U. S. DEPARTMENT OF COMMERCE
BUREAU OF STANDARDS

BISMUTH

CIRCULAR OF THE BUREAU OF STANDARDS, No. 382

U. S. DEPARTMENT OF COMMERCE
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ABSTRACT

As one of the first phases of an investigation seeking to develop and extend the uses of bismuth, a survey of the literature on bismuth has been made. The information resulting is published in the present circular.

The occurrence and distribution of bismuth, its recovery from ores and from by-products in the purification of other metals, methods of refining bismuth, statistics of production, and price ranges are all considered briefly. Physical properties and uses are discussed as well as nearly 30 binary alloy systems of bismuth and several more complex metallic systems containing bismuth. The low melting points of several of these alloys are of particular interest, several of them melting at temperatures considerably below the boiling point of water. A selected and classified bibliography is appended.

CONTENTS

I. INTRODUCTION

This publication is one of a series of circulars published by the Bureau of Standards on individual metals and their alloys with particular emphasis on the physical properties of the metal or alloys. Each circular collects, compiles, and systematizes, for a given metal and its alloys, the information which is scattered throughout a voluminous technical literature.

Previous circulars on Copper, Nickel and Its Alloys, and Light Metals and Alloys all have dealt with metals and alloys which are commercially important and whose uses are manifold and well known. The present circular, on bismuth, is concerned with a metal whose properties are comparatively unknown to the average metallurgist and whose uses at present are limited. This compilation of existing information was prepared as one of the early steps in a current research project on the Extension of the Uses of Bismuth, by J. G. Thompson, research associate for the Cerro de Pasco Copper Corporation.

II. HISTORY

Bismuth is one of the less familiar metals, although it has been known since the middle ages. Modern names, such as "bismuth" (English), "bismuto" (Spanish), and "bismutto" (Italian), all are derived from the German "wismut," "wissmut," "wissmat," and "wissmuth," but the origin of the German name is uncertain. Tafel suggests a derivation from "Wiesen" (meadows) and "muten" (to operate a mine) to identify the metal as a product of the mines which were located in the meadows of the Schneeberg district (1, 2, 238).[1]

The name was known in the thirteenth century (Albertus Magnus), and references to the metal are found in the works of Valentine, Paracelsus, and Agricola during the period from 1450 to 1550. Early specimens of bismuth were impure, and this resulted in frequent confusion of the metal with antimony, tin, and zinc. Modern history of bismuth dates from the middle of the eighteenth century when the work of J. H. Pott, C. J. Geoffroy, and Torbern Olof Bergman showed that bismuth is an individual metal which has many analogies with lead.

III. OCCURRENCE AND DISTRIBUTION

Bismuth is a fairly common element, although it is neither abundant nor widely diffused in nature. H. S. Washington (236) estimates the weight per cent of bismuth in the earth's crust as 10^{-6} or 10^{-7}, of the same order as tungsten and silver, more abundant than selenium, gold, tellurium, or platinum, but less abundant than molybdenum, antimony, mercury, tin, and cadmium. Other estimates (1, 8) agree with this value.

Bismuth is found as native metal associated with tin, copper, cobalt, gold, or other metals and in a variety of ores. The more important ores are bismuthinite or bismuth glance (Bi_2S_3), bismite or bismuth ochre (Bi_2O_3), bismutite (hydrated carbonate), and bismutosphærite (carbonate containing little or no water). Of less importance are pucherite (bismuth vanadate), guanajuatite (selenide),

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[1] The figures given in parentheses here and throughout the text relate to the reference numbers in the bibliography given at the end of this paper.

tetradymite (telluride), and numerous double sulphides containing lead, copper, or silver. It is also found as a natural alloy with gold (Au_2Bi) in maldonite from Australia, and alloyed with silver in chilenite from South America and as bismuth silicate, uranate, and molybdate.

These ores, usually found only in small quantities, are widely distributed. Deposits exist in Europe, Asia, Africa, North and South America, and in Australasia. In general, the ores are less important than the deposits of native metal, the bismuth-tin or bismuth-lead deposits of South America, Australasia, France, and Cornwall; the bismuth-cobalt deposits of Saxony; and the bismuth-gold deposits of Australasia, Norway, and the United States. Bolivia is the principal producer of bismuth and could easily supply all of the present world's demand.

In the United States bismuth minerals have been found in Alaska, Arizona, California, Colorado, Connecticut, Georgia, Maine, Montana, Nevada, New Mexico, South Carolina, Utah, Washington, and Wyoming. No ores are mined in the United States (6), but some bismuth has been produced as a by-product in the refining of lead, copper, gold, and silver ores. It may be recovered from the flue dust of copper smelters or from the slimes of the electrolytic refining of lead. Only one or two plants are reported (7) for 1928 as producers of bismuth in this country, as a by-product in the refining of lead and tin bullion, part of which is from ores of foreign origin.

IV. RECOVERY OF BISMUTH

Bismuth ores, or concentrates, may be treated either by wet or dry processes. The former (1, 11) involve leaching with acid, usually hydrochloric, and precipitation of the bismuth as oxychloride by dilution. The precipitated oxychloride may be reduced to metal by the action of iron or zinc or by fusion with carbon. Dry or fusion processes vary widely in detail, from low-temperature processes in which the low-melting bismuth alone liquefies, trickles down, and is thus separated from the rest of the ore, to complete fusion processes in which the whole of the ore or concentrate is mixed with a suitable slag and melted. The low-temperature processes, now obsolete, were very wasteful, as much of the bismuth, up to 33 per cent, remained in the solid gangue.

In a representative fusion process (11) the ores, concentrated to 50 or 60 per cent bismuth, are roasted to volatilize arsenic and antimony and then smelted in crucibles or in a reverberatory furnace. The charge must be readily fusible, owing to the volatility of bismuth compounds, and usually contains 10 to 20 per cent sodium carbonate with oxides of iron, lime, and old slags with 3 to 5½ parts of charcoal or coke. Reduction occurs at red heat, the temperature is later raised appreciably, and the crude metal is tapped off in iron molds. This crude bismuth contains most of the lead, gold, silver, and antimony and a small amount of the arsenic and copper of the original charge. Most of the copper forms matte, nickel and cobalt form speiss with part of the arsenic, and both speiss and matte contain bismuth. Typical analyses of crude metallic bismuth are given in Table 1. The crude metal may contain lead, copper, arsenic, antimony, sulphur, tellurium, iron, cobalt, nickel, thallium, silver, gold, and tin as impurities.

TABLE 1.—*Analyses of metallic bismuth*

	Crude				Refined					
	Australia	South America			Peru	Bohemia	Bolivia	Saxony		
Bismuth	96.2	96.0	93.37	84.8	99.99	99.32	99.05	99.74	99.77	99.98
Antimony	.8	.2	4.57	5.5	Nil.	------	.56	------	------	------
Arsenic	Trace.		Nil.		Nil.	------	------	.01	------	Trace.
Copper	.5	.1	2.06	3.5	.00065	Trace.	.26	.02	.08	.03
Lead	2.1	3.5	------	4.9	Nil.	.30	------	.11	Nil.	.06
Iron	.4	------	------	Trace.	.001	Trace.	------	Trace.	Trace.	Trace.
Sulphur	------	------	------	Trace.	------	------	------	.04	------	------
Silver	------	(1)	------	[2] .30	.0007	Nil.	.08	.07	.05	------

[1] Contains 34 ounces silver per ton. Also contains 0.2 per cent tin.

[2] Contains 0 0045 per cent gold. Also contains 0.7 per cent tin.

V. REFINING OF BISMUTH

Most of the bismuth which finds commercial application is consumed by the pharmaceutical trade. This use demands "bismuttum purissimum," or bismuth 99.9 to 99.98 per cent pure. Both dry and wet refining processes are employed. The crude metal may be partially refined by exposing it while molten to atmospheric oxygen in order to volatilize or dross the tin, arsenic, antimony, sulphur, zinc, iron, etc. Another method (10) embraces treatment with molten sulphur to eliminate arsenic, antimony, and copper as a matte which is skimmed off. The molten residue is treated with sodium hydroxide and skimmed to remove tellurium and residual arsenic, antimony, and sulphur as sodium compounds. Zinc is added to the molten residue and the copper, silver, and gold concentrate with the zinc in an upper layer, which is skimmed off. Residual zinc is removed by treatment with sodium hydroxide and skimming, and the bismuth is then freed from lead by crystallization.

A number of wet methods of purification are given in the literature (1), the most common form being the solution of impure bismuth in acid followed by the precipitation, by hydrolysis, of the oxysalt. Electrolysis in dilute hydrochloric acid may be employed (13) to produce 99.8 per cent Bi; electrolysis in a fluosilicate electrolyte is claimed (12) to separate bismuth from lead and gold. Mellor (1) quotes A. Classen to the effect that spectroscopically pure bismuth can be obtained by electrolysis from a nitric-acid solution, in which lead and bismuth peroxides are deposited at the anode and crystalline bismuth at the cathode. Distillation in vacuo has been employed as a method of purification (239, 240).

Formerly all of the bismuth for the pharmaceutical trade was refined by wet methods, but material refined entirely by dry processes is now on the market. A major requirement for pharmaceutical uses is absolute freedom from arsenic and tellurium. Representative analyses of refined bismuth are given in Table 1.

VI. PRODUCTION AND MARKET PRICE

The world's production of bismuth is estimated to be about 2,000,000 pounds per annum. The world's consumption of bismuth probably is about 800,000 pounds per annum, of which the United States consumes about 300,000 pounds. Except for the small requirements of the makers of fusible alloys, practically all of the bismuth which finds use is consumed in the manufacture of pharmaceutical preparations. This limited demand is responsible for the limited production; any reasonable increase in the demand could be easily met by the recovery of bismuth as a by-product from smelters and refining processes where bismuth at present either is not recovered or is removed as an impurity and thrown away.

The market price of bismuth has been subject to wide and arbitrary fluctuations. In the last 15 years it has varied between $1 and $3, and at present seems to be fairly stable at about $1.70 per pound.

VII. PROPERTIES OF BISMUTH

1. PHYSICAL PROPERTIES

Bismuth is a coarsely crystalline, brittle metal, usually described as tin white in color, but with a distinct reddish tinge and a high luster. It is the third member of the arsenic, antimony, bismuth subgroup of the fifth group of the periodic table. It has the highest density of the three members of its subgroup, and in many respects is the most metallic of the three. It has the atomic number 83, the next in order above lead, and an atomic weight (14, 15, 16, 17) of 209. Bismuth crystals are trigonal (20) or rhombohedral (24, 27). The cystalline molecule dissolved in lead is diatomic, dissolved in mercury or cadmium it is monatomic (27). Bismuth crystallizes in a rhombohedral face-centered, or deformed simple cubic lattice with the lattice constant $a = 4.726$ Ångstrom units (193). According to Ogg (25) the unit rhomb contains 8 atoms.

