Metallurgy : a textbook for manufacturers, foremen and workers in the metal industries, with a special consideration of detnal metallurgy.

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Metallurgy

A Text-Book for Workers
in the Metal Industries

METALLURGY.

Charles R Tyson
West Town
Dewsbury 1912

METALLURGY:

A textbook for manufacturers, foremen, and workers in the metal industries, with a special consideration of Dental Metallurgy

BY

AD. FENCHEL, D.Sc.

Lecturer on Metallurgy on the Academic and Master Courses of the Trade Board of Hamburg

Translated by H. J. MORRIS, L.D.S.Eng.

Lecturer on Dental Mechanics, Sheffield University.

With 111 Illustrations.

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1911

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AUTHOR'S PREFACE.

SINCE Henry le Chatelier and Carl Barus enabled us to measure high temperatures, physical chemistry has succeeded in establishing the affinities of metals for each other.

The results of these investigations are stated in diagrams which give a full account of all the equilibria or phases existing between different metals.

Le Chatelier, Buckhuis-Roozeboom, Roberts Austen, Heycock and Neville, Wüst, Kurnakow, Martens, and especially Tamman and his pupils, must be mentioned for the work they have done in these investigations.

Photomicrography and the demonstration of the volumetric and electric properties of the alloys gave them a fair control of the results.

Textbooks on metallurgy, and especially on dental metallurgy, often give methods of refining metals and the formulæ of certain alloys, without considering their constitution.

This knowledge has, however, helped the modern metal industry to obtain wonderful results, which have made famous the names of Armstrong, Vickers, Krupp, and others.

The big industrial establishments which employed scientific metallurgists were able to use the fruits of scientific progress, but they kept secret the results gained in their own laboratories.

The present book undertakes to instruct the reader who is not able to understand the scientific literature on the subject without preliminary studies. It may be clearly pointed out that it is meant to be a text- and hand-book for practical men, manufacturers, and dentists, and to give them exact data about their working materials, and the results of modern metallurgical research.

The anatomy and physiology, if the expression may be allowed, of the metals and alloys and the reading of the diagrams are explained.

The reader will further be introduced to the controlling methods and the elements of chemical analysis and electrolysis, which are taught by minute description of the different processes.

In the text each diagram is clearly explained, in order to enable every reader to profit by its results, even without having entered fully into the theoretical detail. Those percentages of the alloys are pointed out there which show properties differing from the average of their components, especially the eutectics, the mixed crystals and the chemical compounds.

I further treat the phenomena of polymorphism, the temperatures at which they make their appearance, and the changes they cause. Special consideration has been given to the dental metallurgy, which deals with gold for plate and casting work, solders and amalgams.

This information will enable everyone who uses metals in his work to avail himself of the newest scientific knowledge of them, and also to undertake systematic research into the properties of alloys of definite percentages and the mixtures between them, and so replace rough and ready methods by accurate scientific data.

Though I have gained confidence through my experience as lecturer for the Hamburg Trade Board, I am fully aware of the difficulty of the undertaking, but I believe that this work is a necessity for all who are engaged in metallurgical processes, as no book of this kind has yet been published.

I shall always be glad to receive hints from readers as to possible improvements in the contents.

D. FENCHEL.

Hamburg, July, 1911.

TRANSLATOR'S PREFACE.

THE object of this translation is to bring before English students the results of the laborious compilation and research of the Author.

This research has been of two kinds, both equally important.

On the one hand, he has with his own hands advanced the frontiers of metallurgical knowledge, and on the other he has, with vast industry, searched out and put in order the records of other investigators in many lands and tongues, much of which has been "buried," so to say, in journals and transactions of societies which are only accessible to a very limited circle of readers. In the revision of the physical and electro-chemical part much valuable help was rendered by Mr. G. B. Brook, of the Applied Science Department of the Sheffield University. That it may prove helpful and stimulating to all workers in metals who read it is the earnest hope of the translator.

H. J. MORRIS,
Lecturer on Dental Mechanics,
Sheffield University.

Orchard Chambers,
27, *Church Street, Sheffield,*
July, 1911.

CONTENTS.

A. General.
B. Special.
C. Practical.

A. GENERAL.

GENERAL PART.

ERRATA.

Page 13.—In table, braced matter to the five lines of 800 Temperature degrees Centigrade *should read* (fig. 8 " C").

,, 17.—Line 7 from foot *should read*, 45 per cent. will crystallize in the eutectic at 400° C.

,, 30.—Line 11 from top, *for* 1·093 *read* 1·096.

,, 54.—Line 15 from foot *should read*, and it also renders it more liable to get rid of oxygen.

,, 59.—Line 10 from top, *for* " 107° C." *read* 1,070° C.

,, 61.—Line 2 from foot, *for* " Cu_2Cd_3" *read* Cd.

,, 74.—Third column of first table, under Phosphorus per cent., the figures *should read*, ·196, ·053; and line 7 from foot, *for* 0·52 B. *read* 0·52 Pb.

,, 76.—Line 10 from top, second column, *should read* 14 – 2·5 ,,

,, 78.—Line 7 from top, under S Per cent. *read* ·013.

,, 81.—Line 7 from foot, the Greek letter *should be* α; and line 2 from foot *for* " 567 per cent." *read* 567° C.

85.—Bottom line, *for* " 1,404° C." *read* 1,454° C.

,, 97.—Line 18 from foot *should read*—

$$AuCl_3 + 3FeSO_4 = Au + FeCl_3 + Fe_2(SO_4)_3.$$

,, 98.—Last line *should read* (quart).

,, 109.—Line 9 from top *should read*, (2) Au_2Pb.

,, 115.—Top line, *for* " 4·52 Zn" *read* 14·5 Zn.

,, 116.—Line 3 from top *should read*, and forms the crystal with Zn.

,, 119.—Line 3 from top, *for* "metallographs" *read* metallography.

,, 122.—In the table, column Variety. line 4 from foot, *for* "$(Fe_3C. + Fe_1)$" *read* $(Fe_3C. + Fe\ \alpha)$.

,, 127.—Line 18 from foot, *for* "with 5 per cent." *read* with ·5 per cent.; and line 2 from foot *read* (5) *Molybdenum*.

,, 131.—Line 9 from foot, *for* " They form a chemical" *read* They form no chemical.

,, 134.—Line 4 from top, *for* "560° C." *read* 566° C.

,, 138.—Line 10 from top, *for* "by weight of pure Al, which" *read* by weight Ni, which.

,, 143.—Line 10 from foot, *for* "CdSb2" *read* Cd_3Sb_2; and line 7 from foot *for* " 192° C." *read* 292° C.

ERRATA.

Page	Line	Present Reading	Corrected Reading
1	9	Monocline	Monoclinic
1	10	Tricline	Triclinic
32	25	three or more atoms	two or more atoms
41	11	element	elements
41	12	constituent	constituents
45	8	silver	silicon
98	21	(alum)	(alumina)
136	26	carbon dioxide	carbon monoxide
144	10	has one valence	has a valency of one
144	10	Mercuro	Mercurous
144	11	Mercuri	Mercuric
156	25	39°C.	—39°C.
162	26	arsenate	arsenide
164	30	grey protoxide	basic carbonate
167	33	H_2WO_4	WO_3
221	7	Sulphide	Sulphur
221	33	globula	globule
224	2	$Al_2\ Cl_3$	$Al\ Cl_3$
224	10	$Al(OH)_2$	Na_3AlO_3
224	26	bromide	bromine
224	32	sulphate	sulphide
225	8	soda (Na_2Cl_3)	soda (Na_2CO_3)
225	32	sulphate	sulphide
226	4	Pure mercury	Mercurous chloride
226	24	Sb_2S reappears	Sb_2S_5 reappears
227	1	sulphate	sulphide
227	26	sulphate	sulphide
230	22	colloidal	finely divided
231	20	$AgNH_4Cl$	$Ag(NH_3)Cl$
231	20	mercuric	mercurous
233	4	stannate of soda (Na_2Sn_3)	stannate of soda (Na_2SnO_3)
233	22	into a chlorate	into the lower chloride
235	5	litharge (PbO_2)	litharge (PbO)
242	foot-note	or FeCl	or $FeCl_3$
244	5	amount	rate of flow
245	34	precipitate	precipitation

METALLURGY.

I. PURE METALS.

THEIR INTERNAL STRUCTURE.

ALL metals consist of combinations of crystals, that is to say, of a number of crystals held together by that form of energy which is called cohesion. Six different systems of Crystals are recognizable :

The Regular.
The Tetragonal.
The Hexagonal.
The Rhombic.
The Monocline
The Tricline

The chief characteristic of these systems is the number of facets and angles at which the crystals meet one another.

The crystals are formed when the metals change from a state of complete molecular freedom (fluid) into the solid state. The cause is the lowering of the temperature, *i.e.*, the withdrawing of energy in the form of heat.

The molecules, free in the liquid metals, give off that energy in the form of heat to their surroundings, which formerly enabled them to move about one another in obedience to the law of gravity.

Some of this energy remains in the crystallized metal as cohesion. This unites the smallest crystallites into crystals and binds the crystals into a solid whole.

This growth is started by the formation of a large number of minute crystals, which are known as crystallites. These are exactly like the future crystals, only on a smaller scale. Upon the sides of these fresh layers of crystallites are deposited and they continue to grow by a process of "accrystallization" till at last they meet and form a solid mass. Symmetrical growth then comes to an end and subsequent deposits are confined to the filling up of the vacant spaces. This is how irregular crystals come to be formed, and it requires a thorough knowledge of crystallography and a goniometer to make out the system to which they really belong.

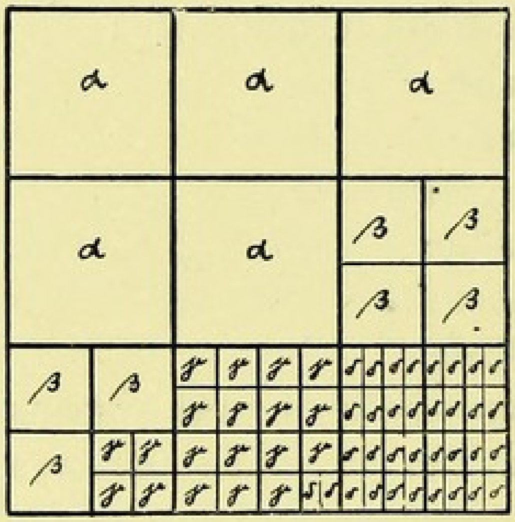


FIG. I.

Let us make a section through the axis of a cube of perfectly crystallized metal—a so-called Hexahedron.

Under proper treatment the surface will show under the microscope a net-like structure of crystals, symmetrically deposited as quadrates. These crystals are the smallest which the eye is able to distinguish as separate units, but knowing how each one has grown, we are able to reconstruct it as follows:—

Each crystal, a, is formed of a large number of crystallites, β ; and we can infer further, from views which are very generally held, that each crystallite, β, is formed of a number of molecules, γ; we must also regard each molecule as composed of at least two atoms.

The properties of hardness, toughness, ductility, etc., found in the finished metal, we must regard as due to the forms of the crystals and the strength of the cohesion which binds crystal to crystal, crystallite to crystallite and molecule to molecule.

The force which binds atom to atom is called chemical affinity. This determines the chemical properties.

II. ALLOYS OF TWO METALS.

(*a*) ABSOLUTE IMMISCIBILITY.

If two metals, which are perfectly immiscible, such as lead and ~~iron~~ aluminium, are melted together, they will separate like oil and water. The heavier will sink to the bottom, and the lighter remain on the top, and so they will crystallize.

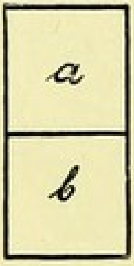


FIG. 2.

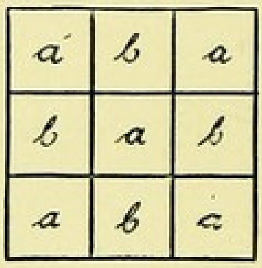


FIG. 3.

(*b*) MIXED CRYSTALS.

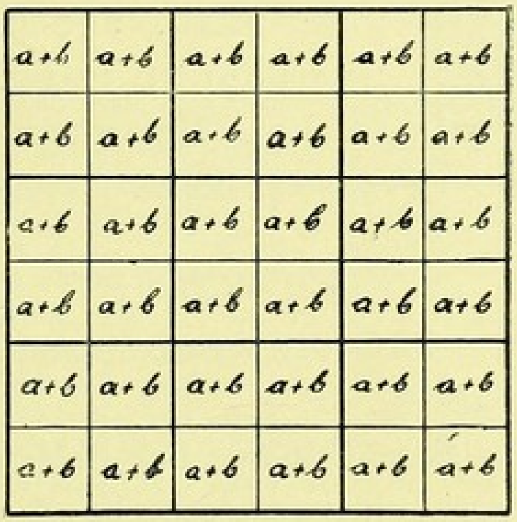
Under this heading we shall consider alloys of metals (*a* and *b*) of different melting points, possessing a physical affinity. In such alloys crystallization will start on cooling in that component which has the highest melting point (*a*), fig. 3.

This metal will start the first minute centres of crystallization.

If now this first crystallite "a" grows by accrystallization equally of crystallites "a" and "b" the completed crystal will be built up of crystallites of both metals deposited alternately (fig. 3).

This crystal is called a "mixed crystal," or "solid solution." It is called a "solution" because the original cohesion of the crystallites "a" to one another is "dissolved" by the interpenetration of the crystallites "b" and *vice versa*.

The force which binds different metals together is called "adhesion." Adhesion destroys the cohesion of the metals concerned, and therefore must be a stronger force. The adhesion between two metals is often confined to a certain range of temperature. Again, the solution of a metal "a" by adhesion to another metal "b" may change the melting point of both.



a+b	a+b	a+b	a+b	a+b	a+b
a+b	a+b	a+b	a+b	a+b	a+b
a+b	a+b	a+b	a+b	a+b	a+b
a+b	a+b	a+b	a+b	a+b	a+b
a+b	a+b	a+b	a+b	a+b	a+b
a+b	a+b	a+b	a+b	a+b	a+b

FIG. 4.

Adhesion between two metals may bring about molecular union (fig. 4). In this case the crystallite first built is formed of molecules "a" and "b."

A mixed crystal under the microscope is as homogeneous as the crystal of a pure metal, and they cannot be distinguished microscopically from one another, especially if they are in a state of molecular union.

(*c*) CHEMICAL COMPOUNDS.

A still more intimate union may take place between two metals. This postulates the existence of units still smaller than molecules.

It was shown that a crystallite was built up of molecules, and a molecule must be regarded as composed of two or more atoms.

A chemical combination then breaks up the molecules and frees the atoms. These units again form new molecules consisting of atoms of both metals.

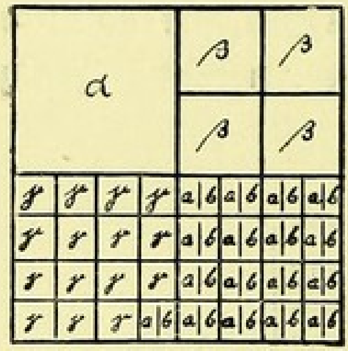


FIG. 5.

The new molecules are a true chemical compound (fig. 5.) It follows that the molecule or crystallite of a true compound of two metals may behave exactly like a unit of a pure metal, and take part in the formation of mixed crystals or eutectics. The meaning of the latter word calls for some explanation.

EUTECTICS.

The sense in which the word "solution" is used has been explained above.

Now, if two different metals are brought into contact, the adhesion between two crystals of different bodies (the expression "body" may signify a pure metal, mixed crystal or chemical compound) is stronger than the cohesion between the crystals of the individual metals.

This condition, however, most frequently occurs in the liquid state only, and then a separation takes place on cooling and crystallizing.

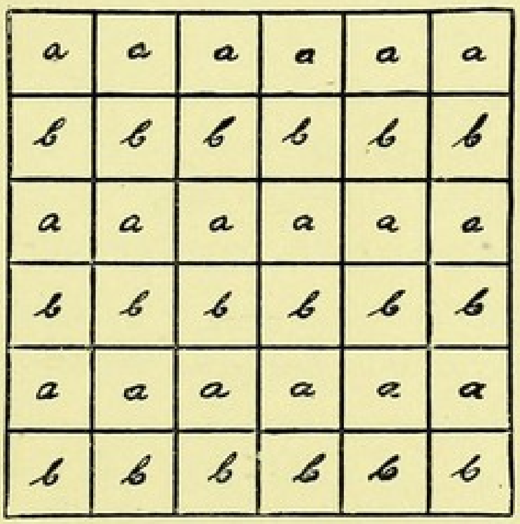
The solution, or break-up of cohesion by adhesion, augments considerably the latent energy of the mixture called a eutectic.

The result of this is that a eutectic possesses so much latent energy that it requires much less added energy (*i.e.*, heat) to free its molecules and make them flow (*i.e.*, melt).

In other words, a eutectic will melt at a lower temperature than either of the metals composing it.

The melting of a metal means the solution of its structural continuity, and a eutectic represents extreme mutual depression of the melting point of two metals melted together.

Microscopically the result shows as alternating layers of crystals "a" and "b," and the slide appears after etching as regular strips, or points of light and dark colour, representing the two metals of which the eutectic is composed. Hence the name eutectic, meaning "well built." Compare fig. 11d.



a	a	a	a	a	a
b	b	b	b	b	b
a	a	a	a	a	a
b	b	b	b	b	b
a	a	a	a	a	a
b	b	b	b	b	b

FIG. 6.

Thermic analysis exposes the properties of eutectics still more fully.

CONCLUSIONS.

Metallic compounds may consist of :—

(1) Similar crystals of one metal.
(2) Mixed crystals of different metals.
(3) Chemical compounds of different metals.
(4) Eutectics of different metals.
(5) Mixtures of 1—4.

If we know the properties of the first four we can infer those of any alloy of two metals.

We have also seen that a microscopical examination will not enable us to distinguish an alloy with certainty; and because pure metals, mixed crystals, and chemical compounds are all homogeneous, they cannot be distinguished either.

We must, therefore, resort to other methods to fill up the gaps left by microscopic examination.

III. THERMIC ANALYSIS OF METALS.

In the preceding paragraphs it has been shown that the crystals of metallic compounds tend to separate when they receive the energy necessary for isolated existence.

Under the influence of a moderate rise in temperature, crystal becomes movable against crystal, and we say that the metal becomes malleable or soft.

The addition of more heat enables the crystallites, and the "molecules" which form them, to become movable, and we say that the metal becomes liquid.

As stated above, a liquid is that condition of a substance in which the smallest parts—the molecules—can move freely amongst one another, according to the law of gravity. A cup filled with fine sand is a good example of this. The grains of sand are comparable to molecules, and you can pour it just as a liquid is poured.

The energy in the form of heat, which a liquid contains, must be given up when it crystallizes on cooling, and as soon as the molecules are reunited to a solid mass they no longer need that energy for an independent existence.

(*a*) CRYSTALLIZATION IN A PURE MEDIUM.

If we take from a known volume of water the same quantity of heat every 10 seconds, that is to say, if we cool it gradually by equal amounts, its temperature will fall every 10 seconds through the same number of degrees.

Therefore, if the temperature is lowered 10° C. every 10 seconds, water, which was originally at 60° C., will be cooled to 0° C. in 60 seconds.

But if the same process is continued further, the temperature will not continue to fall, but will remain at 0° C. for some time, viz., 20 seconds.

During these 20 seconds all the water has become crystallized, that is, it has turned to ice, and at the same time the latent energy, which had made the fluid condition possible before, has been dissipated as heat. It was this latent heat which kept the ice for 20 seconds at 0° C., in spite of continued removal of heat by external agencies.

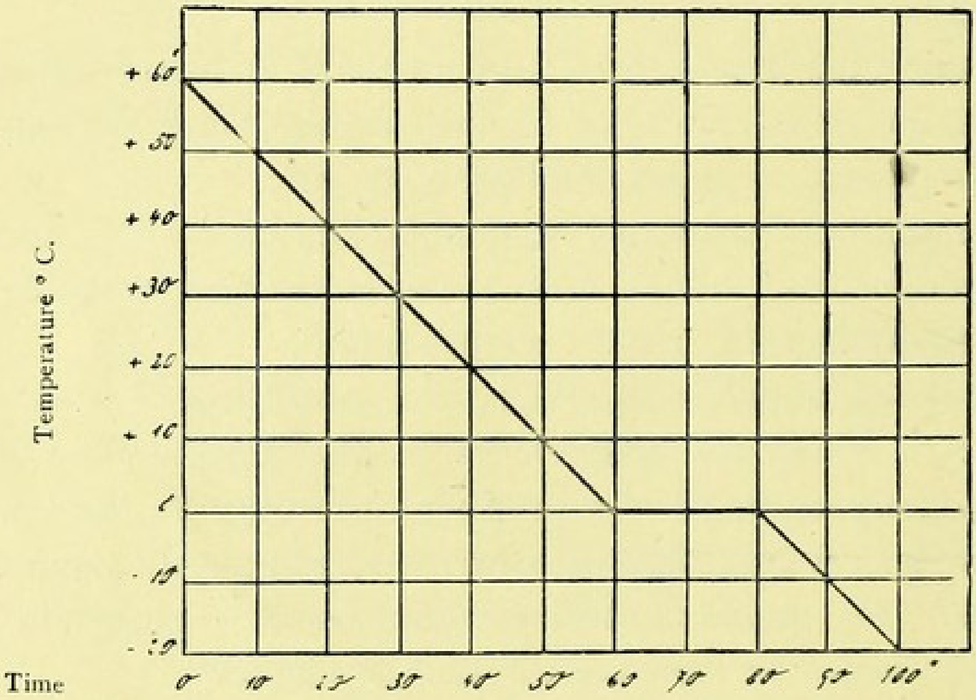


Fig. 7.—Freezing diagram of water.

After all the water has been crystallized the temperature of the ice will fall again at equal rates. The horizontal line in the diagram at 0° C. shows where the process of crystallization takes place (fig. 7).

(*b*) CRYSTALLIZATION IN AN ALLOY OF TWO METALS.

The cooling curve of an alloy of two metals varies according to their chemical or physical relationship.

ABSOLUTE IMMISCIBILITY.

Supposing two totally immiscible metals "A" and "B" are melted together, say 90 per cent. "A" with a melting point at 800° C., and 10 per cent. "B," which melts at 400° C. Suppose also that they both have the same specific heat, that is to say, that equal quantities of them require an equal amount of heat to melt them. This heat is given off on crystallizing.

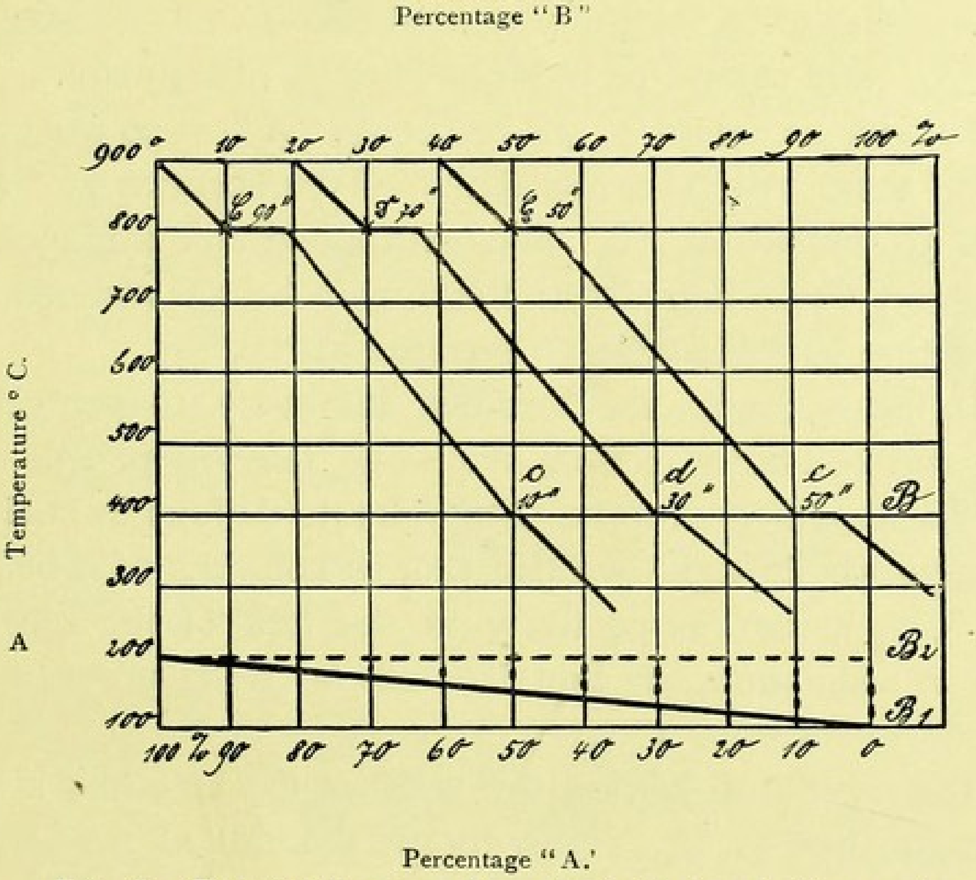


FIG. 8.—Freezing diagram of two absolutely immiscible metals.

They are heated to 900° C., and at that temperature both are fluid.

Now cool them down at regular rates.

At 800° C., the melting point of "A," the steady fall of temperature will halt awhile till all of "A" has crystallized out (fig. 8 "C"), then the temperature will again fall regularly to 400° C. (the melting point of "B") and stay there till that also has crystallized (fig. 8 "c").

If the total amount of retardation came to $C + c = 100$ seconds, or the width of one square in the diagram, we shall find that, as there is 90 per cent. of "A" in the mixture, there will be a retardation of fall on cooling amounting to $\frac{9}{10}$ of the square at 800° C. or 90 seconds at "C," and at "c" of 10 seconds or $\frac{1}{10}$ of a square.

So with a content of 70 per cent., "A" + 30 per cent. "B," there will be a retardation of 70 seconds at "D" and 30 seconds at "d," and with equal amounts (50 per cent. of each ingredient) there will be 50 seconds retardation at "E" and 50 seconds at "e."

If these figures are assumed for every 10 per cent., we can construct a table similar to that on p. 13.

These numbers representing the retardations in cooling (90, 70, 50 seconds) we can plot as columns of a height of 9, 7, 5 mm. respectively at the foot of the scheme of co-ordination, so that the side of a square can be made to measure 1 cm.

The result of joining the ends of the columns is the straight line $A_1 B_1$. Now draw the dotted line $A_1 B_2$ (fig. 8.)

Below the line $A_1 B_1$ we can now read off without any further trouble the percentage content of "A" in a crystallized mixture, and above the line the content of "B." These conclusions are obtained solely from the retardation (*i.e.*, crystallization) times of the metals.

If this diagram is extended to 100 per cent. of "A," and every temperature marked with a circle which shows the first primary crystallization at 800° C., as well as the second crystallization at 400° C., the diagram will appear like fig. 9.

By connecting the points A C D E F G, and the points H, c, d, e, f, B, two parallel lines are made, the first in the abscissa of 800° C., the melting point of A, and the second in 400° C., the melting point of B.

TABLE.[1]

Time in seconds	Temperature degrees Centigrade	
0	900	
10	890	
20	880	
30	870	
40	860	
50	850	
60	840	
70	830	
80	820	
90	810	
100	800	
110	800	
120	800	9·10 seconds cooling retardation in primary crystallisation (fig. 8 "~~b~~") C
130	800	
140 – 190 = 5 ×	800	
200	790	
210	780	
220	770	
230	760	
240	750	
250	740	
260, &c., to	730	
510	420	
520	410	
530	400	1·10 seconds cooling retardation in secondary crystallisation (fig. 8 " c ")
540	400	
550	390	
560, &c., to	380	

---

[1] This table is diagrammatic. As a matter of fact the difference of temperature between melted metals and the surrounding air grows less as cooliug proceeds, and so the rate of cooling is reduced. After the primary crystallisation there is also a change in the specific heat, which causes different retardation in cooling. Consequently a true diagram will not show straight cooling lines, but curves.

At the foot of the diagram we find the facts mentioned above illustrated by the course of the line representing the time of crystallization. This changes according to the percentage of the metals present.

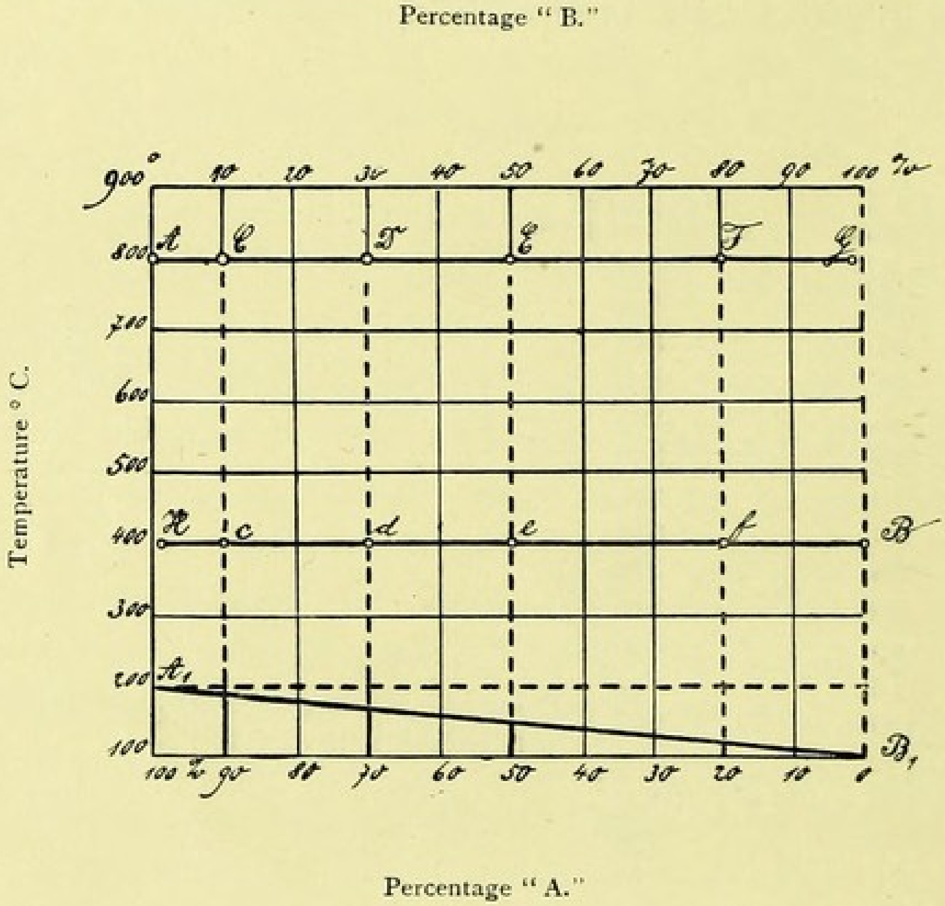


FIG. 9.

In case of absolute immiscibility of both metals in the liquid or solid state, the height of the columns representing the duration of the crystallization of both metals is exactly proportionate to their percentages.

The rationale of this will become clear by what follows.

MISCIBILITY IN THE LIQUID STATE,

Immiscibility in the Crystalline Condition.

If two metals are miscible in the liquid state, that is to say, if they dissolve each other, and immiscible when crystallized (solid), the melting point of either will be lowered by the addition of some of the other metals (fig. 10).

If we add to "A" (melting point 800° C.) 10 per cent. of "B" (melting point 500° C.), the melting point of "A" will be lowered for instance to 700° C. (fig. 10 C).

By adding 20 per cent. it will sink to 600° C. (fig. 10 D).
,, 30 ,, ,, ,, 500° C. (,, F).
,, 40 ,, ,, ,, 400° C. (,, E).

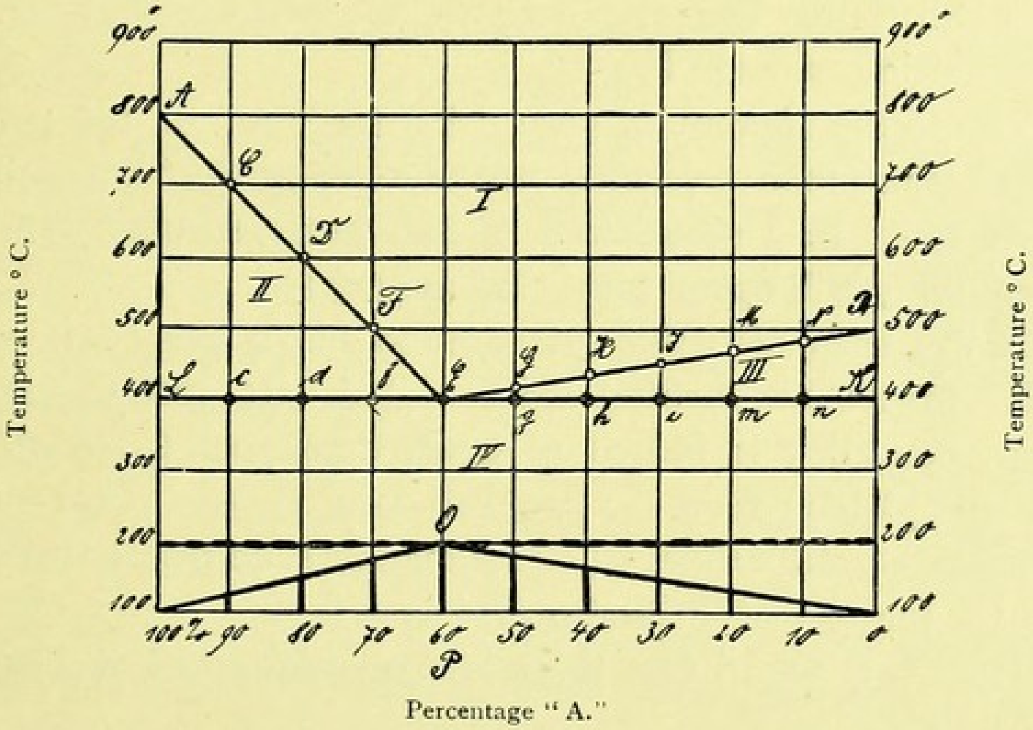


FIG. 10.

If, however, we add "A" to "B" we get a very different diagram. The addition of 10 per cent. of "A" to "B" brings down the melting point from 500° C. to 483·33° C. (fig. 10 N).

By adding 20 per cent. A to B it will sink to 466·66° C. (fig. 10 M.)
,, 30 ,, ,, ,, ,, 450·00° C. (,, T).
,, 40 ,, ,, ,, ,, 433·33° C. (,, H).
,, 50 ,, ,, ,, ,, 416·66° C. (,, G).
,, 60 ,, ,, ,, ,, 400·00° C. (,, E).

Thus we see that with an alloy of 60 per cent. "A" plus 40 per cent. "B," the lowest melting point has been reached, and that the addition of more of "A" to "B" or "B" to "A" will raise the melting point of both.

EUTECTIC.

This lowest melting point of different concentrations of alloys is called their "eutectic." There is also another peculiarity about a eutectic mixture which requires explanation besides the melting point. We will suppose, as before, two metals, "A" and "B," of equal specific heat, liberating the full amount of latent energy on crystallizing at 800° C.

The whole amount of pure "A" (or "A" of 100 per cent.) must then crystallize out at once at 800° C., and there must be a retardation of 100 heat seconds. The same thing will occur with "B" at 500° C.

It has been seen that an addition of 10 per cent. of "B" lowers the melting point of "A" to 700° C. If, now, this alloy is heated to more than 700° C. it will be completely fluid, so we call 700° C. the point of primary crystallization. (These numbers are merely used for the purpose of illustration).

Here it is found that there is a retardation of 75 heat seconds.

But the amount of latent heat represents 100 heat seconds, so that ·25 are not accounted for. Investigation shows that as a matter of fact all the alloy has not been crystallized, but only three-quarters of it, and as the temperature is lowered more there will be a further retardation equal to 25 heat seconds at the point "c."

These twenty-five seconds of the second or rather secondary crystallization are arranged as a column of 2·5 mm. at the foot of the diagram. By these means we can see that at "C" or 700° C., 75 per cent. of what has crystallized is the pure metal, A.

At "C," however, 25 per cent. of a compound has crystallized, whose melting point corresponds with what was found to be the eutectic, E = 400° C.

Now the total quantity of "A" originally amounted to 90 per cent. of the mixture and 75 of these have been crystallized at "C," therefore the remainder of the 25 per cent. crystallizing at "C" must consist of the 15 per cent. of A left plus the whole (= 10 per cent. of the total mixture) of "B."

From this we conclude again that the eutectic consist of 60 per cent. A + 40 per cent. B.

If 20 per cent. of "B" is added to "A" it will cause the melting point of "A" to fall to 600° C.

The alloy composed of 80 "A" + 20 "B," which is quite fluid at a temperature over 600° C., if crystallized at this point, will cause the "A crystals" also to form at this temperature.

The retardation of cooling will amount to fifty seconds, (fig. 10 D) and at 400° C. the remaining fifty heat-seconds will be liberated (fig. 10 d).

Thus the analysis shows 50 per cent. pure A plus 50 per cent. of the eutectic E, which latter consists of the remaining 30 A + 20 B, or 60 per cent. A + 40 per cent. B.

If 30 per cent. of B is added to A (fig. 10 F) there will only be 25 per cent. of "A" separating at 500° C., but 45 per cent. ~~of the eutectic~~ will crystallize in the eutectic at 400° C. (fig. 10 f) and this will be found to consist of 30 per cent. B plus the remaining 45 per cent. of A.

By further raising the proportions to 60 per cent. A + 40 per cent. B there will be found to be only one crystallization, namely, that at 400° C. (fig. 10 E) which is shown by the 100 seconds retardation of cooling at that point.

The line O P. at the foot of the diagram reaches its greatest height (10 mm.) here.

A similar thing occurs on the line E B.

This differs from the other side merely in so far as the melting point of B is lowered (altogether by 100° C. only) on adding 60 per cent of A.

In this case the melting point of B or the primary liberation of latent heat, which is indicated by a circle, only falls 16·60° C. for every addition of 10 per cent., while the crystallizing temperature of the eutectic remains always at 400° C. (fig. 10, g, h, i, m, n).

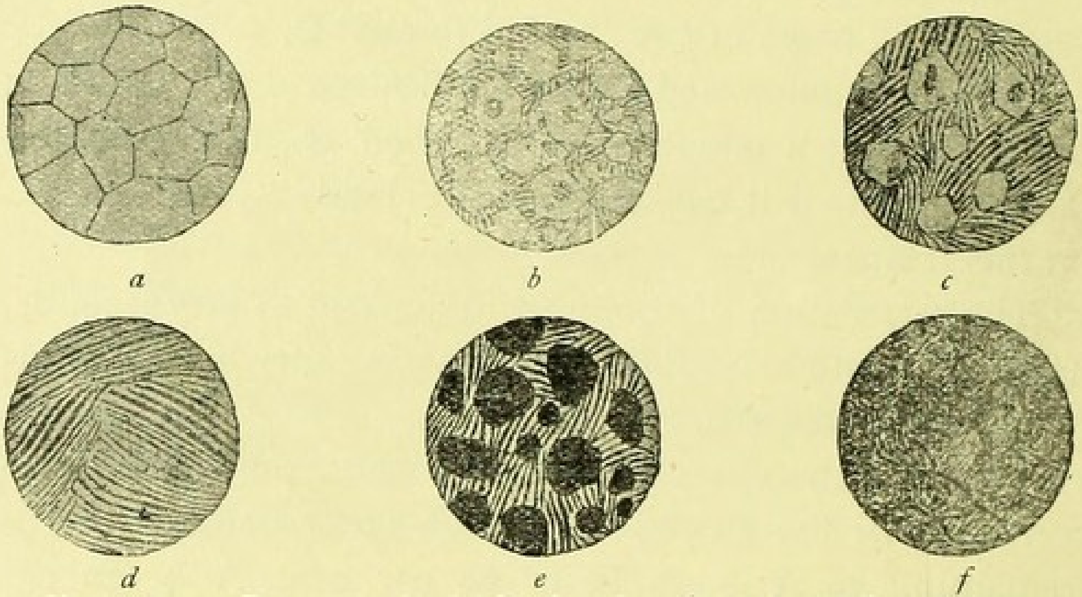


FIG. 11.—*a*, Pure crystals "A"; *b* and *c*, Crystals "A" and Eutectic "E"; *d*, Pure Eutectic "E"; *e*, Crystals "B" and Eutectic "E"; *f*. Pure crystals "B."

A eutectic, therefore, may be described as that alloy of several metallic bodies which always has the same composition, and always the same, viz., the lowest, melting point of all, and a lower one than any constituent.

If now all the points of the primary crystallization are connected by the lines A E and B E and all the points of the eutectic crystallizations by the line L E K we shall have four different conditions shown diagrammatically.

(I) All alloys are liquid.

(II) All alloys contain pure crystals of A and liquid eutectic.

(III) All alloys contain pure crystals of B and liquid eutectic.

(IV) All alloys are completely crystallized.

The eutectic content of a fully crystallized alloy of any composition can be read off at the height of a millimetre from the joined ends of the lines at the foot of the diagram, each square having sides of 1 cm.

Under these circumstances the micrographs of binary alloys of different compositions will show primary crystallization of A and eutectic (fig. 11, *b*, *c*) in the percentages on the left of the eutectic point, and on the right the primary formation of B and eutectic (fig. 11, *e*).

CHEMICAL COMPOUNDS.

The structure of chemical compounds and their appearance under the microscope have been already described.

When a metal or a metallic compound is melted, a sort of molecular division takes place until the molecules are quite free and movable.

In consequence of this a chemical compound, which is atomic in its nature, remains fixed and is not modified unless it is exposed to a stronger chemical affinity, and the molecules of a real compound will behave in the same way towards a pure metal as any other pure metal would.

Let us suppose that there is between A and B a compound AmBn (fig. 12, C). We shall get the same diagram of meltings between this compound and its components A and B as we should with the pure metals. Such a diagram really consists of two diagrams of metals, which do not combine chemically.

Fig. 12 illustrates these points.

(1) On the line A E_1 C.

A = the pure metal A.
C = the chemical compound AmBn, consisting of 65 per cent. A plus 35 per cent. B.
E_1 = the eutectic of both.

(2) On the line B E_2 C.

B = the pure metal B.
C = the chemical compound AmBn.
E_2 = the eutectic between B and C.

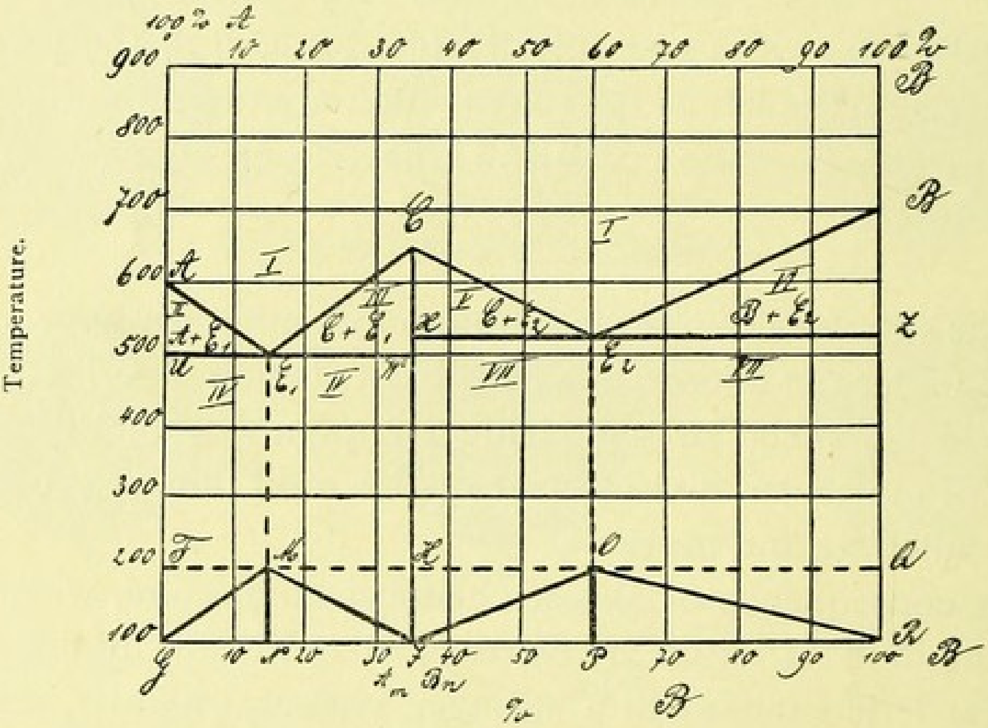


FIG. 12.—Crystallization of two metals with one chemical compound. *A*, Pure metal "A"; *B*, Pure metal "B"; *C*, Chemical compound AmBn; *E_1*, Eutectic A+C; *E_2*, Eutectic C, +B.

The explanation given of the phases shown in Fig. 10 is very applicable to this diagram.

(I) All is fluid above the lines A E_1 C E_2 B.

(II) On the line A E_1 there appears a primary separation of pure A, so that phase II consists of crystals of A + liquid eutectic E_1.

(III) On the line E_1 C there appears a primary crystallization of the chemical compound "C," so that phase III consists of crystals "C" + liquid eutectic E_1.

Below the line U W all is crystallized.

(IV) The remaining liquid eutectic separates out in all cases on the line U W = 500 C.

Phase IV, fig. 12, consists of crystallized + A or C eutectic or pure eutectic.

(V) On the line C E_2 there appears a primary separation of the compound "C."

Phase V contains crystals of the compound C + liquid eutectic E_2.

At all points on the line H E_2 (530° C.) the remainder of the eutectic, which was fluid, now crystallizes out, so we see that the eutectic between C + B always crystallizes completely at E_2 (530° C.). Below H E_2 in this region crystallized C + E_2 is demonstrated.

All the points of line E_2 B indicate a primary crystallization of pure B, consequently in phase VI the "B" crystals are mixed up with liquid eutectic, which crystallizes secondarily at the eutectic temperature (530° C.) indicated by the line E_2 Z.

In phase VII the compound is crystallized again throughout (C + E_2, or B + E_2).

By observing these points of crystallization or retardations on cooling we can make the following deductions (fig. 12).

(1) At F G there is no eutectic and the metal A is 100 per cent. or pure.

(2) At M N the eutectic "E_1" amounts to 100 per cent. and consists of 85 per cent. A + 15 per cent. B.

(3) At H J there is no eutectic, but 100 per cent. of a chemical compound Am Bn (= 65 per cent. A + 35 per cent. B).

