

Summary

1. x-Ray diffraction and microscopic examinations of annealed specimens of antimony–bismuth alloys show them to consist of one phase only, corresponding to a system which forms a complete series of solid solutions.

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(14) Neuburger, *Z. Krist.*, **80**, 103 (1931).

2. The lattice parameter was found to vary linearly with the mole per cent. of the components.

3. Ôtani's curve is believed to be the correct equilibrium solidus for this system.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF NEBRASKA]

The Potentials of the Lead Oxide Electrodes in Alkaline Solution[1]

BY LYLE VERNON ANDREWS AND D. J. BROWN

Glasstone,[2] who measured the lead oxide-lead dioxide electrode, worked with normal solutions of sodium hydroxide only. Since lead oxide acts as an acidic oxide in concentrated alkaline solution, the activity of the sodium hydroxide in the two half cells would be different. It has been shown by Glasstone[2] and Milbauer[3] that lead dioxide in contact with an alkaline solution of lead oxide reacts to form the oxide commonly called red lead, Pb_3O_4 which has also been shown by Glasstone to be lead orthoplumbate, Pb_2PbO_4.

In view of these facts it would seem impossible to obtain a standard potential using lead oxide and lead dioxide in the alkaline half cell. It should, however, be possible to make the measurement in two steps, using lead orthoplumbate as the intermediate product and calculate the oxidation potential.

For a reference electrode, we decided upon the $Hg\text{-}HgO(s)\text{-}OH^-$ electrode.[4] The two cells proposed are

$$\mathrm{Hg\text{-}HgO(s)\text{-}PbO(s)\text{-}KOH\text{-}PbO(s)\text{-}Pb_3O_4(s)\text{-}Pt} \qquad (1)$$

$$\mathrm{Hg\text{-}HgO(s)\text{-}KOH\text{-}PbO_2(s)\text{-}Pb_3O_4(s)\text{-}Pt} \qquad (2)$$

When an electron current passes through the cells from right to left, the following reactions take place

$$\mathrm{Hg + Pb_3O_4 \rightleftharpoons HgO + 3PbO}$$

$$\mathrm{2Hg + 3PbO_2 \rightleftharpoons 2HgO + Pb_3O_4}$$

These equations indicate that the electromotive force of the cells should be independent of the concentration of the alkali.

Lead dioxide was deposited on platinum foil, made rough either by coating with platinum black and then heating in a blast lamp, or by treating the smooth foil with hot aqua regia for a few minutes. The roughened platinum was cleaned with hot concentrated nitric acid, followed by a half hour treatment with hot half normal potassium hydroxide solution. The solution from which the lead dioxide was deposited, contained about 0.5% of lead nitrate and was about 2 normal in nitric acid. A current density of approximately 0.003 amp./sq. cm. was used.[5]

Lead orthoplumbate was prepared by treating lead dioxide, deposited on platinum foil, with a solution 0.5-1.0 normal in potassium hydroxide and almost saturated with lead oxide, for ten to fifteen hours at about 80°. These conditions have been shown by Glasstone[2] and Milbauer[3] to give lead orthoplumbate. The deposit adheres firmly, and forms a coating over the lead dioxide.

Lead oxide, red variety, was precipitated from a hot 12 normal solution of potassium hydroxide[6] by adding powdered lead acetate to the hot alkali. The oxide was washed by decantation with hot 10 normal potassium hydroxide, then washed thoroughly and repeatedly with hot distilled water and dried over sulfuric acid in a vacuum desiccator. Analysis for lead[7] gave 99.7% PbO. A small amount of water was evolved when the oxide was heated strongly.

Potassium hydroxide solution was prepared as described by Ming Chow.[4] Doubly distilled water, distilled in an all-Pyrex still, first from alkaline permanganate and then redistilled from the clean still, was used to prepare all solutions.

Saturated solutions of the oxides were made in 200-ml. round-bottomed, long-necked flasks, fitted with ground-glass stoppers and provided with rubber caps to prevent carbon dioxide from working past the ground-glass stoppers. These flasks were almost filled with solvent, an excess of the solid oxide added and then shaken in a constant temperature air-bath at 25.0 ± 0.2°.

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(1) Original manuscript received January 3, 1933.

(2) Glasstone, *J. Chem. Soc.*, **121**, 1456 (1922); 1469 (1922).

(3) Milbauer, *Chem. Zeit.*, **38**, 587 (1914).

(4) Ming Chow, THIS JOURNAL, **42**, 488 (1920).

(5) Smith, THIS JOURNAL, **27**, 1287 (1905); Fischer and Schleicher, "Elektroanalytisch Schnellmethoden," zweite Auflage, 1926, p. 243.

(6) Smith and Woods, *ibid.*, **45**, 2632 (1923).

(7) Brown, Moss and Williams, *Ind. Eng. Chem., Anal. Ed.*, **3**, 134 (1931).