The density of bismuth is 9.80 grams per cm^3 at 20° C. (29) and 10.067 at the melting point. The density of molten bismuth decreases regularly as the temperature rises, from 10.062 grams per cm^3 at 275° C. to 9.611 at 650° C. Expansion of the metal during solidification amounts to 3.32 per cent of its solid volume at the melting point (30). The compressibility (31) is 2.8×10^{-6}, between 100 and 500 megabars, when the compressibility is defined as the average fractional change of volume caused by 1 megabar pressure. The hardness (32, 33) of commercial bismuth is given as 7.3 on the Brinell scale using a 6.35 mm ball and 40.3 kg load at 60° F., and as 2+ on the Moh scale.

2. THERMAL PROPERTIES

The melting point of pure bismuth is 271° C. (34, 35). An increase of pressure lowers the melting point (36), but it requires 1,000 atmospheres to lower the melting point 3.55° C. (37). The mean specific heat for the metal up to the melting point is 0.0319 calories per gram, the latent heat of fusion 14.1 calories per gram (38). The vapor pressure (42) is 10^{-3} mm of mercury at 540° C., 1 mm at 840° C., and 100 mm at 1,200° C. The boiling point at atmospheric pressure is between 1,440° and 1,500° C. (34, 41, 42). The boiling point rises with increased pressure, and at 17 atmospheres it is 2,080° C. (43). The heat of vaporization (44) is 42,700 calories per gram molecule. The thermal conductivity (46) varies from 0.018 calorie per second per cm^3 per °C. at 100° C. to 0.037 at 400° C. and higher. The thermal conductivity of solid bismuth is less than that of any other metallic element except mercury. The mean coefficient of expansion, from 0 to 100° C., is 0.00000731. The viscosity of bismuth is of the same order of magnitude as for cadmium, tin, and lead (48). The coefficient of viscosity at 23.7° is 13.71×10^8 poises (dynes per cm^2) (47). The surface tension of bismuth is lower than that of tin, cadmium, lead, or antimony (49). It varies from 376 dynes per cm at 300° C. (52) to 343.9 dynes at 779° C. (51).

3. ELECTROCHEMICAL AND ELECTRICAL PROPERTIES

In the electrochemical series bismuth lies just below hydrogen, together with arsenic, antimony, and copper. From this position bismuth is positive to such metals as lead and tin. It is less subject to oxidation than lead or tin and more resistant to corrosion under oxidizing conditions. The electrode potential of bismuth at 25° is −0.314 volt for the BiO^+ ion and −0.298 volt for the $BiOH^{++}$ ion, as compared to the molal hydrogen electrode (55). The hydrogen overvoltage at a bismuth surface, in 2N H_2SO_4 at 25° is 0.388 volt (54), somewhat greater than the corresponding value for antimony (53). Bismuth electrodes show a tendency to passivity in both alkaline and acid electrolytes (56, 57), and the metal is amphoteric (101) in that it dissolves electrochemically at both anode and cathode.

The specific resistance of solid bismuth is 106.5 microhm-centimeters at 0° C. and 267 at the melting point (3, 59). The mean temperature coefficient of resistance from 0° to 100° C. is 0.00446 (63). Electrical resistance of the solid metal increases with pressure (60, 246) and decreases with tension (62). At the melting point the specific resistance of solid bismuth is 267 microhm-centimeters and of liquid bismuth 127. Bismuth and antimony are the only two metals whose resistance is greater in the solid than in the liquid state (61, 64). The ratio of the resistivity just after fusion to the resistivity just before fusion, for most metals, is roughly 2. For antimony this value is 0.75, for bismuth 0.478. Measurements of its resistivity at the temperature of liquid helium show that bismuth is not a superconductor (58). Figure 1 illustrates the changes in the resistivity of pure bismuth caused by the addition of amounts up to 5 per cent of other metals, such as tin, lead, antimony, tellurium, magnesium, and aluminum.

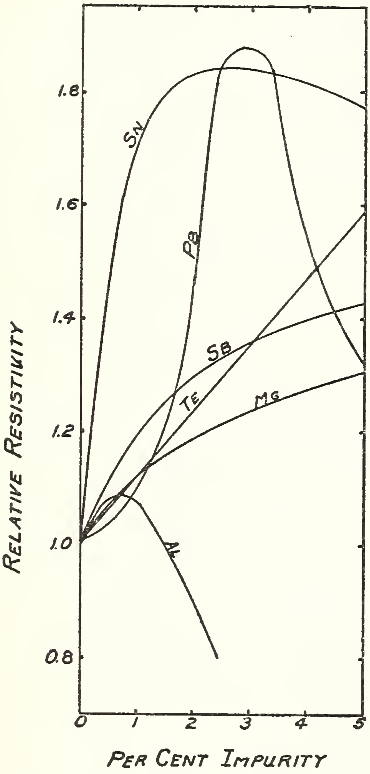

FIGURE 1.—*Effect of impurities on the resistivity of bismuth* (3)

(a) THERMOELECTRIC EFFECTS

Bismuth possesses an unusual thermal e. m. f., about 80 μv per °C. against silver. By coupling pure bismuth with a bismuth alloy containing 5 to 6 per cent tin an e. m. f. of about 120 μv per degree can be obtained (65, 66, 67, 68). A Thomson effect of 676 μv per ° C. for an alloy of bismuth with 1 per cent tin, against copper, has been observed (210). The low melting point and the difficulty of preparing and maintaining wires of suitable size, owing to brittleness and lack of ductility, interfere with the thermoelectric use for bismuth.

(b) MAGNETIC EFFECTS

Bismuth is the most diamagnetic of all metals (72), but the susceptibility decreases with rising temperature (71). An alloy of Cu-Mn-Bi is distinctly magnetic, although all of the components are diamagnetic (231).

The thermal conductivity decreases in a magnetic field (73). The electrical resistance of bismuth increases when the metal is subjected to the action of a magnetic field (the Hall effect) (70, 74, 77 to 83).

4. X RAYS AND RADIOACTIVITY

The absorptive powers of bismuth for X rays have been measured (85, 235) and are similar to those of lead. Exposure to X rays during crystallization does not alter the structure or the properties of bismuth (84). The pure metal does not possess radioactivity detectable by an electroscope (88). Transmutation of bismuth to thallium by treatment with cathode rays was not successful (87).

5. ALLOTROPES

Earlier investigations (98, 99) indicated the existence of at least two allotropic forms of bismuth, with a transformation of the alpha to the beta modification at 75° C. Recent work at the Physikalisch-Technische Reichsanstalt (237) shows that the irregularities in the electrical resistivity and other curves, on which the belief as to the existence of allotropes was based, were due to the presence of impurities and that 99.99 per cent pure bismuth, like spectroscopically pure zinc, gave no indication of allotropic transformation when tested by dilatometric, electrical resistivity, and microscopic methods.

6. MISCELLANEOUS PROPERTIES

Pyrophoric metal can be prepared by the reduction of basic bismuth nitrate (100). A mixture containing bismuth and ammonium citrates is reported to be photosensitive (102). Traces of bismuth in various calcium salts produce a beautiful blue luminescence in a burning jet of hydrogen (103). This might be used as a qualitative test, as it is claimed that 0.00001 per cent bismuth can be detected.

VIII. USES FOR BISMUTH

The use of bismuth compounds, both organic and inorganic, in pharmaceutical and medicinal preparations creates probably 80 per cent of the demand for bismuth. These preparations include powders, salves, and ointments as well as specific remedies. Bismuth compounds have been used in preparing patients for X-ray examination. Bismuth for these uses must be as pure as possible and must be entirely free from certain impurities, such as arsenic. Detailed discussion of the complex and voluminous literature dealing with the medicinal and pharmaceutical uses of bismuth is beyond the scope of this paper. The present investigation is concerned primarily with possibilities for extending the uses of metallic bismuth.

Bismuth is used in the preparation of alloys chiefly to lower the melting point of the mixture and, to a lesser extent, as a hardening agent for lead and tin, or to improve the casting properties of these metals. Bismuth is an essential constitutent of practically all of the low-melting metallic alloys which have been used for fusible plugs, safety devices, tempering baths for small tools and pieces, and solders. Some of these alloys, such as Wood's, Rose's or Lipowitz' metal, melt at or below the temperature of boiling water and have been used as solders; for making delicate castings, such as dental dies from plaster impressions; to hold delicate castings or pieces of irregular shape during machining or testing operations; to furnish gas-tight liquid seals for apparatus, such as nitriding ovens; and for toys, such as the "magic teaspoons" which melt in hot water. Bismuth amalgams, with or without lead and tin, have been used for the production of mirrors whose luster is reported equal to that of silver.

Bismuth added to tin will impart hardness, sonorousness, luster, and fusibility. A 10 per cent addition of bismuth improves the appearance of a tinned joint on hot or cold rolled steel. An alloy for hardening bearing metals contains Sb 70 parts by weight, Sn 25, Cu 3, Bi 2. Bismuth has been used in Britannia metal and pewter. From their relative positions in the electrochemical series, the addition of bismuth up to the limit of its solid solubility in either tin or lead should improve the resistance to oxidation of these metals.

Bismuth alloys—for example, those with lead—whether high or low in bismuth, have good casting qualities and produce good impressions of the mold. For this reason, pure bismuth or Bi-rich alloys have been used in making patterns, and smaller amounts of bismuth (up to 15 or 20 per cent) have been used in stereotype and similar metals. The pure metal and the very rich alloys expand on solidification, but the alloys of lower bismuth content contract. They produce sharply defined castings in spite of this contraction because the presence of bismuth, or of antimony, in the case of lead-antimony alloys, lowers the surface tension and the viscosity of the molten mixture, so that, while still liquid, it follows the contours of the mold.

Bismuth, in amounts up to about 1 per cent, has been added to various brasses and bronzes and to antifriction metals, but smaller amounts of bismuth, or when it is present as an impurity, are usually regarded with extreme suspicion. Small amounts present in copper or gold make them unworkable, and the presence of bismuth in lead which is intended for the manufacture of white lead is objectionable, as it leads to an off-color product.

Bismuth wire, prepared either by extrusion at elevated temperatures (243, 244) or by melting and drawing within glass tubes (245), has been used in thermocouples, pyrometers, galvanometer suspensions, hair lines for microscopes, etc. The high thermal e. m. f. of bismuth can be used to produce a very sensitive thermocouple, but the wire is brittle and difficult to handle. If the wire is prepared by drawing down a glass tube filled with metal, the glass may be removed with hydrofluoric acid or left for insulation and protection.