(4) At O P the eutectic E_2 amounts to 100 per cent., and consists of (40 per cent. A + 60 per cent. B).

(5) At Q R there is no eutectic, but pure B (100 per cent.), fig. 12. Moreover, exact composition of the eutectics containing A, B and the compound C can be estimated by transferring the proportions of the lines G I : G N, and R I : R P from 35 : 15, and 65 : 40 (their percentage contents) upon 100 : X.

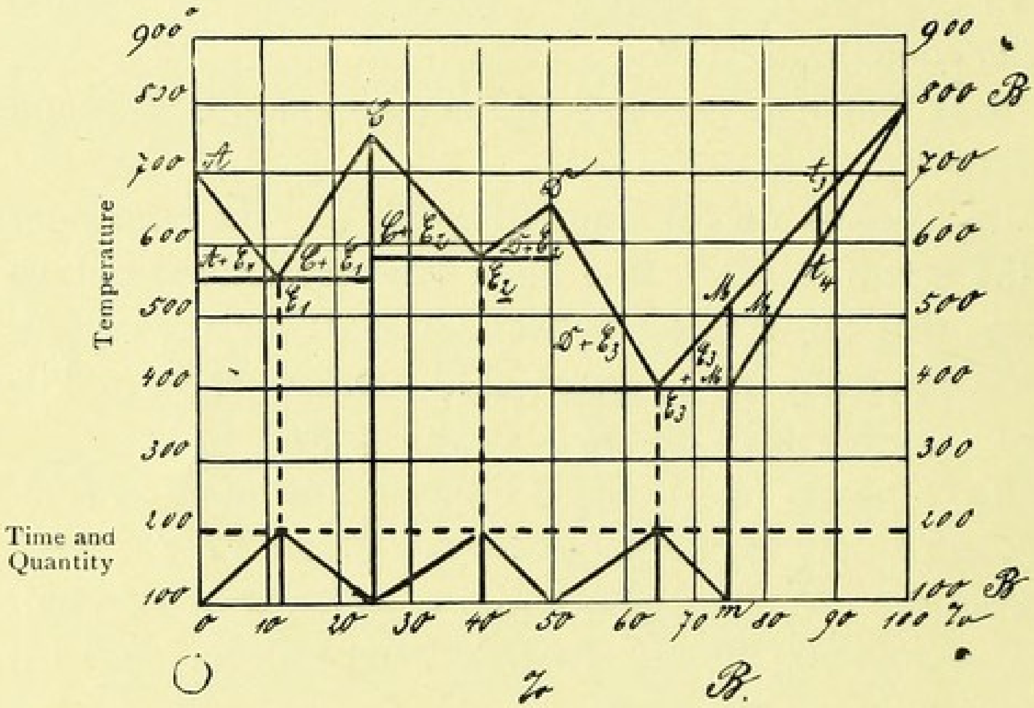


FIG. 13.—Two metals with 2 chemical compounds, 1 series of mixed crystals m—B, and 3 eutectics.

Eutectic E_1 for instance is composed of 15 A + 85 B. We find its content of A and the compound "C" in the following way :—

$$A = \frac{100\ GN}{GI} = \frac{100 \cdot 15}{35} = 42 \cdot 86 \text{ per cent. A.}$$

Accordingly, C = 57·14 per cent.

$$\text{Eutectic } E_2 = \frac{100\ IP}{IR} = \frac{100 \cdot 25}{65} = 38 \cdot 46 \text{ per cent. C} + 61 \cdot 54 \text{ per cent. B.}$$

The length in millimetres of the lines at the foot of the diagram shows this graphically. Thus, if the side of the square measures 1 cm. we can read off at once the contents of the eutectic and see the amount of the primary crystallizations of A, B and C.

The chemical compound "C" has 65 per cent., A + 35 per cent. B (fig. 12).

There may be several different combining proportions chemically, between two metals, in which case the diagram must be divided into more than two parts, and each one analyzed in the way described above (fig. 13).

MIXED CRYSTALS.

Miscibility in the fluid as well as the solid state. (*Compare also page* 237 *electrolysis.*)

Diagram 13, in addition to the two chemical compounds "C" and "D," shows mixed crystals which are in the percentage relationship of m—B (75 to 100 per cent.).

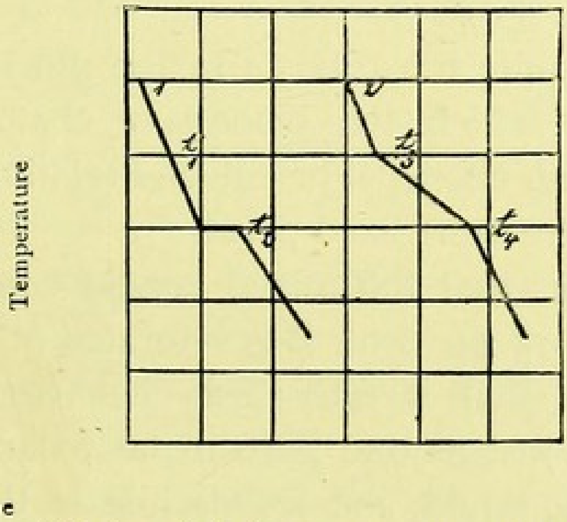


FIG. 14.—Crystallization : (1) of a pure metal ; (2) of a mixed crystal.

The formation of these is indicated by a slower liberation of heat during crystallization and the absence of a eutectic formation on the cooling curve.

In diagram 14, line 1 shows a single crystallization at t_2. Line 2 shows the gradual formation of mixed crystals from t_3 to t_4.

This delayed evolution of heat is explained by the diminishing tendency to crystallize.

There are, however, a great many mixed crystals, which will only develop if the metals are kept for some hours at the crystallizing temperature, and there are other cases in which this fact may be attributed to an alternating crystallization and resolution followed by a secondary formation of the mixed crystals.

For instance, crystallites of B which were formed first were re-dissolved by the accrystallized crystallites of the compound D, and then the molecules unite again to become the crystallites of the mixed crystals.

The line t_3 to t_4 shows that there is an absorption of heat or a reduction of temperature, when the solution takes place, and that there is a formation of mixed crystals going on during the whole temperature interval by the line t_3 to t_4.

This is not quite the same as in the illustrations given previously, in which the secondary crystallizations of alloys having no chemical or eutectic relationship, always took place at the same fixed point.

Fig. 13 shows that the mixed crystal composed of 25 per cent. A + 75 per cent. B is saturated at "m."

This means that it afterwards behaves towards the compound D just as one pure metal to another, and is miscible in the liquid, and immiscible in the crystallized state.

So we get the eutetic E_3 and all the other phases formed between " M " and " D."

POLYMORPHISM.

In many alloys certain combinations, mixed crystals or eutectics, crystallize out at certain temperature.

These always show a fixed melting point and fixed percentage relationships, and have their peculiar microscopical properties.

If, however, the cooling is done very slowly, quite other qualities will appear at another and lower temperature. The internal structure and crystallization may be quite different, and as a result of this the density or hardness may be altered, and also the magnetic and other properties changed.

Note the effects on Gold Coloring

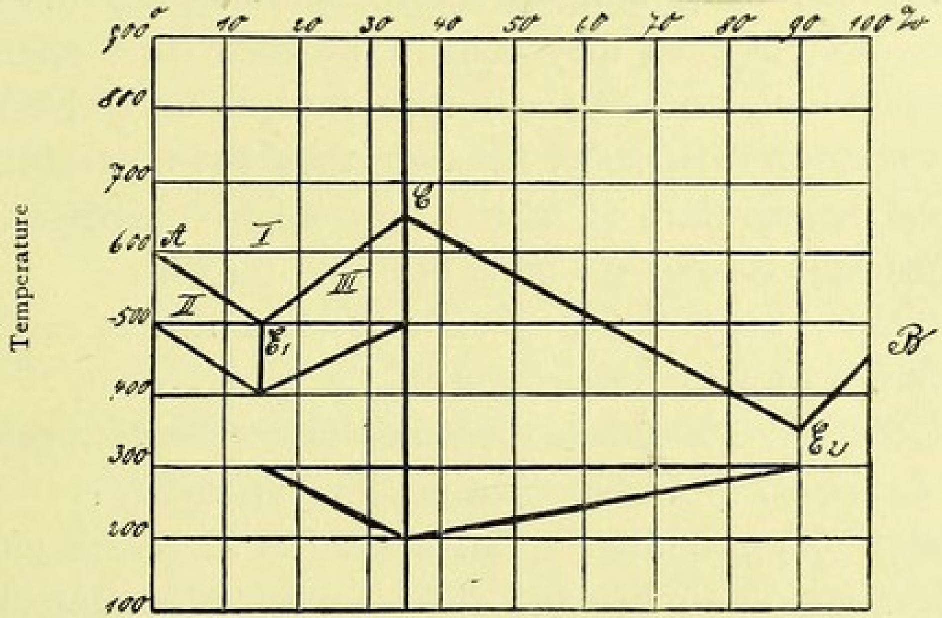


FIG. 15.—Diagram of Polymorphism of compound "C."

There will be a liberation of heat again at this second or re-crystallization, and by drawing the line of the retardation of cooling below the proper curve on the diagram, we shall get two lines showing the liberation of the heat of crystallization. The greatest elevation of this is shown again by a line 10 mm. in length.

In fig. 15 we see between A and B at 35 per cent. the compound "C."

E_1 is the eutectic between C and A. It has 85 per cent. of A, and is entirely crystallized at 500° C.

If the alloy is cooled slowly a different formation (polymorphism) is exhibited at 300° C, which is clearly shown by a microscopic examination. The usual thermic phenomena also takes place at their respective temperatures. For instance, the compound C can be re-dissolved into A and B.

To prevent this polymorphism or re-crystallization the mass must be cooled suddenly as soon as it is hard either at or above the temperature at which these polymorphic changes may occur.

This sudden cooling gives the crystals no time to re-dissolve, and so they remain in their first state of crystallization, and have all the physical and chemical properties of that state, because they have passed the critical temperature at which they might change. The iron-carbon alloys are a good example for this.

At about 1100° C the mixed crystal known as martensite (steel) forms.

At 690° C. martensite becomes ferrite and cementite and the eutectic of these two is called pearlite.

Below 600° C. there is an alteration in the magnetic properties and in between there are quite a number of other changes.

If properties are wanted which are peculiar to the crystals, formed at certain temperatures, then the alloy must be cooled suddenly, either at or above these temperatures and then the crystals will have no time to re-dissolve and re-form.

This is how the various temperings of steel are obtained.

These facts are shown, as was explained above, by drawing or connecting up in the diagram a second line of points representing cooling temperatures. See fig. 15 and also the Silver Tin and Iron-Carbon series.

ISOMORPHISM.

Under the microscope it is often found that different proportions in alloys show the same appearances.

For example, silver alloys containing from 73-100 per cent. silver all look alike, and this caused Behrens to suppose that they represented a regular series of chemical compounds.

As a matter of fact, there is only one chemical compound Ag_3Sn. But there are mixed crystals with pure silver, which are indistinguishable from each other and from pure silver when put under the microscope.

This is called Isomorphism, and it is one more proof that the result of researches by one method need checking by another.

HIDDEN MAXIMA.

The formation of a chemical compound is not always shown by a maximum temperature of crystallization, as would appear from diagrams already given.

In actual working the rising of a temperature, during the crystallization of a compound, is often obscured by the slowness of the crystal formation and other influences.

Only a skilled metallographist can detect it at first sight by the form of a curve or its tangents and by the microscope.

In consequence of this, short notes have been added to the diagrams to direct special attention to such occurrences.

IV. THE PHYSICAL PROPERTIES OF METALS.

It has been shown in the earlier chapters that the structure of metals is altered by the temperature to which they are subjected.

Similarly the other physical characters of single metals are influenced by heating them to different temperatures. Mechanical treatment also may change their properties in many ways.

We shall now deal briefly with the different physical properties of metals. A Table after Wüst will be found on pp. 36 and 37, containing the physical constants of the thirty-three elements which are considered in this volume.

(*a*) THE FREEZING POINT.

The determination of the freezing point has already been dealt with fully in Chapter III., p. 9. It was there shown that on cooling a liquid, at a certain point, the thermometer remains stationary, and the effect of the external cooling is neutralized by the heat given out by the solidification of the liquid substance. No lowering of temperature occurs until the change from the liquid to the solid state is completely effected.

(*b*) SPECIFIC HEAT.

The amount of heat necessary to raise 1 gramme of water through 1° C. is taken as the unit of heat, and is called a calorie. Thus 1 calorie is required to raise

1 gramme of water 1° C. The number of calories necessary to increase the temperature of 1 gramme of any metal by 1° C. varies widely with the metal, and is called the specific heat of that metal.

Thus, to raise 1 gramme of mercury through 1° C., 0·033 calorie is required. The specific heat of mercury is, therefore, said to be 0·033, compared with water as unity.

The specific heat increases with rise of temperature, and attains a maximum just before the melting point of the metal is reached.

It is therefore necessary, in calculating the specific heat of any metal, to know the value of:

(1) Specific heat at room temperature = S.
(2) Specific heat just before melting = S_1.
(3) Specific heat melting point = T.
(4) Room temperature = t.

Then from the equation the specific heat is found.

$$W \text{ (specific heat)} = (T - t)\,\frac{S + S_1}{2}$$

A metal can be poured when the temperature is increased beyond the melting point to a point known as Phase I., at which the material is entirely liquefied (*cf.* fig. 10).

(*c*) THE MELTING POINT.

We have seen that when a metal changes from the liquid to the solid state, heat is evolved. The quantity of heat so given out is definite for a definite weight of the particular metal.

When, however, the reverse process is carried out, that is, in changing from a solid to a liquid, an exactly similar amount of heat is absorbed by the metal in the process of becoming liquid. Thus we find that the temperature of the material, which up to this point has increased uniformly, is arrested, and remains constant until the whole of the material is melted.

This temperature is called the melting point.

(*d*) HEAT CONDUCTIVITY.

The absolute heat conductivity is that amount of heat (expressed in calories) absorbed by a cube of the metal of 1 c.c. volume in 1 second.

A reference to the table on p. 37 shows that the specific heat conductivity of silver is such that the amount of heat imparted to a cubic cm. in 1 second would raise 1 c.cm. of water through 1·1° C. (actually ~~1·093~~). (1·096) -

(*e*) SPECIFIC GRAVITY AND SPECIFIC VOLUME.

The specific gravity of a metal is the weight of a cubic centimetre expressed in grammes.

The specific gravity of metals is usually, for the sake of convenience, compared with the specific gravity of water, which is taken as 1·0000 at 4° C.

The determination is based on the fact that "when a solid body is weighed whilst fully immersed in water, it loses weight equal to the weight of an equal volume of water."

The procedure is as follows :—

(1) The metal is first weighed carefully in air and transferred to a specific gravity bottle. The weight of the dry bottle and when full of water at 4° C. must have been previously ascertained.

(2) The remaining space in the bottle is now filled with water, and the temperature brought to 4° C. The stopper is inserted, the bottle carefully dried and weighed. The weight obtained is that of the bottle + metal + water.

Deduct from this the weight of the dry bottle and the weight of metal taken. The difference represents the weight of water required to fill the bottle when the metal is present. Take this weight from the known lot of water held by the bottle.

This figure represents the weight of water in grammes, displaced by the metal, or its volume in cm^3.

Then specific gravity of the metal is found from :—

$$\text{Specific gravity} = \frac{\text{Weight of metals.}}{\text{Volume.}}$$

This gives the specific gravity compared with water as unity.

If any other medium (alcohol, paraffin) is used, then the specific gravity of the metal with that of the medium is given by

$$\text{Specific gravity} = \frac{\text{Weight of metal taken} \times \text{specific gravity of medium.}}{\text{Divided by weight of medium displaced by metal ;}}$$

or if we call :—

(1) Weight of metal $= G$.

(2) Weight of water displaced by metal $= V$ (volume).

$$\text{Specific gravity} = \frac{G}{V}$$

(3) Specific gravity of medium $= X$.

(4) Weight of medium displaced by metal $= V_1$.

$$\text{Specific gravity} = \frac{G \times X}{V_1}$$

The specific gravity decreases with rise of temperature, since the material expands and displaces a larger volume of water.

The specific gravity of many metals is increased by the process of hammering, rolling and drawing.

The specific volume of a metal is that volume, expressed in c.cms., weighing one gramme.

If the specific gravity be known, the specific volume is easily calculated.

$$\text{Specific volume} = \frac{1}{\text{Specific gravity.}}$$

Similarly, if the specific volume be known, the specific gravity is found from :—

$$\text{Specific gravity} = \frac{1}{\text{Specific volume.}}$$

(*f*) ATOMIC AND MOLECULAR WEIGHTS.

On reference to the table on p. 36, there will be found the chemical symbols given by Berzelius to the elements. The symbol, as a rule, is the initial letter or letters of the Latin or Greek name for the element.

Thus oxygen (Greek, *oxygenium*) is symbolized by the letter O, and hydrogen (Greek, *hydrogenium*) by the letter H.

The use of symbols for chemical substances is so commonly employed that they are here inserted in detail for the benefit of those readers who are not closely conversant with chemistry.

The smallest particle of any substance that can have a free existence is called a molecule.

The mass of material is made up of an infinite number of those tiny particles which we call molecules. These molecules are made up of one or more atoms. The same substance is always uniform, that is, each molecule has the same chemical composition. Some molecules consist of only one atom (e.g., mercury) ; others contain two atoms (e.g., hydrogen and many other gases) ; chemical compounds contain two ~~three~~ or more atoms in the molecule. But it must be remembered that the molecules of the same chemical substance, wherever found, contain the same number of atoms.

The lightest substance known is the gas hydrogen (H), and hence this is taken as the basis of comparison for all the other elements.

The weight of an atom of hydrogen is taken as 1, and the weight of the atoms of all other substances are obtained by comparison with that of hydrogen.

Thus it is found that oxygen is sixteen times as heavy as hydrogen. So that if we write the weight of an atom (or the "atomic weight") of hydrogen as 1, we must write the atomic weight of oxygen as 16.

The "molecular weight" of a substance is found by adding up the weight of the component atoms. Thus, since the molecule of oxygen contains two atoms, its molecular weight must be $2 \times 16 = 32$.

Similarly the molecule weight of hydrogen is $2 \ (1 + 1)$.

Water (formula H_2O) is composed of hydrogen and oxygen. Each molecule of water contains 3 atoms, 2 of hydrogen and 1 of oxygen. Hence the weight of a molecule (or the "molecular weight") of water would be 18.

$$\begin{array}{lcccl} \text{1 molecule } H_2 & = & 1 + 1 & = & 2 \\ \text{1 atom O} & = & 16 & = & 16 \\ \hline \text{1 molecule water} & & & = & 18 \end{array}$$

Or in other words the molecular weight of water is 18.

In conclusion, the atomic or molecular weights of all substances are represented by a number, which is based on the relative weights of the atoms or molecules of such substances when compared with hydrogen.

(*g*) COEFFICIENTS OF EXPANSION AND CONTRACTION.

With increased temperature all metals expand.

The coefficient of expansion represents the increase in length when a metal is raised to 1° C.

If you consider this expansion in the case of a cube, you get expansion along the three axes and the surplus of the diagonals. The value in the latter case is so small as to be negligible.

The expansion along the three axes therefore is that expressed in the coefficient of expansion.

Conversely, a metal contracts on cooling and a coefficient of contraction for each 1° C. can be found.

When metals change from the liquid to the solid state, with few exceptions, a considerable contraction takes place, the molecules being closer to one another in the solid than in the liquid state.

The coefficient of contraction is the percentage of shrinkage of the casting compared with the model from which it is cast, directly after freezing at a temperature just below the freezing point.

(*h*) Tensile Strength.

The tensile strength is represented by the weight, expressed in kilogrammes, exerted along a bar of metal 100 mm. long and 1 mm. square, necessary to break it.

The effect of the strain so exerted is such that at some particular points along the test piece a gradual lessening of the diameter takes place, together with an evolution of heat, and finally the test piece breaks at that point. This phenomenon is known as the "flowing" of metal, and the point at which it begins is called the "point of flow."

The phenomena of flow are also brought about by pressure (*vide* Amalgams).

(*i*) Elastic Limit.

Up to a certain point, if the uniformly increasing load on the bar be removed the stretched bar assumes its original length. A point is reached as the load is increased beyond which the bar no longer possesses this property, and this is termed the point of elastic limit.

(*k*) Hardness.

The degree of hardness of a metal is determined by the ability to effect a scratch on the polished surface by one or other of the agents in the following list. These substances have each a "hardness value" compared with a value of 10 given to the diamond.

Two of such substances can be found, one of which effects a scratch while the one before it in the list does not. Then the hardness figure of the metal lies between those two. The following table is according to Mohs :—

	Hardness number		Hardness number
Talc	1	Felspar	6
Gypsum	2	Quartz	7
Calcspar	3	Topaz	8
Fluorspar	4	Corundum	9
Apatite	5	Diamond	10

A column in the table on p. 37 gives the relative hardness of metals as determined by comparison with Mohs' scale.

(*l*) Alternating Stress.

The capacity of resistance of the metal to a force exerted at right angles to its length. It is measured as the force (expressed in kilogrammes) necessary to break a bar of 1 sq. cm. cross-sectional area.

The test piece is held securely in a vice and the force is applied to the portion projecting.

(*m*) Forging, Malleability, Ductility.

These qualities cannot be represented by a numerical value and are dependent on the internal crystalline structure of the metal.

(*n*) Cohesion and Adhesion.

The force which unites the crystals to each other in any solidified metal is called *cohesion*. This term is con-

TABLE OF THE KNOWN PHYSICAL PROPERTIES

No.	Chemical symbol	Name of the metal	Atomic weight (1907)	Specific weight at ordinary temperature	Freezing point ° C.	SPECIFIC HEAT		Melting heat
						At 15° C.	Near the freezing point	
1	Ag	Silver	107·93	10·50	961·5	0·055	0·076	24·7
2	Al	Aluminium ..	27·1	2·60	657	0·167	0·308	100
3	As	Arsenic ..	75·0	5·73	sublim. at 450	0·076	—	—
4	Au	Gold	197·2	19·32	1063·5	0·030	—	12·6
5	Bi	Bismuth .	208·0	9·80	267·5	0·030	0·030	12·4
6	Ca	Calcium ..	40·1	1·58	780	0·180	—	—
7	Cd	Cadmium ..	112·4	8·64	322	0·054	0·062	13·9
8	Co	Cobaltum ..	59·0	8·6	1500	0·106	0·204	—
9	Cr	Chromium ..	52·1	6·50	1515	0·104	—	—
10	Cu	Copper.. ..	63·6	8·93	1084	0·086	0·118	43·0
11	Fe	Iron	55·9	7·86	1550	0·116	0·162	—
12	Hg	Mercury ..	200·0	13·55	— 39	0·033	0·032	2·8
13	Ir	Iridium ..	193·0	22·42	abt. 1900	0·030	0·040	—
14	K	Potassium ..	39·15	0·87	62	0·166	—	15·7
15	Li	Lithium ..	7·03	0·59	186	0·941	—	—
16	Mg	Magnesium ..	24·36	1·74	632·6	0·246	—	—
17	Mn	Manganese ..	55·0	7·39	1245	0·122	—	—
18	Mo	Molybdenum..	96·0	8·6	Very high	0·066	—	—
19	Na	Sodium ..	23·05	0·98	97·0	0·293	—	31·7
20	Ni	Nickel.. ..	57·7	8·9	1484	0·109	0·161	4·6
21	Os	Osmium ..	19·0	22·48	Abt. 2000	0·031	—	—
22	Pb	Lead	206·9	11·37	326·9	0·030	0·034	5·4
23	Pd	Palladium ..	106·5	11·4	1575	0·059	—	36·3
24	Pt	Platinum ..	194·8	21·50	1780	0·032	0·046	27·2
25	Rb	Rubidium	85·5	1·52	38·5	—	—	—
26	Rh	Rhodium ..	103·0	12·1	Higher than Pt.	0·058	—	—
27	Sb	Antimony ..	102·2	6·62	630·5	0·048	0·054	—
28	Sn	Tin	119·0	7·29	232	0·055	0·059	14
29	Ti	Titanium ..	48·1	3·59	—	0·112	—	—
30	Tl	Thallium ..	204·1	11·85	301	—	—	—
31	V	Vanadium ..	51·2	5·5	—	0·115	—	—
32	W	Tungsten ..	184·0	19·1	Higher than Cr	0·034	—	—
33	Zn	Zincum ..	65·4	7·1	419	0·093	0·122	28·0

* Where two figures are found the first refers to the

of the Metals According to Wüst.

Complete melting heat	Heat conductivity	Average coefficient of expansion lin. 1 to 100° C.	Coefficient of contraction in freezing in %	Resistance kg/mm²*	Hardness	Electric resistance 1,000 m. 1 mm.² Ω	Electric conductivity 0° C.
81·7	1·096	0·000019	—	10 30	2·5 3	15	679000
240	0·35	0·000023	1·6	12 24	2	28	324000
—	—	0·000006	—	—	3·5	350	28600
44·52	0·70	0·000014	—	7—8 28	2·5	21	461000
21	0·02	0·000013	—	—	2·5	1080	9260
—	—	—	—	—	—	75	95000
32	0·21	0·000030	—	—	—	70	144100
—	—	0·000012	—	—	—	97	103000
—	—	—	—	—	—	—	—
154	0·72	0·000017	0·8	20÷24 24÷35	2·5 3	16·7	620000
—	0·17	0·000012	1·0	—	4 5	76	131000
—	0·02	0·000181	—	—	—	941	10630
—	—	0·000007	—	—	6	—	—
26	—	0·000083	—	—	—	66	150500
—	—	—	—	—	—	88	119000
—	0·38	0·000027	—	21·5	—	43	230000
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
60	—	0·000072	—	—	—	48	211000
205	0·14	0·000013	1·0	—	—	70	144200
—	—	0·000007	—	—	—	95	105300
16	0·08	0·000029	1·1	1·2	1·5	195	50400
130	0·17	0·000012	—	—	4·8	107	—
109	0·17	0·000009	—	28	4·3	108	63500
—	—	—	—	—	—	—	—
—	—	0·000009	—	—	—	—	—
—	0·04	0·000017	—	—	3·3	380	27100
27	0·14	0·000023	0·8	3·5÷4	1·5	100	76600
—	—	—	—	—	—	—	54600
—	—	0·000031	—	—	—	180	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
73	0·26	0·000029	1·6	25÷30 15÷20	—	57	186000

annealed metal and the second to the cold-worked one.

fined to the force exerted in binding crystals of the same metal together.

It is a force inferior to that found to exist in alloys of two or more metals, in which we get *mixed crystals*. This force is called *adhesion*.

This force of adhesion generally secures a greater hardness and strength to the alloy than is possessed by the single metals composing it.

As we shall see later on, the alloy sometimes consists of a chemical compound, in which case a further increase in these properties results.

(*o*) WELDING.

Many metals, heated to a point considerably below their melting point, can be united by pressure. This process is called " welding."

Gold may possess this quality to a marked degree even at ordinary temperatures. Hence its application as a " filling " for teeth by dentists.

The properties under letters G to M vary for each metal with its crystalline structure.

The ease with which an internal rearrangement of the crystals can be brought about by heat treatment, resulting in a change of physical properties, also varies with each particular metal.

Easily oxidizable metals should, in the heated state, be freed from traces of oxide, otherwise they cannot be welded together.

(*p*) ELECTRICAL RESISTANCE.

The electrical resistance of any material is measured in ohms. The ohm is the unit of resistance, and is such a resistance as is offered to the passage of the electric current by a column of mercury 1,063 mm. in height and 1 millimetre cross-sectional area.

The resistance thus offered to the passage of the current converts it into heat.

Such substances which convert electricity into heat are called conductors of the first degree, and metals and alloys form the largest proportion of these substances.

The number of ohms which represent the resistance of a wire 1 metre in length and 1 square mm. cross-sectional area is termed the specific resistance.

The specific conductivity is the reciprocal of the resistance. The lower the resistance, the greater the conductivity of the metal.

Electrical conductivity and heat conductivity of metals are generally relative, a metal that is a good conductor of electricity generally being a good conductor of heat.

Electrical resistance of any metal varies with the temperature at which the determination is made.

As the temperature increases, so does the resistance, and *vice versâ* the conductivity diminishes.

The correction for variation for temperature is termed the coefficient of electrical resistance and electrical conductivity, and for the latter is 0·104 decrease of the conductivity for every °C. rise above zero. This coefficient (0·104) is the same as the coefficient of expansion for gases.

Single metals have generally a higher electrical conductivity than alloys. The addition of even small amounts of silver to copper reduces the conducting value of the latter (although silver is a better conductor than copper).

We find the average of the conducting value of their components only in the five examples : SnZn, SnPb, SnCd, PbCd, ZnCd.

(*q*) MAGNETIC PROPERTIES.

Some metals, notably iron, and in a lesser degree nickel and cobalt, become magnetized when touched with a magnet or brought into a magnetic field, say by surrounding the bar of metal by a spiral of insulated copper wire, through which a fairly strong current of electricity is passing. (Such an arrangement is called a solenoid.)

(*r*) COLOUR.

Some metals, even in the thinnest plate, show no evidence of transparency. They absorb all the rays of *transmitted* light.

By reflected light, the rays are all reflected, and hence these metals appear to be white.

Gold, however, reflects the yellow rays, and hence ordinarily is spoken of as a yellow metal. If, however, a very thin sheet of gold be examined by transmitted light, it appears green in colour.

Again, metals in a finely divided state have a different colour to that possessed by the same metal in the form of sheet. Thus gold in a finely powdered form is yellow-brown ; copper is reddish yellow, and platinum is black.

(*s*) METALLIC LUSTRE.

The metallic lustre or polish that the metal is capable of taking is determined by the hardness and close texture of the metal ; the latter quality would appear to depend on the nearness of the crystals of metal to each other.

V. THE CHEMICAL PROPERTIES OF METALS.

Just as the atomic or molecular weight varies with different metals, so also do the chemical properties of one element vary largely from those of another.

We do, however, find series of elements that have similar properties, of which series more will be said under the head of what is known as the periodic table.

If by the union of two or more elements a compound is formed, we find that such a compound is quite homogeneous, made up of a large number of exactly similar molecules of constant composition, and in its properties differs widely from the constituent elements Moreover, the compound so produced is only with difficulty broken down into its constituents by physical means.

It is important to remember that the same chemical compound has an unvarying composition. Thus, common salt, whether found in the ocean, or inland in springs, or prepared in the laboratory, has exactly the same composition, viz., sodium 39·3 per cent., chlorine 60·7 per cent. Further, each infinitesimal molecule of salt has exactly this definite and unvarying composition.

"NOBLE" AND "BASE" METALS.

According to their greater or less affinity for oxygen, the metals are divided broadly into two groups, base and noble.

(1) The noble metals so called are platinum, gold,

osmium, iridium and silver. These metals deoxydize at high temperatures.

(2) The base metals, on the other hand, oxydize more or less readily, many even at the ordinary temperature and are not easily reduced even at high temperatures.

This classification, in my opinion, is hardly warranted on such slight differences in chemical behaviour.

A more fitting comparison between the two series might be drawn, just as the terms negative and positive are used in electricity. There we find a chain of metals, each of which is electro-positive to those that follow.

In the same way the metals might be arranged in a chain, based on the ease with which one metal is displaced in solution by the introduction of a second. The noble metals are the most easily displaced, and hence we should get a chain which had, say, platinum at one end, and magnesium at the other, thus: Pt — Os — Ir — Au — Ag — Pb — Cu — Sn — Zn — Ni — Fe — Mn — Al — Mg. Thus any metal is more or less easily reduced from its compound by any one of the metals that follow it in the list.

This knowledge is applied to the purification of metals when in the molten state.

OXIDATION.

As we have stated, many metals even at a low temperature unite with the oxygen of the air. This process is very much more rapid when the metal is in the molten condition. The oxides so formed, if not removed, dissolve in the molten metal, and destroy or materially alter properties that are essential to the proper working of the metal subsequently. Many metals have the property of occluding gases (*e.g.*, molten silver absorbs quite a large volume of oxygen), and if these gases are permitted to remain in the metal, a further source of trouble or weakness results.

To remedy this tendency to oxidation various means are adopted to separate the surface of the molten metal from the atmosphere.

(1) A layer of coal dust forms an effectual screen. Its effect is to create a "reducing" atmosphere—that is, one which has exactly opposite properties to an "oxidizing atmosphere." The carbon of the coal first burns to carbon dioxide thus: (*a*) $C + O_2 = CO_2$.

Then a second reaction takes place in presence of excess of carbon at high temperature.

(*b*) $CO_2 + C = 2CO$.

Carbon monoxide (CO) is a powerful "reducing" agent.

(2) Borax is also used as a screen in the same way. It does not, however, supply a reducing atmosphere, but possesses the valuable property of dissolving the oxides in the molten metal, forming a slag. This of course entails some wastage of the metal.

(3) Metals of high melting point are covered with powdered glass (sodium calcium silicate), which screens them from oxidation, and less loss is entailed than with borax.

(4) Another method that is adopted is to melt the metal in an atmosphere of hydrogen. This not only prevents oxidation, but reduces any oxides in the metal to the metallic state, combining with the oxygen to form water; for example:—

$$ZnO + H_2 = Zn + H_2O$$

(Zinc oxide + Hydrogen = Zinc + Water)

As hydrogen and oxygen form highly explosive mixtures, the method must be so arranged that all the air in the melting pot has been swept out and entirely replaced by hydrogen before the process of melting begins.

When the gas coming from the outlet that is left for the escape of excess gas burns quietly, without explosion, with a blue flame, it is safe to apply the heat for the melting operation.

For operations on a small scale, a Kipp apparatus is most suitable for the generation of the hydrogen.

Some metals, notably iron, occlude hydrogen, and this must be borne in mind when selecting the protecting agency against oxidation.

If it is impossible to find a means for the prevention of oxidation, the following plan is available. When the metal or alloy is completely melted and ready for pouring, the dissolved oxides are removed by the addition of certain elements. The following considerations, after Wüst, should be observed.

(1) The metal or metalloid added must have a stronger affinity for oxygen than that of the metal whose oxide is to be removed.

The element added then robs the existing metallic oxide of its oxygen and reduces it to the metallic state. The cleaning agent is itself oxidized.

(2) The oxide of the cleansing agent must be insoluble in the molten metal, and such a one should be chosen which will give an oxide lighter or heavier than the metal itself, so as to facilitate its easy removal, either before or after solidification of the metal.

(3) In some cases, traces of the refining agent added in excess of what is needed do materially affect the working qualities of the metal. Such agents must be avoided.

(4) It is essential that the refining agent be miscible with the metal, in order to ensure the complete removal

of the oxides: e.g., nickel is best purified by the agency of magnesium — nickel oxide + magnesium = magnesium oxide + nickel.

These are called deoxidizing processes, and the element added, the deoxidizer.

Thus iron is conveniently deoxidized by manganese, silicon or aluminium. The deoxidation of copper can be effected by aluminium, ~~silver~~ silicon, magnesium, manganese, zinc, and tin, but more easily than any of these by the agency of phosphorus.

In the following list oxide of any particular metal is reduced to the metallic state by the addition to the molten mass of any of the elements preceding it in the list.

(1) Magnesium.
(2) Aluminium.
(3) Silicon.
(4) Phosphorus.
(5) Magnanese.
(6) Iron.
(7) Nickel.
(8) Zinc.
(9) Tin.
(10) Copper.
(11) Lead.
(12) Silver.
(13) Gold.

The use of phosphorus is limited to the deoxidation of those metals which do not dissolve carbon.

The work of Carl Barus and Henry Chatelier has solved the many difficulties that surround the correct measurement of high temperatures and the knowledge of their heterogeneous equilibrium.

Table of the Periodic System.

The following explanation of this marvellous classification of the elements according to the "Periodic law" is due to *Staigmüller*.

This system divides the elements into seven distinct groups, ranged horizontally as shown in the table. The gradual increase of atomic weights from left to right of each horizontal line should be noted.

Vertical lines divide the elements into nineteen groups. The metals or non-metals constituting each vertical series show that each is related in its physical or chemical properties to all the others in the same column.

Thus, on reference to the table it will be seen that the melting points rise or fall from the top member to the element at the bottom of the column.

Similarly the atomic weights increase as we descend each vertical column. In many cases this increase is nearly regular enough to be uniform, making the metal fall in "periods"—hence the name of "periodic law."

From this the following conclusions can be drawn.

(1) The elements composing any vertical column (or natural group) do not form compounds with each other.

Thus, as has been stated, metals in the following groups do not form compounds:

Cu	Zn	Ge	As
Ag	Cd	Sn	Al
Au	Hg	Pb	Bi

An element forms compounds with all members of one of these natural groups or none.

Lead is, however, an exception to this, as it forms two chemical compounds with Au, but none with Ag or Cu.

Si forms a compound with Cu, but none with Ag. Tamman's table, pp. 49, 50, shows all the chemical compounds which have been found between different pairs of metals.

MIXED CRYSTALS.

As a rule the members of a natural group of metals form mixed crystals with one another.

These alloys, and the exceptions to the rule just given, are shown in Tamman's table above referred to (pp. 49, 50).

OTHER INFLUENCES.

A metal is said to be solid, liquid, or gaseous, according as its molecules are able to move about with more or less freedom.

Its various properties as a solid are discussed under the head of Polymorphism.

In the liquid state metals are often able to dissolve gases and to form insoluble gaseous compounds.

These cause bubbles to appear in ingots and so impair their value.

TABLE OF THE PERIODICAL SYSTEM ACCORDING TO STAIGMÜLLER.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
H —259	He under —267	Li 186	Be under Ag	B not melted	C not melted											N —210	O —245	F —223
	Ne	Na 98	Mg 651	Al 687	Si 1430											P 44 and 630	S 115	Cl —102
	Ar —188	K 63	Ca 780	Se	Ti higher than 2200	V 1680	Cr 1515	Mn 1247	Fe 1545	Co 1505	Ni 1484	Cu 1084	Zn 419	Ga 30	Ge 900	As red heat	Se 217	Br —7
	Kr —169	Rb 39	Sr Red heat	Y	Zr higher than Si	Nb 1950	Mo over 2100		Ru over 1950	Rh over Pt	Pd 1587	Ag 961	Gd 322	Jn 155	Sn 232	Sb 631	Te 450	J 113
	X —140	Cs 27	Ba 850	La 810	Ce 623	Nd 840	Pr 940											
				Yb		Ta 2300	W over 2300		Os 2500	Jr 2200	Pt 1780	Au 1064	Hg —39	Tl 302	Pb 327	Bi 268		
					Th		U											

SPECIAL PART.

4

INTRODUCTION.

In this section of the book all the known properties of metals which the author regards as important will be described.

The description of the alloy is accompanied by complete diagrams, arranged (after Bornemann) in atomic percentages. A guiding line is added to these, which makes it possible to read off the weight percentages without further trouble (fig. 16).

Thus, at the point which gives the atomic percentage which it is desired to translate into a weight percentage, a perpendicular is erected on the abscissa (fig. 16, C D).

If from the intersection of the perpendicular with the guide line B D A, a horizontal line is produced to the right (fig. 16, D E) side of the diagram, it will indicate the weight percentage E.

Taking fig. 16 as an example, we see that 65 per cent. of the atoms of A correspond to 45 per cent. of the weight of A.

If it happened that the atomic weights of both metals were the same, then the line A B would be straight (fig. 16, B G A), and the atom percentage would equal the weight percentage.

F G would then be the perpendicular indicating 50 per cent. of atoms, and G H the horizontal showing 50 per cent. of weight.

In describing the properties of alloys, the points which have been emphasized are those relating to chemical affinities, saturated mixed crystals, and eutectics.

Weight percentages and melting points are clearly set forth in the text.

In studying the new properties of alloys, a knowledge of percentage contents of compounds, mixed crystals, and eutectics is valuable, because all others do not possess new properties, but show a mixture of the qualities of these.

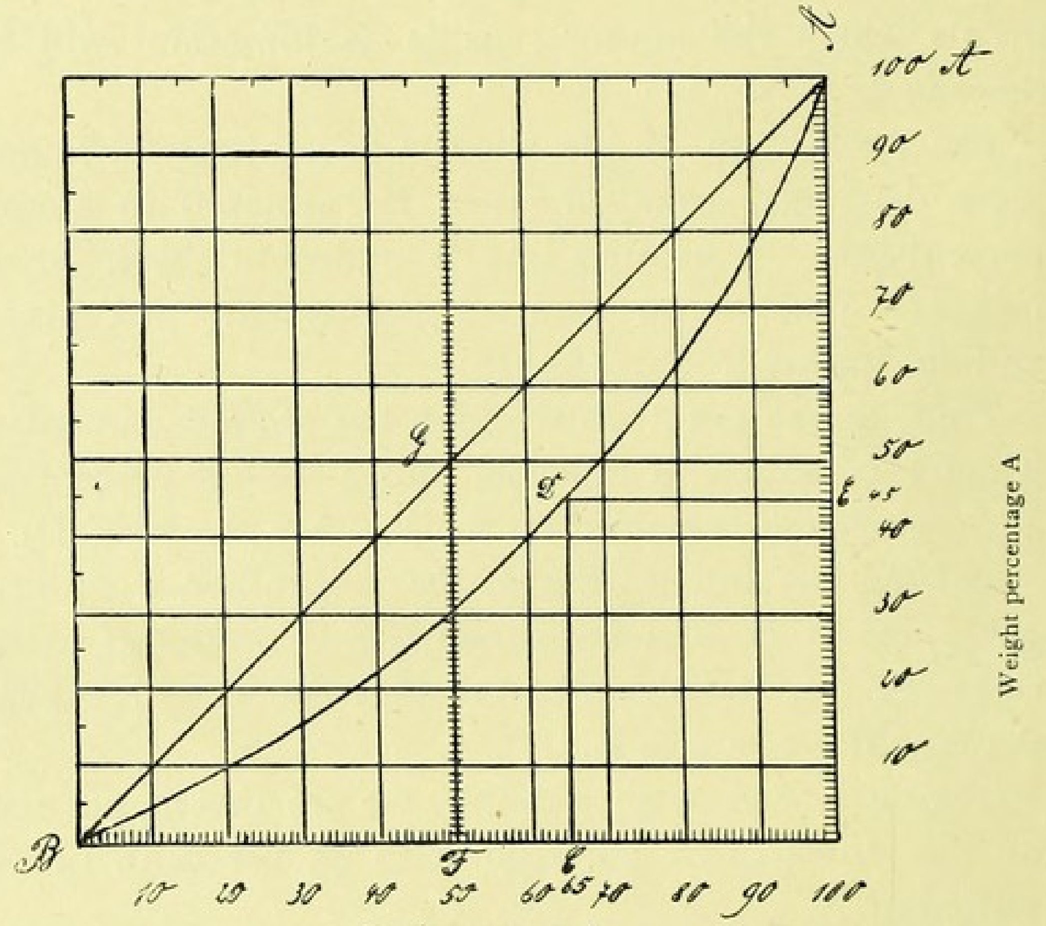


FIG. 16.—Direction for transferring the atomic percentage of the diagrams into weight percentage.

If these things are borne in mind, a rational search can be made for alloys having specially desirable properties, or modifications can be effected in those we already have.

The change of volume, that is to say, the expansion or contraction which may take place when two metals are alloyed, has been treated of separately, because its relation to the structure of the metals has not yet been fully explained.

As regards the order in which the metals are treated, I have taken first the natural group—Cu, Au, Ag—which is of most interest to workers in precious and base metals. In this group the alloys have been arranged alphabetically, according to their chemical symbols. Next to these I have treated iron; for the places of all others I refer to the index.

VI. COPPER AND ITS ALLOYS.

The word copper is derived from the Latin *cuprum*, which in turn takes its name from the island of Cyprus, because it was from there that the Romans obtained most of their copper ores. Its chemical symbol is Cu; see p. 36, No. 10, for its physical properties.

It was known to the Egyptians 2000 B.C., and was alloyed with tin to make bronze.

Servius Tullius minted copper coins.

When heated, it becomes coated with a reddish oxide, which dissolves in the melted copper, and tends to make it springy. Hence Cu must always be protected from oxidation in the way previously described (see Oxidation).

The addition of aluminium makes copper harder and tougher without affecting its ductility, ~~but~~ and it also renders it more liable to get rid of ~~absor~~b oxygen.

Antimony has an unfavourable effect and makes it springy and brittle, as do also bismuth and lead. Iron and nickel do not alter it much.

For the methods of extracting Cu from its ores the reader is referred to Dr. Fischer's "Metallurgy" and other comprehensive works.

The chemistry of the metal is also referred to in the parts of this work devoted to that subject.

Copper amalgams will be discussed with mercury under the heading of "Copper-Mercury."

(1) Copper—Silver, Cu-Ag.

Copper and silver are miscible in all proportions in the fluid state.

Microscopical examination shows that only one homogeneous mixed crystal is formed. Its composition is 1 per cent. Ag, 99 per cent. Cu. Analysis by the thermic process, however, indicates that the saturated mixed crystal ought to contain 6 per cent. Cu + 94 per cent. Ag.

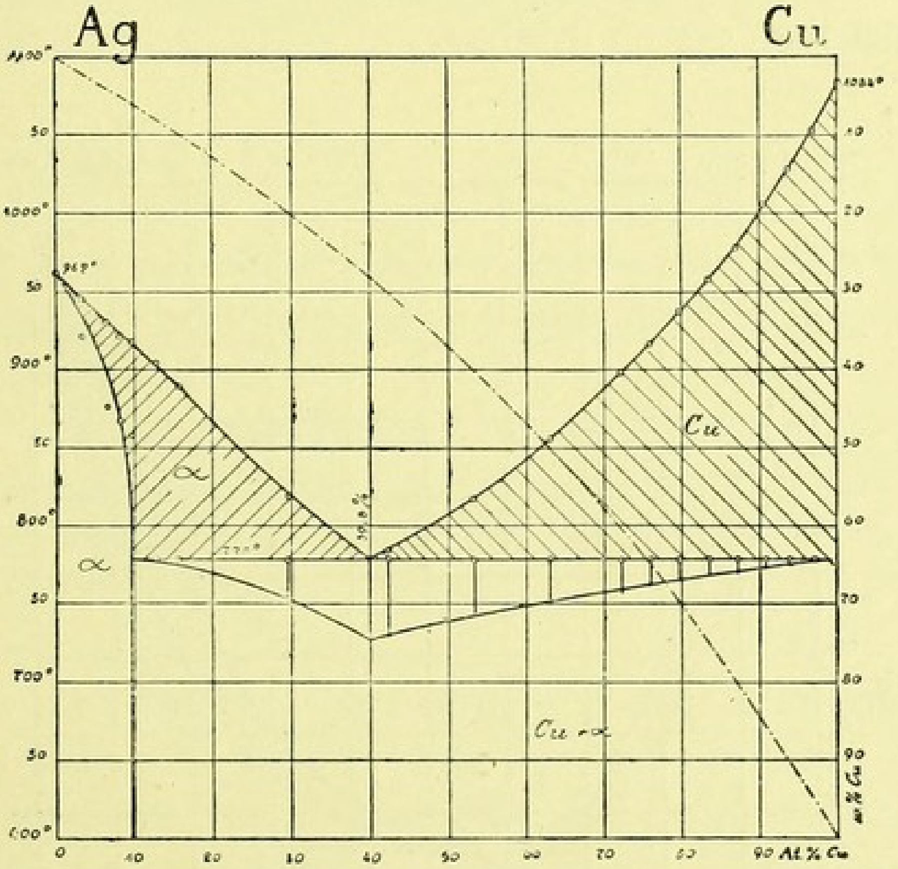


FIG. 17.—Copper—Silver according to Friedrich and Leroux. Atomic percentage by Bornemann.

The metals dissolve very slowly in one another, and Lepkowski states that alloys containing 1 per cent. silver only become really homogeneous after being melted together for 3½ hours at 750° C.

An alloy containing 2 per cent. of silver showed us free silver after being kept fluid for ten hours, 3 and 4 per cent. disappeared after thirty hours, and 5·75 per cent. after forty hours. With 7 per cent. Ag some remained free after eighty hours. This will explain the difference between the findings by the thermic and microscopical examinations.

Alloys containing 97 per cent. and 96 per cent. Ag were found to be homogeneous after eight to ten hours, those with 95 per cent. Ag after forty hours. In those with 94 per cent. Ag copper was to be found free after eighty hours. This indicates that silver diffuses more easily in copper than copper in silver.

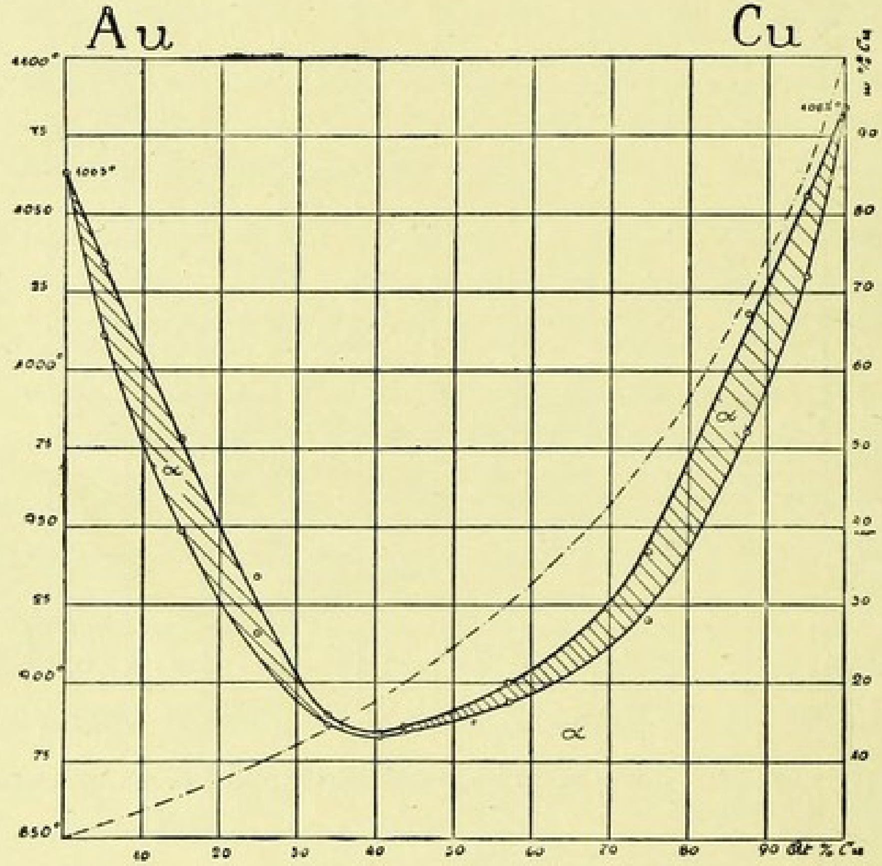


FIG. 18.—Copper—Gold according to Kurnakow and Zemczuzny. Atomic percentage by Bornemann.

The conclusion to be drawn from this is that the perfect alloying of copper and silver takes a long time to effect, and most of the copper-silver alloys of commerce contain free copper and consequently oxidize on the surface.

The eutectic contains 72 per cent. Ag + 28 per cent.

Cu and it melts at 778° C.—the lowest melting point of all the CuAg alloys.

Our diagram shows the result of common alloying, while Lepkowski's researches ought to result in a diagram like Fig. 18 : Au-Cu.

(2) Copper—Gold.

Gold and copper form mixed crystals. These dissolve one another and lower the melting point. There is no eutectic.

According to Kurnakow and Zemczuzny the alloy having the lowest melting point contains 82 per cent. by weight of gold and 18 per cent. by weight of copper, or 60 atomic per cent. gold and 40 atomic per cent. of copper, and it melts at 880° C.

These mixed crystals need a still longer time than those of CuAg to form, and it is therefore advisable to keep the mixture fluid as long as possible and then cool it slowly and hold it just above the crystallizing point for a long time.

The alloy known as Nuremburg gold is composed of 90 per cent. Cu, 7·5 per cent. Al, and 2·5 per cent. gold. It has a colour like that of gold and is not affected by atmospheric conditions.

An alloy composed of eighteen parts Au, thirteen Cu, eleven Ag, and six Pd has a brownish red colour and is extremely hard and resistant to wear. It is used as a substitute for precious stones on the pivots of watches.

The Japanese gold alloy called Shaku-do consists of copper with 1-10 per cent. of gold and a little antimony.

(3) Copper—Aluminium, Cu-Al.

These metals form :—

(1) The chemical compound CuAl consisting of 56 per cent. by weight of Cu and 44 per cent. of Al (according to Gwyer), with a melting point at 622° C.

(2) The compound $CuAl_2$ consisting of 45 per cent. by weight of Cu and 55 per cent. Al, with a melting point at 585° C. (according to Curry), *vide* diagram.

(3) A third chemical compound Cu_3Al (β in the diagram) seems to the writer more like a mixed crystal, and has a composition of 87·6 per cent. by weight of Cu and 12·4 per cent. Al.

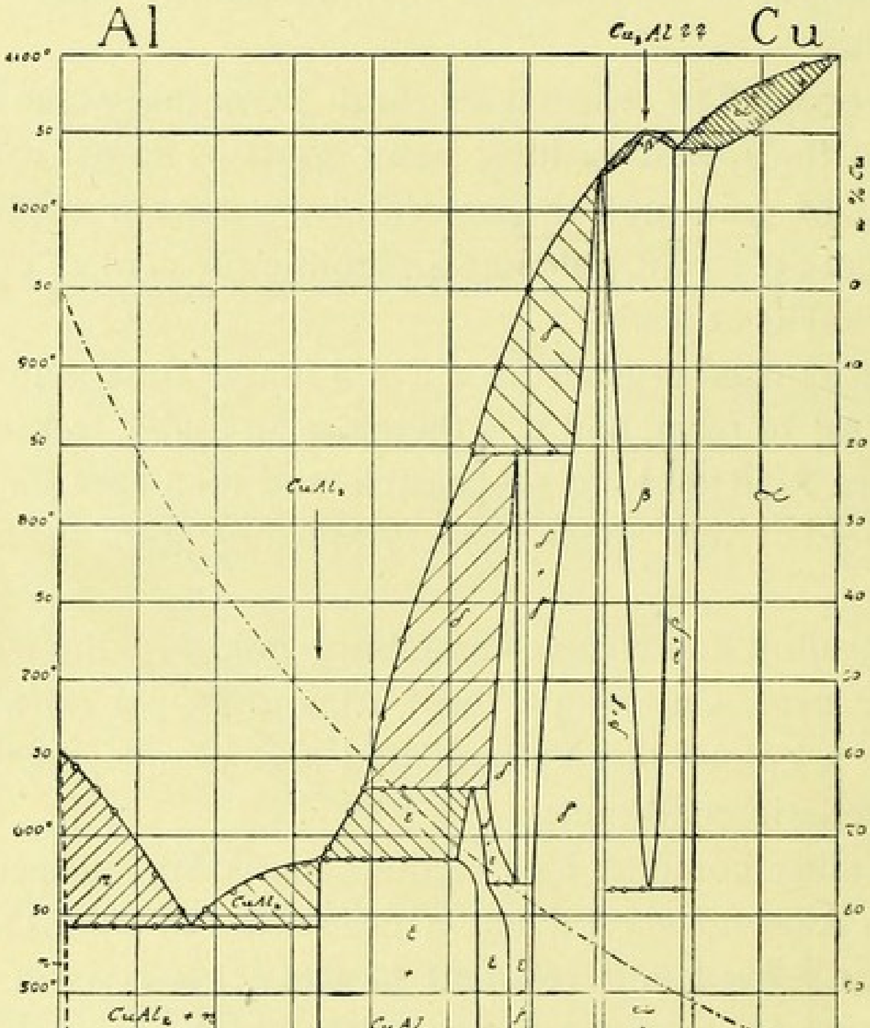


FIG. 19.—Copper—Aluminium according to Curry. Atomic percentage by Bornemann.

Six different mixed crystals have been found, but they, like the compounds, are seldom stable during the cooling off process and continue to change after crystallization has taken place.

Between the compound $CuAl_2$ and the mixed crystal there is a eutectic containing 32·5 per cent. Cu with a melting point at 544° C. This is the lowest melting alloy of any mixture of the two metals.

The mixed crystal "*a*" is the one chiefly used in manufacturing, and this contains up to 11·5 per cent. Al, and melts at 1040° C. It is, however, adequately saturated, and will crystallize without changing in percentages down to 7 per cent. Al.

This latter, which melts at 1070° ~~107~~°C., may be considered the most satisfactory alloy for industrial purposes. It is known technically as "aluminium bronze," and percentages of 1·5-10 per cent. Al are most favoured.

With a content of 10 per cent. Al the bronze can be rolled, hammered, or polished. It has a fine golden colour, and is very hard and resistant to acids and wear.

The so-called Hercules metal consists of: 85·5 per cent. Cu; 2·5 per cent. Al; 10·0 per cent. Sn; 2·0 per cent. Zn.

This alloy is very resistant to salt solutions and organic acids, and is consequently very useful in the manufacture of fruit knives. It should find a good field in dental prosthetic work.

The following alloys also have special qualities :—

11·5—13	per cent.	by weight	of aluminium,	melting	point	1030—1050° C.
13 —16	,,	,,	,,	,,	,,	1030—1050° C.
16 —23	,,	,,	,,	,,	,,	*ca* 900—1000° C
23 —41	,,	,,	,,	,,	,,	,, 630— 900° C.

All these alloys would probably show different properties, according as they were cooled suddenly or slowly after crystallization.

The literature on the subject does not give much information as to how far they are used or can be used in manufactures.

(4) Copper—Bismuth, Cu-Bi.

This pair form no compound, no mixed crystal, and no eutectic which is at all remarkable.

They can be mixed in the fluid state, but separate again on crystallization, so that no practicable alloy can be formed from them.

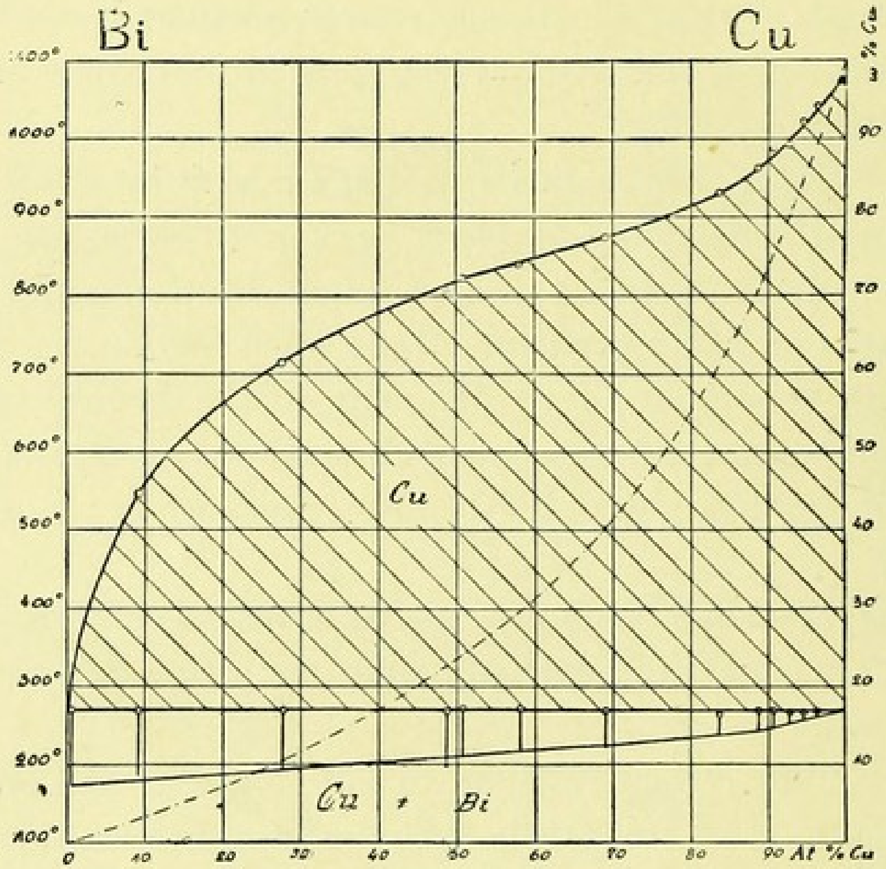


FIG. 20.—Copper—Bismuth according to Teriomin. Atomic percentage by Bornemann.

(5) Copper—Cadmium, Cu-Cd.

Alloys of these metals do not appear to be of great use in manufactures. They are of a grey colour up to 53 per cent. Cd; with 50 per cent. a reddish tinge appears, which increases as the percentage of copper is raised, till they take on a yellowish red colour.

They are soft when the Cd content is high, and become harder as the Cu is increased.

Those with the maximal melting point (the true compounds Cu_2Cd, and Cu_2Cd_3), are very hard and extremely brittle, and have a crystalline fracture.

As the Cu content is increased the brittleness gradually disappears, and the fracture becomes fibrous.

There are two chemical compounds.

Cu_2 Cd —45 per cent. Cd 55 per cent. by weight of Cu, melting point 695° C.
Cu_2 Cd_3—72 ,, Cd 28 ,, ,, Cu, ,, ,, 575° C.

The second compound forms a mixed crystal (*a*) with pure Cd, viz., the compound Cu_2Cd, and it is saturated by 69 per cent. and 72 per cent. Cd.

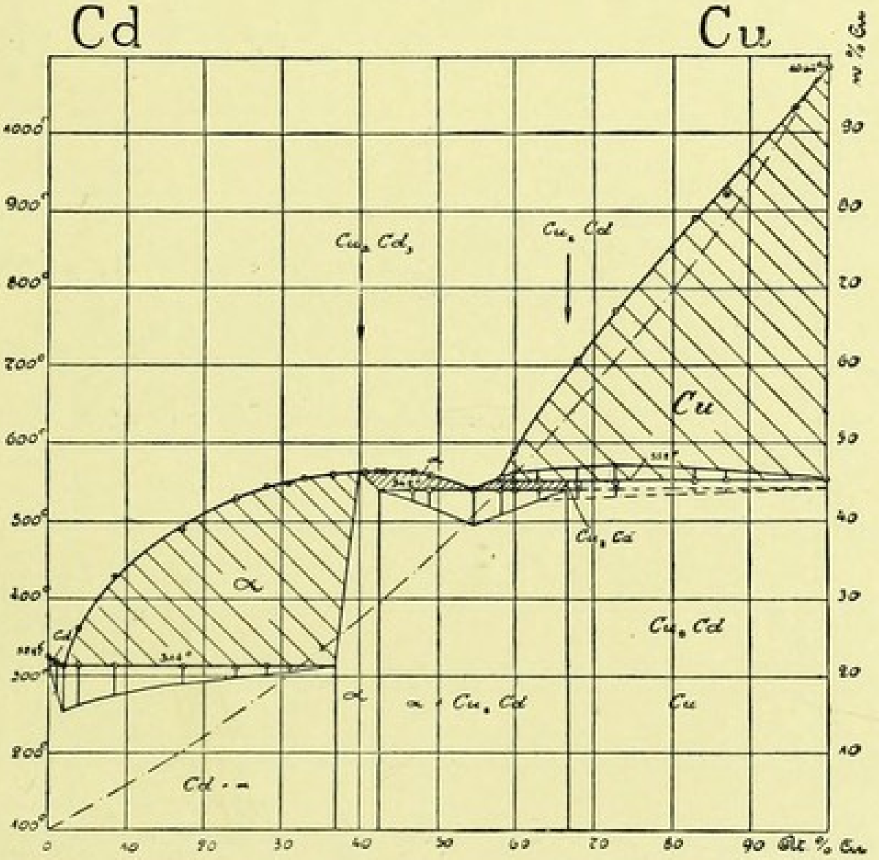


FIG. 21.—Copper—Cadmium according to Sahmen. Atomic percentage by Bornemann.

There are two eutectics.

No. 1 has 58 per cent. Cd + 42 per cent. Cu, and melts at 542° C. It contains the chemical combination Cu_2Cd, and the mixed crystal with 69 per cent. ~~Cu_2Cd_3~~. Cd.

No. 2 consists of 97 per cent. Cd, and 3 per cent. Cu.

It contains pure Cd, and the mixed crystal *a* with its 75 per cent. Cd. It melts at 314°C.

The intermediate phases can be easily understood from the diagram.

(6) Copper—Cobalt, Cu-Co.

These two metals are miscible in all proportions in the liquid state, and they form two mixed crystals, one having 10 per cent. Cu, and the other 95·5 per cent. Cu. They are designated *a* and *γ* in the diagram.

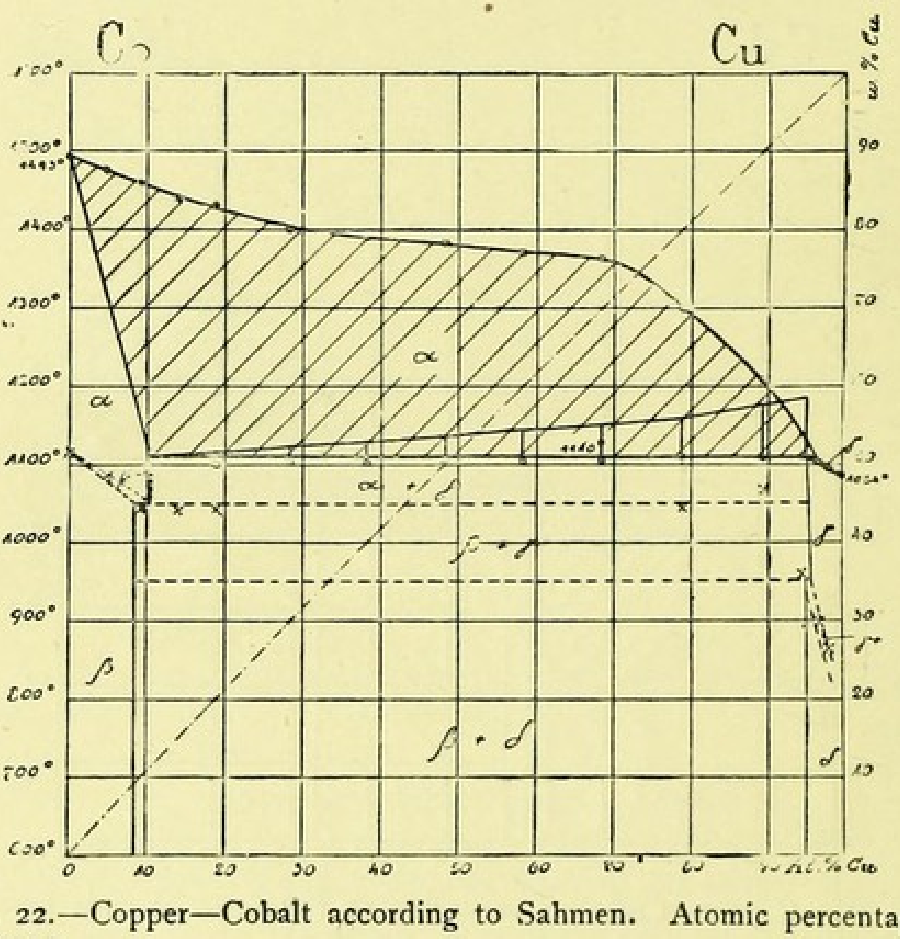


FIG. 22.—**Copper—Cobalt according to Sahmen. Atomic percentage by** Bornemann.

By cooling slowly the *a* crystal will change into the *β* at about 1150° C, and *γ* into *δ* at 950° C.

The pointed line indicates a gradual change of the cobalt crystal from a non-magnetic to a magnetic one.

There are no alloys or eutectics formed which are at all remarkable, and no information to hand with regard to industrial uses, etc.

The hardness of the mixed crystal with excess of Co is "4," and that with excess of Cu "3" according to Moh's scale.

(7) Copper—Chromium, Cu-Cr.

These cannot be mixed either in the solid or liquid states, and so they do not form either alloys or eutectics.

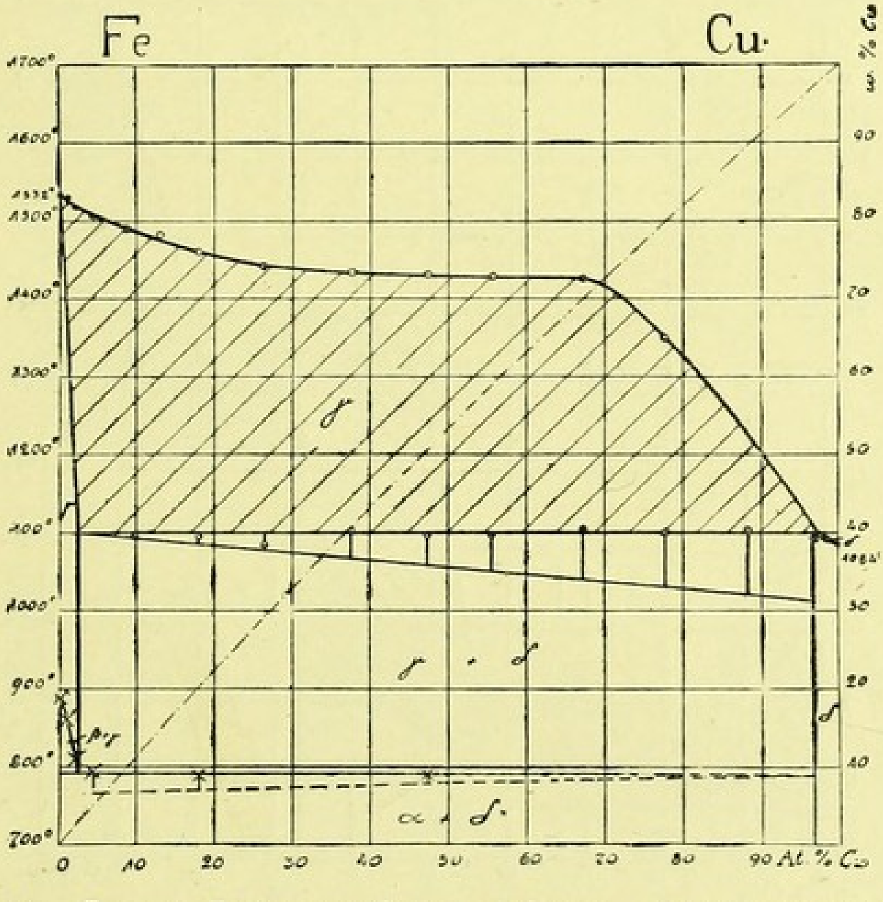


FIG. 23.—Copper—Iron according to Sahmen. Atomic percentage by Bornemann.

(8) Copper—Iron, Cu-Fe.

There are no alloys or eutectics between these two metals, but two mixed crystals are formed, the first, γ, has 0·25 per cent. Cu, and the second, δ, 97-100 per cent. Cu.

The temperature at which the Fe changes (800-900° C.) from γ to $\delta + \beta$ and from β to α (at 790 ° C.) are clearly shown on the diagram.

The addition of very little carbon considerably increases the solubility of Cu in Fe. These compounds, however, do not seem to be of much practical interest.

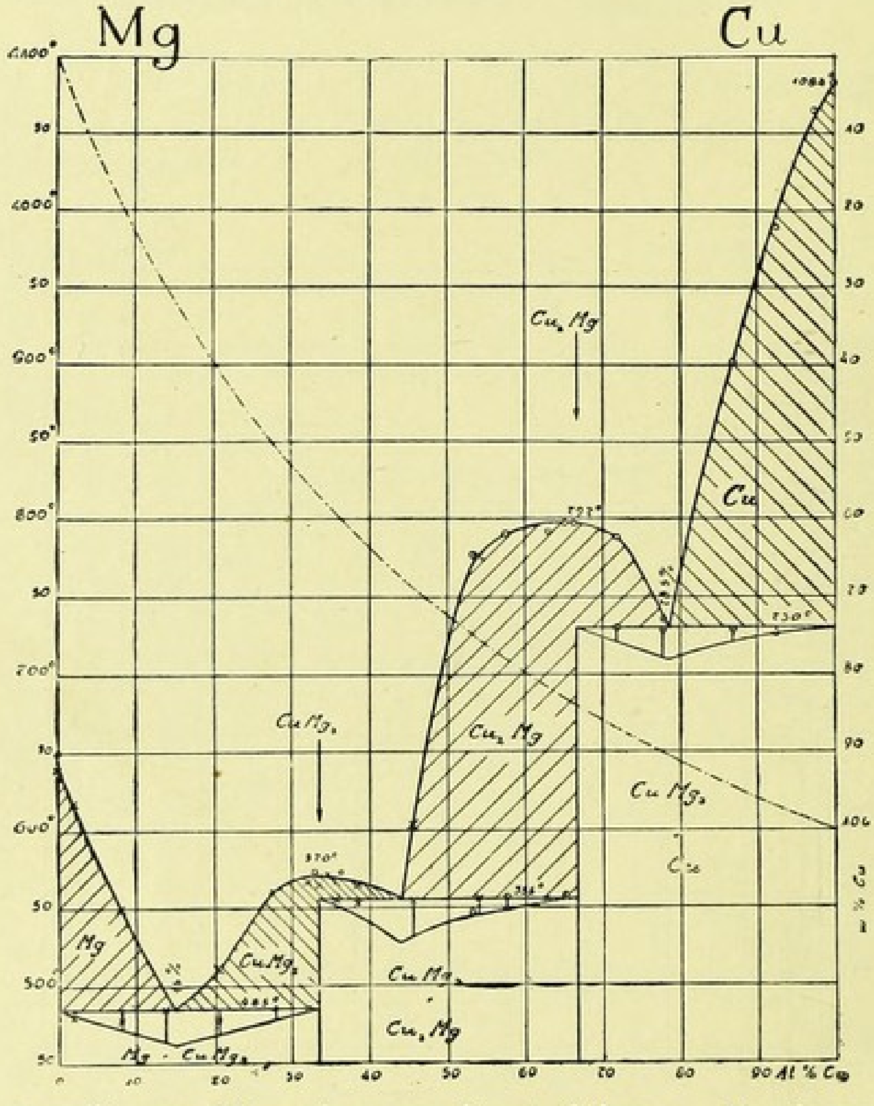


FIG. 24.—Copper—Magnesium according to Sahmen. Atomic percentage by Bornemann.

(9) Copper—Magnesium, Cu-Mg.

These form two chemical combinations :—

$CuMg_2$ with 57 per cent. by weight Cu melting point 570° C.
Cu_2Mg ,, 83·5 ,, ,, Cu ,, ,, 797° C.

These have eutectics with one another and with the pure metals as follows :—

90·5 per cent. by weight Cu 9·5 per cent. by weight, Mg, melting point 730° C.
67 ,, ,, Cu 32·5 ,, ,, Mg, ,, ,, 555° C.
33 ,, ,, Cu 67 ,, ,, Mg, ,, ,, 485° C.

The compounds are very brittle and have the same colour as pure Mg. They are not used industrially.

(10) Copper—Manganese, Cu-Mn.

Between these two there is a complete series of mixed crystals, but no eutectic or chemical combination. The alloy, with about 68 per cent. Cu, shows the lowest melting point, namely 870° C.

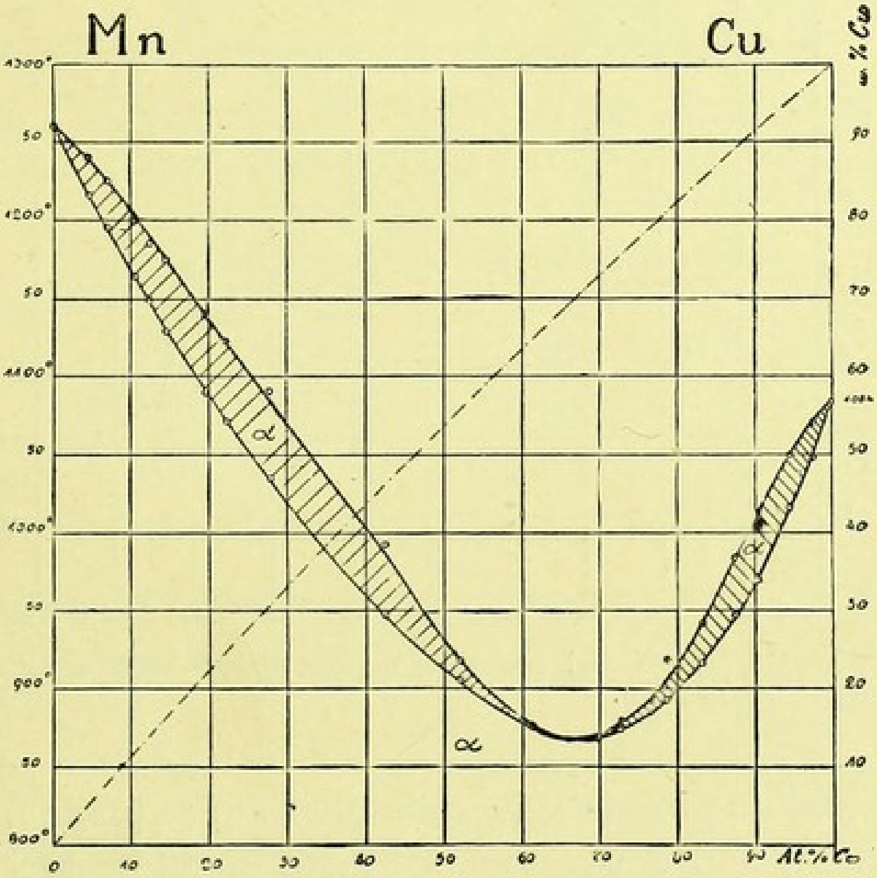


FIG. 25.—Copper—Manganese according to Zemczuzny, Urasow and Rykowskow. Atomic percentage by Bornemann.

(11) Copper—Nickel, Cu-Ni.

These are miscible in all proportions when liquid and form a complete series of mixed crystals, so that there are no eutectic or chemical compounds.

Schmidt used these alloys as dental amalgams, and in respect of colour they are certainly better than ordinary copper amalgams.

Theoretically they are copper amalgams with free nickel, but there is no reason for supposing that mercury is miscible with nickel or forms compounds with it.

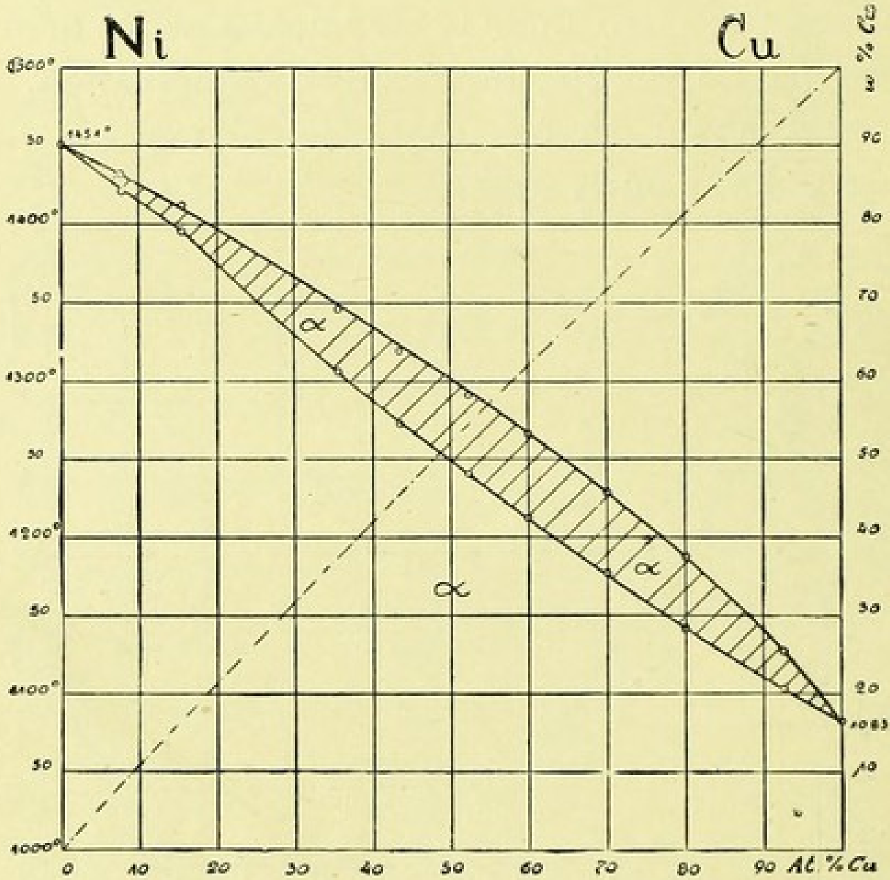


FIG. 26.—Copper—Nickel according to Gürtler and Tammann. Atomic percentage by Bornemann.

They belong to the same natural group as platinum and palladium, and amalgamation ought therefore to be impossible, judging from the analogy of platinum.

Palladium can, however, be amalgamated with difficulty if it is in a finely divided state, freshly precipitated and heated.

The copper-nickel alloys are much used in the industries and are made into coins. They wear very well. Mixed with zinc they are known commercially under such names as nickel silver, argentan, alpaka, German silver, argent allemand.

Silver-plated they are called Alfenide, Peru silver, argyrolith, &c.

German nickel coins are made of Cu 75 per cent., Ni 25 per cent.; American of Ni 12 per cent., Cu 88 per cent.

The whitest alloy contains 57·15 Cu, and 42·85 Ni, but it is most difficult to work.

"German silver" generally contains zinc, viz., Cu 50-66 per cent., Ni 13-18 per cent., Zn 19-31 per cent.

The more Zn it contains, the easier it is to cast, but this makes it less resistant to chemical influences.

Fisher's table of the various kinds of German silver gives the following percentage compositions :—

TABLE OF GERMAN SILVER ALLOYS.

Material	Per cent. copper	Per cent. nickel	Per cent. zinc	Per cent. iron	Per cent. lead	Per cent. tin	Properties and use
Parisian	62·24	16·56	13·42	3·26	0·15	0·22	Good white colour, very hard
Weldable ...	55·89	23·76	19·83	0·05	0·09	0·10	Pressed knife handles, colour like silver 0·806
For casting (*a*) ...	50·79	22·14	27·10	...	0·02	...	Fine art casting, dark silver colour
,, (*b*) ...	59·1	9·7	30·2	...	...	...	White blue, brittle
Sheffield German silver	45·7	17·1	37·2	...	...	...	Easily fusible, weldable with difficulty
High fusing German silver	45·7	34·3	20·0	...	...	...	Workable when cold, though with difficulty
For spoons ...	79·7	13·0	7·2	..	...	0·9	Yellowish, well weldable
English average	57·4	13·0	25·0	3·0	...	...	Very elastic and weldable
Argentan for plate	50·32	18·40	30·14	...	0·05	0·18	...
Chinese argentan	40·4	31·6	25·4	...	...	...	...

The so-called Alpaka silver contains :—

Per cent.	63·94 Cu	Per cent.	·04 Fe
,,	14·56 Ni	,,	·12 Sn
,,	19·24 Zn	,,	·03 Pb
,,	2·05 Ag		

Nickel bronze contains :—

Per cent. 60 Cu	Per cent. 20 Ni
„ 12 Zn	„ 8 Sn

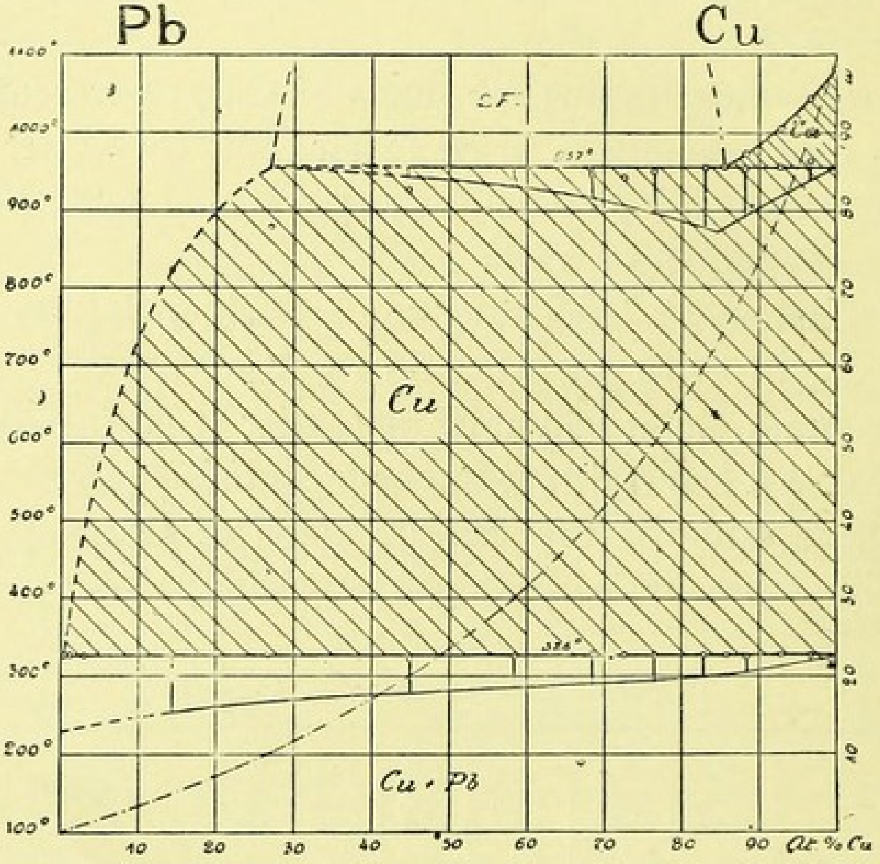


FIG. 27.—Copper—Lead according to Friedrich and Leroux. Atomic percentage by Bornemann.

(12) Copper—Lead, Cu-Pb.

These two form neither compounds nor mixed crystals, and are hardly miscible at all in the liquid state.

On account of this the alloys have practically no importance.

(13) Copper—Palladium, Cu-Pd.

In the liquid state these are miscible in all proportions and form a complete series of mixed crystals, but no eutectics.

According to Ruer, the colour is white, with upwards of 20 per cent. Pd, and the alloys are harder than their

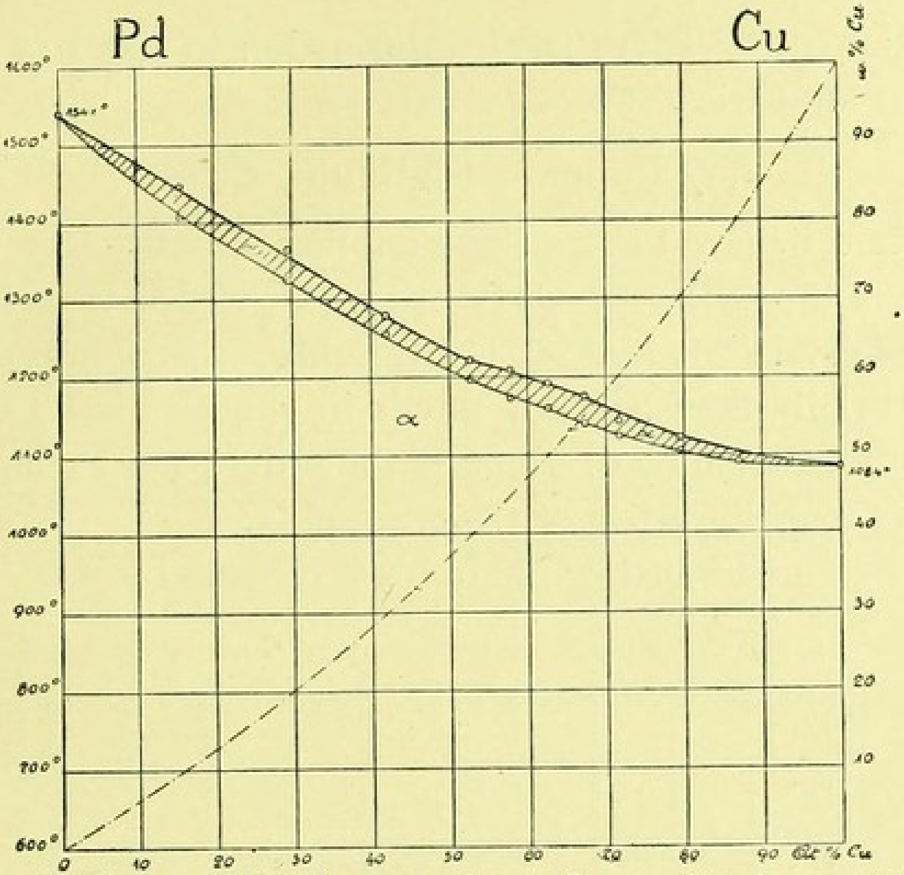


FIG. 28.—Copper—Palladium according to Ruer. Atomic percentage by Bornemann.

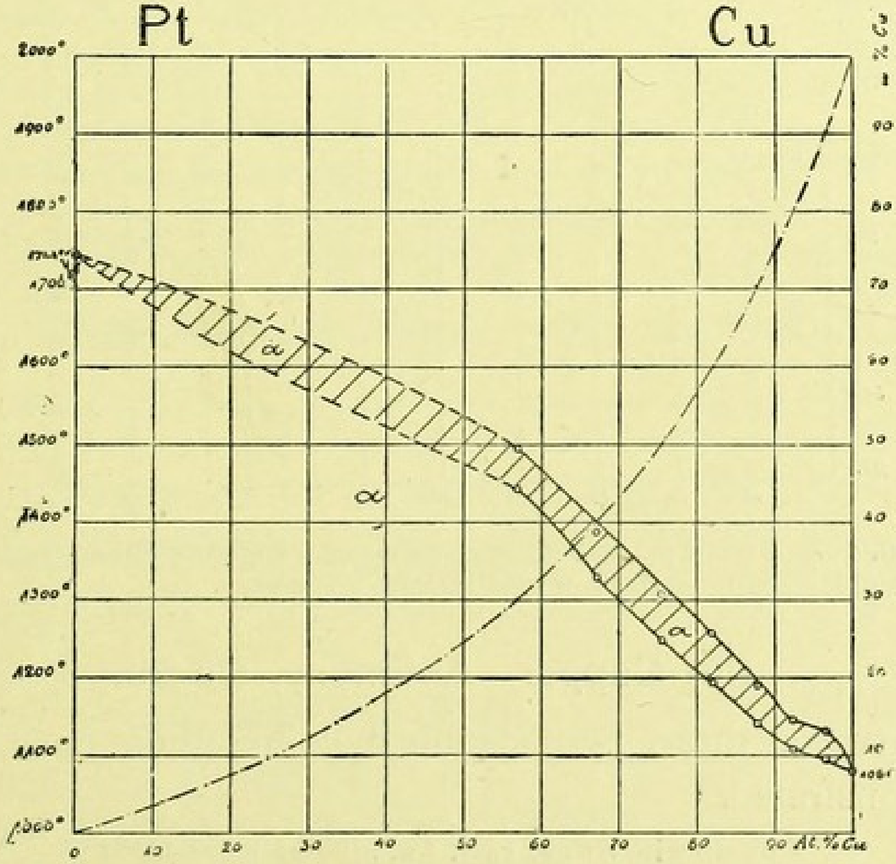


FIG. 29.—Copper—Platinum according to Doerinckel. Atomic percentage by Bornemann.

components. There is no information to hand of their use in industries.

(14) Copper—Platinum, Cu-Pt.

These behave towards one another in much the same way as the NiPd or CuPd pair. A complete series of mixed crystals is formed, but no eutectic or compounds. Industrially they are not much in request, but Cooper states that an alloy of 13 parts Cu and 3 parts Pt has the colour and properties of 18-carat gold.

It might be worth while to try it in dental work.

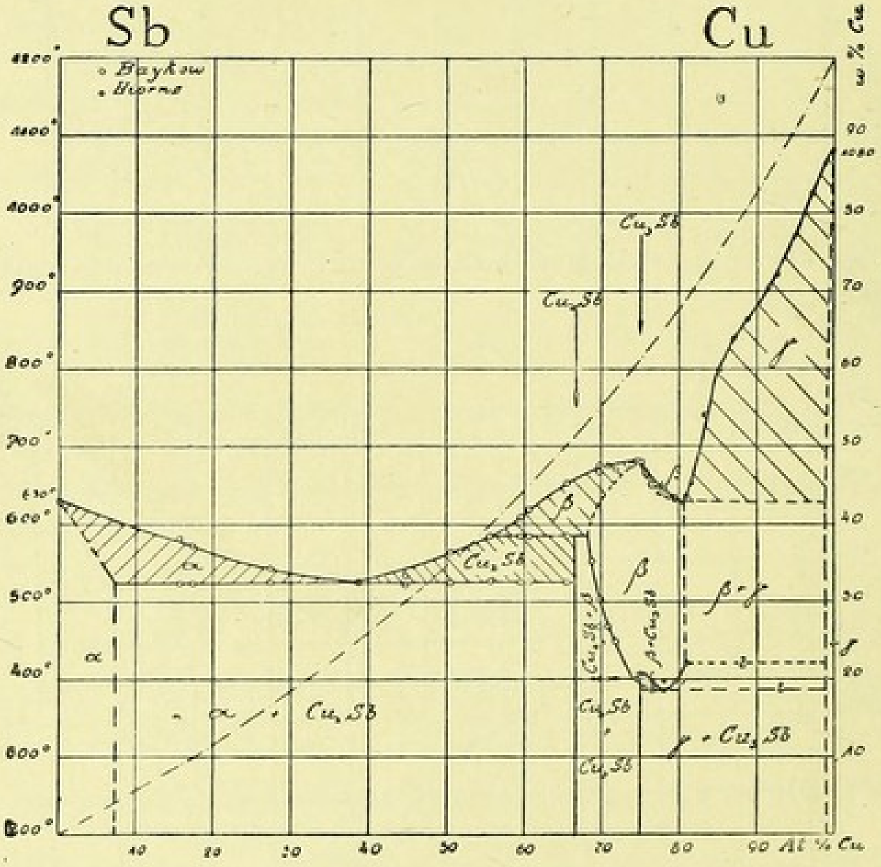


FIG. 30.—Atomic percentage by Bornemann. Copper-Antimony according to a combination from Baykow and Hiorns' researches.