The electrical and thermal conductivities of bismuth are extraordinarily low and the electrical conductivity further decreases when exposed to the influence of a magnetic field. Consequently, bismuth has been used in the construction of instruments for determining the strength of magnetic fields.

It has been reported (153, 154) that bismuth up to 2 per cent, like silicon, increases the electric resistance of steel without diminution of the magnetic permeability or dissipation of energy through hysteresis. Bismuth steels have been suggested as a substitute for silicon steels for transformer sheet. From a study of the iron-bismuth diagram it is difficult to understand how bismuth steels can be made.

Miscellaneous uses for bismuth include the following items: Metallic pencils have been made of an alloy consisting of 90 parts by weight of bismuth, 70 lead, and 8 mercury; in the separation of the metals of the platinum group, fusion with bismuth has been employed to dissolve rhodium; plates of metallic bismuth have been used as a surface for friction and lubrication tests, as these plates are more easily cleaned of grease than is glass.

Bismuth compounds have found some uses outside of pharmaceutical and medicinal preparations. Organo-metallic compounds of bismuth possess decided "antiknock" properties, although they are only about one-third as efficient as lead compounds in this respect. Bismuth trichloride is claimed to render less inflammable some waterproofing materials, such as tar, creosote, and nondrying oils. Bismuth trioxide has had some small use as a pigment and in vitreous enamels, porcelain, and glass, chiefly as a flux to increase the fusibility of coloring oxides or compounds. In these uses it resembles lead oxide, but has the advantage of being nonpoisonous. A mixture of the composition Bi_2O_3:3Zn has been patented as a catalyst in the synthesis of methanol. Catalysts for the oxidation of ammonia have been made by adding bismuth oxide to iron oxide. Bismuth trioxide has been used as a catalyst for the oxidation of hydrocyanic acid. Owing to the volatility of Bi_2O_3, the life of some of these catalysts at high temperatures is short.

IX. BINARY ALLOY SYSTEMS

1. ALKALI METALS-BISMUTH

Bismuth is completely miscible with either sodium or potassium in the liquid state. (Figs. 2 and 3.) Three compounds are formed with potassium and 2 with sodium (2, 104, 105). The high melting points of these compounds, particularly that of Na_3Bi, are surprising in view of the low melting points of the constituents.

2. ALUMINUM-BISMUTH

Bismuth and aluminum (fig. 4) are mutually insoluble (109, 111) except for a possible slight solubility of aluminum in liquid bismuth. Bismuth up to 2 per cent has no noticeable effect on the physical properties of an alloy of Al-Cu (108).

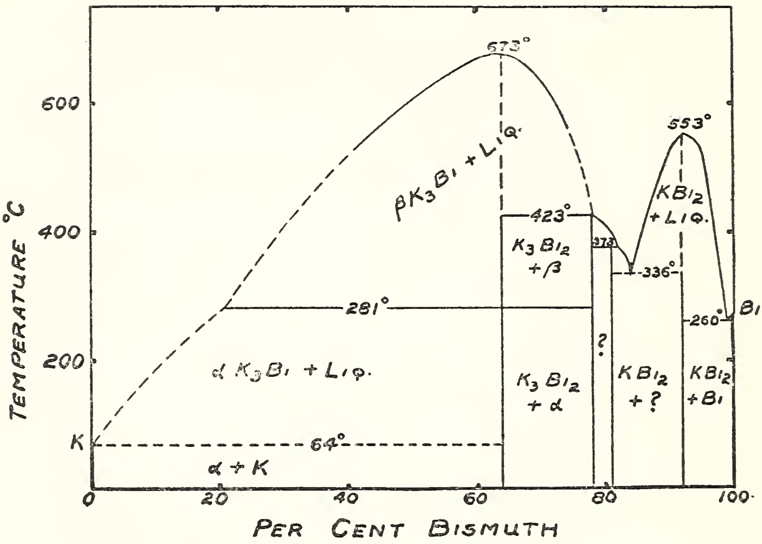

FIGURE 2.—*Potassium-bismuth system (Smith, 3, p. 427)*

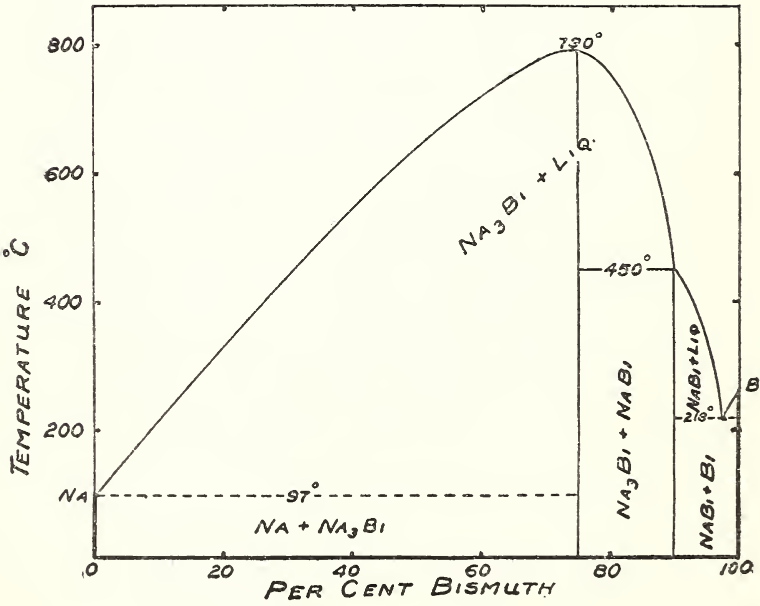

FIGURE 3.—*Sodium-bismuth system (Mathewson, 3, p. 427)*

3. ANTIMONY-BISMUTH

Bismuth and antimony (fig. 5) are miscible in the liquid state and form a continuous series of solid solutions. This system is unique in that the solidus line is practically horizontal between the limits of 40 and 100 per cent bismuth. A horizontal solidus usually indicates a eutectic, but no eutectic exists in this system (2, 71, 109, 113, 114, 115, 118).

4. ARSENIC-BISMUTH

Bismuth and arsenic (fig. 6) are completely miscible in the liquid state (2, 120). If a eutectic is formed it is practically pure Bi. The liquidus is nearly a straight line from almost pure Bi to pure As. Preparation of "bismuth arsenides" has been described (119, 121) although no compounds are indicated in Heike's diagram. The melting point of As in this diagram must have been determined under pressure. Recent data (3) show that As sublimes at about 600° C., under atmospheric pressure.

5. CADMIUM-BISMUTH

The bismuth-cadmium diagram (fig. 7) represents a simple eutectiferous system. The two metals are practically insoluble in each other in the solid state, the solid solubility in each case being not over 0.1 per cent (109, 126). The Bi-Cd alloys, like Bi-Pb, show maximum hardness at about the eutectic composition, but lose this maximum hardness on long annealing at 130° C. (124).

6. CALCIUM-BISMUTH

The bismuth-calcium diagram is not complete. The eutectic, at the bismuth end, contains very little calcium. One or more compounds are probable (129).

7. CARBON-BISMUTH

Carbon is practically insoluble in bismuth (2). At 1,490° C. bismuth will dissolve only 0.023 per cent carbon (130).

8. CERIUM-BISMUTH

Bismuth and cerium (fig. 8) form four compounds, $BiCe_3$, Bi_3Ce_4, BiCe, and Bi_2Ce (132). As in the case of Na and K alloys, the compounds of Ce and Bi have surprisingly high melting points. This is particularly noticeable in the case of the compound Bi_3Ce_4, whose melting point is considerably above the boiling point of pure bismuth.

9. CHROMIUM-BISMUTH

These two metals are immiscible in both the solid and liquid states throughout the ranges indicated by the solid lines in Figure 9. Presumably Bi and Cr are immiscible throughout the entire range of composition, but the data are not complete.

10. COBALT-BISMUTH

The system (fig. 10) is not complete (134). The two metals do not form compounds and are immiscible in the solid phase. Liquid bismuth dissolves a small amount of cobalt.