(15) Copper—Antimony, Cu-Sb.

Between these, two chemical compounds have been demonstrated.

Cu_3 Sb with 61 per cent. Cu, melting point 600° C.
Cu_2 Sb ,, 51 ,, Cu, ,, ,, 660° C.

A saturated mixed crystal α is formed of 4 per cent. Cu and 96 per cent. Sb, and this has a eutectic with Cu_2Sb, which is composed of 26 Cu 74 Sb, melting at 525° C.

The mixed crystal γ is saturated with 99 per cent. Cu, 1 per cent. Sb, and it forms with Cu_3Sb a eutectic having 69 per cent. Cu and 31 per cent. Sb.

This melts at 630° C.

At a temperature of 630° C. a transformation takes place of γ into $\beta + \gamma$ and there are other changes at 415° C. and 388° C. which are shown in the diagram.

Sudden cooling will preserve the properties of the crystals first formed at the higher temperatures.

There are no known applications of these alloys in the industries.

(16) Copper—Tin, Cu-Sn.

These metals form some very important alloys which are known commercially as bronze.

(1) The chemical compound Cu_3Sn, melting at 720° C.; composition, 61·7 per cent. Cu; 38·3 per cent. Sn.

(2) There has been a good deal of discussion about the alloy Cu_4Sn, as many metallurgists consider it to be identical with the mixed crystal ϵ. Altogether five mixed crystals have been identified, of which the most important are:—

(1) The α crystal, containing 77·5—100 per cent. Cu. This is saturated with 88 per cent. Cu. The great majority (88—100 per cent. Cu) of these mixtures are stable, which means that they do not change while cooling.

The crystals with 77—88 per cent. Cu crystallize first into $\alpha + \beta$ crystals, and then β changes to ϵ. With 64·5—77 per cent. Cu, they finally become pure ϵ crystals.

To prevent this transformation, the casting must be cooled suddenly as soon as it crystallizes, that is, at 700—800° C.

(2) The γ crystal, containing 61·7—48 per cent. Cu, changes at 620° C. into the δ crystal.

(3) The δ crystal has 61·7—8 per cent. Cu. It again re-crystallizes into the compound Cu_3Sn after cooling under 400° C.

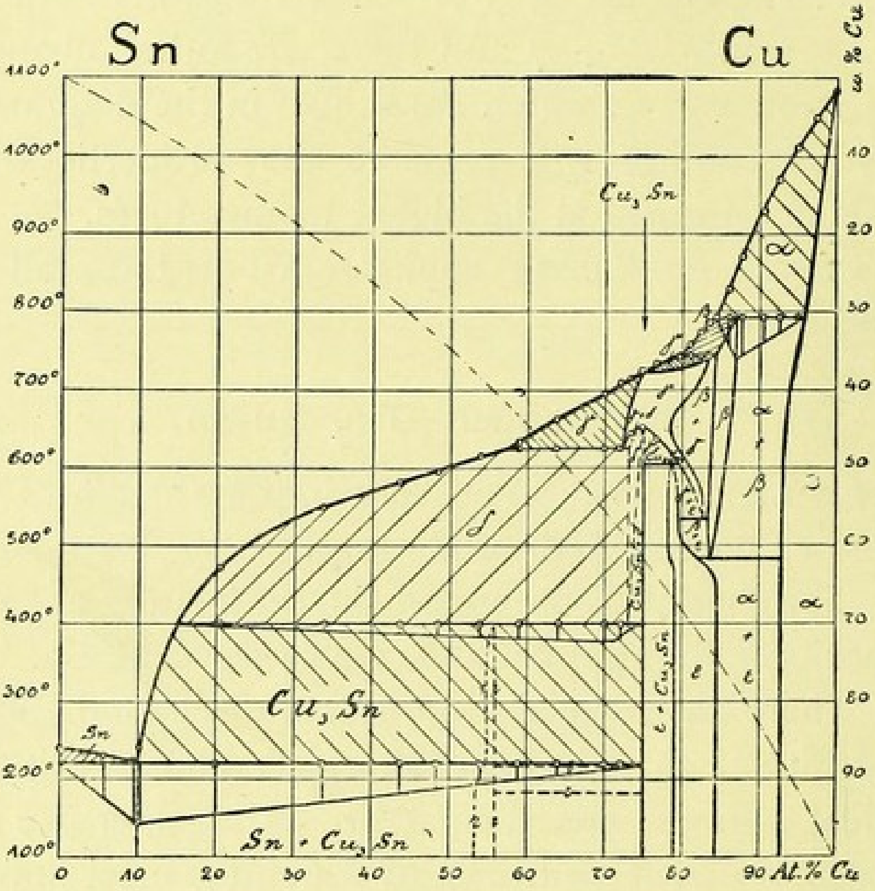


FIG. 31.—Combined from the researches of Shepherd and Blough, and of Giolitti and Tavanti. Atomic percentage drawn by Bornemann.

The reason is the diminished solubility of tin in copper below that temperature.

The eutectic with 6 per cent. Cu melts at 220° C. Below this temperature all ordinarily cooled alloys, having from 0—61·7 per cent. Cu, show the combination Cu_3Sn + pure Sn; from 61·7—67 per cent. Cu, $\epsilon + Cu_3Sn$; from 67—75 per cent. Cu they crystallize as pure ϵ crystals; from 74·5—88 per cent. Cu form $\alpha + \epsilon$ crystals; and 88—100 per cent. Cu form pure α, as pointed out before.

The special requirements of many industries are met by many different alloys, of which the best known are given below.

But to the author it seems that by a careful observance of the points given above with regard to retaining certain special properties in compounds and mixed crystals by sudden cooling, a better use might be made of them.

The big works which employ skilled metallurgists have found many of these things out, but they keep their methods secret.

The Method of Alloying.—The copper is brought to the melting point, and then melted tin is poured into it and stirred. The tin loses about 25 per cent. by oxidation.

DR. TH. FISCHER'S TABLE OF PROPERTIES.

Cu	Sn	Colour of alloy	Fracture	Properties
%	%			
99	1	Light red ...	Granular ...	Soft and tough.
95	5	Reddish yellow	Finely granular	Harder.
90	10	...	Coarsely granular	Files well.
80	20	Light golden yellow	Rather coarse ...	Harder, but can be filed.
75	25	Pale yellow ...	Smooth... ...	,, ,, ,,
65	35	Greyish white	Not so smooth...	Breaks easily; hard to file.
50	50	,, ,,	Less smooth ...	Breaks easily.
40	60	Dull white ...	,, ,, ...	Easier to file and polish.
30	70	,, ,, ...	Rather flaky ...	,, ,, ,,
20	80	,, ,, ...	,, ,, ...	Files and polishes easily.
10	90	White ...	Granular ...	Files easily.

Small quantities can be melted in a crucible, but larger amounts must be dealt with in a puddling furnace. The fuel used should contain no sulphur. To make it pour more easily, a little zinc is sometimes added to the bronze, but should never exceed 2 per cent.

Phosphor Bronze.—By adding ·05 to ·2 per cent. phos-

phosphorus the alloy will be completely deoxidized, but no phosphorus will be found in it after crystallization. Composition :—

	Copper Per cent.		Tin Per cent.		Phosphorus Per cent.
(*a*)	90·86	...	8·56	...	~~1·96~~ ·196
(*b*)	94·71	...	4·39	...	~~0·53~~ ·053

Tungsten Bronze.—By alloying 10 per cent. wolfram with 90 per cent. Cu, a very resistant bronze is obtained, which is used for bearing necks of axles and telegraph wires.

Gun Metal.—This should have but the least possible additions of zinc and phosphorus.

Origin		Copper Per cent.		Tin Per cent.
French	...	90·09	...	9·90
Prussian	...	90·9	...	9·1
English	...	89·3	...	10·7
Turkish	...	95·20	...	4·71

Engineers' Bronzes.—These have the following compositions according to the properties required :—

Use		Zinc		Tin		Copper
Locomotive axle boxes ...	...	8·0	...	10·0	...	82·0
Railway carriage axle boxes	...	2·0	...	20·0	...	75·0
Steam pipes	...	2·0	...	17·0	...	80·0
Tops	...	2·0	...	10·0	...	88·0
Carriage wheel sockets ...	...	2·60	...	9·7	...	87·7
Mechanical instruments ...	...	5·10	...	12·8	...	81·20
Small cast goods	...	—	...	5·88	...	94·12
Malleable shovels	...	16·4	...	33·6	...	50·0

Bell Metal.—This contains 77 to 80 per cent. Cu, and 20 to 23 per cent. tin ; silver bell metal : 41·5 Cu, 58·5 Sn ; tamtam : 78·51 Cu, 20·27 Sn, 0·18 Ag, 0·52 Pb; speculum-metal : 40 to 70 Cu + 60 to 30 Sn.

Fischer thinks that the best alloys are those composed of 68·21 per cent. Cu + 31·79 per cent. Sn (Cu_4Sn ?). German and French copper coins are composed of 95 Cu + 4 Sn + 1 Zn. The admixture of lead in any quantity makes bronze worthless for industrial purposes.

(17) Copper—Zinc, Cu-Zn.

The copper-zinc alloys play an important rôle in manufactures. They are known by such names as messing-brass, tombac, delta, aich, and sterro-metal, the latter having small percentages of iron, tin, lead, manganese, and phosphorus.

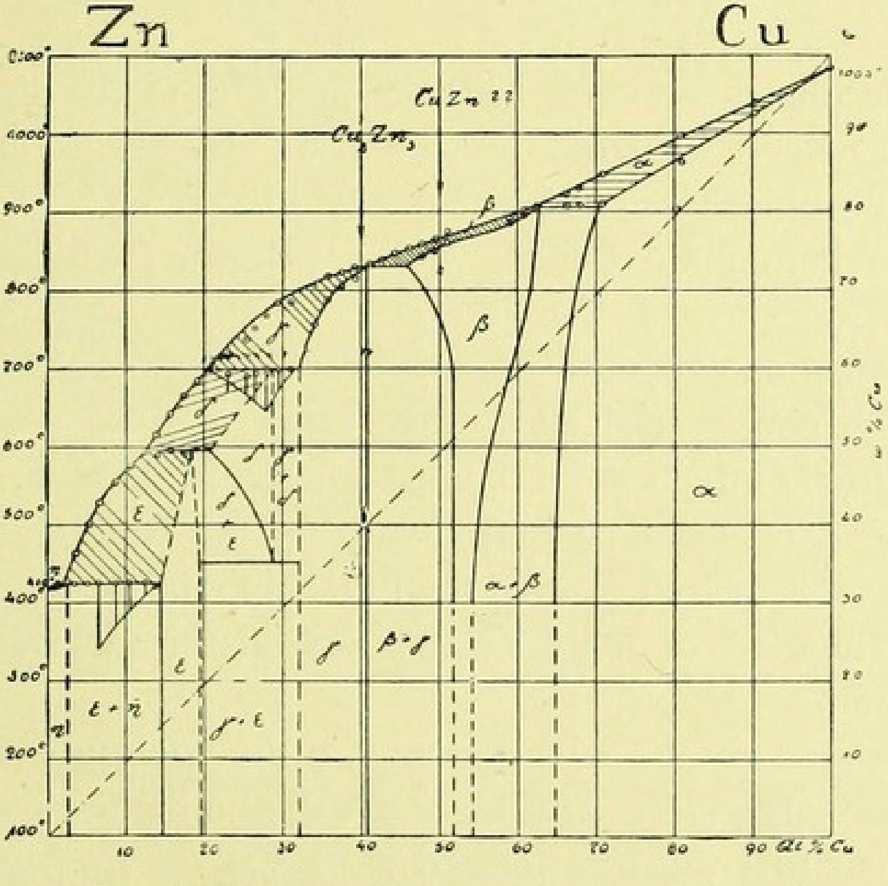


FIG. 32.—Copper—Zinc, combined from the researches of Shepherd and Tafel. Atomic percentage by Bornemann.

The two metals form a series of mixed crystals, which all show a homogeneous structure under the microscope, and many investigators, including Le Chatelier, regarded them as a series of true compounds.

Shepherd and Tafel, however, think that there are no real chemical combinations.

Bornemann is certain of the existence of the compound Cu_2Zn_3, but uncertain about CuZn. Tamman believes in the existence of $CuZn_4$ besides.

According to Shepherd, there are six different mixed crystals formed by alloying these metals, and their composition after complete crystallization is as follows :—

	Per cent.		Per cent.
$\alpha =$	100 – 64 Cu	Between	
$\beta =$	54 – 51 ,,		54 – 64 Cu $= \alpha + \beta$
$\gamma =$	40 – 31 ,,		51 – 40 ,, $= \beta + \gamma$
$\delta =$	unstable		
$\epsilon =$	19 – 14 ,,		31 – 19 ,, $= \gamma + \epsilon$
$\eta =$	2·5 – 0 ,,		14 – ~~25~~ 2·5 ,, $= \epsilon + \eta$

The phases between these are mixtures of the different kinds of crystals, some of which are able also to change polymorphically at various heats while cooling.

The compound Cu_2Zn_3 would be formed with 39 per cent. Cu.

In manufactures the *α* and *β* crystals play the chief part. All the commercial alloys take more than 50 per cent. and most of them more than 64 per cent. Cu.

The *α* crystal is saturated with 70 per cent. Cu + 30 Zn, and if there is less Zn than this amount the alloy will be composed of unsaturated *α* crystals of various composition.

Between 70 and 64 per cent. Cu the cooling *α* crystal will dissolve more zinc than it will at a higher temperature, so that the first formed *β* crystal returns again to the *α* phase.

Certain conclusions can be drawn from these figures as to the properties of the different alloys. Briefly put, the properties of the *α*, *β*, *γ*, *δ*, *ϵ* crystals vary within the limits indicated, according as the Cu decreases and the Zn increases, until the respective crystals are fully saturated.

Manufacturers found many of these things out a long time ago in actual working, and that is why we find these compositions of the alloy in everyday use at the present time.

Tombak.—Alloys having 18 per cent. zinc are known by the name tombak, and it is their golden yellow colour which makes them popular. They melt at 1,000° C. By adding a little tin the melting point is lowered and they take on more of the characteristics of bronze.

Sheet-brass is made of the purest copper and zinc. It contains 27-37 per cent. Zn and melts at over 900° C. It is used in the manufacture of wire and sheets.

Cast brass contains up to 40 per cent. Zn. It is made from scrap and is seldom pure.

Fine cast brass is pure.

Mosaic gold contains (see also under "Tin," page 139), according to Fischer, from 33·3-36·7 per cent. Zn and melts at about 900° C. It is so called from its colour.

The melting points of alloys rich in zinc are as follows :

With 60 per cent. Zn melting point 840°C.
70 per cent. ,, ,, ,, 780°C.
83 per cent. ,, ,, ,, 670°C.

The addition of Fe and Mn, &c., make the brass almost as hard and elastic as steel, as well as very resistant to atmospheric effects.

Tin and lead lower the melting point a good deal and make it cast more easily.

Various ternary and quaternary alloys owe their existence to the properties conferred by these various additions.

Aich's metal is golden yellow and as hard as steel :

Cu Per cent.	Zn Per cent.	Fe Per cent.
60 – 60·2	38 - 38·2	1·6 – 1·8

Stereo metal is tougher and harder than steel :—

Cu Per cent.	Zn Per cent.	Fe Per cent.
55·33	41·80	2·66 rest loss.
60	38·13	1·50 ,,

Delta metal is malleable when red hot, it is hard and tough. It is prepared by dissolving Fe in Zn (soluble up to 8 per cent.), which is then added to the melted brass.

Cu 60 per cent., Zn up to 40 per cent., Fe up to 3 per cent. and other variations:

Cu Per cent.	Zn Per cent.	Pb Per cent.	Fe Per cent.	Mn Per cent.	S Per cent.
55·94	41·61	0·72	0·87	0·81	~~0·13~~ ·013

Durenametal of the Dühren works consists of:—

Cu Per cent.	Zn Per cent.	Sn Per cent.	Fe Per cent.	Al Per cent.
65	30	2	1·5	1·5

Aluminium brass has an addition of 1·5-8 per cent. Al. It is hard and elastic and, like phosphor bronze, is very resistant to acids and gases.

VII. SILVER AND ITS ALLOYS.

(See Table, page III, 36-37).

Silver (Ag. 107·93) was widely known in prehistoric times, and was used in Egypt for coinage before the Christian era.

Distribution.—Silver ores are found in nearly all parts of the world, generally in association with ores of other metals.

They are found in combination with sulphur, selenium, tellurium, antimony, arsenic, and the halogens chlorine, bromine, iodine, and even in sea-water and sea-weed.

Refining.—In ancient times this was done by first alloying with lead. In the 16th century various amalgamating processes were introduced into Peru, such as the Patio, Kröhnke, Tina and Caro processes.

In Europe (Saxony) it was not till the end of the 18th century that the process of amalgamation in vats was used to free the silver from the ores.

In the 19th century the salt lixiviation process was discovered by Augustin and Ziervogel, after whom the method is named. The ore is converted into chloride by roasting with salt (NaCl), then dissolved and precipitated.

At the same time Pattison discovered a way to melt out of very poor ores the eutectics, which are richer in silver but become fluid at 305° C. and separate at this temperature from the lead, which crystallizes between 305° and 327° C. (see diagram, AgPb, page 89).

Quite recently electrolytic methods have been introduced.

The zinc desilverization process: At high temperature zinc combines chemically with lead and silver.

The Zn combination consists of a union of AgZn and Pb, which forms a ternary compound, and where gold is present the quaternary AgAuPbZn.

These two melt at much higher temperature and have a lower specific gravity then their eutectic, so that they can be almost completely skimmed off with the ladle. The fluid remainder is poor in silver.

Pure silver is white in colour. It is harder than gold and copper, and next to gold is the most malleable of the metals.

Its melting point is 961° C. It is inclined to oxidize during melting, and when it cools the oxygen escapes (spits), or remains enclosed in the form of bubbles, making the metal porous. For this reason pure silver is unsuitable for castings.

The difference in specific gravity between the cast and cold-worked metal is remarkable.

Thus the specific gravity of cast silver is 10·454-10·511; of cold-worked is 10·554-10·567.

Pure silver remains white on exposure to the air, but in the presence of sulphurous gases it becomes coated with a dark brown sulphide.

This can be avoided by keeping silver articles wrapped in paper which has been soaked in acetate of zinc.

Contact with human excreta, such as sweat, &c., which contain chlorines, causes a chloride to form on silver, which can, however, be easily washed off with ammonia.

The metal is completely dissolved by dilute nitric, and by strong sulphuric acid. Strong hydrochloric acid has hardly any effect at all.

(1) Silver—Aluminium, Ag-Al.

These metals form :—

(1) The chemical compound Ag_2Al, with 89 per cent. by weight of Ag and 11 per cent. Al. It melts at 720° C.

(2) The compound Ag_3Al, with 92 per cent. Ag and 8 per cent. Al. Melting point 770° C.

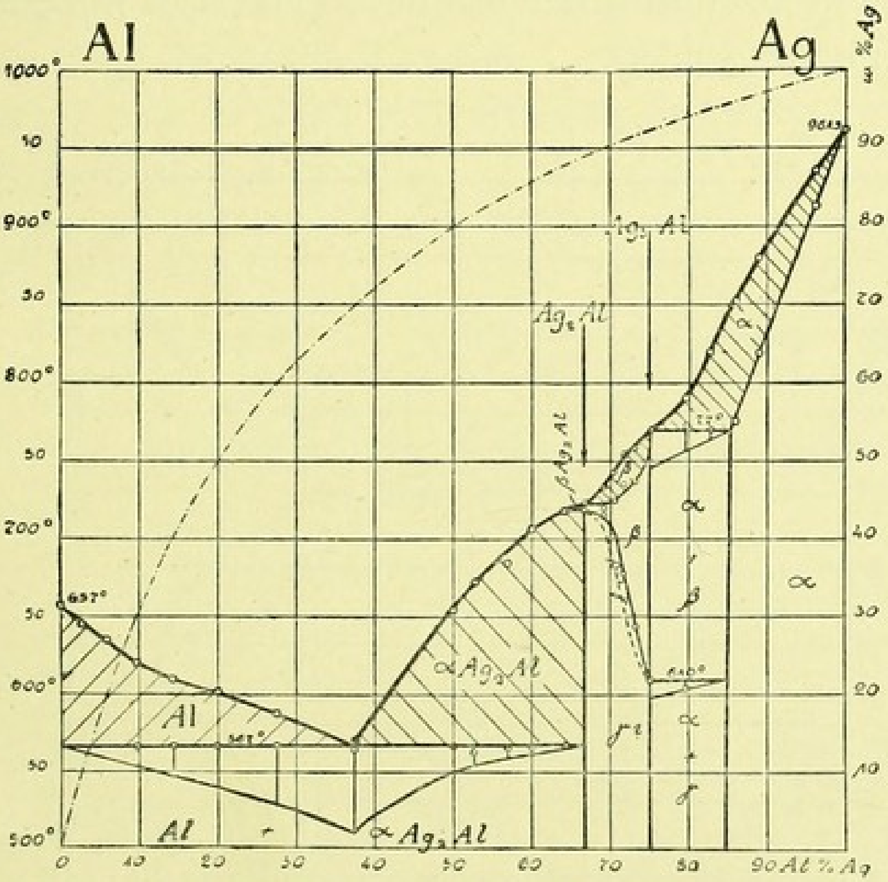


FIG. 33.—Silver—Aluminium according to Petrenko. Atomic percentage after Bornemann.

(3) The mixed crystal a ~~α~~, which is a solid solution of Ag_3Al with Ag.

(4) The mixed crystal β, formed by the two compounds.

(5) The eutectic of 70 per cent. Ag, and 30 per cent. Al, melting at 567° C ~~per cen~~t. This is formed between Ag_2Al and pure Al.

The mixed crystal *α*, containing up to 4 per cent. Al, remains constant on cooling.

With 4 to 7 per cent. Al the *α* crystal changes into *α* + *β* at 770° C. The *β* changes into *γ* probably between 710° C. and 610° C.

All alloys having up to 7 per cent. Al (according to Petrenko) keep their colour on exposure to the air.

The author has been unable to find that these alloys are put to any industrial use beyond that of ingredients in aluminium solders.

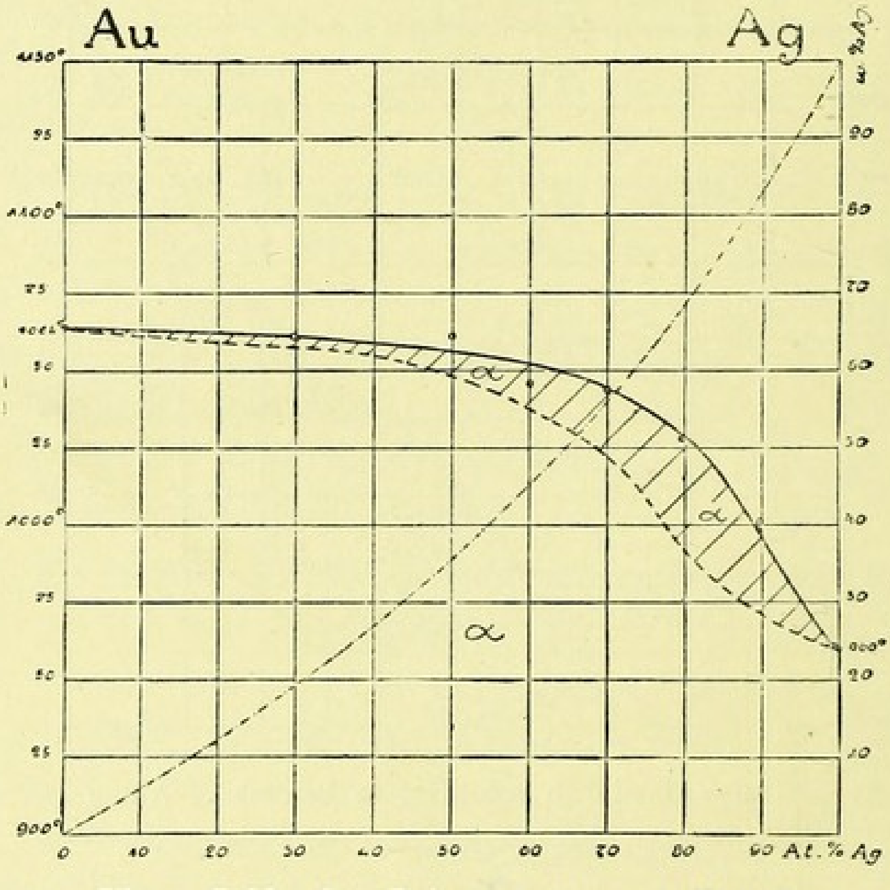


FIG. 34.—Silver—Gold, after Roberts-Austen and Kirk Rose. Atomic percentage after Bornemann.

(2) Silver—Gold, Ag-Au.

These metals are miscible in all proportions in the fluid and crystalline state, and form a complete series of mixed crystals.

It is noteworthy that the melting point of gold is hardly lowered at all, even by the addition of silver in amount up to 50 per cent.

An alloy of 60 Ag-40 Au requires more than 1,050° C. to melt it.

This circumstance, coupled with the fact that these metals mix easily in comparison with the copper alloys (*see* copper-silver, copper-gold), makes silver the best metal for alloying with gold.

Moreover, the tensile strength of gold is considerably increased by the addition of Ag.

Copper may be used for colouring purposes, but only in the smallest quantities.

The annexed diagram will explain a few other minor points.

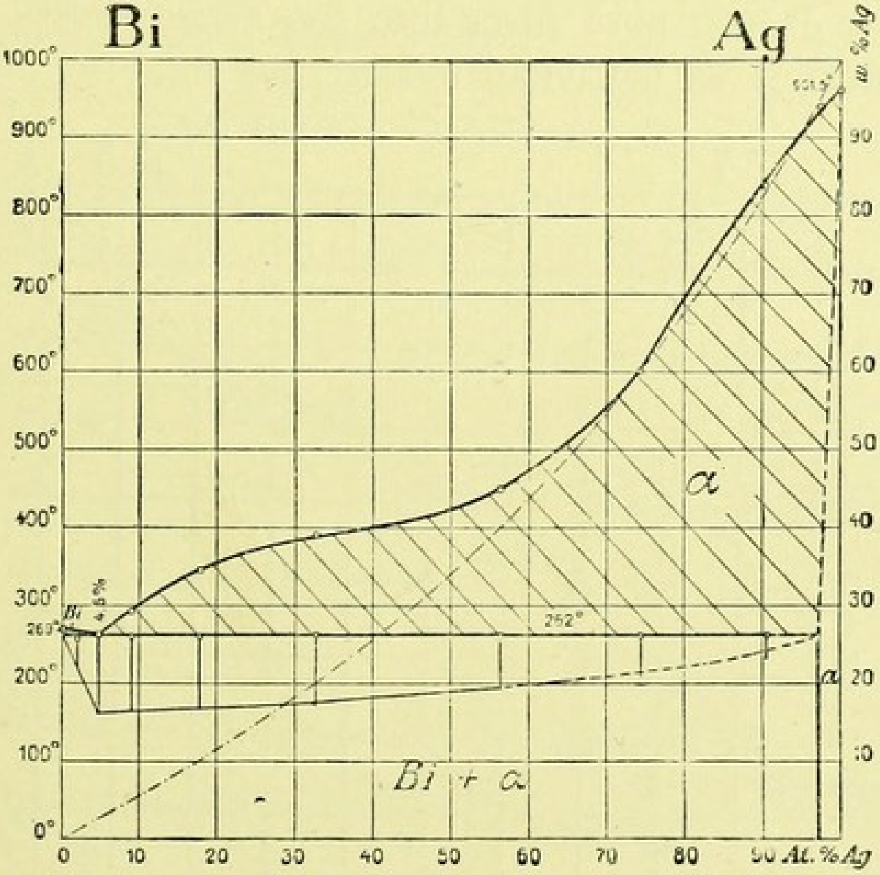


FIG. 35.—According to Petrenko. Atomic percentage by Bornemann.

(3) Silver—Bismuth, Ag-Bi.

These are miscible in all proportions in the liquid state.

They form mixed crystals with 2½ to 100 per cent. Ag, which are saturated in proportions up to 95 per cent. Ag, with 5 per cent. Bi, and crystallize out as such.

The eutectic is composed of 97·5 Bi, 2·5 Ag, and it melts at 262° C.

The composition of the crystallized alloys can be easily seen from the diagram.

They consist up to 2·5 per cent. by weight of Ag, of Bismuth + eutectic (*α* + Bi), with 2·5 to 95 per cent. Ag of *α* + eutectic (Bi + *α*), over 95 per cent. Ag of pure *α*.

On account of their bismuth content, these alloys have an interest for dentists in relation to the amalgam (tin-silver) problem.

They change pure silver into the mixed crystal, and so influence its behaviour towards the tin.

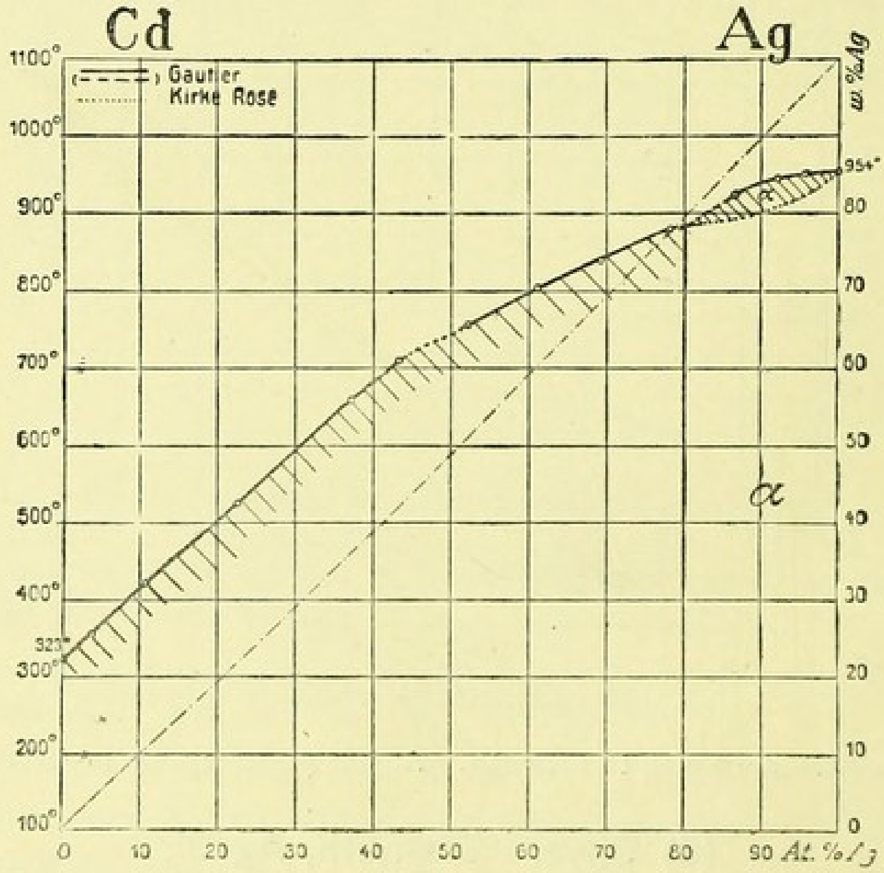


FIG. 36.—According to Gautier and Kirk Rose. Atomic percentage by Bornemann.

(4) Silver—Cadmium, Ag-Cd.

The diagram shows that these alloys have not been much studied, as the crystallization of the alloys with silver at less than 80 per cent. has been stated only at their beginning.

The combination Ag_4Cd most probably exists (79 per cent. Ag, 21 per cent. Cd by weight) and forms mixed crystals with pure Ag as well as pure Cd.

According to Wood, an alloy of 1 to 2 parts Ag with 1 part Cd is so malleable that it can be beaten very thin. Silver and Cd in equal parts are also very malleable, but by no means so tough.

Two parts Cd and 1 part Ag make a brittle alloy.

Cadmium is also used as an ingredient in some of the tin-silver amalgams and in solders.

(5) Silver—Cobalt, Ag-Co.

These two metals cannot be mixed in any state, so that any commercial use of them is out of the question.

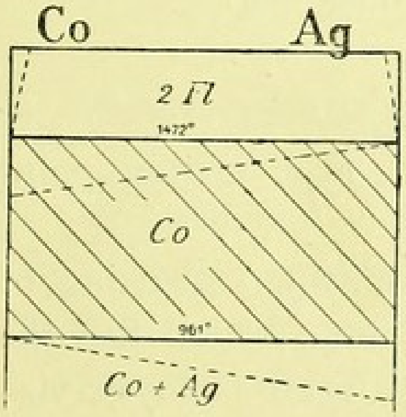


FIG. 37. – According to Petrenko.

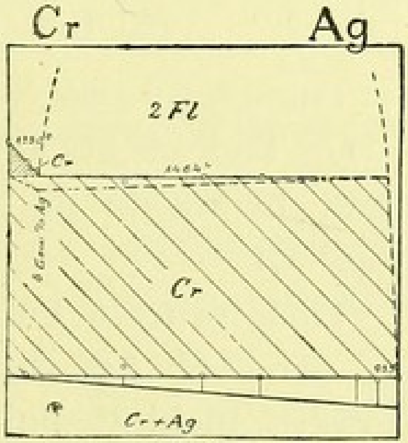


FIG. 38. — According to Hindrichs.

(6) Silver—Chromium, Ag-Cr.

These two metals are well-nigh immiscible either solid or liquid, because chromium will crystallize out of a molten mixture at 1,464° C., and silver at 953° C.

1454° C.

A slight lowering of the melting points suggests a limited mixture in liquid state, having at any rate less than 5 per cent. Cr + 5 per cent. Ag each. Apparently these alloys are of no practical use.

(7) Silver—Iron, Ag-Fe.

The remarks *re* silver-cobalt apply also to this pair. The alloys are useless. This shows that silver is no good for soldering iron.

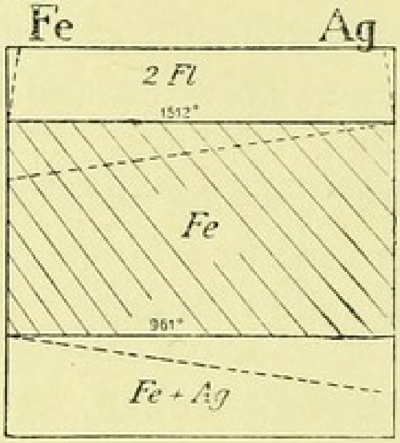


FIG. 39.—According to Petrenko.

(8) Silver—Magnesium, Ag-Mg.

These form two combinations :—

(1) The chemical compound Ag_3Mg having 60 per cent. by weight Ag and 40 per cent. Mg ; melting point 540° C.

This forms a eutectic with pure Mg, consisting of 48 per cent. Ag, with 52 per cent. Mg., which has the lowest melting point of all the AgMg alloys, viz., 469° C.

(2) The chemical combination AgMg, having 82 per cent. Ag, 18 per cent. Mg ; melting at 820° C.

(3) These two compounds together form the mixed crystal *a*, which forms also on the Ag side, *i.e.*, between Mg Ag, and Ag.

(4) The mixed crystal β forms a eutectic of 90 per cent. Ag, and 10 per cent. Mg, melting at 750° C., with:—

(5) The β crystal of pure silver + the compound AgMg.

The diagram shows the behaviour clearly.

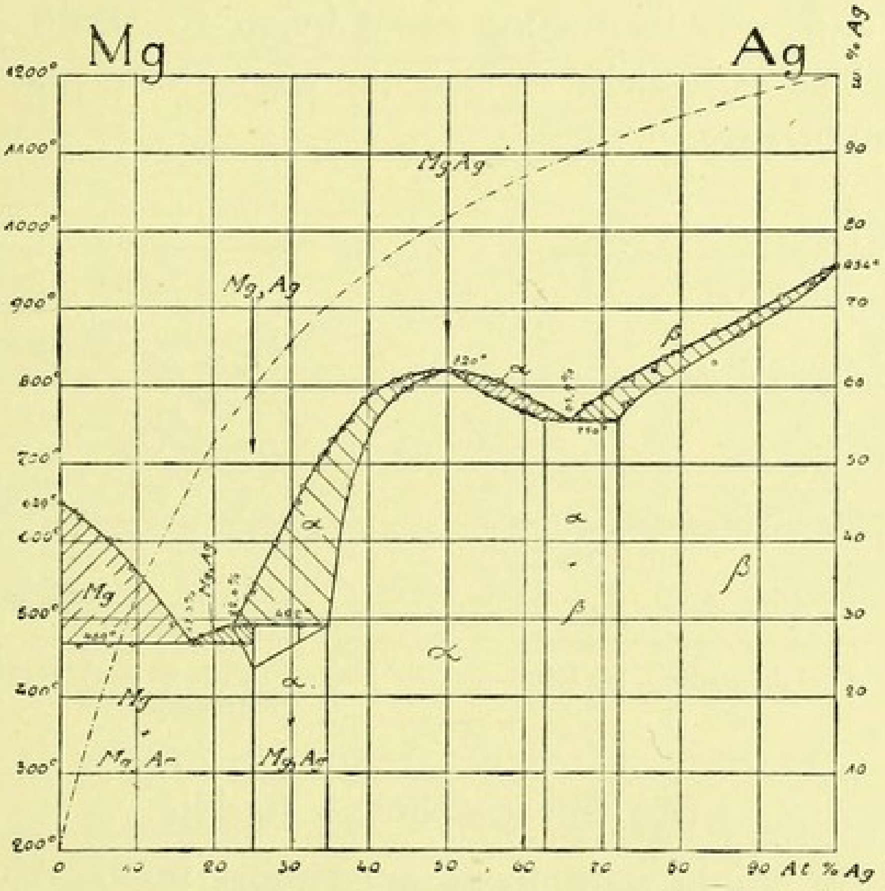


FIG. 40.—According to Zemczuzny. Atomic percentage by Bornemann.

The addition of Mg makes Ag harder and less malleable. The compounds are very brittle, and so are the alloys, which are rich in Mg.

The latter will decompose water more easily than will pure Mg.

A freshly cut surface of a 91 per cent. Ag alloy has a yellowish colour. Parkinson expresses a negative view with regard to the possible use in the trades of these alloys, because they are brittle and easily affected by exposure to the air.
]

(9) Silver—Manganese, Ag-Mn.

This pair resembles Ag-Co, Fe-Cr and others.

About 8 per cent. Ag will dissolve in Mn in the liquid state, and this brings its melting point down to 1,145° C.

Two per cent. Mn will dissolve in Ag in the liquid state and lower its melting point by 10° C. Both metals crystallize separately, so that the alloys have practically no importance.

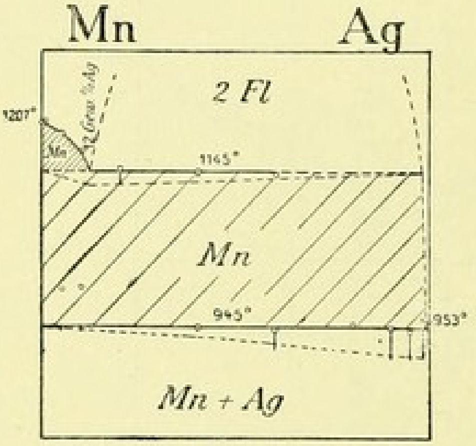


FIG. 41.—According to Hindrichs.

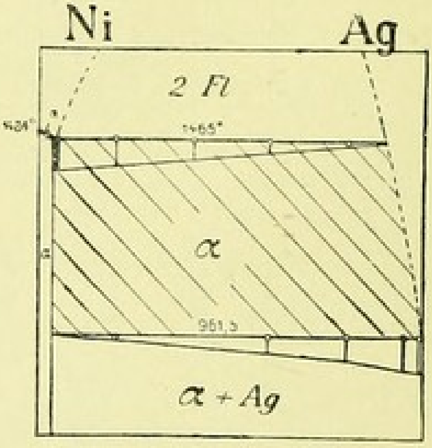


FIG. 42.—According to Petrenko.

(10) Silver—Nickel, Ag-Ni.

In the liquid state these are almost immiscible. Ni will take up to 4 per cent. Ag and form the mixed crystal *a*. Molten silver will dissolve up to 10 per cent. Ni, but it crystallizes out again at its own melting point.

The mixed crystal *a* should have a sphere of usefulness because the 4 per cent. Ag has an ennobling influence upon Ni.

(11) Silver—Lead, Ag-Pb.

Silver and lead mix in the liquid state in all proportions.

The eutectic between them consists of 98 per cent. Pb and 2 per cent. Ag, and melts at 305° C.

There are no chemical compounds or mixed crystals.

In consequence of this a lead alloy containing silver can be ennobled by melting out the eutectic, while the same process permits the extraction of richer eutectic out of very poor ores.

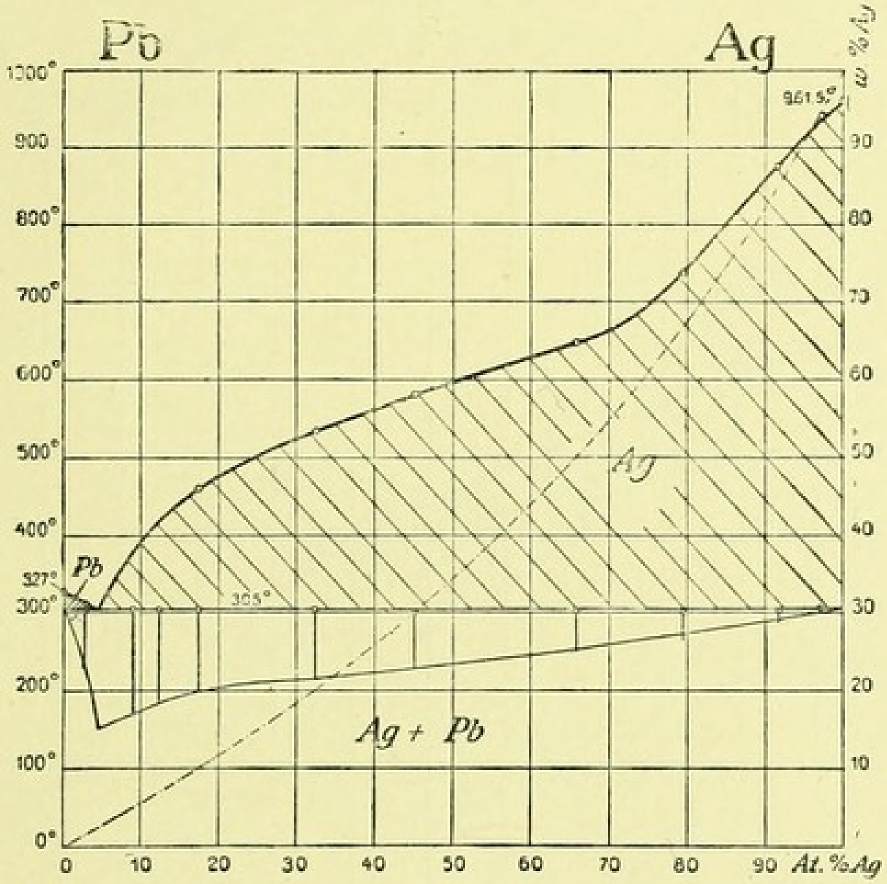


FIG. 43.—According to Petrenko. Atomic percentage by Bornemann.

The zinc process of refining has been described above. The quartation method of cupelling gold with lead and litharge, after first alloying with Ag, may be mentioned, but apart from this these alloys do not appear to be used in the trades.

(12) Silver—Palladium, Ag-Pd.

These two form a complete series of mixed crystals. They make very hard alloys which take a beautiful light polish.

The author has not been able to discover that these alloys are used at all in any trades.

The addition of Pd to Ag might be used with advantage to raise the melting point of the latter, but to obtain perfect homogeneity in the result Ruer says that very slow cooling is necessary—several hours, in fact.

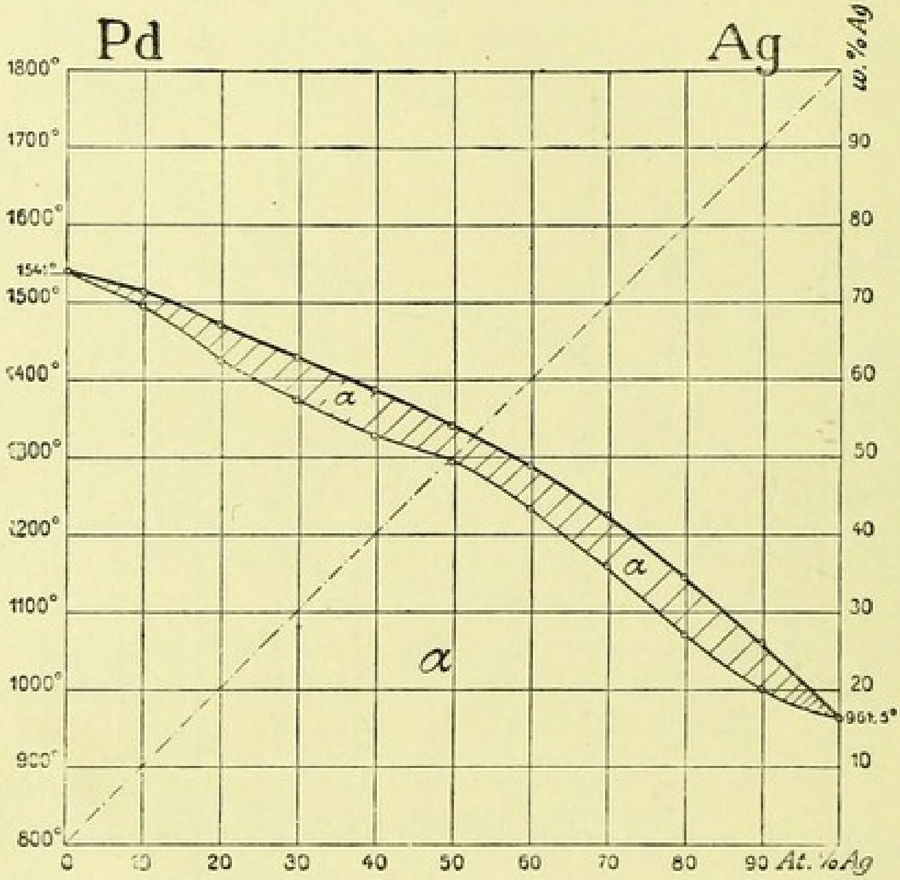


FIG. 44.—According to Ruer. Atomic percentage by Bornemann.

(13) Silver—Platinum, Ag-Pt.

All alloys between these two metals have not been thoroughly worked out, because proportions of Pt of over 80 per cent. are difficult to deal with owing to their high melting point.

The *a* crystal is noteworthy. This forms in the alloys from 52·5-100 per cent. Ag.

Doerinckel says that the saturated mixed crystal is very like the formula Ag_2Pt, but an actual chemical combination has not been proved.

It is this *a* crystal which is used for the making of dental plates under the name of dental alloy.

Its most distinct properties are obtained with 47·5 Pt and 52·5 Ag, but this does not necessarily mean that it is better for dental purposes than that ordinarily sold for such work, which at best consists of not more than 33·3 per cent. Pt and 66·6 per cent. Ag.

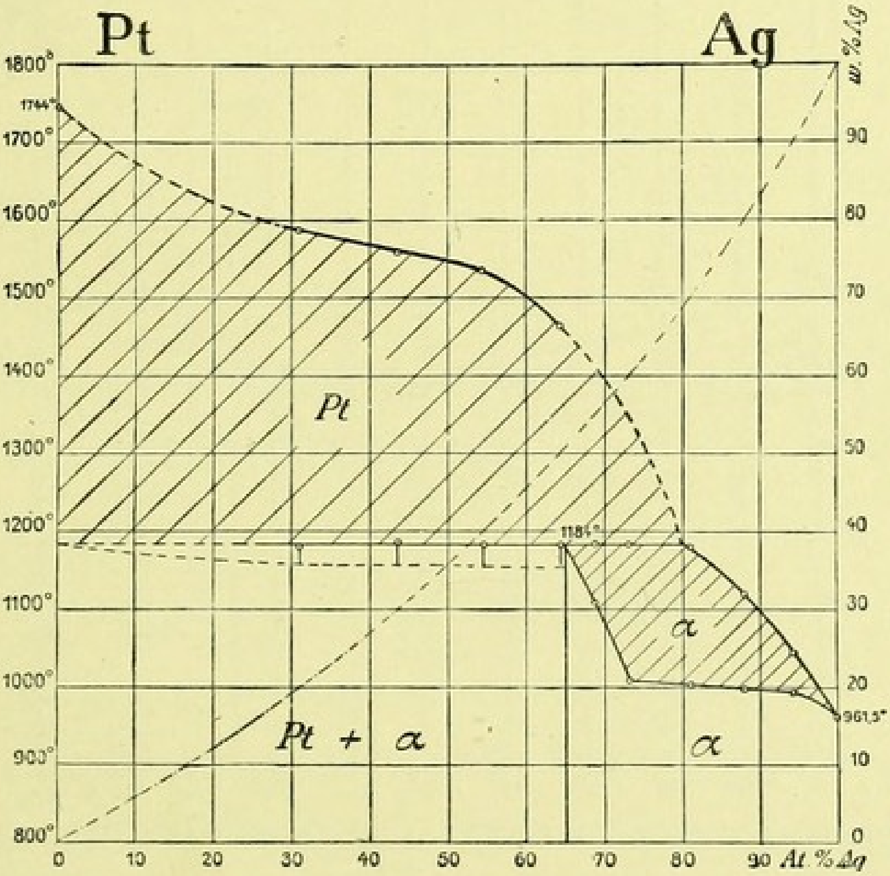


FIG. 45.—According to Doerinckel. Atomic percentage by Bornemann.

The objection to this alloy in dental work is its brittleness in comparison with 18-carat gold, and in consequence of this many dentists have abandoned its use entirely.

Another factor against it is the enormous increase in the price of Pt, which used to be cheap, so that now dental alloy is rather neglected.

Its melting point with 47·5 Pt is 1184° C.; it should be kept fluid a long time and not cooled quickly.

(14) Silver—Antimony, Ag-Sb.

These metals form the compound Ag_3Sb, having 72·5 per cent. Ag, 27·5 Sb, and crystallizing at 560° C.

This compound forms the mixed crystal with pure Ag, which is saturated at 85 per cent. Ag + 15 per cent. Sb, thus showing a close analogy to the Ag-Sn alloys.

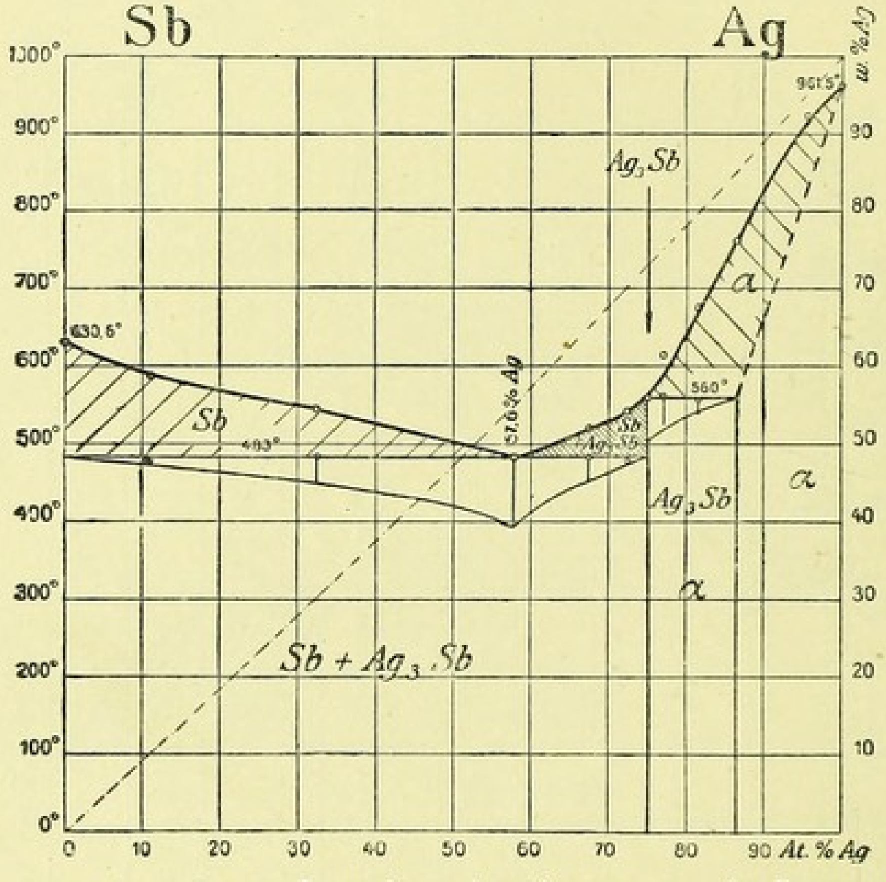


FIG. 46.—According to Petrenko. Atomic percentage by Bornemann.

There is also a eutectic here which consists of 55 per cent. Ag, 45 per cent. Sb, and melts at 483° C.

The mixed crystal *a* can only be obtained by cooling very slowly. These alloys do not appear to be used commercially.

(15) Silver—Tin, Ag-Sn.

Silver and tin form the compound Ag_3Sn.

Between Ag_3Sn and Ag, there is a mixed crystal *a*, which does not change during cooling, if the silver stands at more than 82 per cent.

Below 480° C., α + Ag_3Sn divides into β + Ag_3Sn while at 232° C. Ag_3Sn also undergoes a change.

Petrenko concludes from this, that the alloy from 82 per cent. Ag to 48 per cent. Ag must be cooled suddenly to preserve the mixed crystal which he shows in his diagrams.

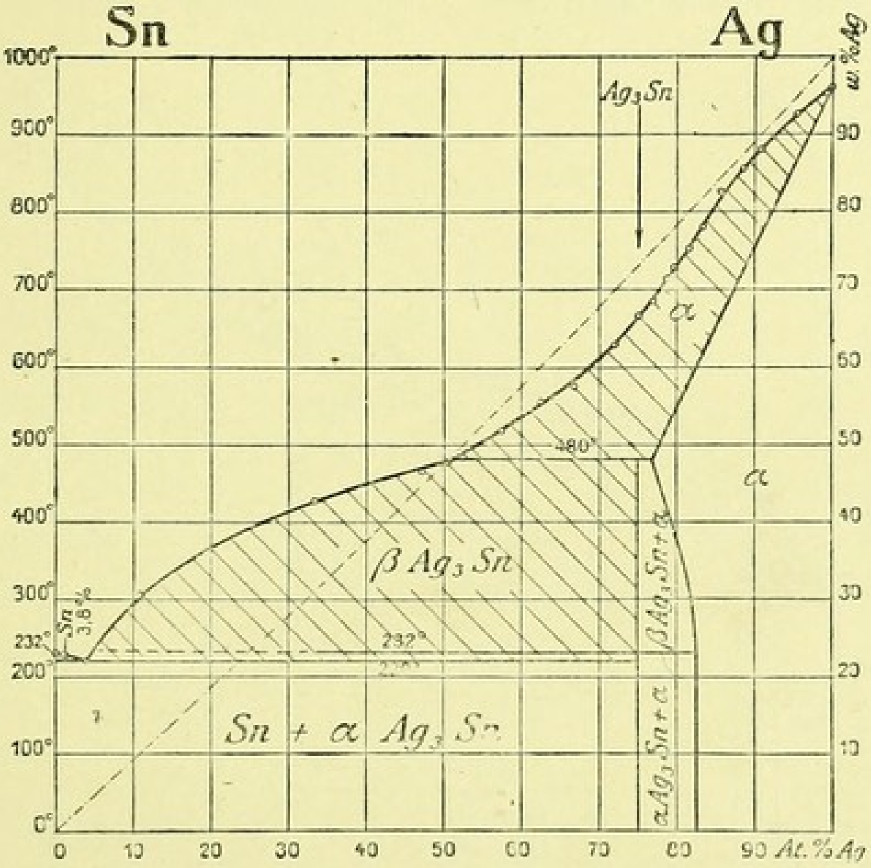


FIG. 47.—According to Petrenko. Atomic percentage by Bornemann

Ag 3·8 per cent., Sn 96·2 per cent., form a eutectic melting at 220° C.

The tin-silver alloys will further be discussed in the chapter on amalgams.

(16) Silver—Zinc, Ag-Zn.

The mutual reactions of these metals have not yet been completely worked out.

Only the alloy Ag_2Zn_3 and AgZn have been demonstrated with any certainty. Neither of these changes while cooling, and they show homogeneity of structure under the microscope only after very slow reduction of temperature.

There is a doubt as to the existence of Ag_3Zn_2 and Ag_2Zn_5, because two different kinds of crystals are in evidence, and there is no actual proof of polymorphism given by cooling curve.

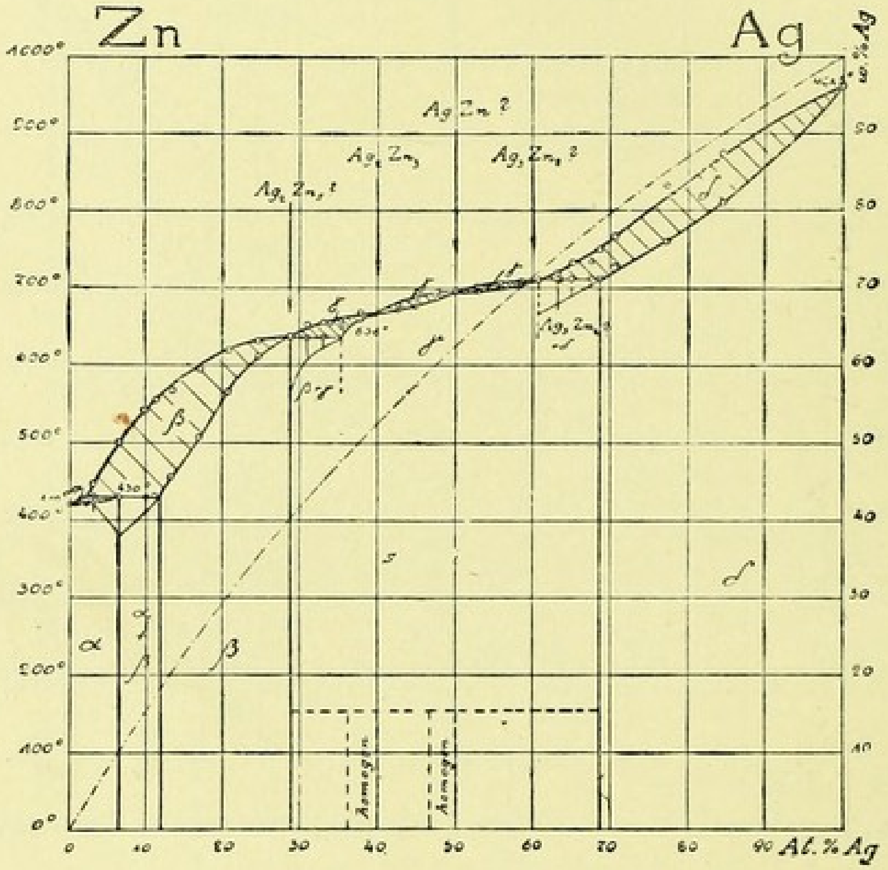


FIG. 48.—According to Petrenko. Atomic percentage by Bornemann.

Two kinds of crystals are found in these alloys with :

21·7-37·7 per cent. by weight.
51—60 ,, ,,

The ones between are homogeneous.

The different compounds form mixed crystals with one another and with the pure metals. They are marked in the diagram as *a*, *β*, *γ*, *δ*.

One per cent. Zn is often added to Ag to prevent oxydation and to avoid the so-called spitting during crystallization.

According to Fischer an alloy of two parts Zn and one of silver (β crystal) closely resembles pure silver and is easy to work. The melting point is about 630° C.

This may be the doubtful chemical compound Ag_2Zn_5 (60 per cent. Zn, 40 per cent. Ag) which melts at about 635° C.

VIII. GOLD AND ITS ALLOYS.

For gold-silver ref. "Silver." For physical properties *see* table p. 36-37.

Gold, Au (atomic weight 197·2, specific weight 19·32, melting point 1,063·5), has always been considered the most precious of the metals because of its colour and lustre, and because it is unaffected by exposure to atmospheric influences.

Recently, however, it has had to take second place to platinum in some respects, as the latter now costs more than £250 per kilo.

In the most ancient times of which we have historical records, and probably even before that, gold was used for jewellery and other small *objets d'art*, and for gilding and as a medium of exchange (coin).

Sixteen hundred years B.C. gold was mined in Ethiopia and Nubia, and Herodotus mentions places in the Altai and Ural mountains and on the Indus and in Gaul, where it was found in the sands of rivers.

The Romans also had rich goldfields, and in later times the discoveries in America and Australia and in Southern and Western Africa have greatly augmented the world's supply of the precious metal.

Long before Christ gold was used by the dentists of those days, and the Law of the Twelve Tables permitted it to be buried with the dead.

Where the gold is found "pure" in quartz or river sand, it is first separated by washing from the lighter sands, &c.,

with which it is mixed, and then the remaining mass is melted to obtain the regulus of nearly pure gold.

As much of it may be lost in the washing process, the water is generally passed afterwards over baths of mercury which retain the gold as an amalgam.

The process of amalgamation is often used for the extraction of gold. The mixing is done by means of iron balls moving around in an iron bowl.

Sulphur, antimony or arsenical combinations of gold have to be roasted before amalgamating with mercury.

For the extraction of gold combined with silver in crude lead the reader is referred to the practical part of this book under "Cupellation."

Very poor ores containing from ·001 per cent.—·01 per cent. gold are generally treated by a wet process and the gold precipitated as chloride.

$$AuCl_3 + 3FeSO_4 = Au + FeCl_3 + Fe_2(SO_4)_3.$$

By this process, which will be referred to again, almost all the gold is extracted.

The cyanide process also has now become practicable since the introduction of the electric deposit method of Siemens and Halske.

In a watery solution of potassium cyanide metallic gold will form a soluble aurous cyanide of potassium.

Under the influence of atmospheric oxygen the following reaction takes place, according to Elsner:

$$2Au + 4KCN + H_2O + O = 2AuK(CN)_2 + 2KHO.$$

The lye holding the gold is now made to flow through containers in which there are iron (anodes) and lead plates (cathodes) arranged alternately, so that the liquid must flow around all of them in a serpentine line.

The cyanide is deposited on the iron plates and the gold goes to the lead, which is melted in a furnace and separated into lead oxide and gold.

Formerly the gold was extracted from the solution simply by adding zinc.

Gold Refining.

When gold is obtained in the crude state it always contains silver. There are several ways of refining it, of which the most commonly used are as follows:

(*a*) *Melting with Sulphur.*—A very early and simple method. The silver combines with the sulphur to form a sulphide and the gold remains at the bottom of the pot.

The gold goes through this process again, while the amalgam of sulphur and silver is melted up with lead and iron into litharge, and from this the silver is extracted.

(*b*) *Where there is much gold, sulphide of antimony instead of pure sulphur is used.*—The amalgam then consists of sulphide of silver and the regulus of a mixture of gold and antimony, from which the antimony is liberated by roasting and the silver treated as before.

Any gold remaining in the silver is extracted by the wet process.

(*c*) *Cementation method.*—Iron—silver mixtures containing gold are heated with common salt (NaCl), green copperas ($FeSO_4$=ferrous sulphate) and brick-dust (alum).ma

Free chlorine is given off, which forms a chloride with the silver and is absorbed by the brick-dust.

The gold remains as regulus with about 10 per cent. Ag.

(*d*) *Miller's method, with small percentages of Ag.*—Chlorine gas is passed through the molten metal till orange-yellow gases appear.

The AgCu and Au become converted by this means into chlorides, which separate and rise to the surface while the gold regulus remains at the bottom.

(*e*) *Quartation.*—In this process silver is added to the alloys till it is in the proportion of one to three gold (~~quartz~~). (quart)

The alloy is then rolled out thin and heated in a glass or platinum crucible with nitric acid, specific gravity 1·25 — 1·35.

Dense red fumes of nitric peroxide are given off, and when these cease the silver nitrate can be poured off, leaving the gold behind. This is now melted with potassium nitrate and borax.

The $AgNO_3$ solution is precipitated with NaCl and the silver from its chloride which remains after filtering is separated with Zn.

$$AgNO_3 + NaCl = NaNO_3 + AgCl.$$

(*f*) *Affinage.*—This process is best for alloys containing .3—60 per cent. Au, but not more than 10 per cent. Cu.

The alloy, which has been rolled out thin, is boiled in an iron vessel with concentrated H_2SO_4 (sulphuric acid). The silver and Cu are converted into sulphates and the gold remains behind.

$$2Ag + 2H_2SO_4 = Ag_2SO_4 + 2H_2O + SO_2.$$
$$Cu + 2H_2SO_4 = Cu\ SO_4 + 2H_2O + SO_2.$$

When the reaction is complete the sulphates are poured off and the gold is washed and melted with sodium bisulphate or nitrate of potash to free it from any remaining Ag.

If there is any Pt present it will combine in the dross and form a platinic oxide of potassium. The sulphate of silver can be diluted and precipitated as metal with metallic Cu.

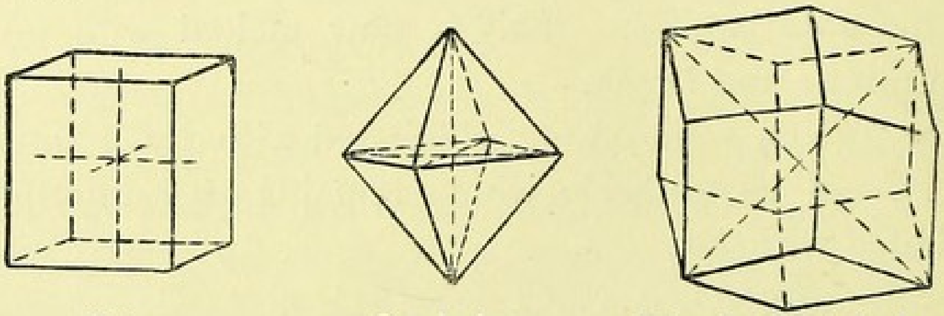
The concentrated copper lye is crystallized into $CuSO_4$ or blue vitriol.

Gold which is absolutely pure chemically is obtained by precipitation from the chloride.

Two parts HCl specific gravity 1·16, with 1 part HNO_3 specific gravity 1.45, go to form the so-called aqua regia.

One part of gold is dissolved in 3 to 4 parts by weight of the liquid, which is then evaporated.

When the liquid becomes of a deep ruby colour it is allowed to cool and the gold chloride crystallized out (fig. 49).



Cube. Octahedron. Rhombadodekahedron.

FIG. 49.

This then is washed several times with alcohol and thoroughly dried.

The chloride is next dissolved in distilled water to which a few drops of HCl are added to precipitate any Ag which may be left.

The solution is allowed to stand a few days and filtered. It should still have a slightly acid reaction.

Pure gold is precipitated from the solution by the addition of (any of the following) oxalic acid, sulphurous acid, sulphate of iron or hydrogen dioxide.

If oxalic acid is used the solution must be slightly warmed. This agent throws down the gold in spongy masses of most diverse structures. The formula reads like this :—

$$2AuCl_3 + 3H_2C_2O_4 = 6HCl + 6CO_2 + 2Au.$$

Precipitation with oxalic acid has the disadvantage of causing the gold to form like a skin on the vessel walls. This inconvenience can, however, be avoided by covering them first of all with filter paper.

If hydrogen dioxide is used there is none of the previous difficulty, but a flaky and easily filtered precipi-

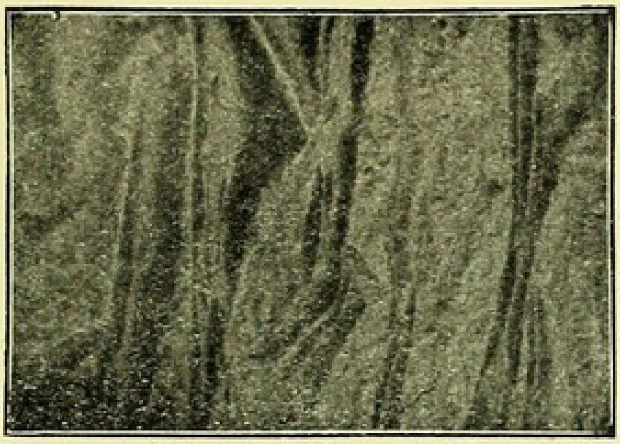


FIG 50.—Orange gold for gilding $\frac{1}{900}$ mm. alloyed with copper and silver. x 160. (Zeiss, Apochromat, in short setting, 8 mm.)

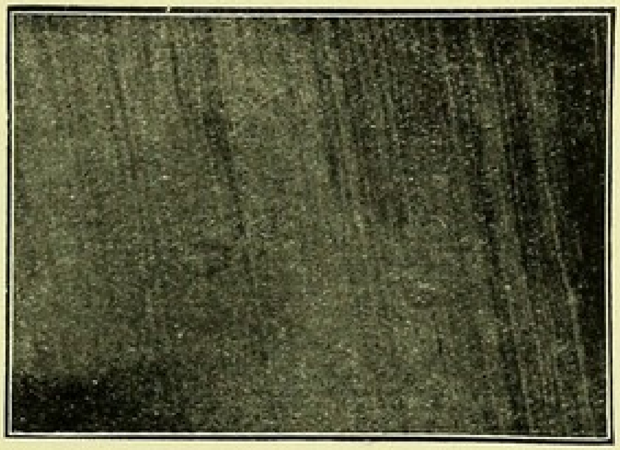


FIG. 51.—Dental gold foil, No 40, non-annealed. x 160.

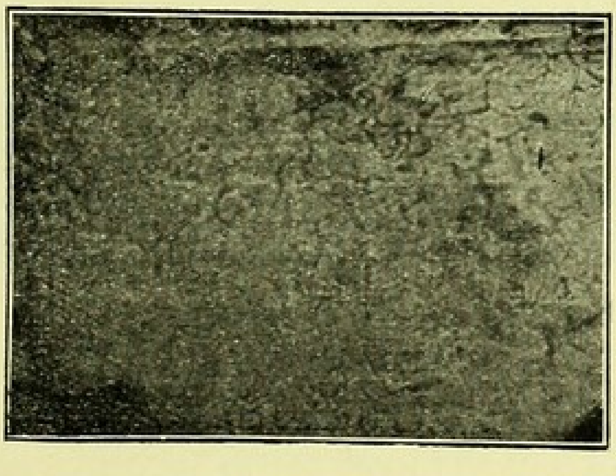


FIG. 52.—Dental gold foil, No. 40, annealed. x 160.

tate of pure gold is obtained (figs. 50, 51, 52, 53) after addition of sodium or potassium nitrate.

This is filtered and the filtrate tested with a few drops of stannous chloride ($SnCl_2$) which gives a purple colour if any gold remains, in which case more H_2O_2 would be used and the process repeated.

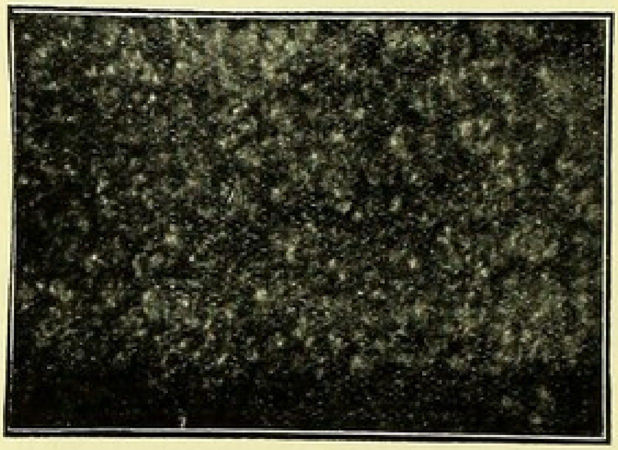


FIG. 53.—So-called Solila gold. x 160.

FIG. 54.—So-called Velvet gold. x 160.

The precipitate is next dried and then boiled with water and again dried and afterwards melted.

Sulphurous acid and sulphate of iron precipitate the gold in the form of a brown powder.

Fine gold is not much used because of its extreme softness.

For gilding it is beaten into foils as thin as $\frac{1}{9000}$ mm. and these allow the green rays of light to pass through.

Thicker foils from $\frac{1}{80}$ to $\frac{1}{800}$ mm. are used by dentists for the filling of teeth.

It is a peculiar property of the gold by virtue of which the crystals are separated by heating and when cooled can still be welded together with the hammer.

Other metals, if at all, are weldable but white hot.

Gold extracted by electrolysis can be used in the same way as the other gold if heated.

These gold crystals exhibit the most diverse forms according to the manner in which they are obtained (figs. 53 and 54).

(1) Gold—Aluminium, Au-Al.

Four compounds have been demonstrated :—

(1) Al_2Au, melting at 1,060° C., the same as pure gold, though the alloy only consists of 78·5 Au and 21·5 Al, and thus corresponds to 19-carat gold.

It forms a eutectic with pure Al (8 per cent. Au, 92 per cent. Al), melting at 647° C. According to Bornemann (p. 58) the compound is purple coloured.

(2) $AlAu_2$, melting point 625° C., contains 93·3 Au, 6·7 Al, and is equivalent to 22·4-carat gold.

It forms a eutectic with Al_2Au (AlAu ?), having 91·5 Au and 8·5 Al, which melts at 569° C.

(3) Al_2Au_5, melting point 550° C. ; this contains 94·5 Au, 5·5 Al.

(4) $AlAu_4$, melting point 545° C., containing 96·5 per cent. Au and 3·5 per cent. Al.

The two last form a eutectic having 96·3 Au and 3·7 Al, which melts at 327° C.

The low melting point (327° C.) with a content of 3·7 Al is in remarkable contrast with the high one (1,060° C.) at a content of 21·5 per cent. Al. These alloys would seem to be worth trying in dental work.

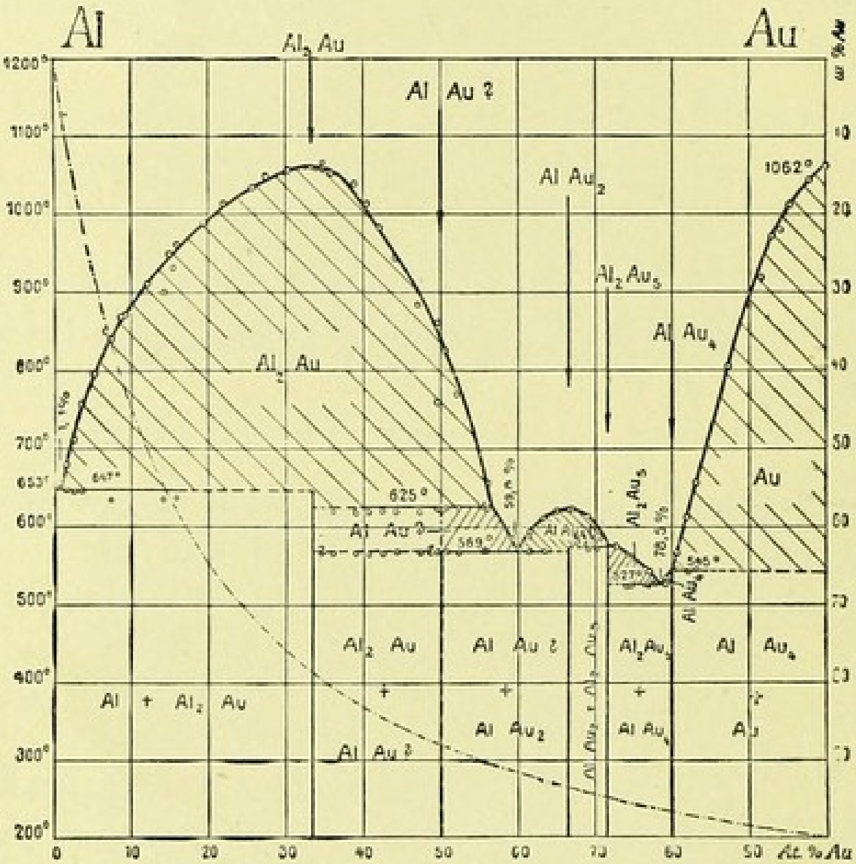


FIG. 55.—Gold—Aluminium according to Heycock and Neville; atonic percentage by Bornemann.

The author's personal trials of them indicate that with a high percentage of Au they become too hard and brittle.

AuAl alloy is known to commerce as Nuremburg gold, and has a composition of 90 per cent. Cu with 10 per cent. of the compound Al_2Au (*vide* CuAu).

(2) Gold—Bismuth, Au-Bi.

These form the mixed crystal *a* which is saturated with 96 per cent. by weight of Au and 4 per cent. Bi.

Between the *a* crystal and pure Bi lies the eutectic having the composition of 18·8 per cent. by weight of

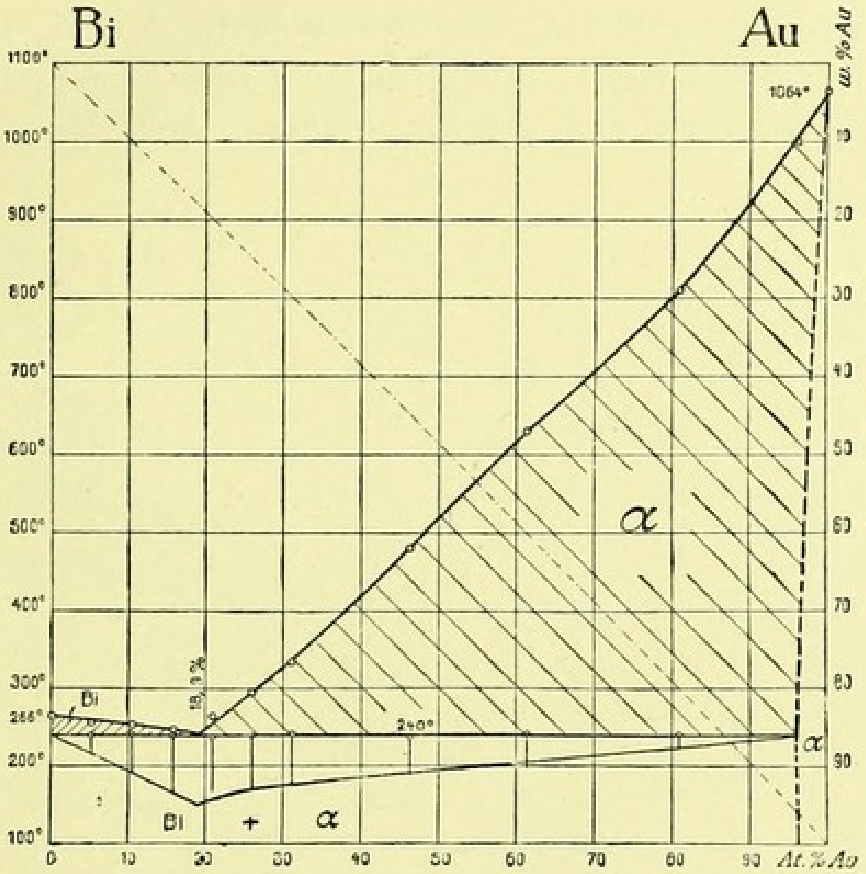


FIG. 56.—Gold—Bismuth according to Vogel. Atomic percentage by Bornemann.

Au and 81·2 Bi, melting at 240° C., so that the crystallized alloy consists between 0 and 18·8—96 per cent. Au of the mixed crystal and the eutectic. The pure γ crystal contains over 96 per cent. of pure gold.

Bi is used to lower the melting point of Au for solders and casting.

(3) Gold—Cadmium, Au-Cd.

These alloys are only used as solders. They form two chemical combinations:

(1) Au_4Cd_3, melting point 623° C. This contains 70 per cent. Au and 30 per cent. Cd.

The compound forms the γ crystal with pure Au, which is saturated at 82 per cent. Au and 18 per cent. Cd.

(2) $AuCd_3$, melting point 493° C. This consists of 36·5 Au with 63·5 Cd and forms with Au_4Cd_3 the β crystal. There is a eutectic with pure Cd which has 12·5 per cent. Au, 87·5 per cent. Cd, and melts at 303° C.

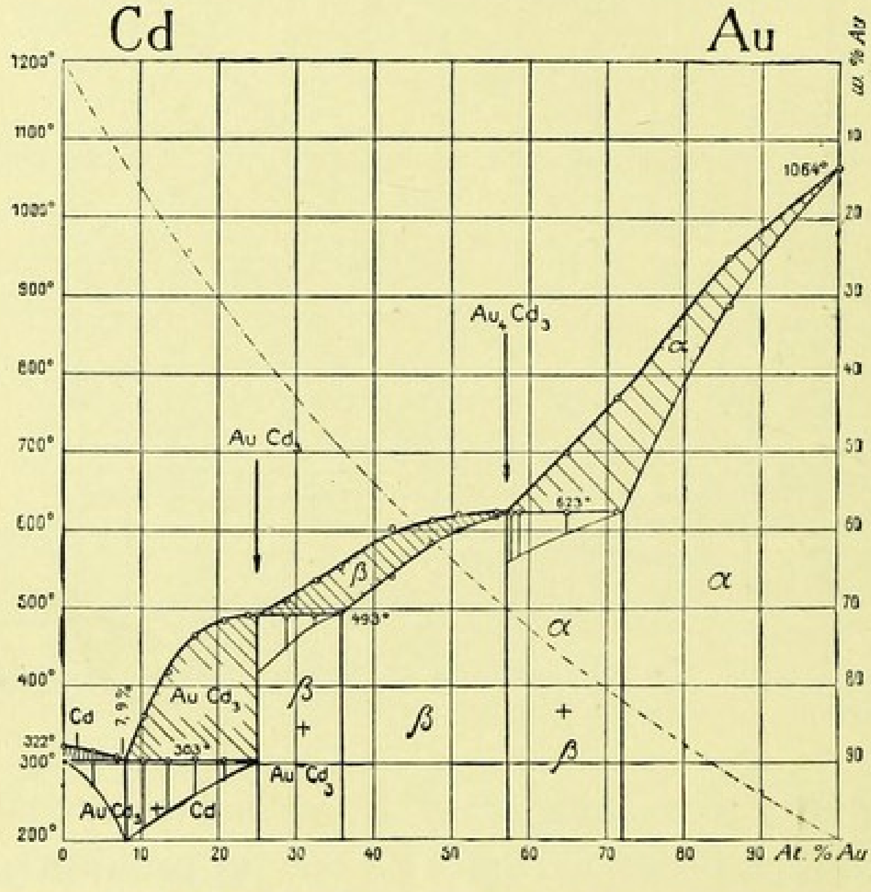


FIG. 57.—Gold—Cadmium according to Vogel. Atomic percentage by Bornemann.

The objection to the use of Cd for lowering the melting point of gold is that it has also a low boiling point, namely, 763° C.

The result is that there are often porosities in soldered work, because this temperature is easily exceeded in that operation.

Better ways of lowering the melting point of Au are to be found by the use of Zn, Bi, Sb and Sn.

(4) Gold—Iron, Au-Fe.

These two form mixed crystals with a hiatus in the series. The transformation of the γ crystal into γ + δ at 1,168° C. and into β + δ at 832° C. and into α + δ at 740° C. are shown clearly in the diagram (see also "Iron," p. 117).

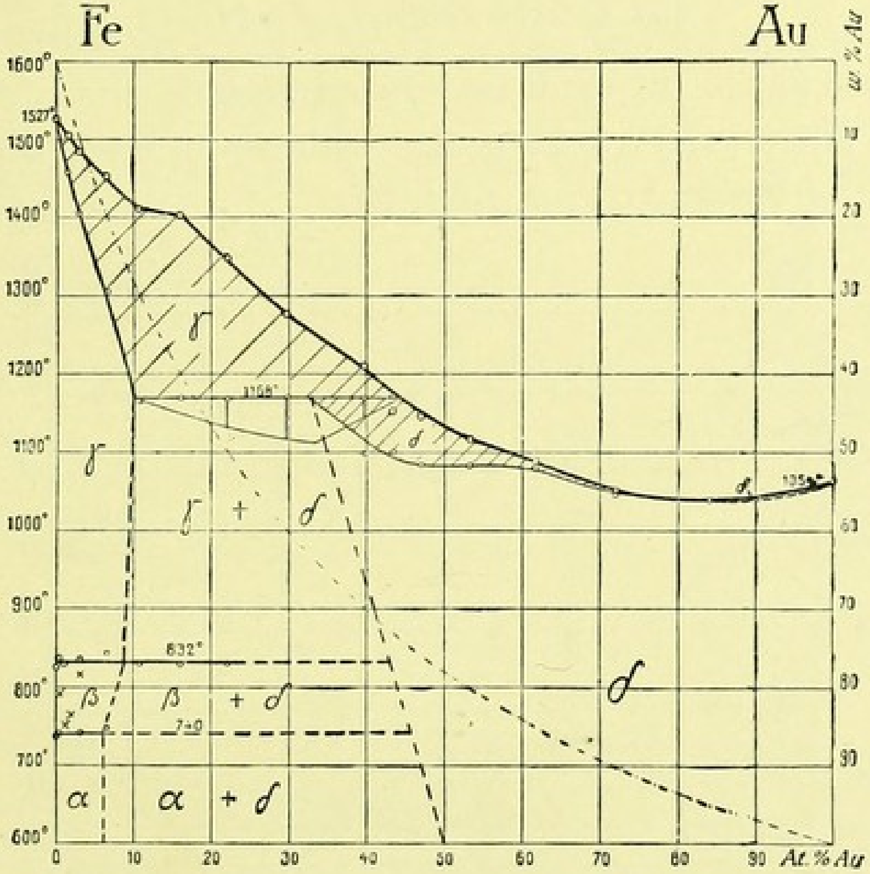


FIG. 58.—Gold—Iron according to Isaac and Tamman. Atomic percentage by Bornemann.

The δ crystal having 82—100 per cent. by weight of gold cools without changing.

According to Bornemann, the colour of the alloys is like that of iron up to 73 per cent. by weight of Au. Between 73 and 100 per cent. Au it varies from a faint yellow to that of pure gold. Hardness according to the Scale of Mohs :—

0	per cent. by weight Au	4·5	per cent.
5	,, ,, ,,	4·0	,,
10	,, ,, ,,	5·0	,,
70	,, ,, ,,	4·0	,,
80	,, ,, ,,	3·5	,,
90	,, ,, ,,	2·5	,,
100	,, ,, ,,	2·5	,,

(5) Gold—Nickel, Au-Ni.

These appear to form two mixed crystals.

(1) The crystal *α* is saturated with about 6 per cent. by weight of Au and 94 per cent. Ni.

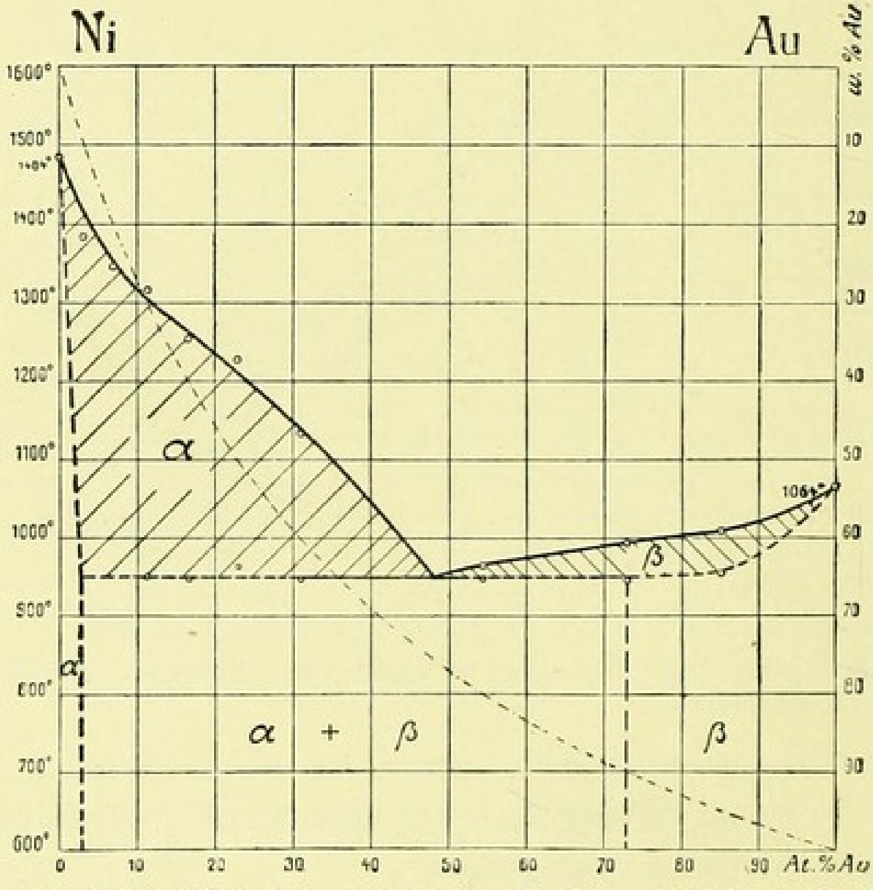


FIG. 59.—Gold—Nickel according to Levin. Atomic percentage by Bornemann.

(2) The *β* crystal with about 90 per cent Au and 10 per cent. Ni.

The two crystals form a eutectic having 75·5 per cent. Au and 24·5 per cent. Ni, which melts at 950° C.

These alloys are worth trying in dental work.

A change in the magnetic properties of Ni is observable at 323° C., which continues till 90 per cent. of gold is added to it.

(6) Gold—Lead, Au-Pb.

The diagram shows two compounds:

(1) $Au_{2}Pb$~~$_{2}$~~ having about 34 per cent. by weight of Au melting at 300° C.

(2) AuPb with about 65 per cent. Au and having a first crystallization at 565° C.

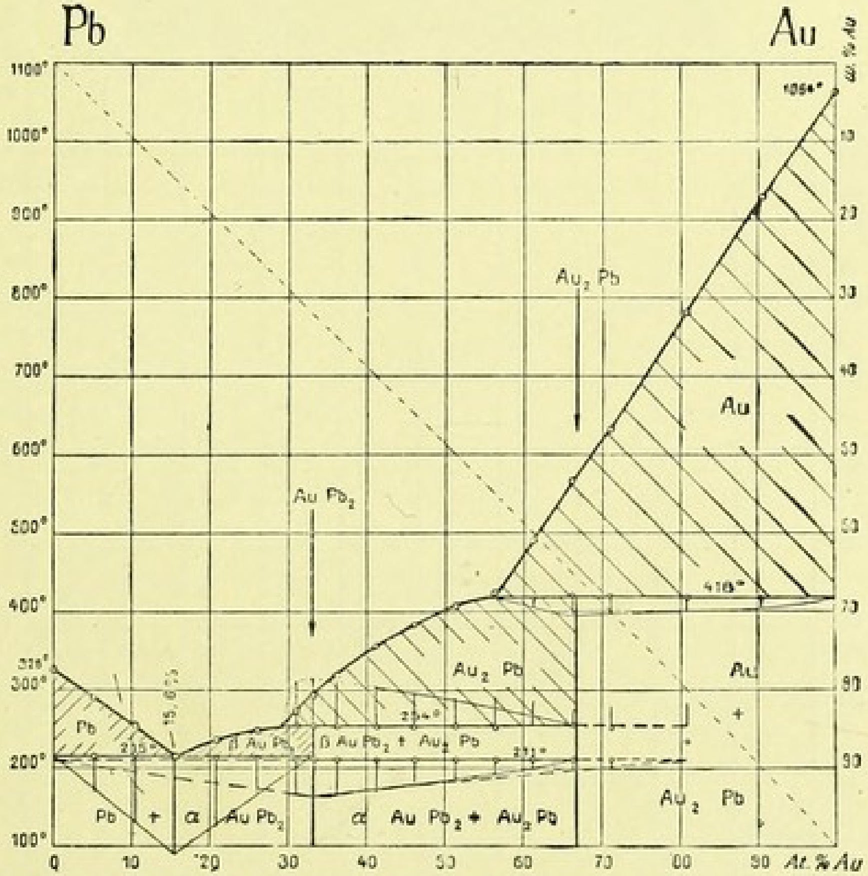


Fig. 60.—Gold—Lead according to Vogel. Atomic percentage by Bornemann.