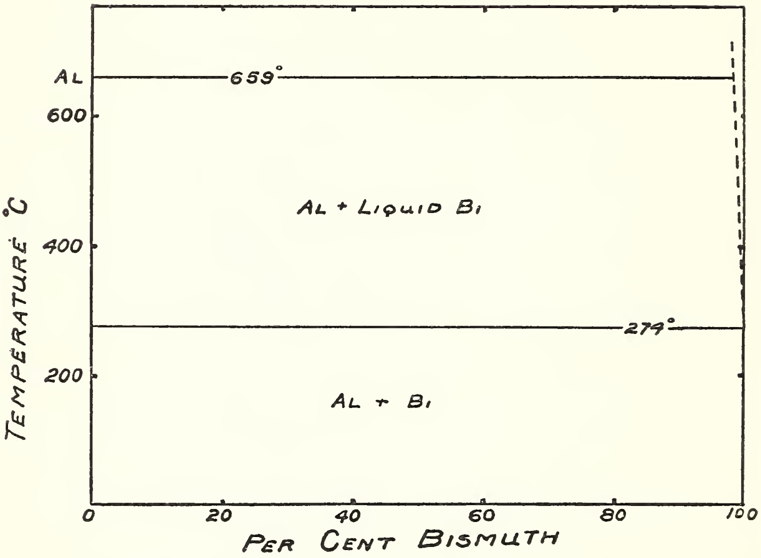

FIGURE 4.—*Aluminum-bismuth system (Gwyer, 106, p. 104)*

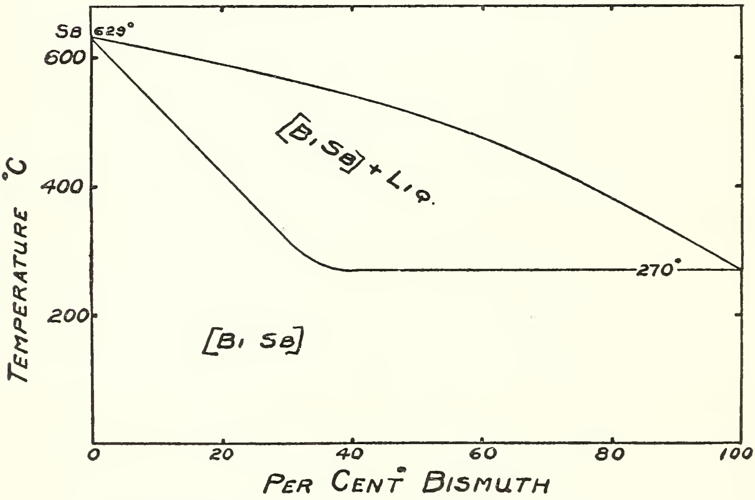

FIGURE 5.—*Antimony-bismuth system (Cook, 115)*

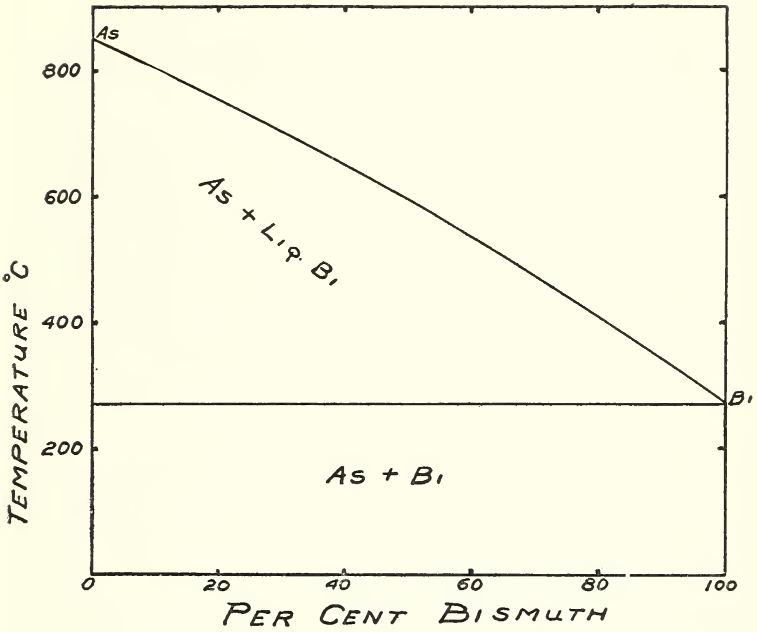

Figure 6.—*Arsenic-bismuth system (Heike, 120)*

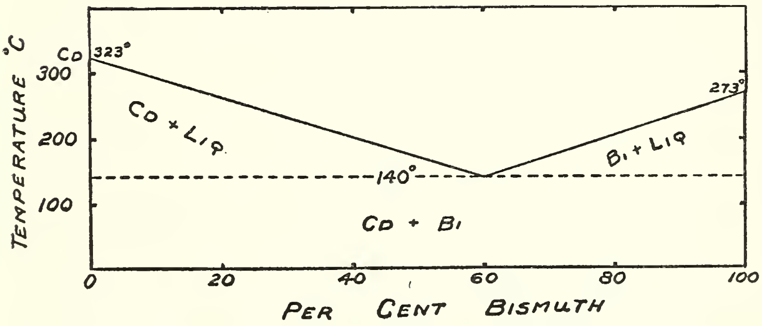

Figure 7.—*Cadmium-bismuth system (Petrenko and Fedorov, 3, p. 426)*

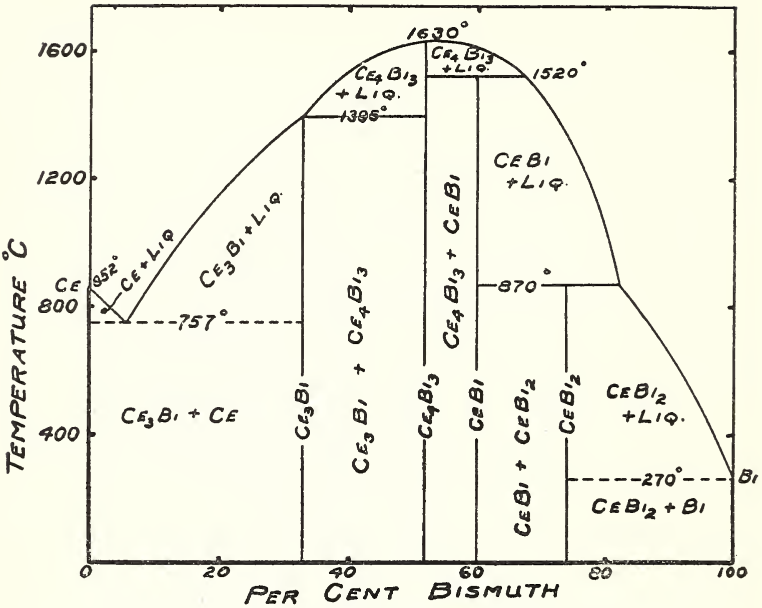

Figure 8.—*Cerium-bismuth system (Vogel, 3, p. 427)*

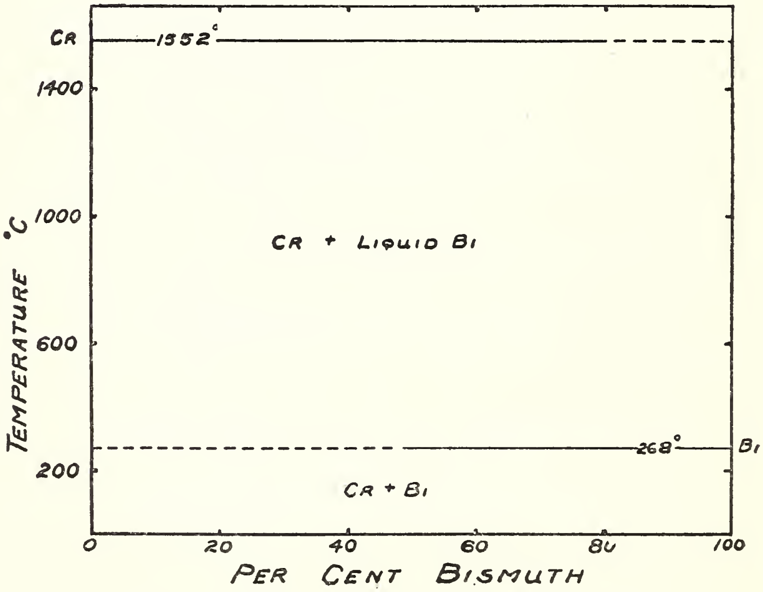

Figure 9.—*Chromium-bismuth system (Williams, 133)*

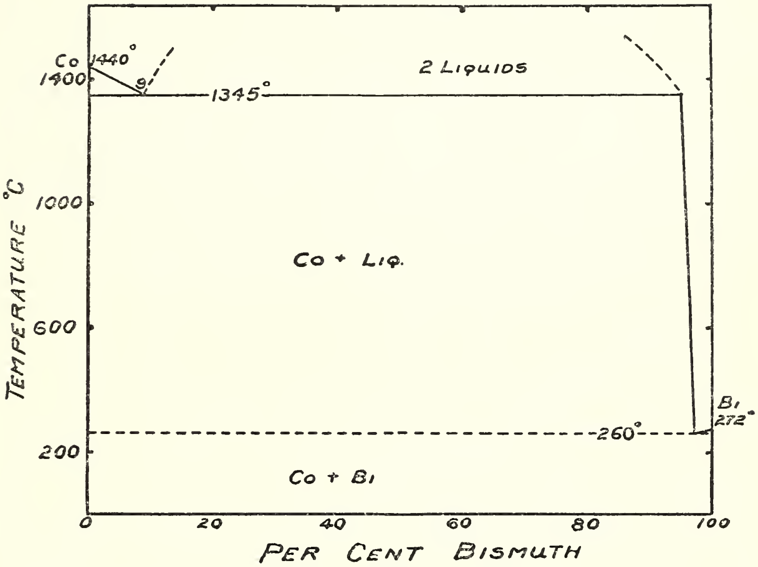

Figure 10.—*Cobalt-bismuth system (Lewkonja, 134)*

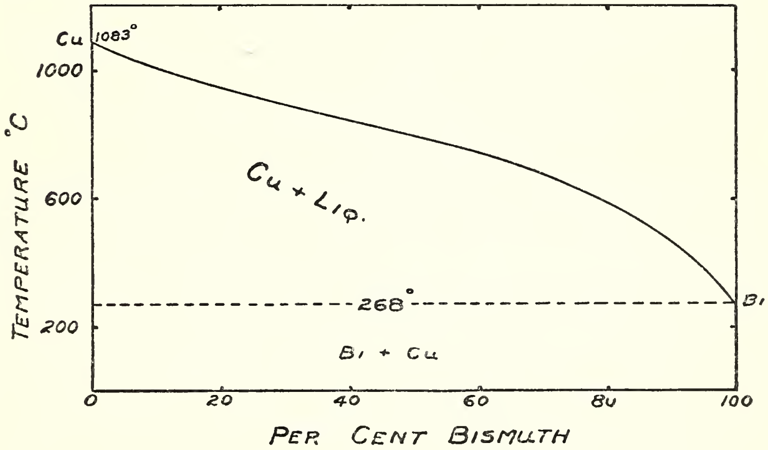

Figure 11.—*Copper-bismuth system (Jeriomin, 3, p. 427)*

11. COPPER-BISMUTH

The liquidus curve (fig. 11) is continuous from copper to bismuth; no compounds are formed (2, 4, 141, 142, 146, 147). If there is a eutectic it lies close to pure bismuth. The two metals are almost mutually insoluble in the solid state (4, 141, 146), the limit of solubility being of the order of 0.1 per cent. This insolubility of bismuth in solid copper explains the well-known brittleness imparted to copper by small amounts of bismuth. Any Bi present in solution in molten Cu is precipitated during solidification as a film of pure Bi around the copper crystals, and the behavior of the resulting metal is then governed by the properties of the brittle films of bismuth. As little as 0.002 per cent Bi makes copper noticeably brittle (148) and more than 0.005 per cent interferes with wire drawing (145). From 0.02 to 0.05 per cent Bi renders copper both cold short and red short (137, 139, 140, 145). The objectionable effects of small amounts of bismuth in copper can be overcome by the addition of arsenic until the metal contains at least three times as much arsenic as bismuth and lead, and in no case less than 0.6 per cent As (148). Phosphorus also may be added to correct this brittleness (135). Small amounts of nickel intensify the effects of Bi (141, 144), but the addition of more than 4 per cent Ni, or of manganese, overcomes the deleterious effects of Bi on the mechanical properties of copper (142). Copper sheet, containing from 0.05 to 0.25 per cent bismuth and from 0.16 to 0.69 per cent arsenic, used as roofing material on English churches and public buildings, showed remarkable resistance to atmospheric corrosion (136).