When cooling ordinarily the alloys are not usually homogeneous, but very slow cooling will alter this.

The eutectic, which melts at 215° C. is composed of lead and $AuPb_2$ and has about 15 per cent. by weight of Au.

The compounds are very brittle. $AuPb_2$ is easy to polish.

(7) Gold—Palladium, Au-Pd.

These form an unbroken series of mixed crystals.

The colour of the alloys with 10 per cent. of Pd is almost white. According to Mohs' scale their hardness is as follows :

100 per cent. Au about 2·5
30 ,, ,, ,, 3·5
0 ,, ,, ,, 3·0

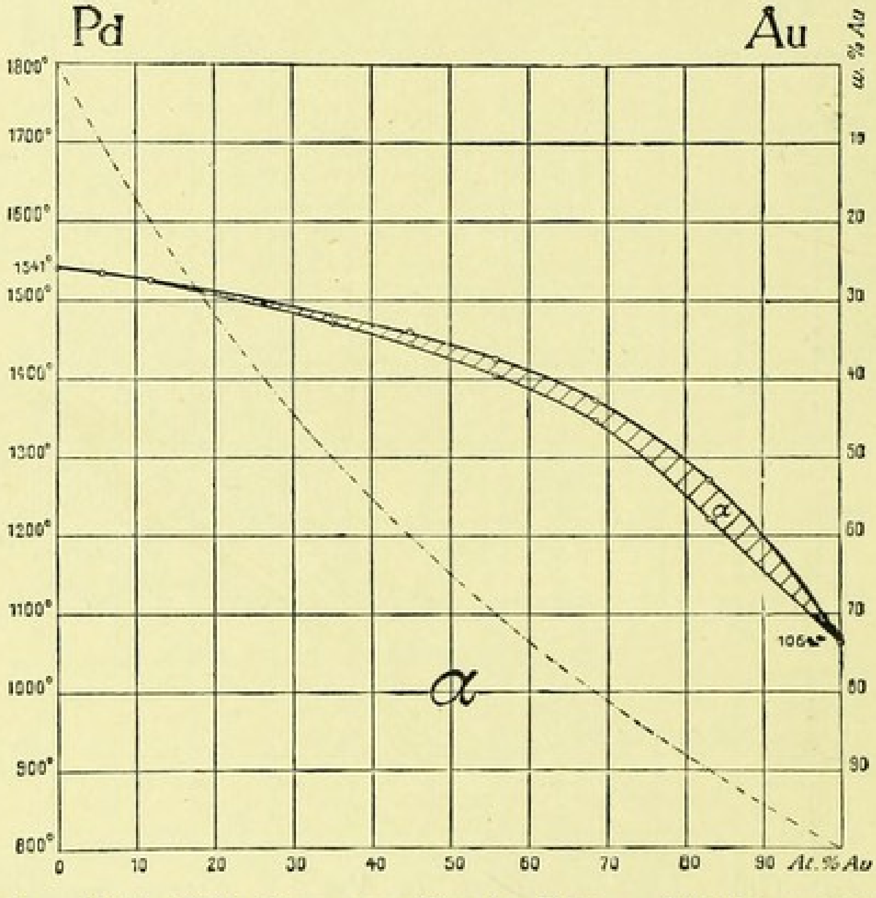


FIG. 61.—Gold—Palladium according to Ruer. Atomic percentage by Bornemann.

(8) Gold—Platinum, Au-Pt.

These form an unbroken series of mixed crystals. From 40—100 per cent Pt the form of the diagram is the result of extrapolation.

According to Bornemann their hardness steadily increases with 20—30 per cent. Pt till it equals that of pure Pt, and then increases again up to 50 per cent. Pt till it equals that of calcareous spar. It then falls again to the Pt level.

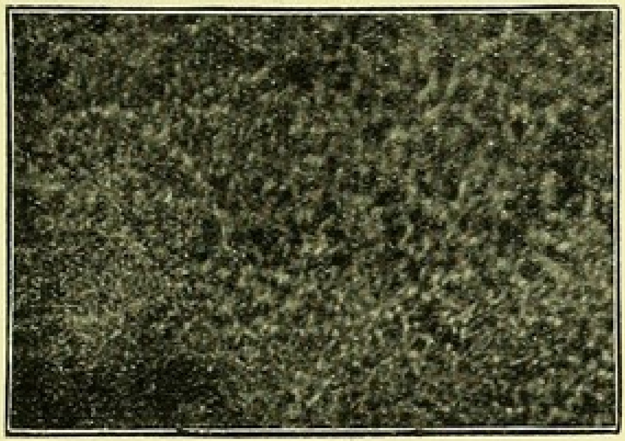


FIG. 62.—Platinum—Gold foil. × 160.

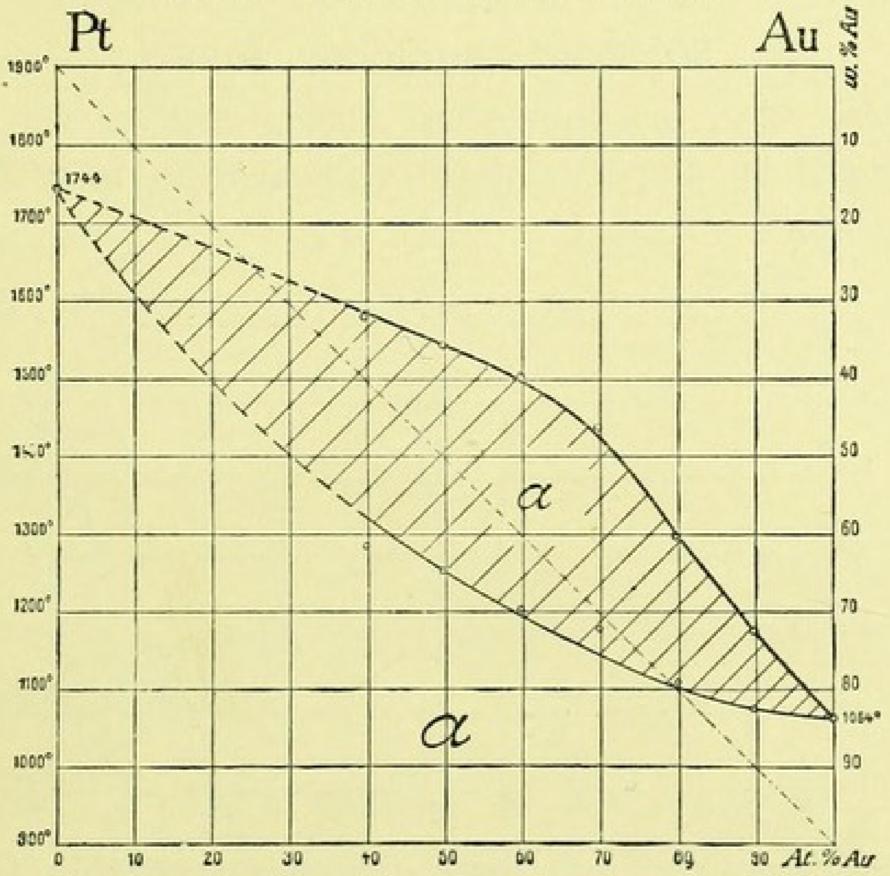


FIG. 63.—Gold—Platinum according to Duerinkel. Atomic percentage by Bornemann.

The alloys are used in dentistry to make gold more springy and tough for clasps and crowns.

Platinized gold makes fillings of a lighter shade than those of pure gold, but as they have a bluish tinge their appearance is not really good.

Pt is mixed with gold either by melting in the oxy-hydrogen flame or by using the foils together when filling teeth.

(9) Gold—Thallium, Au-Tl.

These alloys are of no practical use, as they form neither compounds nor mixed crystals.

They are miscible in the liquid, but immiscible in the solid state, and they form a eutectic, having 27·5 per cent. Au and 72·5 Tl, which melts at 131° C.

Thallium is polymorphic and has two phases.

(10) Gold—Antimony, Au-Sb.

These form the compound $AuSb_2$, with 44 per cent. by weight Au, 56 per cent. Sb, equivalent to 10·56 carats of fine gold.

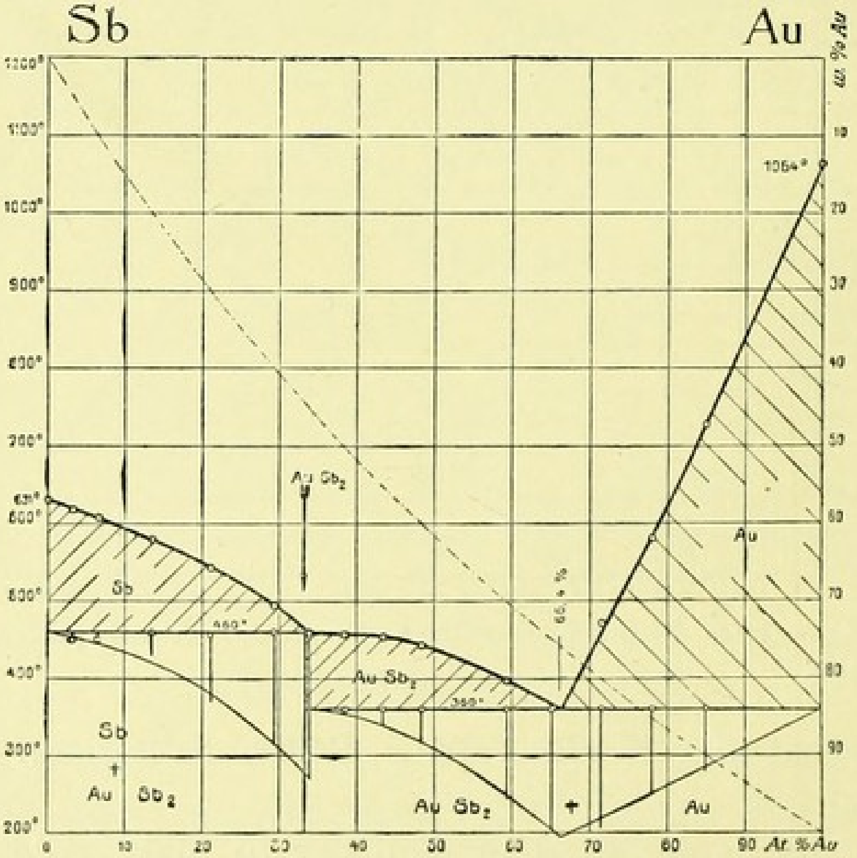


Fig. 64.—Gold—Antimony according to Vogel. Atomic percentage by Bornemann.

Between this compound and pure gold there is a eutectic of 76 per cent. Au and 24 per cent. Sb, melting at 360° C.

The compound $AuSb_2$ is very hard and brittle.

It is used for the purpose of lowering the melting point of casting golds, and solders.

(11) Gold—Tin, Au-Sn.

This alloy is interesting on account of the extraordinary drop in the melting point of Au, which takes place when tin is added to it. This is worth trying in gold solders.

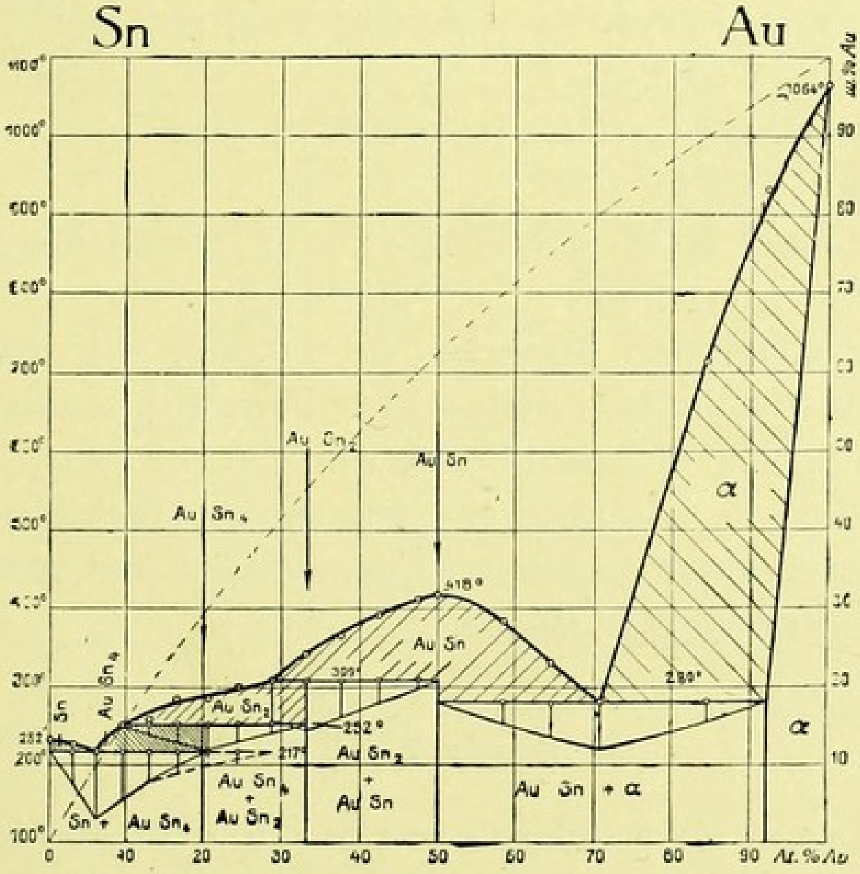


FIG. 65.—Gold—Tin according to Vogel. Atomic percentage by Bornemann.

Three chemical compounds are formed :

(1) AuSn, consisting of 63 per cent. Au and 37 per cent. Sn and corresponding to 15·12 carats gold. The

melting point is 418° C., and the colour greenish white. It is as brittle as glass and resists acids very well.

The compound forms a eutectic with pure gold, which has a yellowish white colour, and a composition of 81·5 Au and 18·5 Sn, and it melts at 280° C.

(2) $AuSn_2$ contains 45·5 per cent. Sn, equal to about 11 carats fine gold. It melts at 340° C.

(3) $AuSn_4$ has 29·5 Au, 70·5 per cent. Sn, about equal to 7-carat fine gold. Melting point 290° C. The eutectic which forms between this compound and pure tin has 10 per cent. Au and 90 per cent. Sn, and it melts at 217° C.

The mixed crystal α is formed by 5 per cent. Sn and 95—100 per cent. Au.

This mixed crystal is saturated by 5 per cent. Sn, and freezes at 910° C.

It should be an excellent alloy for dental inlay work because of its colour.

The compound AuSn and its mixtures with pure Au, particularly the α crystal, are well worth considering as casting golds for dental bridge work.

Brittleness, hardness, and resistance to acids are properties common to all these compounds, but AuSn has them in the highest degree.

(12) Gold—Zinc, Au-Zn.

Alloys of gold and zinc are of importance chiefly on account of their use in solders.

They form three chemical compounds :

(1) AuZn, melting point 744° C. This consists of 75 per cent. by weight of Au, and 25 per cent. Zn.

Between these compounds and pure gold, viz., between their two saturated crystals α and β respectively, there is a eutectic composed of 85·5 Au, and ~~4·5~~ 14·5 Zn, melting at 672° C.

These alloys lying between 63·5 and 85·5 per cent. Au, which form the β crystal, are remarkable for their reddish colour, and this, together with their low melting point, seem to make them peculiarly adaptable as a base for hard soldering.

They are equivalent to 15—20·5 carat gold.

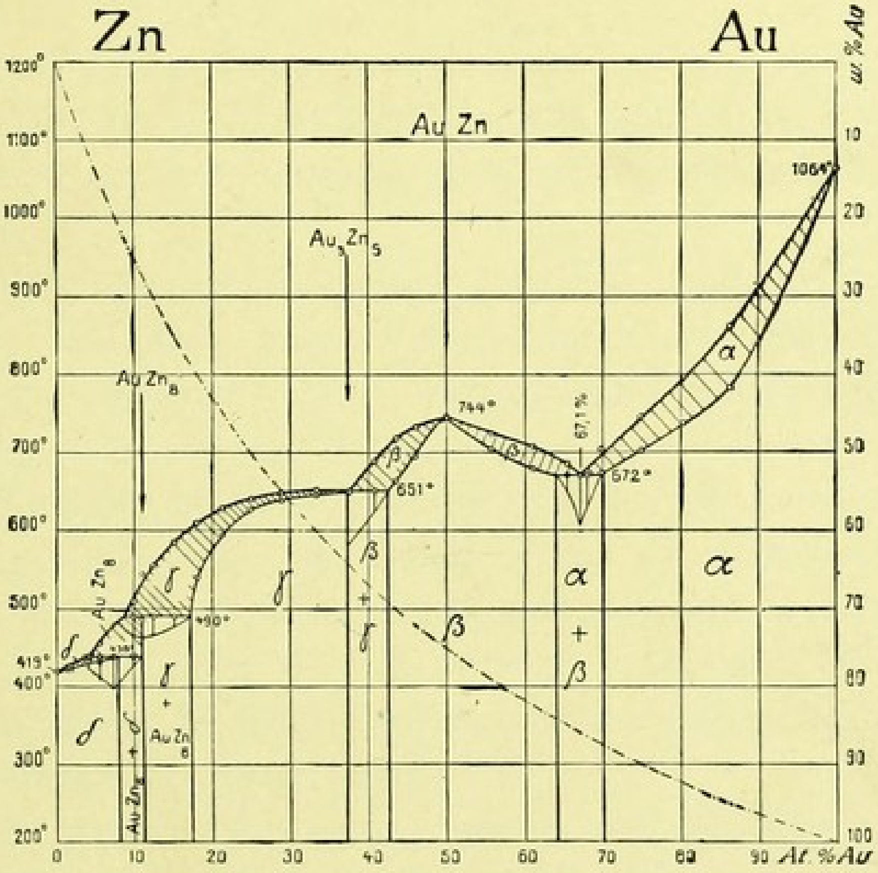


FIG. 66.—Gold—Zinc according to Vogel. Atomic percentage by Bornemann.

The properties of gold-tin alloys are most remarkable in the compound AuZn, which has about 75 per cent. Au, and is 18 carats fine.

(2) The compound Au_3Zn_5, melting point 651° C., contains 63·5 per cent. Au and 36·5 per cent. Zn. It is very hard and will scratch cast steel. Also it forms with AuZn in the β, and with $AuZn_8$ the γ crystal.

(3) The compound $AuZn_8$, melting point 490° C., consists of 26 per cent. by weight Au and 74 per cent. Zn, and forms the [illegible] crystal with Zn.

Alloys having higher percentages of Zn are practically worthless.

The alloying has to be done by adding the molten gold carefully and in small quantities to melted zinc, so as to avoid loss of Zn.

IX. IRON AND ITS ALLOYS.

(*See also under Gold, Silver, Copper, Nickel, &c. For physical properties see table, pp. 36-37.*)

Iron (Fe) has been known from the earliest time of which we have any historical records, and without doubt was used in those remote ages which are called prehistoric.

In the seventeenth century, smith's work improved greatly, and this improvement was continued in the eighteenth century, mainly owing to the introduction of furnaces.

In England, at about this time, the use of charcoal for melting began to be superseded by the use of mined coal.

The discovery of coke, and the invention in 1764 of the steam engine, gave a great impetus to all sorts of iron manufactures by making the workers independent of water power for their forges.

Sheffield owes its pre-eminence in steel industry originally to the fact that it has many small rivers near it, which have been dammed up at intervals and made to turn water-wheels for forging and grinding. Most of these grinding "hulls" have now been abandoned in favour of motors and engines in the city itself. The same may be said of Solingen, which is also located in the vicinity of small streams.

Another advance was made when the hot blast was introduced.

At the end of the eighteenth century steel was being worked by the puddling process, and by melting it in silica-lined furnaces most of the carbon in the iron was converted into Co_2 by the escaping oxygen.

At about this time too the cementation process was invented by Huntsman. This consists in heating up layers of iron and carbon alternately, and to this day it gives to the cast steels of Messrs. Krupp a world-wide fame.

The Bessemer process, which consists of freeing the molten iron from excess of carbon by blowing air through it, was invented in 1855.

The production of "acid Bessemer" requires high-grade ores, but "basic Bessemer" is made from impure ores. Thomas' improvement — the introduction of a basic lining for furnaces—dates from about 1899, and is a great help in the production of steel.

Iron is never found in the pure state, but the ores are always mixed with other metals or metalloids, and thence arise the differences in the qualities of ores of different lands.

The metalloids found with the ores are carbon, silicon, sulphur, phosphorus and oxygen; and the metals, manganese, copper, chromium, nickel, tungsten, aluminium, vanadium.

When mixed artificially with Fe these metals will produce alloys of many different properties. The most important of these by far are the alloys of Fe with C. They form—according to the percentage used—"cast" steels, "mild" steels, and "wrought" steels, &c., and the whole subject is so vast, and the industries connected with it are so great, that it has a literature to itself.

Chemically pure "Fe" can only be obtained by de-oxidizing pure iron oxide with a stream of hydrogen.

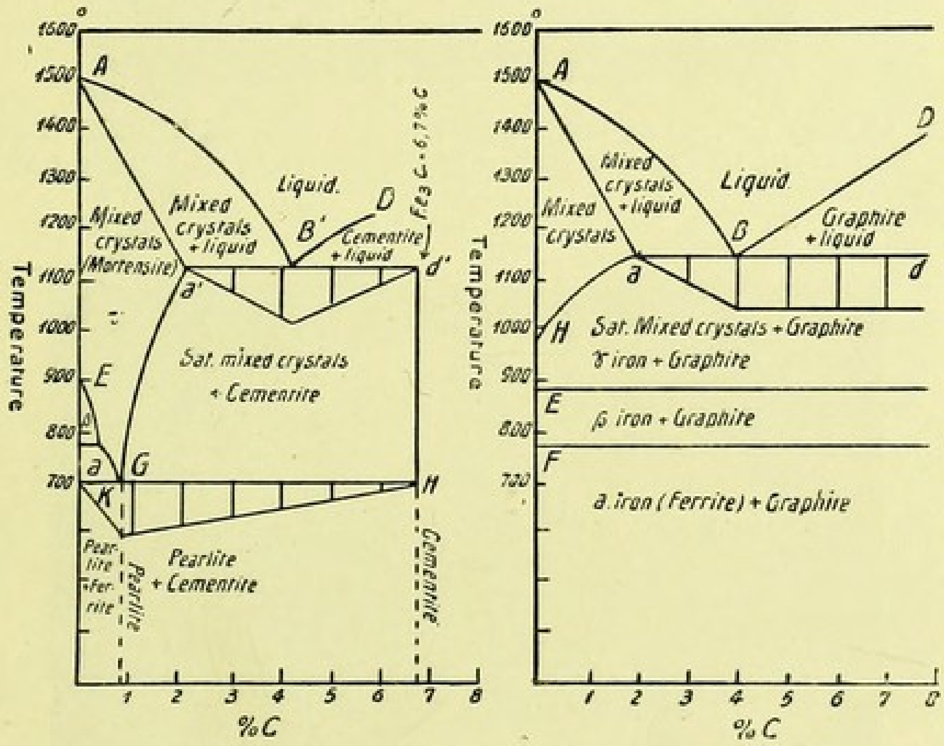
Iron obtained in this way must be melted *in vacuo.*

The difficulties of its preparation prohibit its use technically, though it is of great interest from a scientific point of view. In metallography it is used for thermo elements for low temperatures in connection with constantan (Cu-Ni).

IRON—CARBON, FE-C.

(*According to Goerens and Ruer*).

The iron carbon alloys are classified according to their content of C into "raw" iron, with more than 1·8 per cent. carbon, "wrought" iron, "malleable" iron, and steel with less than 1·8 per cent. C.



1. 2.

FIG. 67.—1. An unstable system as developed under normal cooling. 2. Complete stability after retarded cooling and retention at 1600° C. (After Ruer).

The following explanation of technical terms will enable the student to follow the diagram more easily.

Ferrite.—By ferrite is meant chemically pure iron known as *α* form. The *β* and *γ* forms are not constant.

Cementite is the chemical compound Fe_3C. This is pure Fe plus 6·7 per cent. carbon.

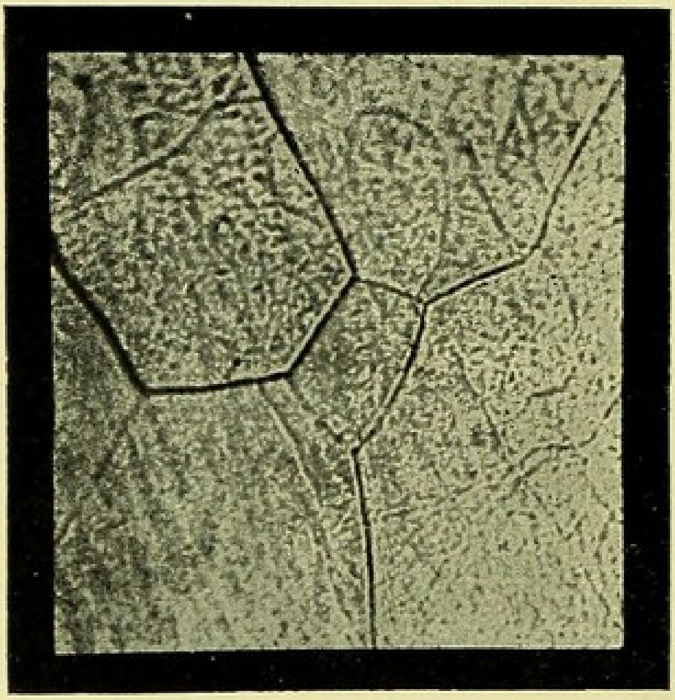


FIG. 68.—Ferrite. The single grains are lined by an irregular polygonal line. Each crystalline grain is etched by the treatment with picric acid.

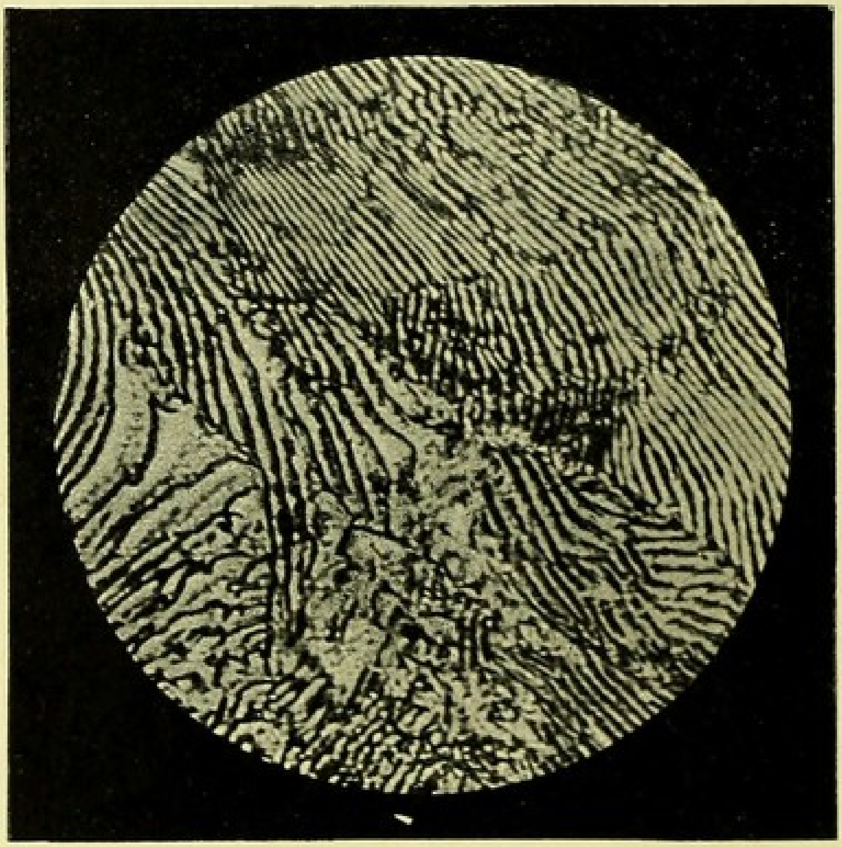


FIG. 69.—Eutectic steel. Lamellar pearlite, -- Cementite (light) + Ferrite (dark). × 400. After Goerens.

Pearlite is the eutectic between cementite and ferrite. It contains 0·85 per cent. C, and forms at 690° C.

Martensite is a mixed crystal between γ iron and cementite. It is saturated with 2·1 per cent. C; it can only keep its carbon over 690° C. Under a slow process of cooling it gives off its C and changes into pearlite and ferrite (with less than 0·85 per cent. C), or pearlite and cementite (with more than 0·85 per cent. C), or with 0·85 per cent. carbon into pure pearlite.

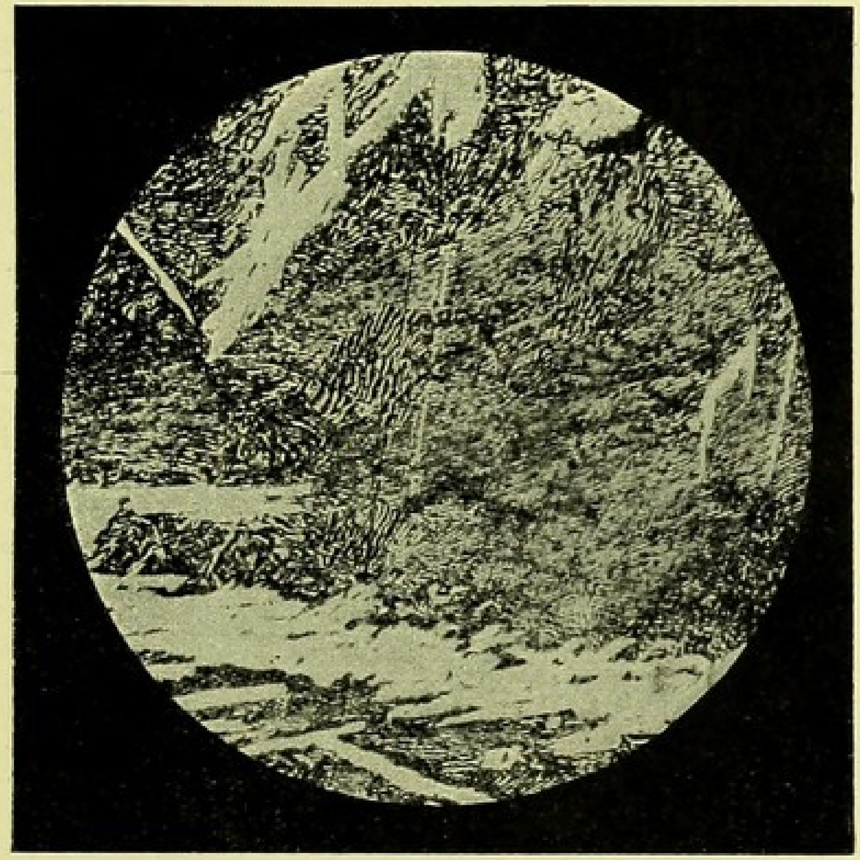


FIG. 70.—Annealed steel for instruments (tools) = Light Cementite imbedded in pearlite. × 400. After Goerens.

Graphite.—If alloys with more than 4 per cent. C are cooled very slowly, and kept for a long time at about 1100° C. they will give off a form of pure C which is known as graphite.

The cementite then separates into iron and graphite, and by further prolonging the cooling process the γ crystal also changes to β and α, so that when the whole system finally comes to rest, the cold iron is found to consist of pure ferrite *a* and graphite. The properties of these various states of iron are given in the following table by Ruer, so that one can see at a glance the comparative hardness, &c., of mixtures cooled suddenly at different temperatures.

Variety	Hardness	Tincture of iodine colours	10 per cent. H_2SO_4
Ferrite (Fe) ...	Softest of all ...	Faint or not at all	Dissolved easily with evolution of H
Cementite (Fe_3C)	Hardest of all; No. 6, according to Mohs' scale harder than a steel needle	Not	Does not dissolve
Pearlite-eutectic (Fe_3C. + Fe_4) $Fe_3C + Fe\,a$)	Medium	Not noticeable ...	Partly dissolves
Martensite mixed crystal (cementile + Fe γ)	Varies with content of C; always softer than cementite	Yellowish brown	Dissolves with formation of H and compounds of C + H

There is a distinction between raw irons with more than 1·8 per cent. carbon.

(1) "Grey" iron, which contains carbon in the form of graphite.

(2) "White" iron, in which carbon is only present in the chemical compound (cementite) Fe_3C.

"Grey" iron is formed when there is more than 4 per cent. C or else during the cooling process when that is prolonged at high temperatures.

Moreover the Fe-C alloys have a stronger tendency to form graphite in the presence of silicon.

"White" iron is formed by normal cooling of the alloys of 1·8-4 per cent. C, but in the presence of manganese it may be formed with as much as 5 per cent. C.

The following modifications have still to be mentioned.

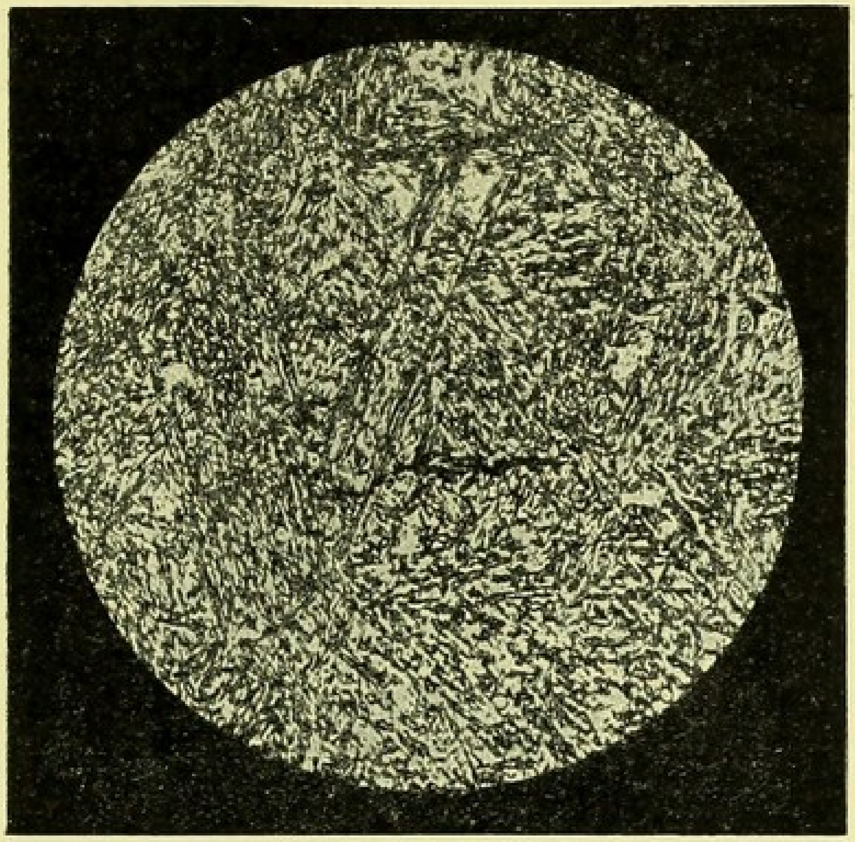


FIG. 71.—Martensite chilled. x 100. After Goerens.

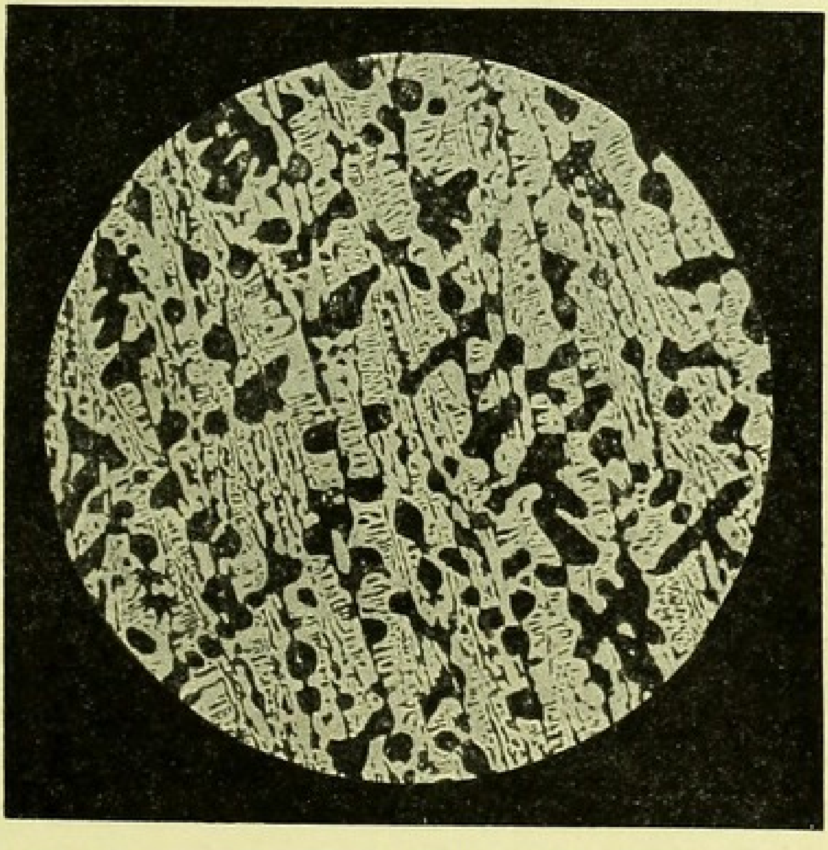


FIG. 72.—Cementite (light) and pearlite (dark) = white iron. x 50. After Goerens.

Sorbite.—It may happen sometimes through pressure or sudden cooling that the eutectic pearlite has not been fully formed, and there is still some ferrite and cementite free, so that the general condition of the iron is of irregularity both chemical and physical.

This state is known as sorbite.

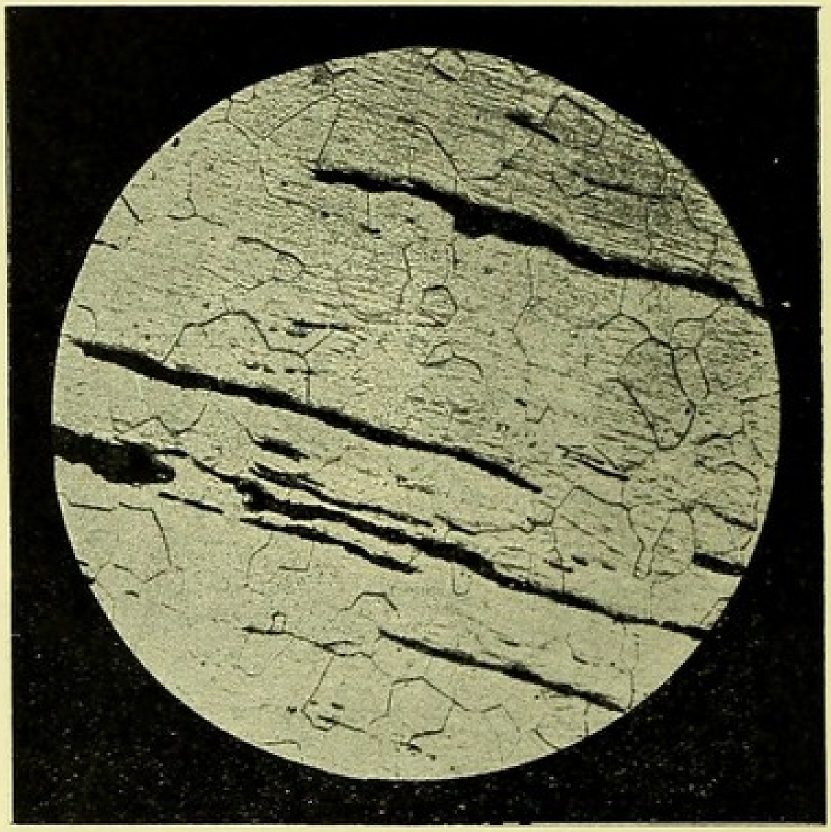


FIG. 73.—Malleable iron (light) is shown by etching with nitric acid. Dark veins of slag. × 50.

Trostite.—If steel is cooled suddenly at the point of polymorphism = 680° C. in the presence of free cementite another analogous modification appears, which Osmond has called trostite.

It is only found near martensite and its nature is not yet fully understood.

Austenite plus martensite is found with more than 1·10 per cent. C, when the molten iron is reduced suddenly from a higher temperature by means of ice water.

It is somewhat softer than martensite and colours differently in etching.

Hydrochloric acid gives a light brown colour on martensite, but austenite remains unchanged.

Sorbite, trostite and austenite do not appear in the diagram of the carbon iron alloys because they represent incomplete reactions and cannot therefore be regarded as homogeneous bodies.

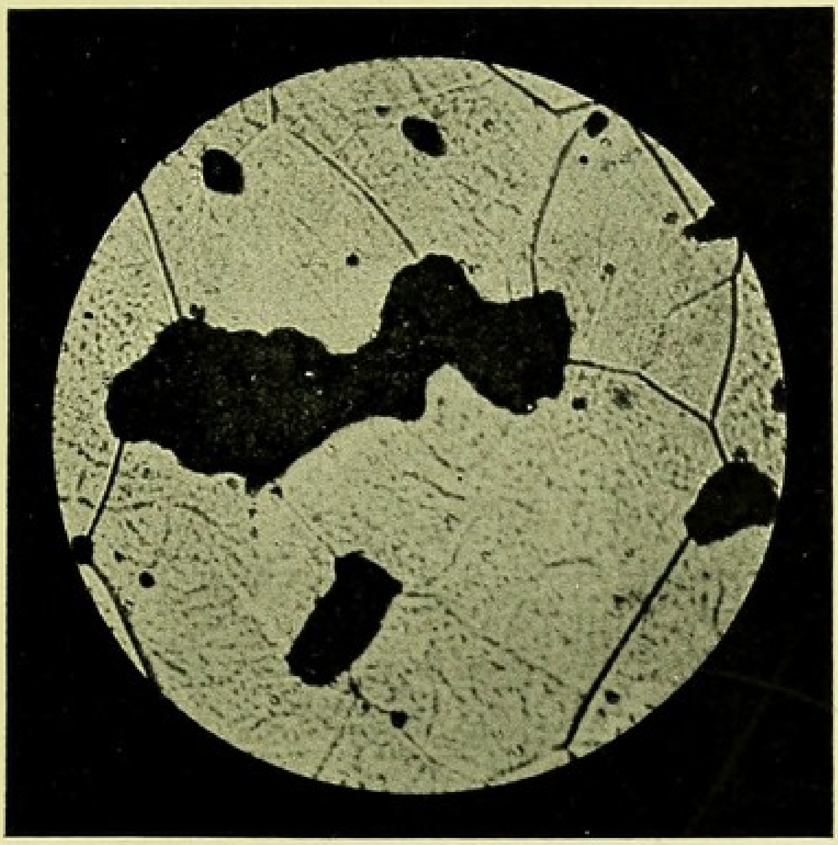


FIG. 74.—Same as fig. 73, cut in transverse direction. x 500.

These brief explanations will make the diagrams easier to follow.

SPECIAL STEELS.

By the addition of various metals such as chromium, nickel, cobalt, manganese, tungsten and molybdenum steels of extraordinary hardness are being made.

Fischer describes some of them as follows :—

(1) Nickel steel is very resistant both mechanically and chemically.

It is made by introducing ferronickel or pure nickel into irons poor in carbon.

The best kinds have 3 per cent. Ni and ·4—·5 per cent. C.

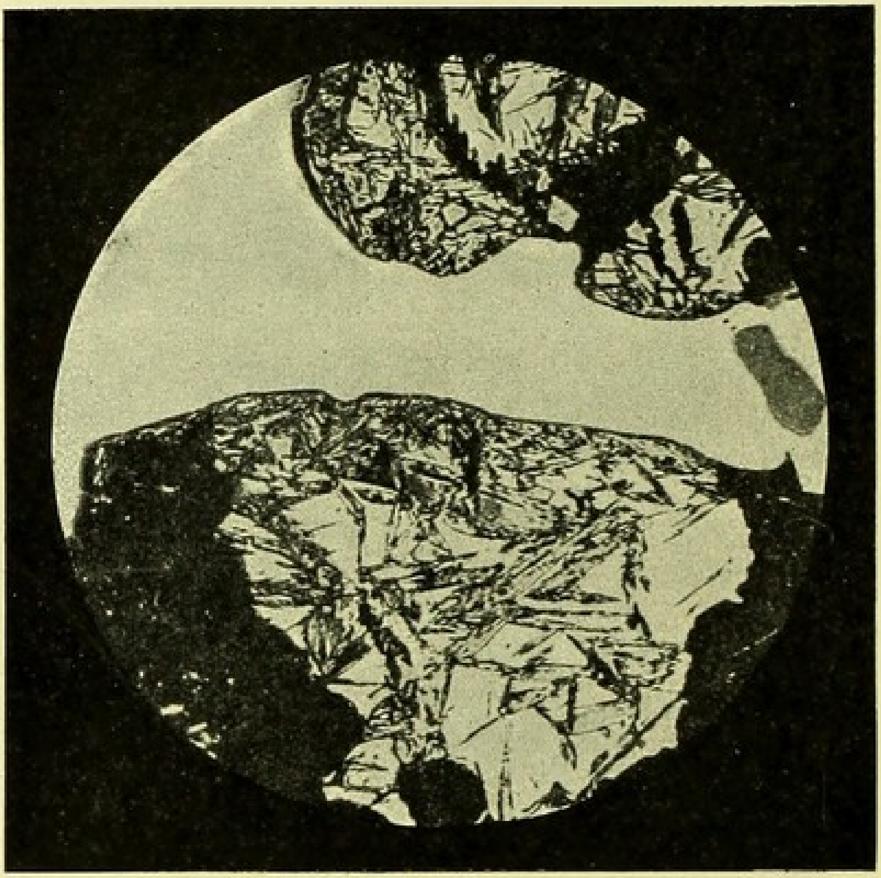


FIG. 75.—Broad white field = cementite; black fields = trastite; grey sharp needles crossing each other = martensite; between these = light austenite. x 500.

This steel when lightly tempered and hardened in oil without being rolled or forged (only cast) will show an average resistance of 70 kg. on 1 square mm. or will take a tensile stress of 70 kg. on a section of 1 sq. mm.

Alloys of Fe containing 10—16 per cent. Ni, 3—8 per cent. Mn, and 1·5 per cent. C are said to be extremely tough.