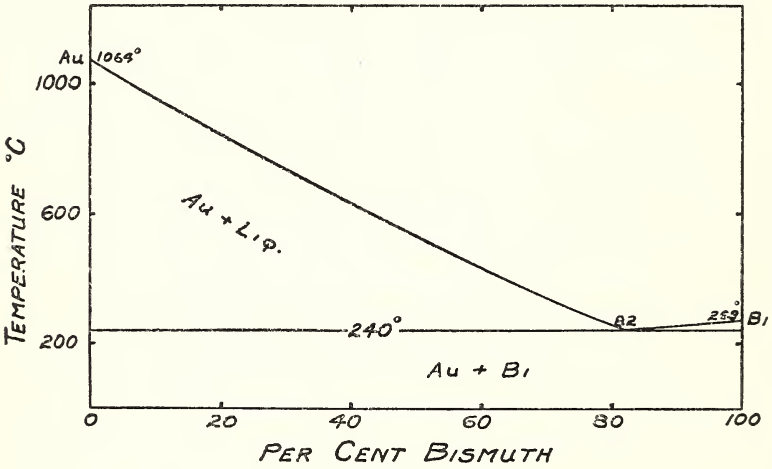

Figure 12.—*Gold-bismuth system* (*Vogel, 242*)

12. GOLD-BISMUTH

Bismuth and gold (fig. 12) are miscible in the liquid state and form a eutectic which melts at 240° C. at 82 per cent bismuth. Vogel's original diagram (241) shows that gold is insoluble in solid bismuth, but indicates possible solid solution of bismuth up to about 4 per cent in gold. Rose (242) states that less than 0.025 per cent Bi is soluble in gold and that bismuth even in this amount is very injurious in the ordinary commercial applications of gold, as it renders the gold brittle and unworkable. Microscopic examination shows a condition similar to that encountered in copper which contains bismuth. The crystals of practically pure gold are soft and malleable, but are surrounded by films of pure, brittle bismuth which shatter when attempts are made to work the alloy either by hammering or rolling. This brittleness of gold, like that of copper, can not be removed by annealing. It is interesting to note that the natural alloy "maldonite" which consists essentially of gold and bismuth in the proportion of 2 Au to 1 Bi is malleable. The fact that gold containing 0.01 per cent bismuth can not be rolled is confirmed by Nowack (149).

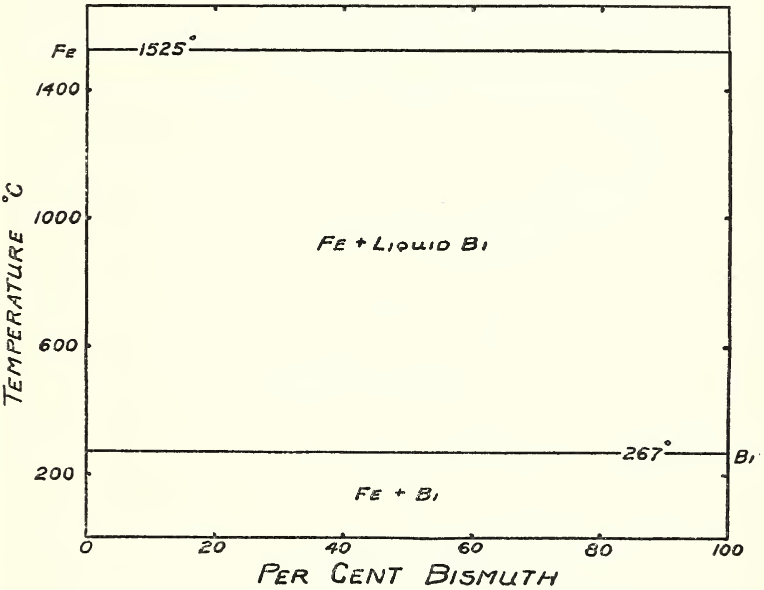

Figure 13.—*Iron-bismuth system (Isaac and Tammann, 155)*

Vogel's original diagram, therefore, appears to be in error, and has been corrected as follows: The solid solubility of bismuth in gold should be less than 0.025 per cent, instead of the 4.5 per cent indicated. In other words, the solidus line should extend from pure bismuth to pure gold and the composition of the solid phase should be shown to be pure gold and pure bismuth.

13. IRON-BISMUTH

Bismuth and iron (fig. 13) are said to be completely insoluble in each other in both solid and liquid states (2, 4, 151, 155). In spite of this apparent complete immiscibility the literature reports that bismuth has a "bad effect" on steel (152), but bismuth up to 2 per cent in steel (153) acts like silicon to reduce eddy current losses; also that "bismuth steels" can be forged (154), but these steels contained only a trace of Bi, although 10 per cent was added to the charge.

14. LEAD-BISMUTH

The equilibrium diagram of this system (fig. 14) has been studied by thermal and magnetic analysis (2, 156, 159, 160, 161). All agree that the system is a simple eutectiferous one with no compounds. Recent work (156) places the eutectic at 58 per cent Bi, with a melting point of 125° C., and the liquidus curves as almost straight lines from the eutectic to the melting points of the pure metals. There is limited solid solubility of each metal in the other, but the limits are somewhat in question. Lead is soluble in bismuth to the extent of about 3 per cent at the eutectic temperature and somewhat less at room temperature. About 37 per cent bismuth is soluble in lead at 125° C. and about 17 per cent at room temperature. Additions of bismuth harden lead, but to a lesser extent than does antimony. Di Capua and Arnone (124) found maximum hardness at the eutectic composition and also found that prolonged annealing caused the disappearance of this maximum hardness. Mallock (158) found that the hardening effect of bismuth is greater above 70 per cent than it is below that amount. Bauer (157) reports the hardening effect of small amounts (less than 2 per cent) of bismuth on lead and thinks that these additions also promote a tendency to intercrystalline corrosion in lead water pipes. The viscosities of lead-bismuth mixtures are less than values calculated from the rule of mixtures (164). The temperature coefficient of viscosity of lead-bismuth alloys is surprisingly small (48), being even lower for the higher concentrations of bismuth than that for pure Bi. These factors, combined with the low surface tension of Bi and Bi alloys (49), account for their good casting properties. The magnetic susceptibility (71), thermal conductivity (165), and electrical conductivity (166) of lead-bismuth alloys have been studied. The effects of small amounts of lead on the electrical resistivity of bismuth are shown in Figure 1.

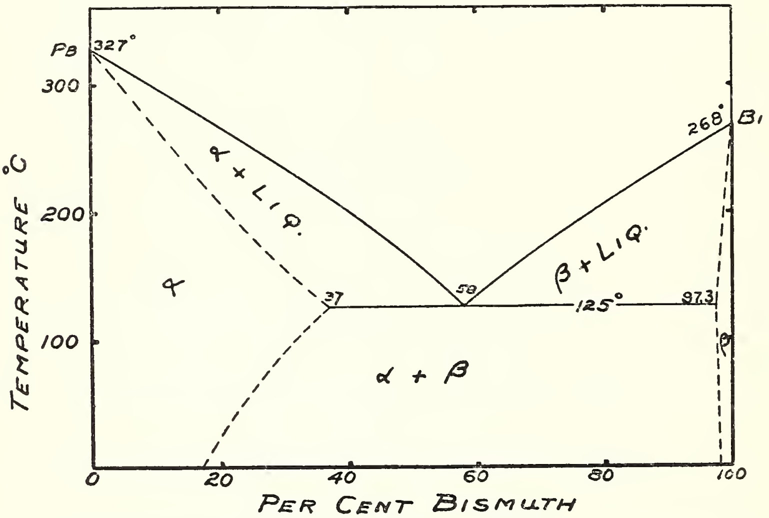

FIGURE 14.—*Lead-bismuth system* (*Cowan, Hiers, and Edwards, 156*)

15. MAGNESIUM-BISMUTH

Bismuth and magnesium (fig. 15) form a compound Mg_3Bi_2 (168, 169, 170), and this compound forms a eutectic with magnesium, at 65 per cent Bi. There may be limited solid solubility at both ends of the diagram (167), but it is negligible in amount.

16. MANGANESE-BISMUTH

Bismuth and manganese are only partially miscible in the liquid state, forming two liquid layers (116, 171, 172, 173). In the diagram published by Bekier (173) (shown in fig. 16), there are three horizontals, one at the level of the bismuth-rich eutectic extends from pure Bi to the vertical line which indicates a compound at about 58 per cent Bi; another extends from the liquidus to pure manganese at 450°; and the third forms the solidus for the 2-liquid-layer system, and extends from about 60 per cent Bi to pure manganese, at 1,240°. The melting point of the manganese-rich eutectic coincides with that of pure manganese. Bekier mentions Dieckman's compound, BiMn, 81.9 per cent Bi, which is magnetic but which loses its magnetism on heating to 360° or 380°. This compound is not shown in the diagram.

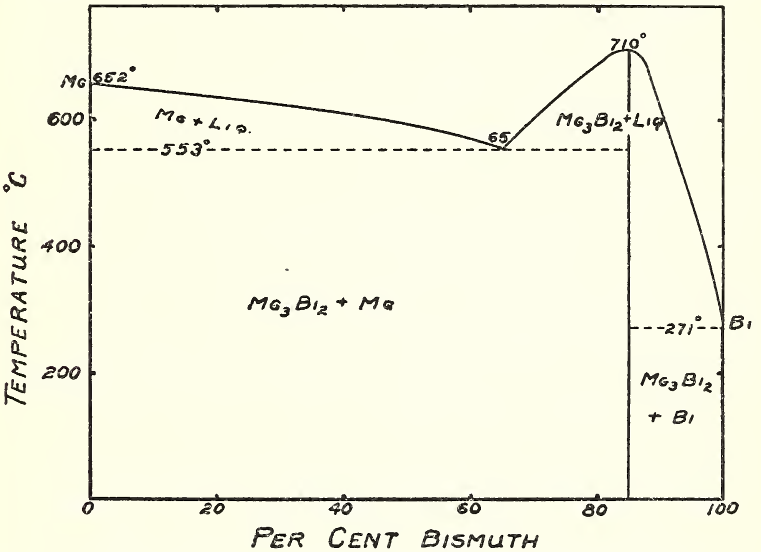

Figure 15.—*Magnesium-bismuth system (Grube, 3, p. 427)*

The diagram of Parravano and Perret (172), as reproduced in the International Critical Tables (3), agrees with Bekier's diagram with only minor changes in the temperatures. However, a more recent diagram, that of Siebe (171), differs in several respects from the others. The horizontal at the bismuth-rich eutectic is extended across the diagram; the compound at 58 per cent Bi does not appear; two additional horizontals are introduced, at 89 per cent bismuth at 597° and at 80 per cent bismuth at 1,040°; the region of existence of two liquid layers extends from the manganese-rich eutectic at 0.5 per cent Bi to 77 per cent Bi, instead of to about 60 per cent, as shown in the other diagrams; a difference of 15° is shown between the melting points of pure manganese and of the manganese-rich eutectic.

All agree that both eutectics lie within about 0.5 per cent of pure Bi and pure Mn, respectively. The solubility of bismuth in manganese is not over 0.5 per cent. Siebe reports that the hardness of the alloys increases with the manganese content and that alloys containing from 0.5 to 9.0 per cent manganese were magnetic. Manganese has been suggested (142) as an addition to copper which contains bismuth, to counteract, through the formation of Bi-Mn compounds, the brittleness which bismuth imparts to copper.

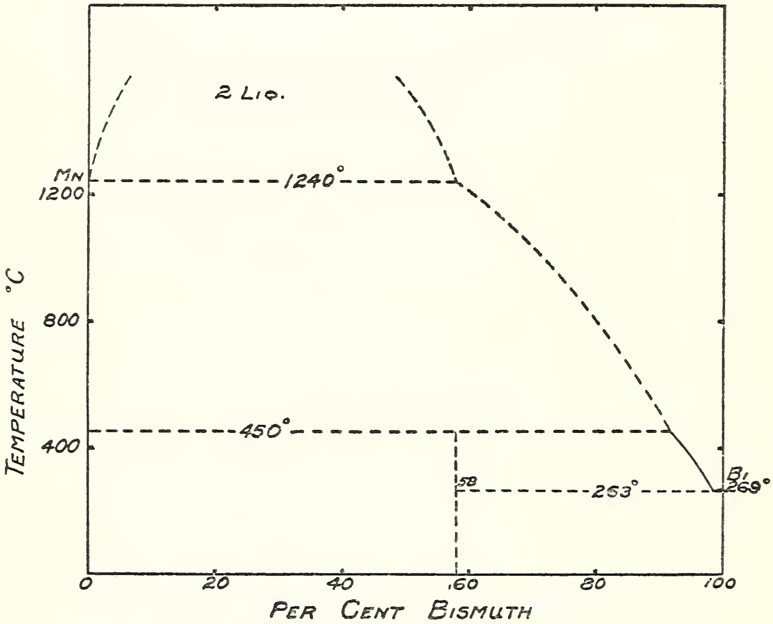

Figure 16.—*Manganese-bismuth system (Bekier, 173)*

17. MERCURY-BISMUTH

The system bismuth-mercury (fig. 17) is not of great importance. The heat of solution of bismuth in amalgams (176) and the vapor pressure of certain amalgams (177) have been studied. Bismuth amalgam has been used (174) in volumetric analysis as a reducing agent for the determination of vanadium and molybdenum or molybdenum and iron.

18. NICKEL-BISMUTH

The diagram (fig. 18) is based on the work of Voss (3, 180), but it has been modified in view of later work. There are no peaks in the liquidus to indicate compounds, but on further cooling of the partly solidified melt two compounds, NiBi and $NiBi_3$, appear at 638° C. and at 472° C., respectively (2, 179, 180, 181). If there is a eutectic between Bi and $NiBi_3$ it lies close to pure Bi. Bismuth-nickel alloys may be worked at temperatures about 50° below the solidus tem-

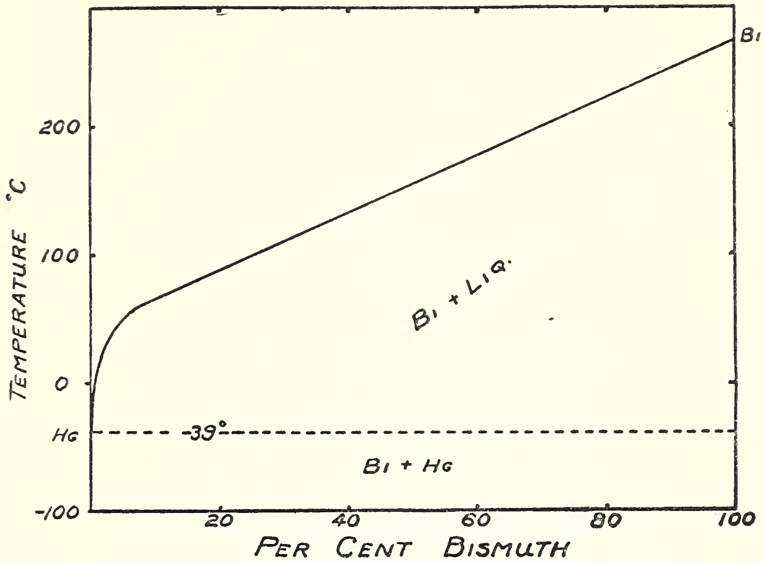

FIGURE 17.—*Mercury-bismuth system* (*Puschin, 3, p. 427*)

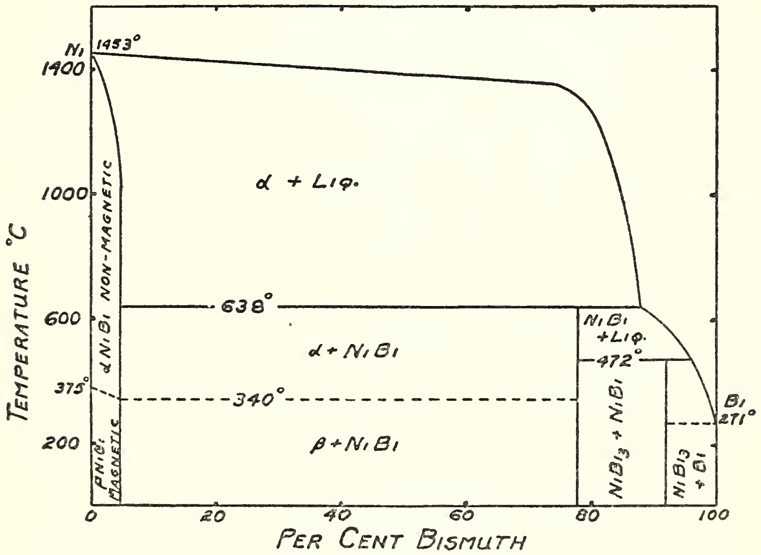

FIGURE 18.—*Nickel-bismuth system*

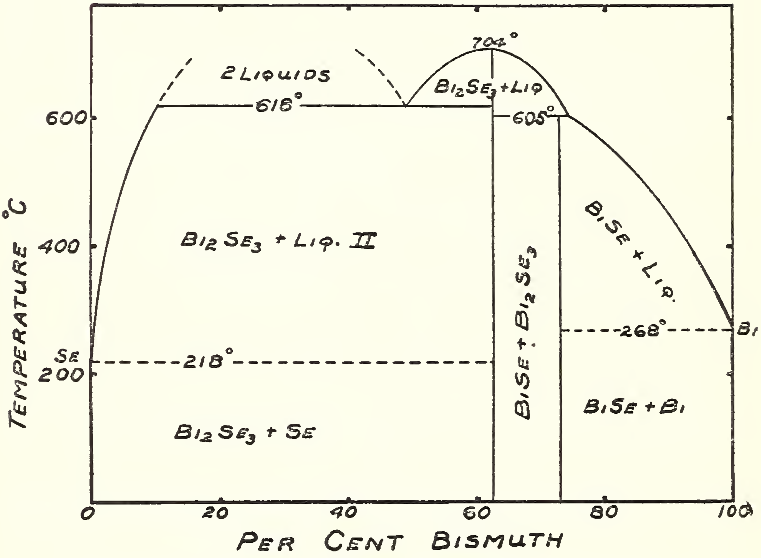

Figure 19.—*Selenium-bismuth system* (*Tomoshige, 183*)

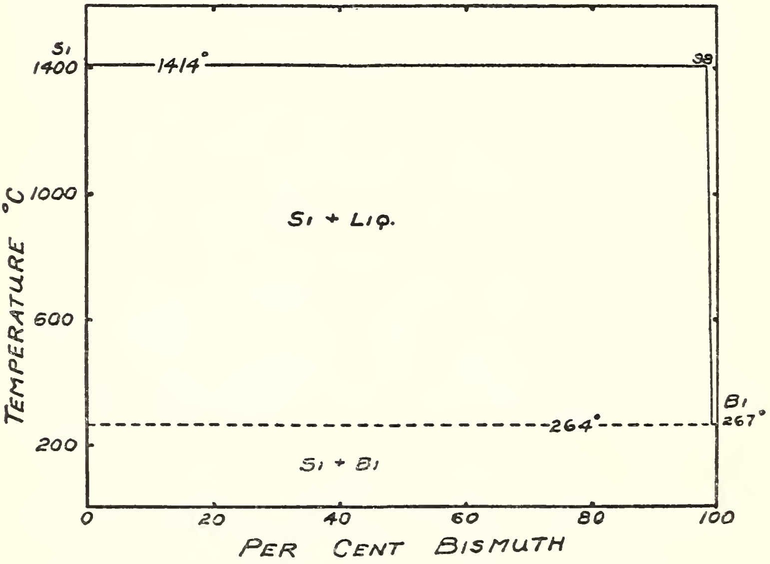

Figure 20.—*Silicon-bismuth system* (*Williams, 133*)

perature (178). The addition of nickel has been suggested (142) to compensate for the presence of bismuth in copper on the basis that concentration of the bismuth in a compound, such as $NiBi_3$, prevents the formation of the objectionable films of pure Bi which envelop the Cu crystals.

19. PLATINUM-BISMUTH

There are no bismuth-platinum compounds (182).

20. SELENIUM-BISMUTH

Bismuth and selenium (fig. 19) form two compounds, BiSe and Bi_2Se_3 (116, 183, 184, 185). Between the limits of 10 and 49 per cent bismuth two liquid layers are formed. There is a eutectic at 618°, and at 605° a peritectic transformation occurs.

21. SILICON-BISMUTH

Bismuth and silicon (fig. 20) are practically immiscible in the liquid state (133, 186) except for a slight solubility of silicon in liquid bismuth (2). Silicon is soluble in solid bismuth to the extent of about 0.8 per cent.

22. SILVER-BISMUTH

Bismuth and silver (fig. 21) are completely miscible in the liquid state and form a eutectic at about 95 per cent Bi which melts at 260° C. (2). The solid solubility of Bi in Ag is low; Ag is insoluble in Bi (168). Bismuth-silver alloys tarnish more readily than pure silver (187).

23. SULPHUR-BISMUTH

This system has been established up to 15 per cent sulphur (2, 185, 189), but beyond this amount the mixtures lose sulphur when heated. One compound, Bi_2S_3, has been definitely established and another, BiS, is probable. One eutectic, having a melting point of 270° C., exists at a concentration of 0.14 per cent sulphur. There is no solubility of sulphur in solid bismuth. The affinity of bismuth for sulphur is less than that of copper, iron, or mercury, but greater than that of cadmium, antimony, tin, lead, or zinc.

24. TELLURIUM-BISMUTH

This system (fig. 22) has been thoroughly investigated (71, 109, 159, 161, 185, 190, 191, 192). The two metals are completely miscible in the liquid state, but there is no solid solubility. One compound is formed, Bi_2Te_3, which contains 52.2 per cent bismuth and melts at 585° C. There are two eutectics, at 264° with 1 per cent Te and at 389° with 86 per cent Te.