(2) Manganese steel is made in a similar way to nickel steel by adding pure Mn or Ferro-manganese to molten steel.

It contains 2—20 per cent. Mn and is very hard, and tough, and these properties are not altered by heating to a dull red.

This alloy does not appear to be affected by the polymorphism which the pure iron carbon compounds show.

(3) Chromium steel gives a maximum of hardness and toughness with ·5 per cent. chromium and 1 per cent. C. More chromium impairs these qualities and makes it more brittle.

By combining Mn, Ni and C, steels can be produced of such extreme hardness that no tool will touch them.

Analyses of such steels show :

Carbon	0·37	per cent.
Silicon	0·08	,,
Sulphur	0·01	,,
Phosphorus	0·03	,,
Manganese	2·88	,,
Chromium	0·42	,,
Nickel	6·98	,,

(4) Tungsten steel is used in making tools where hardness is the chief desideratum. About 5 per cent. of tungsten is added to the molten metal.

(5) *Molybdenum steel* is often used instead of tungsten steel because it stands forging and hardening better.

X. ZINC AND ITS ALLOYS.

(*See also under Copper, Gold, &c. Physical properties table*, p. 36, No. 33).

Zinc is a bluish-white metal having a crystalline fracture. The specific gravity is : cast, Zn 6·85 ; hammered, Zn 7·15 ; rolled, Zn 7·2—7·3.

In ancient times sheet Zn was in use, and it was known as Mosseanocean brass (ὀρειχάλκος of Aristotle), because copper was worked up with an ore containing zinc which was found in the country of the Mosseanoceans. Hence its German name "Messing."

Zn is rarely found in the pure state. The one called galmei is a siliceous rock which contains 68 per cent. zinc oxide. Noble galmei or zinc spar is a carbonate of Zn ($ZnCO_3$), containing about 52 per cent. of the metal. Zincblende or sphalerite, which is a sulphide of Zn (ZnS), is found in large deposits and veins generally in association with iron or cadmium.

Red zinc ore, red zinc oxide, or zincite is an oxide rich in manganese and iron.

But with the exception of this, which is used to obtain the pure oxide, ores are smelted for the zinc.

The ores are first of all freed as far as possible from useless and undesirable earthy mixtures, by disintegration and sifting and exposure to the air.

The ores are next converted into zinc oxide, the galmei is burnt and the sulphide roasted.

The sulphur which is liberated as an oxide has to be rendered innocuous if it is not to be used in the manufacture of sulphuric acid, &c.

The zinc oxide thus obtained is freed from its oxygen by reduction in heat, and so reduced to metallic zinc, which boils at 1040°C.

This is distilled and condensed in fireclay receivers.

The metals (impurities) which come over into the condensers first are those which boil at a lower heat than zinc, such as cadmium, arsenic, lead, antimony.

They form a sort of zinc dust, which is used in paints but not as pure zinc.

Any adhering lead can be easily melted off.

Zinc can be rolled and drawn at 100—150° C. and the sheets and wire are usually made by heated rolls.

It is much used as protective covering for iron sheet and wire against rust (galvanizing). On exposure to the atmosphere zinc becomes coated with a basic carbonate which prevents further disintegration.

When heated in the air it oxidizes at 500°C. and burns with a bluish flame, forming zinc oxide.

Its affinity for oxygen is used for the purpose of ridding other metals of their oxides by the addition of Zn to them.

In consequence it is much used in solders to make them more fluid and most of it is then liberated as oxide.

According to Fischer the commercial zinc of Silesia has the following composition :

Zinc ...	...	98·918 per cent.
Lead ...	...	0·595 ,,
Iron ...	...	0·120 ,,
Cadmium	...	0·062 ,,
Copper	...	Trace
Silver ...	...	0·001 ,,
Arsenic...	...	0·031 ,,

Antimony	...	0·012 per cent.
Sulphur	...	0·002 ,,

(1) Zinc—Aluminium, Zn-Al.

These form two mixed crystals.

(1) 0-4 per cent. by weight Al.

(2) 50-100 per cent. by weight Al.

Between these two mixed crystals there is a eutectic having 4·9 per cent. by weight of Al and

95·1 per cent. ,, ,, ,, Zn

Melting point 381°C.

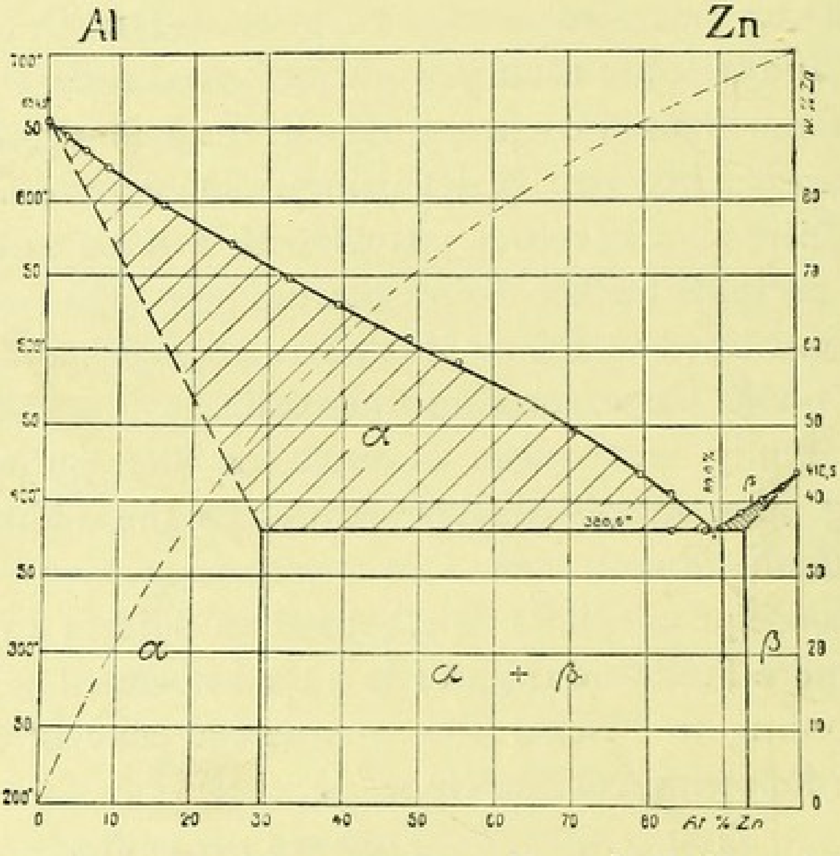


FIG. 76.—Zinc—Aluminium according to Heycock, Neville and Shepherd. Atomic percentage by Bornemann.

(2) Zinc—Bismuth, Zn-Bi.

These are almost immiscible together either in the solid or liquid state, excepting the alloys having from 0—3 per cent. by weight of Zn.

They form the *a* mixed crystal.

Other alloys of Zn and Bi will only mix at temperatures over 800° C.; and this is shown in the diagram by the high dotted arch.

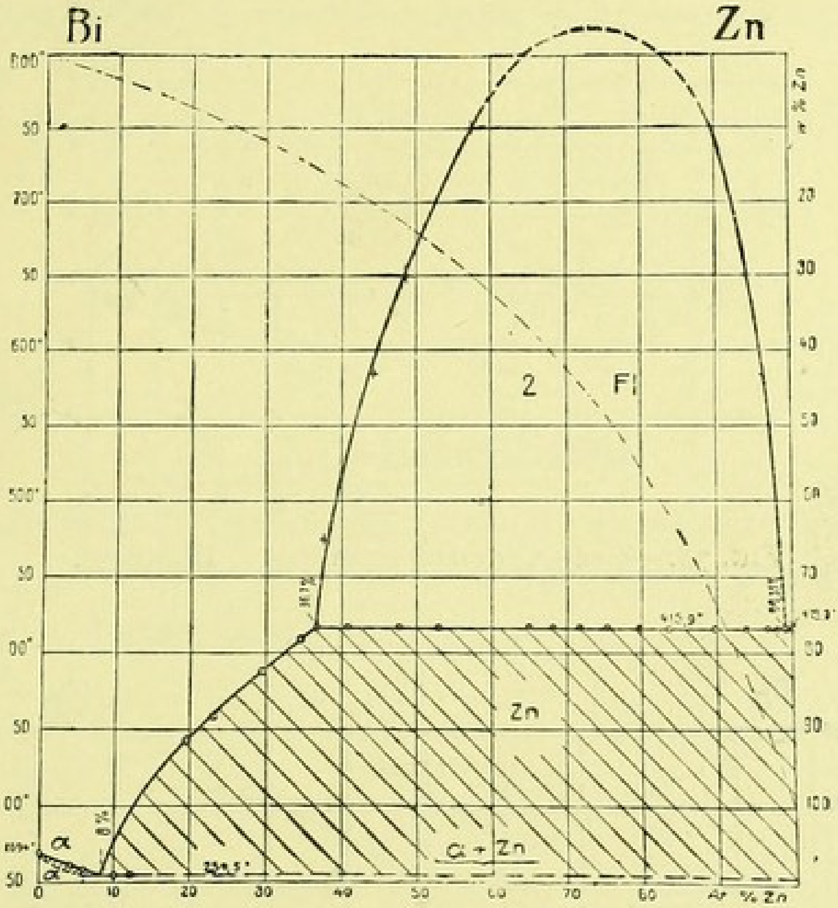


FIG. 77.—Zinc—Bismuth according to Heycock, Neville, Spring and Romanoff.

(3) Zinc—Cadmium, Zn-Cd.

These are miscible in all proportions in the liquid state. They form no chemical compound. There is a eutectic composed of 82·4 per cent. by weight of Zn, 17·6 per cent. Cd, melting at 260° C.

The addition gives to Zn a fine granular structure, but the resulting brown colouration of the oxide makes its presence undesirable in the manufacture of pure white zinc oxide.

Zinc—Mercury, Zn-Hg.

(See Amalgams, p. 160.)

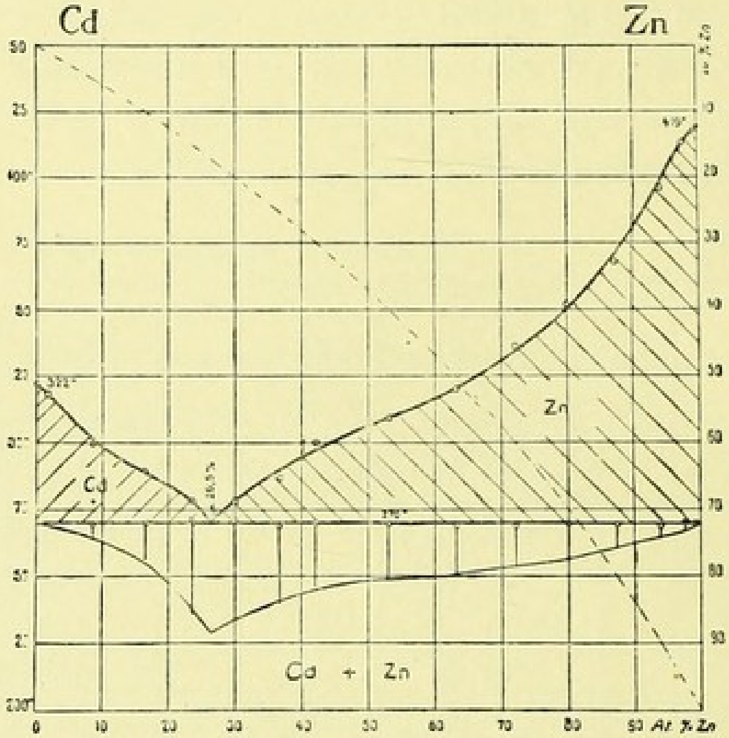


FIG. 78.—Zinc—Cadmium according to Hindrichs.

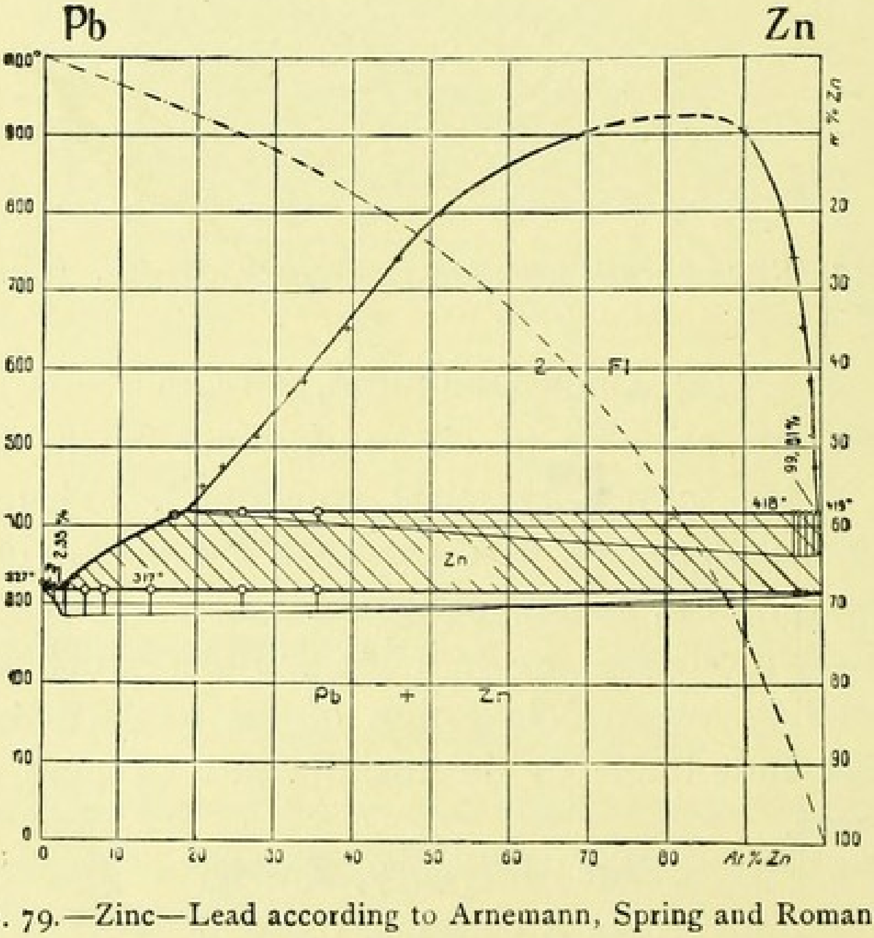


FIG. 79.—Zinc—Lead according to Arnemann, Spring and Romanoff.

(4) Zinc—Nickel, Zn-Ni.

Tafel has demonstrated the chemical compound $NiZn_3$, having 23 per cent. by weight of Ni.

This forms a mixed crystal, with pure Zn, which is saturated, according to Voss, with 14·5 per cent. by weight of Ni.

According to Tafel there are three mixed crystals :

With 77—87 per cent. Zn
,, 53—60 ,, ,,
,, 0—42 ,, ,,

The melting should be done in an atmosphere of hydrogen.

(5) Zinc—Lead, Zn-Pb.

These metals are insoluble in one another in any state, and are like ZnBi in that only very high temperatures render the liquid metals miscible at all.

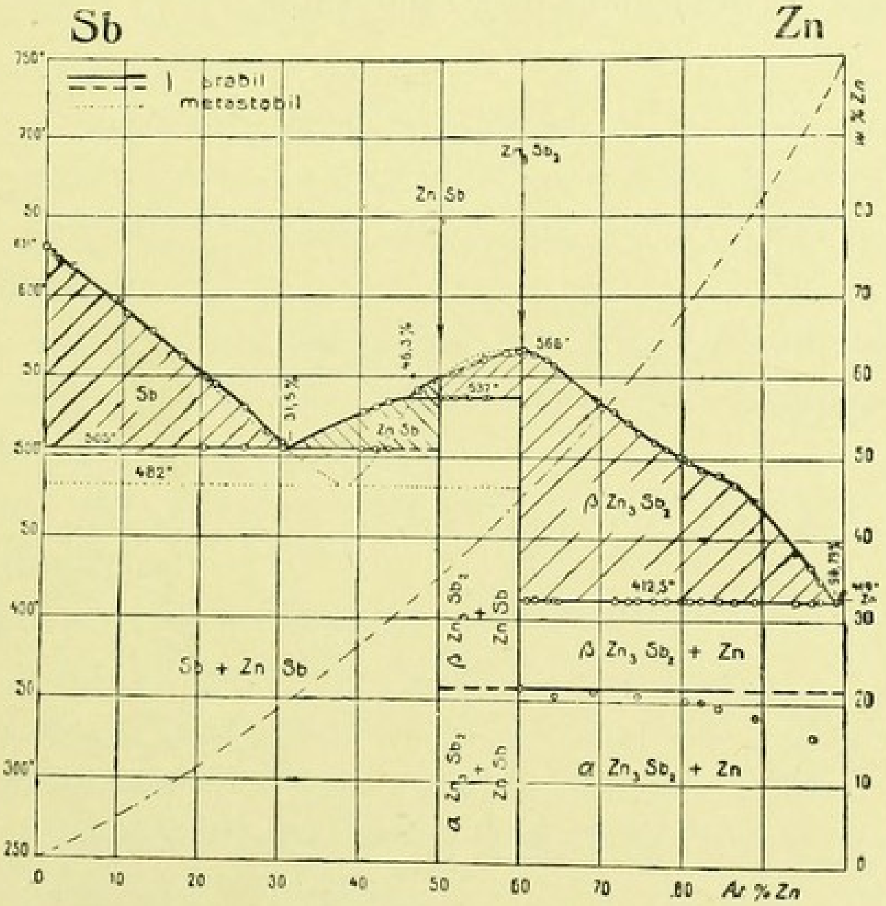


FIG. 80.—Zinc—Antimony according to Zemczuzny. Atomic percentage by Bornemann.

(6) Zinc—Antimony, Zn-Sb.

This pair form two chemical compounds :

(1) Zn_3Sb_2, having 44 per cent. by weight Zn ; 56 per cent. Sb. Melting point, 566° C.

(2) ZnSb with 35·5 per cent. by weight of Zn.

Between these compounds, as well as between Zn_3Sb_2 and pure Zn, and also between ZnSb and pure antimony, there are eutectics.

The compounds are hard and brittle.

(7) Zinc—Tin, Zn-Sn.

These are miscible in all proportions in the fluid state, but they form no true chemical compound. There is a eutectic, having 16 per cent. by weight of Zn and 84 per cent. Sn, which melts at 190° C.

It is quite likely that ZnSn would make a better soft solder than the usual ZnPb compound.

XI. NICKEL AND ITS ALLOYS.

Ni is a greyish-white metal, hard and ductile, and it can be rolled and drawn into very thin sheets and wires.

Being itself unaffected by atmospheric influences, it is used as a protecting covering for other metals.

It belongs to the same natural group as Fe, and, like iron, it combines with Si and C.

Organic acids have also no effect on it, and this makes it very useful as a protective covering for cooking vessels as well.

Up to the middle of the eighteenth century nickel was only known in Europe in the form of the Chinese nickel-copper alloy, called peckfong.

It was re-fused in 1776 by Bergmann, and was obtained from various ores—at first chiefly from arsenic combinations or "Red" nickel, which has 43 per cent. of the pure metal.

The extraction of the metal was very difficult, and the price very high till the middle of the last century, when rich deposits were discovered in America.

About 1870 the great garnierite mines of New Caledonia were discovered.

These are still producing garnierite, which is a silicate of Ni and Mg, having a Ni content of 10 per cent.

Ten years later the Canadian magnetic pyrites were opened up, and their ores yield up to 15 per cent. Ni.

Meteorites also have been found containing as much as 50 per cent. of pure nickel.

It is also a constituent of many metallic ores, and is found in their slags after refining. From these it is extracted by methods similar to those employed on nickel ores proper.

The extraction is effected either by the wet or dry method.

In the dry way it is first roasted several times. This separates the sulphur-iron compounds, leaving behind the cobalt-nickel, combined with arsenic and sulphur.

The cobalt is removed next, and refined.

Finally, the so-called concentration stone remains, and this contains about 75 per cent. Ni in the form of a protoxide.

Another process is called after Bessemer.

In this a stream of air is blown through the molten mass to oxidize the iron and convert it into slag. The arsenic and Sb evaporate, and the remainder contains 75 per cent. Ni, 24 per cent. S, and 1 per cent. impurities.

The Mond method is peculiar. It takes advantage of the fact that a nickel carbon oxide compound, called nickel tetra-carbonyl, boils as low as 43° C.

The nickel ores are oxidized by roasting, the oxides heated to 350° C., and reduced to pure metal by means of hydrogen. This metal, however, is unusable, on account of certain physical properties. So it is cooled to 50° to 60° C., and treated with carbon ~~dioxide~~ monoxide. The nickel tetra-carbonyl thus obtained is evaporated, and led at a temperature of 200° C. into chambers containing granular nickel.

The heat decomposes the compound, and pure nickel is precipitated on the grain nickel already in the chambers.

In the wet process the nickel ores are first ground up, and then dissolved in HCl, or H_2So_4.

The iron is precipitated as protoxide, and filtered out, and a solution of soda is then added to the filtrate.

This precipitates the Ni in the form of a carbonate.

The HCl can be recovered from the chlorides, which are left.

Details of these wet processes are hard to obtain, as they are kept secret by the users (manufacturers).

Protoxide of nickel, when obtained, either by the wet or dry process, is reduced to the metallic form by heating with charcoal, and then it is worked into squares with about 85 per cent. of pure nickel.

From this, by Fleitmann's method, pure nickel is obtained by melting it with zinc oxide and ·05 per cent. Mg.

Garnier advises the addition of lime and carbon to the molten mass.

When finished the metal is 97—98·5 per cent. pure Ni and it has a little cobalt and traces of iron.

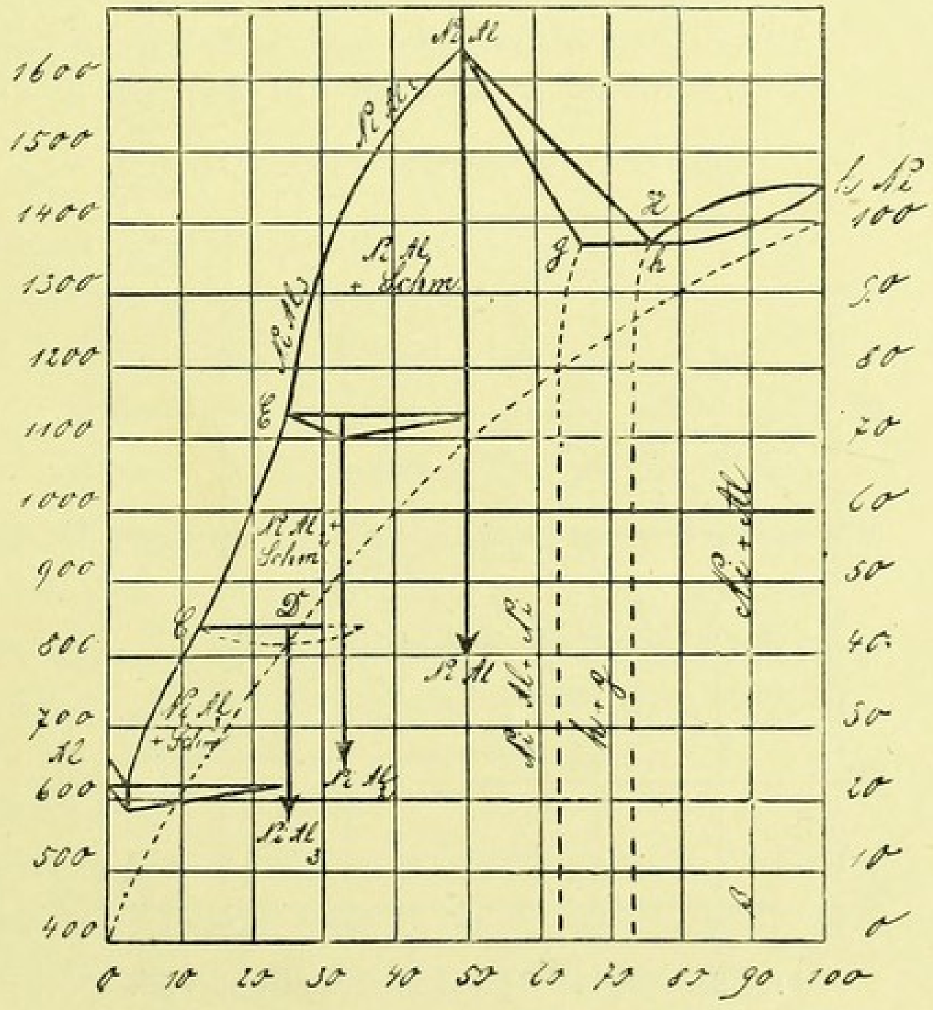


FIG. 81.—Nickel—Aluminium according to Gwyer.

(1) Nickel—Aluminium, Ni-Al.

These form three chemical compounds:

(1) AlNi contains 68·4 per cent. by weight of Ni and 31·6 per cent. Al; it melts at 1640° C. (near to Pt), and forms a eutectic with 6 per cent. by weight of Al and 94 Ni, melting at 1371° C.

(2) $NiAl_2$ consists of 52 per cent. by weight Ni, 48 per cent. Al. Melting point 1430° C.

(3) $NiAl_3$ has 41·9 per cent. by weight Ni. It forms a eutectic with 7·5 per cent. by weight of ~~pure Al~~ Ni, which melts at about 630° C.

(2) Nickel—Bismuth, Ni-Bi.

These are miscible in all proportions in the liquid state. The existence of one compound ($NiBi_3$) is established, but a second (NiBi) is doubtful.

There is also a mixed crystal having 99·5 per cent. by weight Ni.

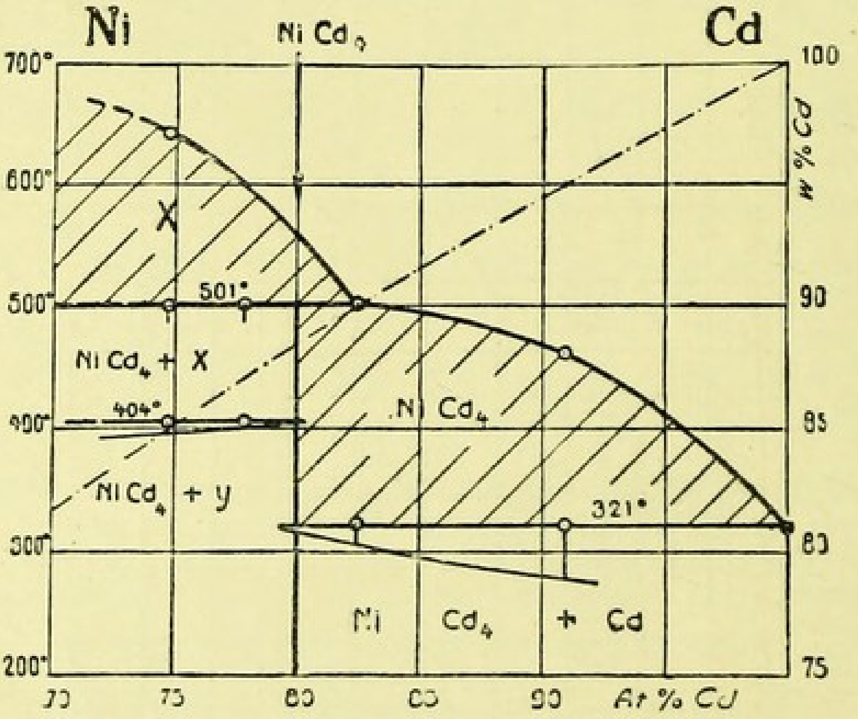


FIG. 82.—Nickel—Cadmium according to Voss.

(3) Nickel—Cadmium, Ni-Cd.

Nickel and cadmium are miscible in all proportions in the liquid state.

There is one chemical compound, $NiCd_4$.

It is very difficult to prepare on account of the low boiling point of Cd, so the diagram only shows percentages of Ni up to 17 per cent.

(4) Nickel—Chromium, Ni-Cr.

These form two almost unbroken series of mixed crystals, one series with excess of nickel from 42—100 per cent. and one with excess of chromium from 58—100 per cent.

An alloy of 42 per cent. Ni and 58 per cent. chrom. has the lowest melting point, namely 1290° C. Losses in melting are state d for chromium only.

(5) Nickel—Antimony, Ni-Sb.

These form two compounds.

(1) NiSb, 32·83 per cent. Ni.	Melting point	1158° C.
(2) Ni_5Sb_2, 54·97 per cent. Ni.	,, ,,	1170° C.

(6) Nickel—Tin, Ni-Sn.

According to Gautier these form the compounds :

(1) Ni_3Sn_2 with two eutectics.

Voss discovered two compounds besides which separate on melting, but there is some doubt about them.

(2) Ni_3Sn.

(3) Ni_4Sn.

(4) A mixed crystal saturated with 86 per cent. Ni.

Between Ni_3Sn, melting at 1310° C., and the mixed crystal there is a eutectic which melts at 1150° C.

Voss demonstrated many allotropic modifications and magnetic changes, and hiatus in the series of mixed crystals of these metals.

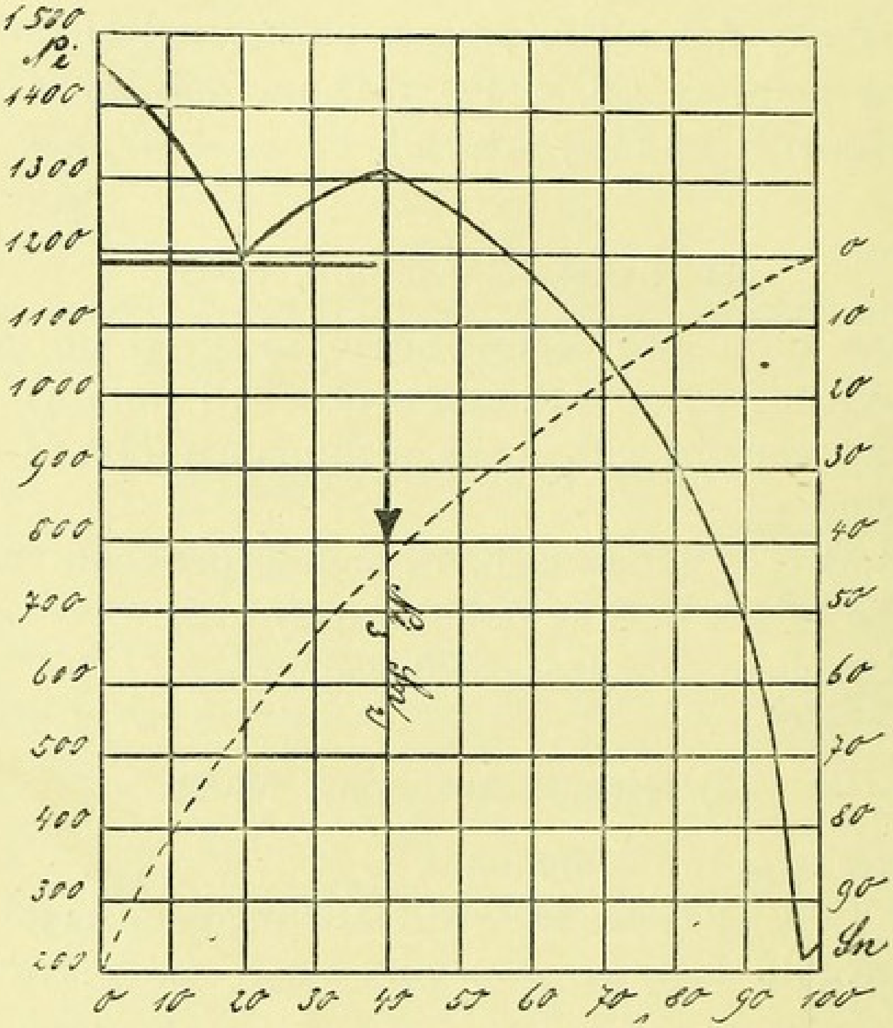


FIG. 83.—Nickel—Tin according to Voss.

(See also under COPPER, SILVER, GOLD, &c.)

XII. VARIOUS ALLOYS.

(1) Lead—Bismuth, Pb-Bi.

These metals mix well in the liquid state, but separate on cooling.

The eutectic, consisting of about 60 per cent. by weight of Bi and 40 per cent. Pb, melts at 127° C.

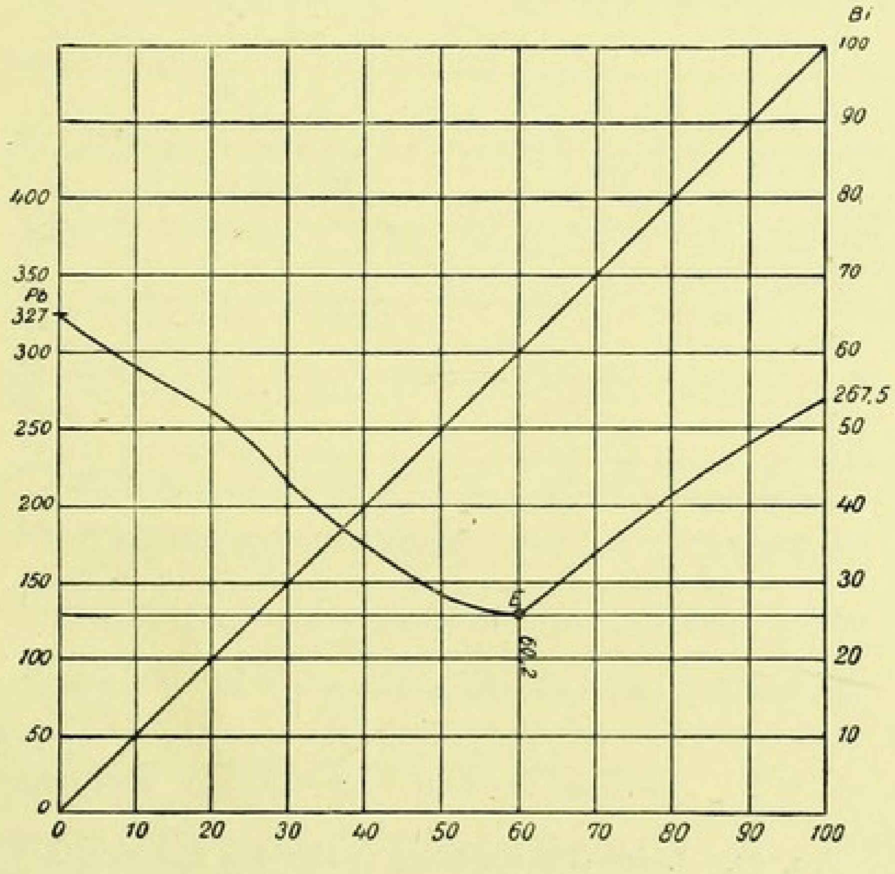


FIG. 84.—Lead—Bismuth according to Kapp.

(2) Lead—Tin, Pb-Sn.

This pair form no chemical compound.

The metals mix in the liquid state, but crystallize out separately.

There is a eutectic of 70 per cent. by weight of Sn and 30 per cent. Pb which has the lowest melting point of all the PbSn alloys, namely 180° C. "E" (see fig. 85).

These alloys are used as soft solders in many trades, and there are two varieties of them—one melting below 200° C. and the so-called "strong" solders which melt at higher temperatures.

The diagram shows that one can have solders melting at any point up to 232° C. either rich in Pb or Sn as desired.

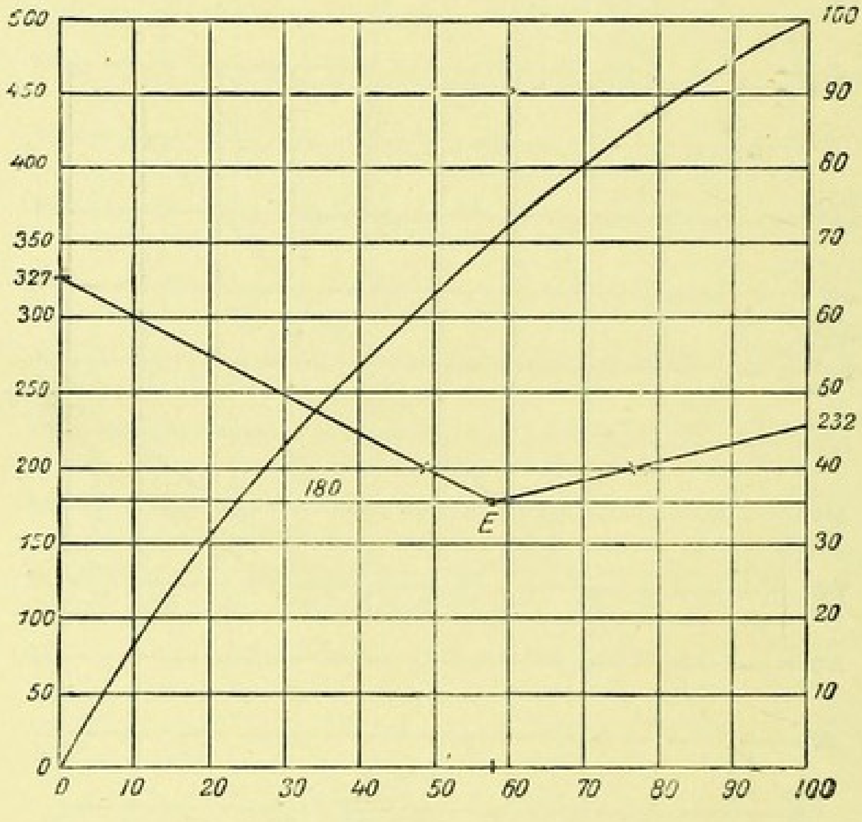


Fig. 85.—Lead—Tin according to Heycock and Neville.

The latter, for example, is used in soldering preserved fruits in tins where more than 10 per cent. lead is not permissible.

There are also two solders melting at 200° C., one of which has 62 per cent. tin, while the other has 82 per cent. Sn.

In addition to its low melting point the eutectic has another property peculiar to all eutectics—the melting point is uniform.

On this account it is called "soaking solder."

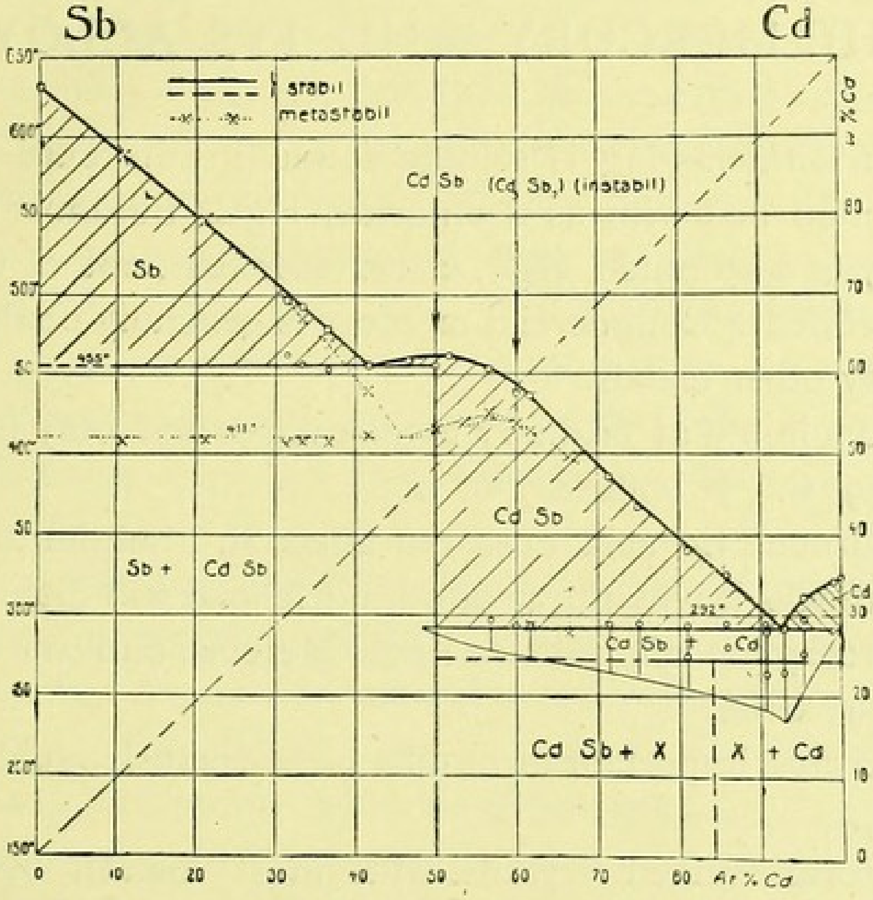


FIG. 86.—Antimony—Cadmium according to Treitschke.

(3) Cadmium—Antimony, Cd-Sb.

These are miscible in all proportions in the fluid state. There are two chemical compounds. Cd_3Sb_2 and CdSb. The former of these two is not stable.

There are two eutectics, one having 92 per cent. by weight of Cd and melting at 292° C., and a second one with 40 per cent. by weight of Cd, melting point 455° C.

(4) Antimony—Tin, Sb-Sn.

These form one chemical compound, SbSn, and two series of mixed crystals :

(1) 0—8 per cent. by weight of Sn.

(2) 90—100 per cent. by weight of Sn.

XIII. MERCURY AND ITS ALLOYS.

Distribution.—Hg is seldom found in the pure state. It is often met with as a chloride, HgCl, but most commonly as a sulphide, HgS, called cinnabar, out of which it is refined. Commercial mercury is generally contaminated by other metals.

It is a liquid at ordinary temperatures and only freezes at —39° C. It boils at 360° C.

Hydrochloric acid does not affect it. Sulphuric acid only attacks it when heated, but nitric acid will dissolve it.

Mercury has one valence in the Mercuro and two in the Mercuri series.

The most important of its salts is the corrosive sublimate $HgCl_2$.

It forms mixed crystals with most metals, but the various alloys with silver and gold are said to be chemical compounds.

Its behaviour in ternary alloys has not yet been fully determined.

With regard to the volume of mercury alloys Bachmetjeff says that all amalgams have a greater volume than the ideal average of their components, with exception of cadmium and copper, which have a less (see chapter on Specific Volume).

This, however, is denied by many writers on the subject, as will appear later from studies which have been made of the different metals with Hg.

On the question of the diffusion of various metals in

Hg, Humphry says silver and copper diffuse the quickest —about 600 times more quickly than Zn.

Most of the earlier writers conclude as to the solubility of metals in Hg by their contents in the eutectics fluid at normal temperatures, and so find very low figures.

The eutectics freeze, as a rule, at very low temperatures (at less than —39° C.), and they fill the gaps between the primary crystals, so that these can be worked as a paste (in manufacture of mirrors and dental amalgams).

The osmotic pressure of the Hg brings about a crystallization of the first formed compounds, viz., Ag_3Hg_2 or mixed crystals with excess of Hg recrystallize to Ag_3Hg_4, and in this way the excess Hg is withdrawn from the fluid eutectic till the whole mass is crystallized.

This is the simple explanation of the hardening process of dental alloys, about which so much has been written.

The phenomena of expansion and contraction can be calculated numerically by means of the tables and diagrams on specific volumes given later.

The doubt and uncertainty of many dentists with regard to their amalgams arises from the fact that most of these as commonly sold are not true amalgams at all, but merely give a superficial amalgamation of the filings used in the mix.

The amalgam lies as a sort of cement between these metallic particles, and then a series of physical and chemical changes commences, which may have far-reaching results where bad or carelessly prepared alloys are used for filling teeth.

(1) Osmosis brings about a change in the distribution of the Hg.

Result.—A change in the shape of the mass.

(2) Infiltration of saliva between the uncemented and porous particles causes the formation of electric currents.

Result.—Solution and discoloration of the filling and tooth.

(3) The pure unamalgamated metals on the surface form sulphides.

Result.—Discoloration on the surface of the filling.

These misfortunes increase in proportion to the primary difficulty of alloying the metals with the Hg. In other words, the higher the melting point of an alloy the harder it is to make a good amalgam of it.

The author has fully explained and demonstrated his views on this subject in various articles elsewhere, and those seeking a deeper knowledge of it are referred to the literature on p. 264.

Up to the present time the most serviceable and popular amalgams for dental uses have been made from the tin-silver alloys.

The writer has found out that those having 48 per cent. by weight of silver and 52 per cent. Sn have proved most satisfactory in respect of colour, stability, and edge strength.

By introducing mercury vapour into the molten alloy its melting point is considerably lowered, and a way prepared (chemically) for the complete amalgamation which follows later.

All alloys prepared in this way really amalgamate, because all crystals already contain mercury, and the molecules of the metals capable of joining have started amalgamation already.

There are a lot of undecided and uncontrolled points still. After this explanation I think it is clear to everybody that it would be useless to give some quires of formulæ of amalgams, of which, if wanted, about one hundred or more will be found in older text-books of dental metallurgy.

Only Black, Flagg and Kirby have worked systematically on amalgams.

Black's researches, however, show such important errors in the light of more recent work that his results are of little use in the advancement of this science.

His chief error lay in not establishing, first of all, what a true amalgam was, but in devoting himself to the study of mere metallic mixtures joined superficially by amalgam.

Moreover, the amounts of mercury used were so different as to preclude any effective comparison of results.

In the third place he has only given the surface changes of his test blocks, and not even stated the temperature at which his measurements were made.

The cubic expansion of tin amalgams according to Cattaneo = $\cdot 0_3 125$ (Landolt and Börnstein); my own measurement gives $\cdot 0_3 33$—and this is an important factor which cannot be ignored.

For these reasons, therefore, it is impossible to place much reliance on Black's results.

In accordance with the general plan of this book the following pages will be found to contain the results of all researches to date, which may be of use to anyone proposing to do original work on amalgams.

The alloys are dealt with in alphabetical order, according to their chemical symbols.

(1) Silver—Mercury, Ag-Hg.

There are on record the results of various researches on these metals.

Crookewitt demonstrated the following chemical compounds: Ag_5Hg_{16}; $AgHg_2$; $AgHg_3$; $AgHg_4$.

Joule established the existence of $AgHg_2$.

Souza evaporated liquid amalgam to dryness, and found that $Ag_{13}Hg$ remained, and by various other methods he proved the compounds: (1) $Ag_{13}Hg$; (2) $Ag_{11}Hg$.; (3) Ag_4Hg.

Merz and Veith heated silver amalgams with 80 per cent. Hg and found:—

After 20	hours	2·3 – 6·45	per	cent. Hg	remained
,, 50	,,	3·89 – 5·4	,,	,,	,,
After about 70	,,	1·24 – 2·37	,,	,,	,,

The difference of the results depended upon whether the heating was done in sulphur, Hg, or diphenyl vapours.

The different investigators prepared their amalgams in different ways.

One method is to dissolve Ag in Hg.