25. THALLIUM-BISMUTH

The bismuth-thallium diagram (fig. 23) is complicated (109, 191, 195, 197, 198, 199). The compound Bi_5Tl_3 is readily identified when encountered in the course of magnetic examination of the system. Other compounds, such as $BiTl_3$, Bi_2Tl, Bi_3Tl_2, have been reported, but their existence is doubtful. There are three eutectics, namely, at 5 per cent Bi (300°), 46 per cent Bi (180°), and 78 per cent Bi (200°).

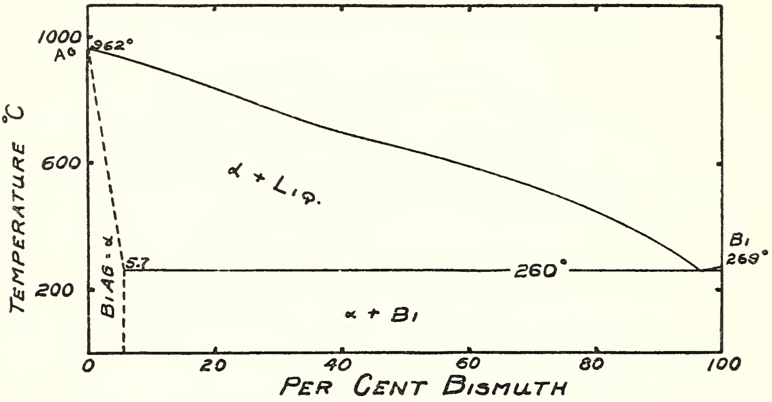

FIGURE 21.—*Silver-bismuth system* (*Petrenko, 3, p. 421*)

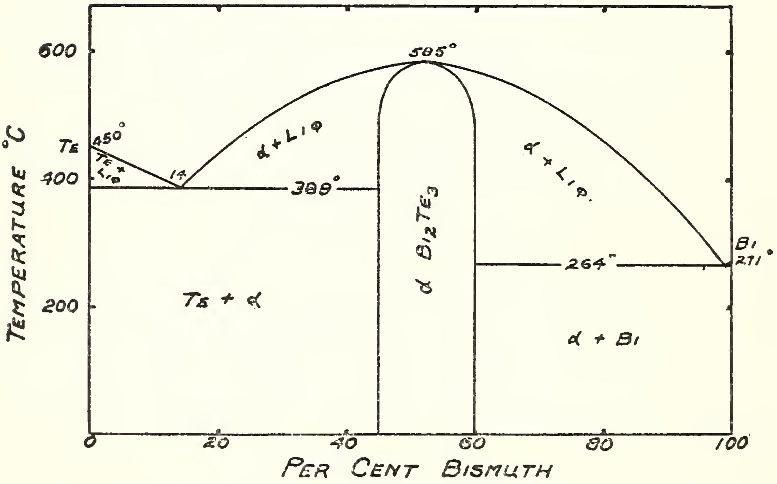

FIGURE 22.—*Tellurium-bismuth system* (*Endo, 71*)

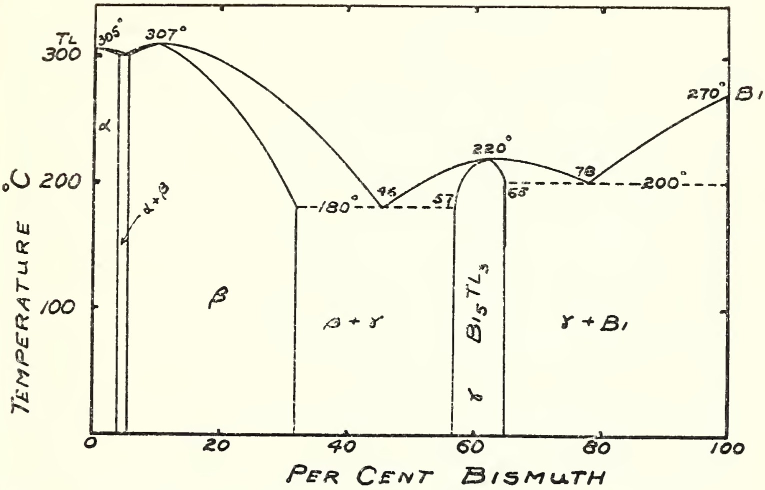

FIGURE 23.—*Thallium-bismuth system (Kurnakov, Zemczuzny, and Tararin, 197)*

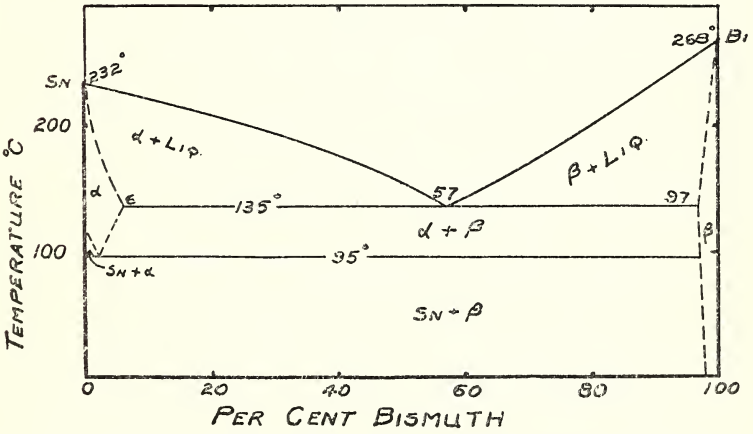

FIGURE 24.—*Tin-bismuth system (Cowan, Hiers, and Edwards, 200)*

26. TIN-BISMUTH

This system (fig. 24) also has been thoroughly investigated (2, 4, 71, 159, 160, 161, 168, 200, 201, 212). The metals are completely miscible in the liquid state, and the system (200) is essentially of the simple eutectiferous type with the two branches of the liquidus meeting at the eutectic point, 57 per cent bismuth and 135° C. Tin is soluble in bismuth to the extent of about 3 per cent at eutectic temperature and about 2 per cent at room temperature. Tin will dissolve 6 per cent Bi at the eutectic temperature, but this solubility decreases with decreasing temperature and a eutectoid inversion takes place at 95° C. Bismuth-tin alloys are all diamagnetic (202). These alloys show maximum hardness and maximum castability at the eutectic composition (143, 204, 207), and the eutectic mixture shrinks 0.8 per cent on solidification (203). Bismuth-tin alloys evolve heat, due to molecular transformations in the solid state (213). The 50–50 alloy has been known as "cutlanego" and its oxide has been used in white enamels. From 5 to 10 per cent bismuth in a tin coating makes it whiter and brighter and cuts down the loss of tin due to drossing (206, 216). However, it is also reported that 0.056 per cent Bi increases the drossing loss of tin. The addition of small amounts of tin to pure bismuth has remarkable effects on the electrical and thermoelectric properties. The electrical resistivity of pure bismuth increases remarkably when small amounts of tin are added. (Fig. 1.) Bismuth alloyed with 1 per cent tin has a thermal e. m. f. against copper of 676 μv per ° C. as compared to 58 for pure Bi under the same conditions. Above 2 per cent tin the thermal e. m. f. decreases (210).

27. ZINC-BISMUTH

Bismuth and zinc are completely miscible in the liquid state only at high temperatures (2, 4, 127, 161, 218). The diagram published by Curry (218) (shown in fig. 25) places the limit of complete miscibility at about 820° C. Between 820° and 417° C. and the limits of 0.5 and 85 per cent Bi two liquid layers are formed. There are two eutectics, one at practically pure zinc, the other at 97.3 per cent Bi. Curry found solid solubility of about 3 per cent zinc in bismuth; Mathewson and Scott (127) deny this, but Endo (161) established, by means of magnetic analysis, the solid solubility of Zn in Bi at about 2 per cent. Bismuth is insoluble in solid zinc. Bismuth-zinc alloys have been suggested for use as pencil "leads" (217).

X. TERNARY, QUATERNARY, AND MISCELLANEOUS ALLOYS

A number of ternary or more complex alloy systems have been investigated, mainly either for the production of low-melting solders or to eliminate the difficulties caused by the presence of bismuth as an impurity in copper. The bismuth-lead-tin system is the most important in the solder group. The ternary diagram (4, 5, 222) shows complete miscibility in the liquid state, limited solubility in the solid state, and no compounds. The ternary eutectic, melting point 96° C., occurs at the composition 52.5 per cent Bi:32 per cent Pb:15.5 per cent Sn as shown in the melting-point diagram. (Fig. 26.) Rosenhain (221) has constructed a solid model in three dimensions for the

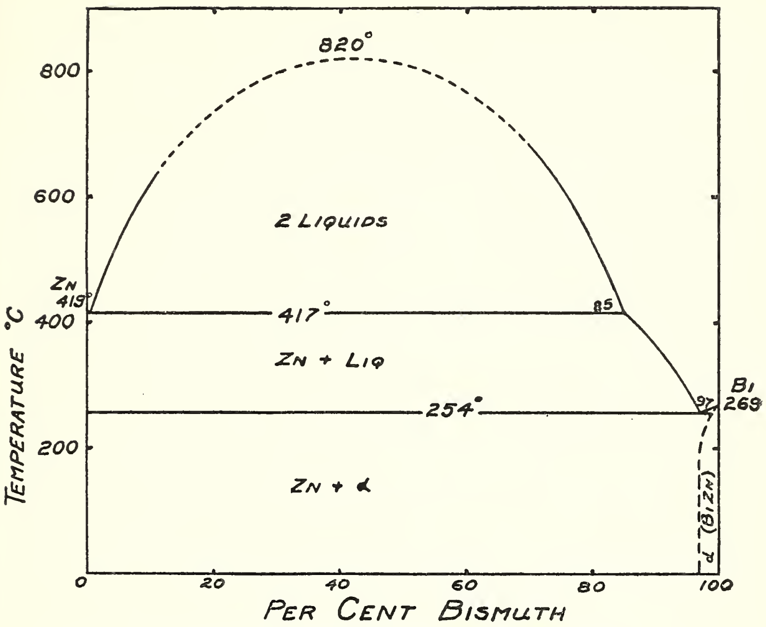

Figure 25.—*Zinc-bismuth system* (*Curry, 218*)

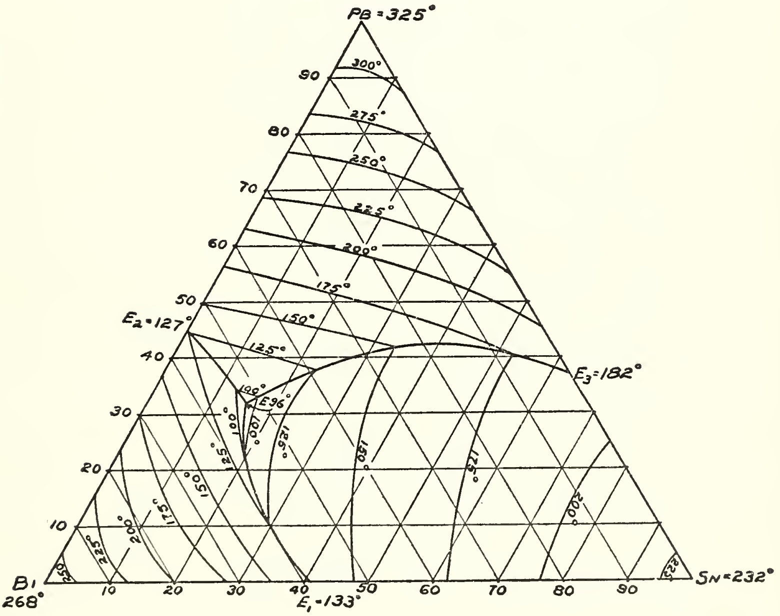

Figure 26.—*Melting point diagram for the system lead-tin-bismuth* (*Heyn-Grossman, Physical Metallography, p. 59*)

system, assuming values for the solid solubilities. Di Capua (219) has determined the hardness of some of the alloys, and Hargreaves (32) reported very marked softening produced by cold working. The addition of cadmium lowers the melting point of bismuth-lead-tin alloys still further; the quaternary eutectic (116, 223) consisting of 49.5 per cent Bi:27.27 per cent Pb:13.13 per cent Sn:10.10 per cent Cd melts at 70° C.

The ternary system Bi-Pb-Cd (128, 224), in the absence of tin, forms a eutectic with a melting point of 91.5° C. at the composition 51.65 per cent Bi:40.2 per cent Pb:8.15 per cent Cd. The systems Bi-Pb-Zn (225) and Bi-Pb-Sb (226) have been studied. In the latter system bismuth in small amounts has little effect on the solid solubility of antimony in lead or on the dispersion hardening of these alloys. Small amounts of antimony have little effect on the solid solubility of bismuth in lead, but larger amounts of antimony remove Bi from solution.

The bismuth-tin-zinc system (227) forms a eutectic at 56 per cent Bi:40 per cent Sn:4 per cent Zn, which melts at 130° C. Bismuth, cadmium, and zinc (127) form a eutectic at 59.8 per cent Bi:39.4 per cent Cd:6.8 per cent Zn, melting point 143° C. Bismuth, tin, and cadmium (228) form a eutectic at 39.3 per cent Bi:33.2 per cent Sn:27.5 per cent Cd, which melts at 103° C. In this case the relative proportions are given in atomic percentage; on the basis of per cent by weight the composition of this eutectic is 53.9 per cent Bi:25.8 per cent Sn:20.3 per cent Cd.

Investigations of the bismuth-copper-sulphur system (229, 230) show that copper has a greater affinity than bismuth for sulphur, which fact is utilized in the refining of bismuth. The bismuth-copper-nickel system is complicated (142). Small amounts of nickel intensify the bad effects of bismuth in copper, but the addition of 4 per cent Ni removes them through the formation of Ni-Bi compounds. Manganese should behave similarly to nickel. The bismuth-copper-magnesium system also is complicated (142); a dark-blue ternary compound of unknown composition is formed. Magnesium seems to act as a good scavenger for copper. The addition of calcium (142) to bismuth and copper forms a dark-gray constituent containing Ca and Bi. In air this constituent powders and falls out leaving pits. Calcium, therefore, is not a useful addition to correct for the presence of bismuth in copper.

Bismuth-copper-antimony (116, 232) and bismuth-lead-silver (233) alloys have been investigated, but are of no importance. The bismuth-copper-manganese alloy, which consists of 39 per cent Bi:43 per cent Cu:17 per cent Mn (231), is interesting as the ternary alloy is distinctly magnetic, although all of the individual components are diamagnetic. An alloy of 2 Bi:3 Cu:25 Sn:70 Sb has been patented (234) for addition as a hardening agent to metals, such as lead.

The accompanying tables show some of the low-melting and other possibly useful alloys of bismuth. Table 2 lists a number of readily fusible alloys arranged in order of their melting points, as compiled from the literature. It appears that only those mixtures which contain mercury will melt below 70° C. The lowest melting mixture of solid metals is the quaternary eutectic of Bi-Pb-Sn-Cd, which melts at 70° C. The melting points given in this and subsequent tables are taken from the literature and have not all been verified.

TABLE 2.—*Low-melting alloys*

Alloy	Bi	Pb	Sn	Cd	Hg	Melting point °C.	Melting point °F.
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	°C.	°F.
Fusible metal	20	20	-----	-----	60	(1)	
Do	53.5	17	19	-----	10.5	60	(140)
Woods metal	50	25	12.5	12.5	-----	70	(158)
Fusible metal	50	28.6	14.3	7.1	-----	70	(158)
Do	46.9	25	12.5	9.4	6.2	70	(158)
Eutectic	49.5	27.27	13.13	10.10	-----	70	(158)
Fusible teaspoons	44.5	30	16.5	-----	5–10	(2)	
Eutectic	51.65	40.2	-----	8.15	-----	91.5	(196)
Do	52.5	32	15.5	-----	-----	96	(204)
Rose metal	50	28	22	-----	-----	100	(212)
Eutectic	53.9	-----	25.8	20.3	-----	103	(217)
Do	58	42	-----	-----	-----	125	(257)
Do	56	-----	40	-----	Zinc 4.	130	(266)
Do	57	-----	43	-----	-----	135	(275)

[1] Liquid at ordinary room temperatures.

[2] Melt in hot water.

Table 3 illustrates a graduated series of alloys suitable for constant temperature baths, if each alloy were kept just at its melting point. Some of these alloys have been suggested as baths for tempering small steel tools.

A series of boiler plug alloys with graduated melting points is listed in Table 4. Table 5 illustrates alloys which may be used for delicate castings. The statement that "these alloys expand strongly" during solidification probably should be interpreted simply to mean that their casting properties are good, due to low surface tension or viscosity of the liquid metal. It is doubtful if any of them actually expand during solidification.

Table 6 illustrates the use of bismuth in type metals. Table 7 lists some amalgams for "silvering" glass. Solders containing 1 part Bi:3 Pb:2 Sn or 2.5 parts Bi:3 Pb:2 Sn have been recommended for sealing glassware.

TABLE 3.—*Melting-point series*

Melting point °C.	Melting point °F.	Parts by weight Bi	Parts by weight Pb	Parts by weight Sn	Parts by weight Cd
70	(158)	7	4	2	1
		5	4	2	2
75	(167)	8	8	3	10
77	(171)	8	6	1.5	1
82	(180)	7	4	4	1
95	(203)	2	-----	3	1
		5	-----	3	1
		3	-----	2	1
100	(212)	8	6	3	-----
108	(226)	8	8	3	-----
118	(244)	8	8	6	-----
122	(252)	8	8	8	-----
130	(266)	8	10	8	-----
132	(270)	8	12	8	-----
143	(289)	8	16	14	-----
151	(304)	8	16	16	-----
154	(309)	8	24	24	-----
160	(320)	8	26	24	-----
165	(329)	8	28	24	-----
171	(340)	8	30	24	-----
177	(351)	8	32	24	-----

TABLE 4.—*Boiler plug alloys*

Melting point	Parts by weight			Melting point	Parts by weight		
	Bi	Pb	Sn		Bi	Pb	Sn
°*C.* °*F.*				°*C.* °*F.*			
100 (212)	8	5	3	149 (301)	8	16	12
113 (236)	8	8	4	154 (309)	8	22	24
123 (254)	8	8	8	160 (320)	8	32	36
130 (266)	8	10	8	167 (332)	8	32	28
132 (270)	8	12	8	172 (342)	8	30	24
143 (290)	8	16	14				

TABLE 5.—*Alloys for delicate castings*

No.	Parts by weight		
	Bi	Sn	Pb
1	6	3	13
2	5	2	3
3	2	1	1
4	8	3	5

TABLE 6.—*Type metals*

Metal	Bi	Pb	Sb	Sn	Cu	Ni
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Type	22.23	50.0	27.77			
German type	29.58	65.1	5.82			
Krupp type	1.0	59.6	18.0	12.0	4.7	4.7
Stereotype	15.0	70.0	15.0			

TABLE 7.—*Amalgams for silvering glass*

No.	Parts, by weight			
	Bi	Pb	Sn	Hg
1	2	2	2	2
2	2	2	2	4
3	2	2	2	18

XI. OUTSTANDING PROPERTIES OF BISMUTH

A review of the literature of bismuth, aside from the pharmaceutical and medicinal literature, indicates that items of outstanding interest are as follows:

Atomic weight.— The atomic weight of bismuth (209) is the highest of any of the elements which are at all common.

Expansion.—Bismuth is one of the few metals which increase in volume during solidification. This expansion of bismuth amounts to 3.32 per cent of its solid volume at the melting point.

Thermal conductivity.—The thermal conductivity of bismuth, 0.018 calorie per second per cubic centimeter per° C. at 100° C., is less than that of any other metallic element except mercury. The thermal conductivity, already low, is further decreased by exposure to a magnetic field.

Electrical and magnetic properties.—Bismuth is the most diamagnetic of all metals. An alloy of copper, manganese, and bismuth is distinctly magnetic, although all the components are diamagnetic. Bismuth and antimony are the only metals whose electrical resistance is greater in the solid than in the liquid state. The electrical resistance of solid bismuth is increased by exposure to a magnetic field. Bismuth is one of the seven metals which are abnormal in that their electrical resistance increases with increasing pressure. The resistivity of bismuth is remarkably affected by the presence of small amounts of metallic impurities, as shown in Figure 1.

Thermoelectric properties.—Bismuth coupled with silver produces a thermoelectric effect of about 80 μv per ° C. This rises to about 120 μv per ° C. for bismuth against a bismuth-tin alloy containing 5 to 6 per cent tin, and even higher for other combinations, such as a bismuth-tin alloy against copper.

Casting properties.—Additions of bismuth lower the surface tension of metals such as lead and tin. Molten alloys which contain bismuth consequently flow freely in a mold and produce sharply defined castings.

Low-melting alloys.—Bismuth is notable for its ability to lower the melting points of many metallic alloys. Several alloys which contain bismuth melt at temperatures lower than that of boiling water. In contrast to these low melting points is the fact that some metallic compounds of bismuth, particularly with alkali metals and with cerium, have surprisingly high melting points.

XII. BIBLIOGRAPHY

The classification of the ensuing bibliography is not complete in all cases. Original articles frequently contain material of interest in more than one section of this paper. Such an article is classified according to the first reference made to it in the text and is not repeated in subsequent classifications. Additional references in some cases will be found in the "miscellaneous" section of the bibliography. For these reasons, a reader interested in the bibliography of any particular section of the paper should refer to the text as well as to this bibliography.

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