Gouy says that ·0003 per cent. Ag will dissolve in Hg at ordinary temperatures.

Surplus mercury is evaporated from the mass, which is then ready for investigation.

Maey worked in this way, and the writer is of the opinion that his results need controlling, because his method of condensing the porous amalgam is not one to which no objection can be taken, especially with regard to his volumetric results, which will be referred to on p. 169 *et seq*.

Other investigators separate silver amalgam from a watery solution of nitrate of silver by adding Hg to it. This causes the silver to separate out of the solution and by shaking it up with the Hg an amalgam is formed. The solution must be heated up to 82° C.

After squeezing out the superfluous Hg in leather a crystalline mass is obtained, the chemical composition of which has been already stated.

Ogg found that the combination was Ag_3Hg_4.

Reinders prepared silver amalgams by mixing a solution of nitrate of silver with nitrate of mercury, and he also obtained Ag_3Hg_4, though at first he had the compound Ag_3Hg_2.

Ag_3 Hg_2 will form with 44·7 per cent. Ag, but where there is excess of Hg, then Ag_3Hg_4 will be formed with 71·2 per cent. Hg.

The volumetric changes of the silver mercury alloys are shown by Maey's diagram of specific volumes (see chapter on Specific Volume).

The larger proportion in which I demonstrate the diagram shows the desirability of control tests, though it certainly shows Ag_3Hg_4, as well as Ag_3Hg_2 being at variance with the ideal volumetric average of the components.

A microscopic research along the same lines would clear up these points most quickly.

(2) Aluminium—Mercury, Al-Hg.

The results of many writers are in agreement as to these two. One may mention Tissier, Cossa, Casamajor, Wislicenus, Kaufmann, Konowaloff and Biernacki.

They agree that pure Al will quickly amalgamate with Hg with evolution of heat.

This amalgam decomposes water, liberating hydrogen, and forms a hydrate of aluminia $Al(HO)_6$, which grows in fantastic forms from the surfaces of the amalgam.

Aluminium amalgam is of no use in dental work.

(3) Gold—Mercury, Au-Hg.

Crookewitt demonstrated the compound $AuHg_4$, which has a specific gravity of 15·412. The average of the coefficients gives 14·6, so that there must be a considerable contraction in the mass.

Sonnenschein described a natural amalgam found in the mines, and having 39·02 and 41·63 per cent. Au, as $AuHg_3$.

This formula is not correct, as it is equivalent only to about 24 per cent. Au.

Au_2Hg_3 is the formula which would correspond better to the weight.

Henry demonstrated Au_4Hg.

Souza obtained an amalgam having about 10·02—10·5 per cent. Hg from a solution of Au in Hg by evaporating the Hg to dryness. The formula of this is Au_9Hg.

He also obtained amalgams described as Au_9Hg and Au_8Hg by other methods.

Chester formed a gold amalgam on the surface of pure gold with 6 per cent. Hg.

Merz and Veith showed the loss of Hg from gold solutions through long heating in different atmospheres to be finished at 33 per cent. Hg.

Kasanzeff found that Au was soluble in Hg up to ·126 per cent. (Gouy gives ·0013 per cent.).

By partially dissolving the Hg in HNO_3 he obtained gold amalgams having 8·4—18·4 per cent. Hg.

These he regarded as solid solutions (mixed crystals) and this hypothesis is probably near the truth.

Microscopic and volumetric investigations have not yet been made.

(4) Bismuth—Mercury, Bi-Hg.

Puschin has investigated the bismuth amalgams most thoroughly after thermic and microscopic and electrical methods, and as a result of his work he is convinced that there are no compounds formed, but only physical mixtures between these two.

Calvert and Johnson give the following compounds and specific gravities :—

(1)	Hg_2Bi	(about 66 per cent. Hg)	specific gravity	11·208
(2)	$HgBi$	(49 ,, ,,)	,,	10·693
(3)	Hg_2Bi_3	(39 ,, ,,)	,,	10·474
(4)	$HgBi_2$	(32 ,, ,,)	,,	10·350
(5)	Hg_2Bi_5	(28 ,, ,,)	,,	10·240

Maerz and Veith dissolved 20 per cent. Bi in 80 per cent. Hg and stated that by prolonged heating all the Hg was again evaporated.

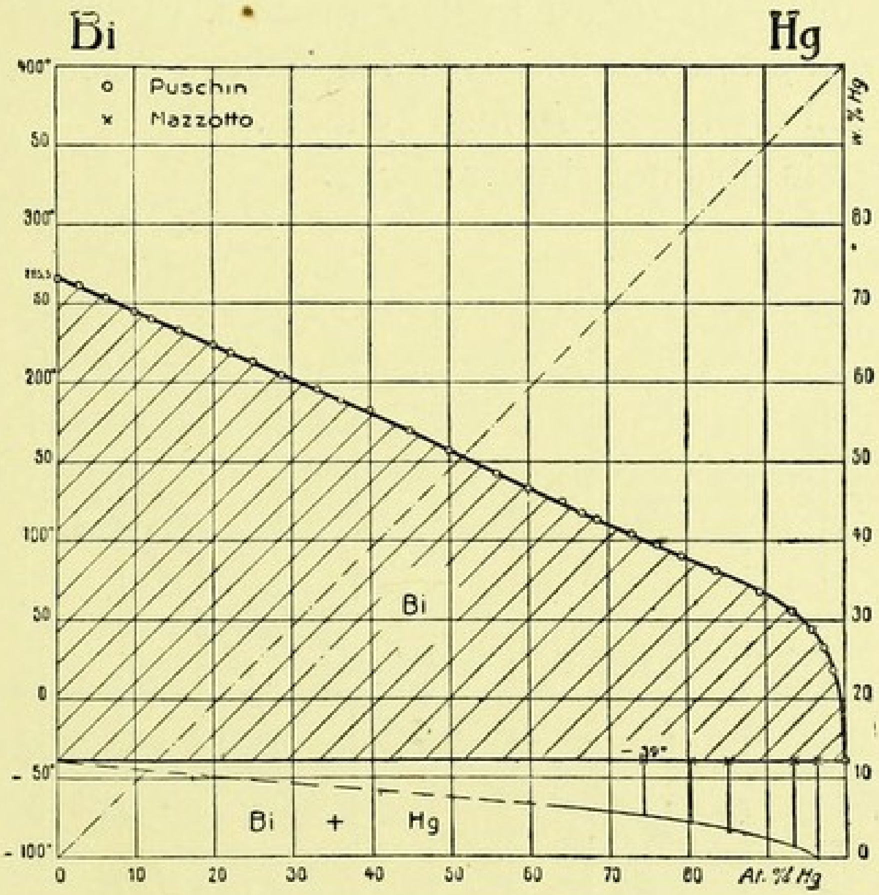


FIG. 87.—Bismuth—Mercury according to Puschin and Mazotto; atomic percentage by Bornemann.

Gouy states that Bi is soluble in Hg to the extent of ·012 per cent.

The volumetric diagram (see Specific Volumes) gives the specific volume according to the measurement of Calvert and Johnson, which show a maximum of variance with the average which would prove the existence of a chemical compound according to Maey.

But the correctness of Puschin's views is unassailable, though the volumetric investigations should be controlled by other workers with a view to discovering what part porosity plays in increasing the volume.

(5) Cadmium—Mercury, Cd-Hg.

Bijl and Roozeboom have studied the cadmium amalgams with regard to their thermic, volumetric, and electrical properties, and conclude that two different series of mixed crystals are formed by them.

Puschin obtained similar results.

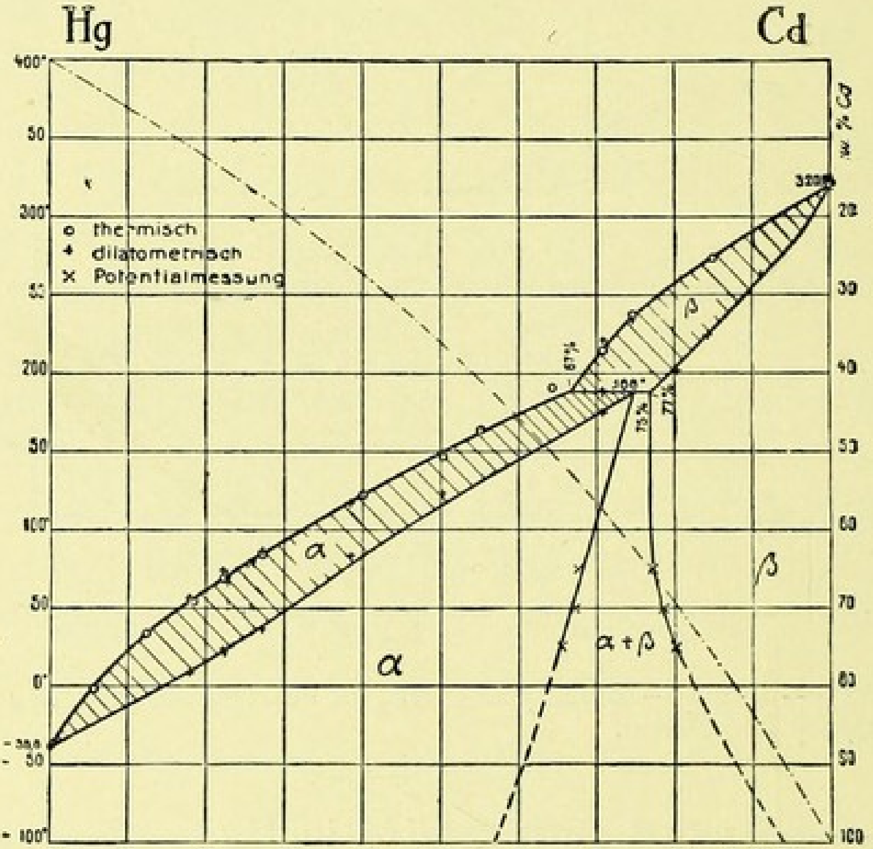


FIG. 88.—Cadmium—Mercury according to Bijl.

With more than 62 atomic per cent. (48 per cent. by weight) of Cd Puschin found that small hexagonal crystals appeared. With less than 62 atomic per cent. of Cd crystals formed like stars or snowflakes.

On this account Puschin also supports the theory of two different series of mixed crystals.

B. Wood found that a 50 per cent. Cd amalgam was tough and malleable, but with 66·66 per cent. Cd it is just as malleable, though not so tough.

According to Merz and Veith all the Hg may be driven from a cadmium amalgam by prolonged heating.

Crookewitt discovered the compound Cd_2Hg_5, spec. gravity 12·615, and Kerp, Böttger and Winter demonstrated $Cd_2 Hg_3$, but these results may not be correct.

Schumann discovered a saturated Cd amalgam having a specific gravity of 12·55, which crystallized in fine needles.

Its apparent specific gravity was 12·05, but this was owing to the inclusion of bubbles.

The composition is not given.

For the specific volume of cadmium amalgams the reader is referred to p. 176.

(6) Copper—Mercury, Cu-Hg.

C. Michaelis kept 1 gr. of Cu for several days in boiling Hg and found a solution of the copper of only 0·025 per cent. Cu.

Gouy found the saturated solution contained only ·041 per cent. Cu. Souza combined Cu_6Hg and $Cu_{14}Hg$ according to the mode of preparation employed, and the latter was found to be constant within wide limits of temperature.

Maerz and Veith heated a copper amalgam with 80 per cent. Hg for some time, and all the Hg evaporated.

Puschin regards them as isomorphic mixed crystals rather than chemical compounds.

But a reference to my photograph of pure Cu amalgam will show plainly that there are two distinct structures present, which seems rather to contradict Puschin's views (see "Dental Cosmos," 1908).

It has not been found possible to give an account of the chemical and physical properties of these amalgams of Cu to which no objection could be taken, because of the great difficulties which the problem presents. These difficulties arise from the wide difference which there is between the evaporating point of Hg and the melting point of Cu.

But something may be done perhaps with the aid of photography.

Essig states that Cu will not combine with Hg without heating.

Humphreys asserts that Cu is quickly diffused in Hg (600 times more quickly than Zn), but as a matter of fact it only dissolves to a very small extent (0·03—0·05 per cent.) at 27° C.

But at higher temperatures Hg will dissolve more Cu; this, however, re-crystallizes on cooling, but whether as pure Cu or amalgam is not stated.

Joule has stated that fluid amalgams of Cu have a greater specific gravity than Hg; in other words, Cu amalgam contracts considerably during its formation.

The phenomena commonly observed in working dental (copper) amalgams are as follows:—

(1) The amalgam which is solid at normal temperatures divides on heating to 200—300° C. into a liquid and a solid.

(2) The fluid will not freeze immediately, but only after the lapse of some time.

(3) The separation of the liquid and the solid does not take place as soon as the temperature is raised, but only after a little time has elapsed, say half a minute.

The writer, from his own microscopic examinations of these amalgams, is of the opinion that they have two structural elements and consist of an alloy which contains :—

(1) A primary amalgam of high Cu content and high melting point, which is either a compound or a mixed crystal.

(2) A secondary amalgam, probably a eutectic, with more Hg and a lower melting point than the primary crystals.

The latter is melted by heating and is then mixed with the primary amalgam to form the mass which is used for filling teeth.

The slow hardening indicates that it is not a simple process of crystallization, but that either polymorphic changes take place or a considerable undercooling delays the setting.

This is another promising field for research, as volumetric and microscopical investigations in this department have yet to be made.

According to Schumann, Cu amalgam is easily prepared as follows :—

Pure Hg is poured into a beaker containing a solution of copper sulphate ($CuSO_4$) and a sheet of iron is put into it.

The Cu in the $CuSO_4$ is replaced by the Fe, forming $FeSO_4$, and the Cu amalgamates with the Hg.

The copper solution must be frequently renewed and the excess of Hg can be removed by squeezing the amalgam in a piece of leather.

(7) Magnesium—Mercury, Mg-Hg.

The results of Wanklin, Chapman and Parkinson agree with regard to magnesium amalgam.

It will form slowly at normal temperatures. On heating a violent reaction takes place and the amalgam forms quickly.

With 5 per cent. Hg the amalgam becomes explosive and decomposes water energetically.

(8) Nickel—Mercury, Ni-Hg.

There is only one communication, that by Wünsche, on record with regard to these. Nickel amalgam was prepared by electrolysis from $NiSO_4$, but when an attempt was made to melt it a separation took place.

Wünsche prepared amalgams in various ways with the following percentages of Ni :—

(1) 3·75 per cent. Ni.
(2) 1·73 per cent. Ni.
(3) 1·51 per cent. Ni.
(4) 8·2 per cent. Ni.

A solid plastic amalgam was obtained by expressing the superfluous Hg from a very thin mix, and Wünsche regards this as a chemical compound.

Thermic, microscopic, and volumetric examinations have not yet been made.

(9) Lead—Mercury, Pb-Hg.

According to Puschin, Fay, North, and Jänecke, these metals form the mixed crystal α, which is saturated with 35 per cent. mercury.

All alloys containing more Hg than this freeze primarily as mixed crystals, and finally the surplus of mercury at −39° C.

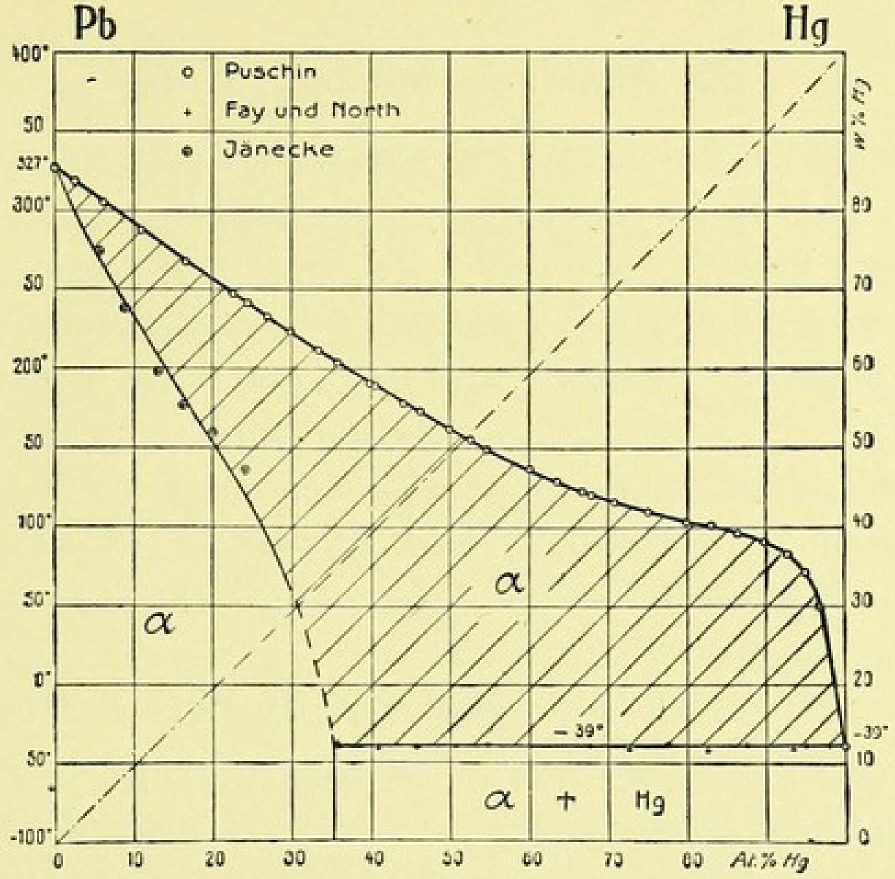


FIG. 89.—Lead—Mercury according to Puschin, Fay, North, and Jänecke. Atomic percentage by Bornemann.

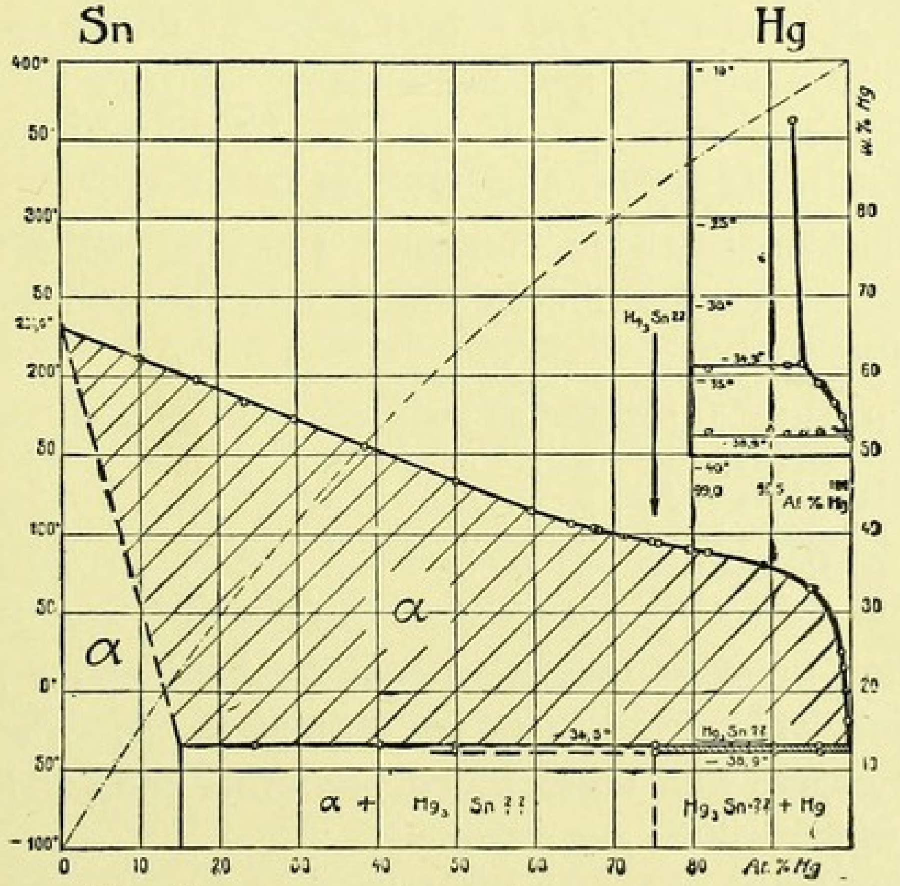


FIG. 90.—Tin—Mercury according to Heteren. Atomic percentage by Bornemann.

(10) Platinum—Mercury, Pt-Hg.

Tarugi has obtained amalgams with 1 per cent., 50 per cent., and 99 per cent. Pt, by acting on the chlorides of Hg and Pt with Mg.

The result was a black amalgam of platinum, but he was unsuccessful in his attempts to dissolve metallic Pt in Hg.

Joule states that he obtained the compound $PtHg_2$.

Thermic, microscopic, and volumetric examinations have not yet been made.

(11) Tin—Mercury, Sn-Hg.

A study of the records about these shows :—

(1) Joule made Sn_7Hg = 80·6 by weight of Sn, by expressing the superfluous Hg from a plastic mix under high pressure.

(2) Horsford allowed a bent piece of tin to suck up Hg like a syphon, and this made a saturated amalgam (which lost nothing on exposure to the air), with a formula of Sn_8Hg (82·6 per cent. Sn).

Fluid tin amalgam contained 1·55 Sn. Calvert and Johnson recorded the following formulæ and specific gravities :—

(1) $HgSn$	37·5	per cent.	by weight	Sn,	specific gravity	10·255
(2) $HgSn_2$	54·54	,,	,,	,,	,,	9·314
(3) $HgSn_3$	64·3	,,	,,	,,	,,	8·805
(4) $HgSn_4$	70·6	,,	,,	,,	,,	8·510
(5) $HgSn_5$	75·0	,,	,,	,,	,,	8·312
(6) $HgSn_6$	78·0	,,	,,	,,	,,	8·151

These numbers indicate a considerable increase in the volume, which is about 11 per cent. at HgSn. Also they fail to agree with those which the writer himself found, and which will be given below.

In addition to these the following combinations are mentioned in the literature on the subject: (1) $SnHg_5$; (2) Sn_3Hg_5.

The names of the authors as well as a complete list of their works are given in my papers quoted above.

Thermic analysis has led Puschin and Heteren to think that there is a series of mixed crystals between Sn and Hg, and the former of these writers speaks also of Isomorphism in this connection.

Heteren supports Cohen's findings with regard to allotropy, and the grey modification of tin at 20° C., which is a point for amalgam makers to remember.

Without wishing to contradict these writers I should like to state my own results, which I obtained on cooling mixtures down to room temperatures.

80·6 Sn and 19·4 per cent. Hg forms a homogeneous crystal which corresponds to the symbol $HgSn_7$.

With more tin two kinds of crystals appear, one of which is darkened by etching with HCl for twelve hours, while the other remains light-coloured.

With less Sn and more Hg the alloy will have one kind of crystal only surrounded by a liquid eutectic, which consists of 1·5 per cent. Sn, and 98·5 per cent. Hg, so that with 80·6 per cent. Sn we must either have a saturated mixed crystal or the compound Sn_7Hg, which is what Joule found (Horsford, Sn_8Hg).

Coming now to the volumetric changes (see volumetric diagram), I have only given an expansion of 1·5 per cent. with 99 per cent. Sn. This is not in agreement with Calvert and Johnson's figures.

The expansion of tin amalgams with 40 per cent. Hg according to my measurements amounts to ·00033 of their volume.

(12) Zinc—Mercury, Hg-Zn.

Cattaneo says that Zn amalgams shrink, but that the shrinkage is less in proportion as the mercury content is reduced.

Gouy found that ·018 per cent. of Zn will dissolve in Hg.

Crookewitt prepared a solid amalgam with 29·4 per cent. Zn. Calvert and Johnson mention the formula HgZn (24·8 per cent. by weight of Zn), with a specific gravity of 11·304.

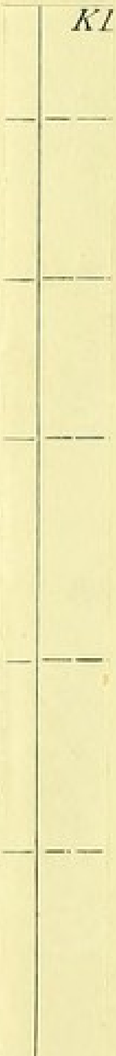
Merz and Veith assert that prolonged heating drives off all the Hg.

Puschin regards all Zn amalgams as physical mixtures, and this is also Maey's opinion. He did not find much variation in the volume (see diagrams of specific volumes).

THE BEHAVIOUR OF THE METALS TOWARDS ONE ANOTHER, ACCORDING TO TAMMAN.

	Ag	Au	Mg	Zn	Cd	Hg	Al	Tl	Sn	Pb	Sb	Bi	Mn	Fe	Co	Ni	Pd	Pt	Cr	Si
Cu ...	f ~ 0 KL 6-95 Cu	f ~ 0 K ~	f ~ $CuMg_2$, Cu_2Mg KL 0-100	f ~ Cu_2Zn_3 $CuZn_4$ KL 2, 5-70 Cu?	f ~ Cu_2Cd_3 Cu_2Cd? KL 0-100 Cu	Ag_3Hg_4 AgHg Ag_2Hg_3	f ~ $AlCu_3$, AlCu, Al_2Cu KL 4-71 and 88, 5-91 Cu	f 3-33 Cu 0 KL 0-95 ? Cu	f Cu_3Sn Cu_4Sn, CuSn KL 0-93 Cu	f L 16-61 Cu KL 0-97 Cu	f ~ Cu_2Sb, Cu_3Sb KL 0-90 ? Cu	f ~ 0 KL 0-100	f ~ 0 K ~	f ~ 0 KL 2·5-97 Fe	f ~ 0 KL 4-90 Co	f ~ 0 K ~	f ~ 0 K ~	f ~ 0 K ~	f L 2-98 Cr 0 KL 0-100	f ~ Cu_3Si $Cu_{10}Si_4$ KL 4-100 Si
Ag ...		f ~ 0 K ~	f ~ AgMg, $AgMg_3$ KL 0-72	f ~ Ag_3Zn_2 AgZn, Ag_2Zn_3 $AgZn_3$ KL 10-78 Ag	f ~ probably compounds	--	f ~ Ag_3Al, Ag_2Al KL 0-95 Ag	f ~ 0 KL 0-90 Ag	f ~ Ag_3Sn KL 0-73 Ag	f ~ 0 KL 0,3 up to 100 Ag	f ~ Ag_3Sb KL 0-85 Ag	f ~ 0 KL 0-95 Ag	f L 2-87 Mn 0 KL 0-100 Mn	f L 0-100 0 KL 0-100	f L 0-100 0 KL 0-100	f L 10-98 Ni 0 KL 0-96 Ni	f ~ 0 K ~	f ~ 0 KL 48-95 Pt	f L 5-91 Cr 0 KL 0-100	f ~ 0 KL 0-90 Si
Au ...				f ~ AuZn, Au_3Zn_5, $AuZn_8$ KL 19-88 Au	f ~ Au_4Cd_3 $AuCd_3$ KL 0-81 Au	—	f ~ Au_4Al Au_5Al_2, Au_2Al, $AuAl_2$, AuAl	f ~ 0 KL 0->95 Au	f ~ AuSn, $AuSn_4$ $AuSn_2$ KL 0-96 Au	f ~ Au_2Pb $AuPb_2$ KL 0-100 Au	f ~ $AuSb_2$ KL 0-1	f ~ 0 KL 0-95 Au	—	f ~ 0 KL 37-72 Fe at 20° KL 20-82 Fe	—	f ~ 0 KL 5-80 Ni	f ~ 0 K ~	f ~ 0 K ~	—	—
Mg ...				f ~ $MgZn_2$ KL 0-100 Mg	f ~ MgCd K ~	—	f ~ Al_3Mg_4 KL 0-35 and 55-100 Mg	f ~ Tl_2Mg_3 $TlMg_2$, Tl_2Mg_3 KL 0-92 Mg	f ~ Mg_2Sn KL 0-100 Sn	f ~ $PbMg_2$ KL 0-100 Mg	f ~ Mg_3Sb_2 KL 0-1	f ~ Mg_3Bi_2 KL 0-100	—	—	—	f ~ $NiMg_2$, Ni_2Mg KL 0-100	—	—	—	f ~ Mg_2Si KL 0-100 Si
Zn ...					f ~ 0 KL 0-100 Cd	f ~ 0 KL 0-67 Zn	f ~ 0	f L 2-95 Tl KL 0-100 Zn	f ~ 0 KL ? 0-100	f L 1-99 Zn 0 KL ? 0-100	f ~ Zn_3Sb_2 ZnSb KL ? 0-100	f L 2-90 Bi 0	—	f ~ at 20% Fe researched, $FeZn_7$, $FeZn_3$	$CoZn_4$	$NiZn_3$ KL 0-14 Ni	—	—	Chemical compound X	—
Cd ...						f ~ 0 KL 62-65 Cd	f L 9-100 Cd 0 KL 0-100 Cd	f ~ 0 KL ? 0-100	f ~ X KL ? 0- 00	f ~ 0 KL ?	f ~ Cd_3Sb_2 CdSb KL 0-100	f ~ 0	Mn not soluble in boiling Cd	—	—	$NiCd_4$	—	—	Cr not soluble in boiling Cd	—
Hg ...								f ~ Hg_2Tl KL ?	f ~ $HgSn_2$ KL 0-95 Sn	f ~ 0 KL 0-65 Pb	—	f ~	—	—	—	—	—	—	—	—
Al ...								f ~ 0-100 Al 0 KL 0-100 Al	f ~ 0 KL 0-100 Al	f L 5-100 Pb 0 KL 0-100	f L ? AlSb slow formation KL	f L 2-92 Bi 0 KL 0-100	f L 14-42 Mn Al_3Mn? $AlMn_3$?	f ~ $FeAl_3$ KL 66-48 and 40-0 Fe	f ~ Co_3Al_{13} Co_2Al_5 CoAl KL 90, 5-80 and 68,5-0 Co	f ~ $NiAl_3$, $NiAl_2$, NiAl KL 87, 5-81 and 68,4-0 Ni	—	—	f L 4-55 Cr $AlCr_2$? KL ?	f ~ 0 KL 0-100 Si
Tl ...									f ~ 0 KL ?	f ~ $PbTl_2$ KL 6-23 Pb	f ~ Tl_3Sb KL ?	f ~ Bi_5Tl_3 $BiTl_3$ KL 0-66 and 92-93 Tl	—	f L 0-100 0 KL 0-100	f L 2-99 Co 0 KL 0-100	f L 0-90 Ni 0 KL 0-98 Ni	—	—	—	f L 0-100 Si 0 KL 0-100 Si
Sn ...										f ~ 0 KL 0-100	f ~ SbSn KL 8-50 and 53-90 Sb	f ~ 0 KL 0-97 Sn	f ~ $SnMn_4$ $SnMn_2$ SnMn ? KL 0-92 Mn	f ~ compound X KL 0-81 Fe	f ~ Co_3Sn_2, Co_3Sn_4? KL 0-100	f L 3, 5-18 and 30-45 Ni Ni_3Sn_2, NiSn, Ni_4Sn? KL 0-85 Ni	—	f ~ Pt_3Sn PtSn $PtSn_2$ Pt_2Sn_3, KL ?	f L 0-87 Cr 0 KL 0-95 Cr	f ~ 0 KL 0-100 Si
Pb ...											f ~ 0 KL 0-100	f ~ 0 KL ? 0-100	f L 12-90 Mn 0 KL 0-100 Mn	f L 0-100 0 KL 0-100	f L 0-100 0 KL 0-100	f L 16-72 Ni 0 KL 0-96 Ni	f ~ $PdPb_2$ PdPb, Pd_3Pb, Pd_2Pb KL 0-77 Pd	f ~ X, PtPb, X	f L 10-75 Cr 0 KL 0-100 Cr	f L 0-100 Si 0 KL 0-100 Si
Sb ...												f ~ 0 KL 0-50 ? Bi	f ~ Sb_2Mn_3 $SbMn_2$, KL 0-31, 41-49 and 53-100	f ~ Fe_3Sb_2 Fe_2Sb KL 0-41 and 45-95 Fe	f ~ CoSb $CoSb_2$ KL 0-100	f ~ Ni_4Sb_3 NiSb, Ni_5Sb_2, Ni_4Sb KL 0-92,5 Ni	—	—	f ~ Sb_2Cr SbCr KL 0-30 and 32, 5-90 Cr	f ~ 0 KL 0, 3-99 Si
Bi ...														f L 0-100 0 KL 0-100	f L 0-100 0 KL 0-100	f ~ $NiBi_3$ NiBi ? KL 0-99,5 Ni	—	—	f L 0-100 0 KL 0-100	f L 2-100 Si 0 KL 0-99, 2 Bi
Mn ...														f ~ 0 K ~	—	f ~ Chem. compounds K ~	—	—	—	f ~ Mn_2Si, MnSi KL 10-100 Si
Fe ...															f ~ 0 K ~	f ~ $FeNi_2$? K ~	—	—	f ~ compound X KL depends upon the temperature of the alloy	f ~ FeSi KL 20-100 Si
Co ...																f ~ 0 K ~	—	—	f ~ K ~ chemical compound X	f ~ Co_2Si Co_3Si_2, CoSi, $CoSi_2$ KL 9-92, 5 Co
Ni ...																	—	—	f ~ 0 KL 42-43 Ni	f ~ Ni_3Si Ni_2Si, Ni_3Si_2 NiSi $NiSi_2$ KL 0-14 and 19-100 Si

f ~ = Miscibility in liquid state in all proportions.
f L = Hiatus of miscibility in the liquid state.
0 = No chemical compound.
K ~ = Complete series of mixed crystals.
KL = Hiatus in the series of mixed crystals.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XIV. OTHER METALS.

The alloys of these metals have already been described. For physical properties see table, pp. 36-37.

(1) Aluminium, Al.

Aluminium is one of the most important components of the earth-crust, and was prepared first in 1827 by Wöhler, and in 1854 Bunsen made it by electrolysis.

Its lightness and beautiful white colour caused it to be used for many purposes for which it was not really suitable, as it is not very resistant to chemical influences, either acid or alkaline.

But its alloys were found to have many desirable properties and have been put to various uses. They are described under "Gold," "Silver," "Copper," &c.

For dental purposes an alloy of 85 aluminium, 10 nickel and 5 zinc may be useful, as its chief property is its great hardness. It is much used for hard-wearing parts of engines.

Oxide of aluminium Al_2O_3 is used as corundum (blue, sapphire, red rubin). Amorphous oxide of aluminium is obtained by raising it to a high temperature, and it is used as a base for dental silicate cements in conjunction with silicon and calcium.

(2) Bismuth, Bi.

Bismuth is a brittle metal of reddish sheen and has properties similar to those of antimony.

It fuses at 264° C. and evaporates at 1100 to 1400° C. The specific gravity is 9·747 when crystalline, 10·055 when liquid. We find, therefore, that it contracts on melting, and expands on crystallization like ice.

Of all metals it is the poorest conductor of heat and electricity and has the least specific heat, the highest specific resistance (1080).

It is precipitated from its salt solutions by zinc, iron, copper, lead.

We use bismuth only as an alloy in soft solders, and in type metals for clichés, and as a constituent of dental amalgams, &c. These alloys are dealt with in various chapters (see Index).

(3) Cadmium, Cd.

Cadmium is a white metal resembling tin, and it can be cut with a knife.

With sulphur it forms a yellow sulphide. Its melting point is 322° C., and its evaporating point 780° C.

In alloys it often lowers the melting point considerably, and is therefore a frequent constituent of solders. Its low evaporating point, however, makes it necessary to carefully avoid overheating all solders containing it, or porosity will be the result (see Solders). Some time ago cadmium was much used in dental amalgams (see Amalgams). It is precipitated from its salt solutions by zinc.

(4) Cobalt, Co.

This metal is rarely found pure (in meteors for example), but mostly as an arsen~~ate~~ide ($CoAs_2$).

It is obtained chiefly as a by-product in the treatment of nickel ores.

Protoxide of cobalt, when heated with alumina, gives the well-known Thénard's blue, and when heated with oxide of zinc the cobalt green of Rinman is obtained.

Metallic cobalt has a very high fusing point, and it absorbs carbon dioxide and oxygen. This makes it difficult to melt.

A very small addition of magnesium for reducing purposes makes it cast well. The metal is very hard and resistant to acids, and it is magnetic, and remains so even when raised to a red heat.

Compounded with iron it makes a very good steel.

The solid solutions of cobalt-chromium are very hard, and steel tools will hardly touch them even at 1000° C.

These alloys will be of great value to makers of war material when they can be produced more cheaply.

They were thoroughly studied and described by Lewkonja of Göttingen (see Literature). In France there is a patent issued for watch-springs and small tools made of it. Pure cobalt is weldable and ductile. (For alloys with gold, silver, &c., see these metals.)

(5) Manganese, Mn.

Manganese is never used pure on account of its low resistance to atmospheric influences.

It is prepared by reducing its oxides.

In making manganese steel we use ferro-manganese. This is prepared by melting the ores with iron and charcoal, and keeping them several hours at a white heat. A regulus of ferro-manganese is thus obtained.

Pure manganese is so hard that it will scratch glass and steel. It will take high lustre and polish, but it is oxidized slowly by cold water and quickly by hot. In alloying it is used for bronze in addition to its iron compounds.

(6) Lead, Pb.

Lead was used in very early times for many of the purposes for which it is used to-day, such as for pipes, weights, and for fixing other metals into stone.

It is obtained almost exclusively from its sulphur compounds, galena or lead sulphide (PbS).

Various methods are in use.

(1) The precipitation may be done by melting with iron, which forms a ferrous sulphide and deposits the lead.

(2) The roasting method is done by changing the ore partly into plumbic oxide and partly into lead sulphate—a third part remains unaffected. These are melted in a retort from which all air is excluded, and the plumbic oxide and lead sulphate reduce the sulphide, leaving pure lead.

$$2PbO + PbS = 3Pb + SO_2$$
$$PbSO_4 + PbS = 2Pb + 2SO_2$$

The lead used in the extraction of silver is purified from the latter, and from copper by addition of zinc.

The crystals of the resulting compound have a low specific gravity, and rise to the surface, from which they are easily skimmed off.

Lead may be separated from iron zinc and nickel by passing steam through them to oxidize them.

Tin, arsenic and antimony are got rid of in this order by long exposure to a current of air, which also causes oxidation.

Lead is a very soft metal; it may be scratched with the finger-nail, and may be rolled and hammered into thin sheets and foils. Its surface oxidizes in a damp atmosphere and forms a basic carbonate ~~grey protoxide~~. The chemical industries make great use of lead on account of its resistance, even when warm, to hydrochloric and sulphuric acids.

In metallurgical laboratories lead is used for cupelling silver and gold from their alloys with base metals. Water pipes and accumulator plates are made of it.

Its alloys, especially with antimony, make good type metal. Lead—tin makes a soft solder, and is used for various other purposes.

The salts of lead give several colours; its oxide is used as an enamel for clay; chemically pure oxide of lead is also used for producing flint-glass for lenses.

(7) Platinum, Pt.

On account of its resistance to all chemical agents platinum is indispensable for chemists.

The metal is found in ores mixed with 20 to 25 per cent. iridium, osmium, iron, copper, but it is easily separated from these. A small percentage of iridium increases its valuable properties. It is best melted with an oxyhydrogen-blowpipe. Small quantities may be easily melted with ordinary illuminating gas and oxygen.

Platinum is weldable at a red heat. The price of platinum has been raised from £20 per kilogram in 1890 to £250 per kilo. in 1910. This enormous rise in price causes a constant search to be made for a cheaper substitute, especially for the pins of artificial teeth.

The alloys of platinum with gold, silver and copper are given with the metals.

Cooper made an alloy of 81 per cent. copper, 19 per cent. platinum, which is said to have the properties of 18-carat gold. Cooper's mirror metal is made of 35 copper, 6 platinum, 2 zinc. Hard-wearing pens which are not affected by ink are made of 1 copper, 3 silver, and 4 platinum.

Bearings of watches which are not affected by magnetism are made of platinum, copper, and nickel.

(8) Antimony, Sb.

This metal has a white colour, it is laminated, brittle and easily ground in a mortar to powder. When melted and cooled rapidly it forms very fine crystals.

It is precipitated from its solutions by metallic zinc as a black powder, which is used to give a black iron-like colour to plaster casts.

The metal is used for making thermo-electrical piles. Alloyed, it makes most metals harder (printing types). In Japan it is much used for making castings, and is coloured artistically by etching and annealing.

(9) Tin, Sn.

A white metal showing good resistance to atmospheric influences. It is soft, ductile, and easily cast into form.

Tin is generally obtained from its oxide (SnO_2), more rarely from its sulphide (SnS_2). The ore (cassiterite) is broken, separated as far as possible by washing from its admixtures, roasted in the open air, and reduced by being melted with carbon, which takes off the oxygen as CO_2.

The metal thus prepared is of a coarse-crystalline structure, creaks when bent, is harder than lead and softer than gold.

Heated to 200° C. it becomes so brittle that it is easily powdered.

Its internal microscopic structure depends upon the temperature at which it is cast, and the rate of cooling.

At 20° C. tin changes to an allotropic condition, the so-called grey tin. This grey modification is the cause of what is called tin-disease in church organ pipes. Organs should always be kept above 20° C., as at this temperature the grey tin recrystallizes into the white form.

To this cause also is due the dirt found in mixing dental amalgams. It is of no use to wash such fillings, but a simple warming of the ready-mixed filling in a test tube is an efficient means of getting the amalgam white again.

Sulphide of tin is used for giving a bronze appearance to metals, and oxide of tin is used as an enamel for pottery and metals.

Many household articles are made of tin, which is generally alloyed with lead for that purpose (pewter). The same combination serves as soft solder. Tin mercury as an amalgam (see Amalgam) or tin-foil is used for making mirrors.

It is also used for galvanizing iron and copper, which are protected in this way against external influences (oxidation, &c.).

Commercial tin is generally contaminated by arsenic, antimony, copper, iron, lead. According to Wüst the best brands are those from Malaga, Banka and Billiton and the Chinese brand "Novah." Next to these come the English, Saxon and Bohemian tins.

Nearly all tin ingots have cavities in their interiors which are often filled with water. In melting them it is advisable to cut the blocks in two to avoid explosions.

The peculiar property which tin has, of making other metal brittle, caused it to be known in the Middle Ages as the "*diabolus metallorum*" or devil of the metals.

Its alloys with other metals are discussed with them.

(10) Tungsten, W (Wolfram).

Tungsten is a grey metal which changes into tungstic acid (H_2WO_4) if heated in the air or brought into contact with water.

WO_3

This acid may be reduced to the metal by being melted in a crucible with potassium cyanide and charcoal, or by being heated in a current of hydrogen.

With steel, tungsten is alloyed as ferro-tungsten, which is made in a similar way to ferro-manganese, by heating the acid with the metals and reducing by melting it with charcoal and aluminium.

XV. THE SPECIFIC VOLUME OF ALLOYS.

The specific volume of alloys was the object of scientific investigation in early times.

A fairly complete collection of results is to be found in the tables of Landolt and Börnstein, pp. 308 *et seq.* Many of these are stated only as specific gravities, and have to be corrected into specific volumes in order to show the results in diagrams, as the two figures are in no way interchangeable.*

The specific volume is however the more important of the two, as the specific gravity is really the result of changes of volume by expansion or contraction brought about by alloying.

The conversion is very simple :

$$\text{Specific volume} = \frac{1}{\text{specific gravity}}$$

$$\text{Specific gravity} = \frac{1}{\text{specific volume}}$$

Maey was the first to employ estimations of specific volumes in order to establish the existence of chemical compounds between two metals. His observations, how-

---

* The specific gravity of a body is the weight of 1 c.c. expressed in grammes. The specific volume is the expression of the quantity of 1 grm. in cubic centimetres.

Thus if the specific gravity of a body is equal to 10 this means that 1 c.c. of it has a weight of 10 grm. The quantity of 1 grm. of this body is therefore equal to $\frac{1}{10}$ or ·1 c.c., or its specific volume is equal to ·1.

ever, are not always confirmed by the results of other methods, and several theoretical reasons make them questionable.

But a great number of Maey's results have been confirmed by other observers using different methods. I regret to say that the correlation of Maey's diagrams has not always been clear to me.

This has induced me to draw new diagrams, using either Maey's or the figures which are given in Landolt and Börnstein.

I have entirely omitted Maey's conclusions regarding the existence of chemical compounds, as they are of no importance to practical people, for whom this book has been written. For such it is sufficient to know the variations in form which take place, and their amount.

Those metals which expand or contract when alloyed so little as to make the amount negligible have been separated into three divisions according to Maey.

Those which are known to show considerable variations of volume are shown diagrammatically.

I. *Alloys which show a slight Expansion as well as Contraction :—*

(1) Bismuth—Antimony	—	at	37·1	per cent.	Sb.
	+	„	22·7	„	„
(2) Bismuth—Tin	+	„	3·3	„	Sn.
	—	„	62·5	„	„
(3) Cadmium—Tin	+	„	80·5	„	„
	—	„	14·7	„	„
(4) Lead—Tin	+	„	16·0	„	„
	—	„	69·5	„	„
(5) Lead—Silver	+	„	11·5	„	Ag.
	—	„	67·6	„	„

(6) Silver—Copper	+ at	5·6	per cent.	Cu.
	— ,,	50·35	,,	,,
(7) Gold—Copper	+ ,,	6·8	,,	,,
	— ,,	1·99	,,	,,
(8) Gold—Silver	+ ,,	76·5	,,	Ag.
	— ,,	12·0	,,	,,
(9) Gold—Tin	+ ,,	37·0	,,	Sn.
	— ,,	22·7	,,	,,
(10) Iridium—Platinum	+ ,,	95·0	,,	Pt.
	— ,,	66.7	,,	,,

II. *Alloys which show only slight Contractions* :—

(1) Bismuth—Cadmium,	at	51·8	per cent.	Cd.
(2) Silver—Bismuth,	,,	49·0	,,	Bi.
(3) Mercury—Lead,	,,	50·8	,,	Pb.
*(4) Mercury—Tin,	,,	53·7	,,	Sn.

III. *Alloys showing slight Expansion only* :—

(1) Tin—Antimony,	at	51·4	per cent.	Sb.
(2) Tin—Zinc,	,,	75·0	,,	Zn.
(3) Lead—Cadmium	,,	8·3	,,	Cd.
(4) Lead—Antimony	,,	54·1	,,	Sb.

The greatest changes in all these alloys never exceed 1 per cent. of their volume.

The following diagrams will explain themselves. They show the alteration from the average line, connecting the two ordinates, which corresponds to the specific volumes of the components.

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* This statement is not supported by Holzmann's and my own results. Compare diagram 12, fig. 102.

(1) Gold—Silver, Au-Ag.

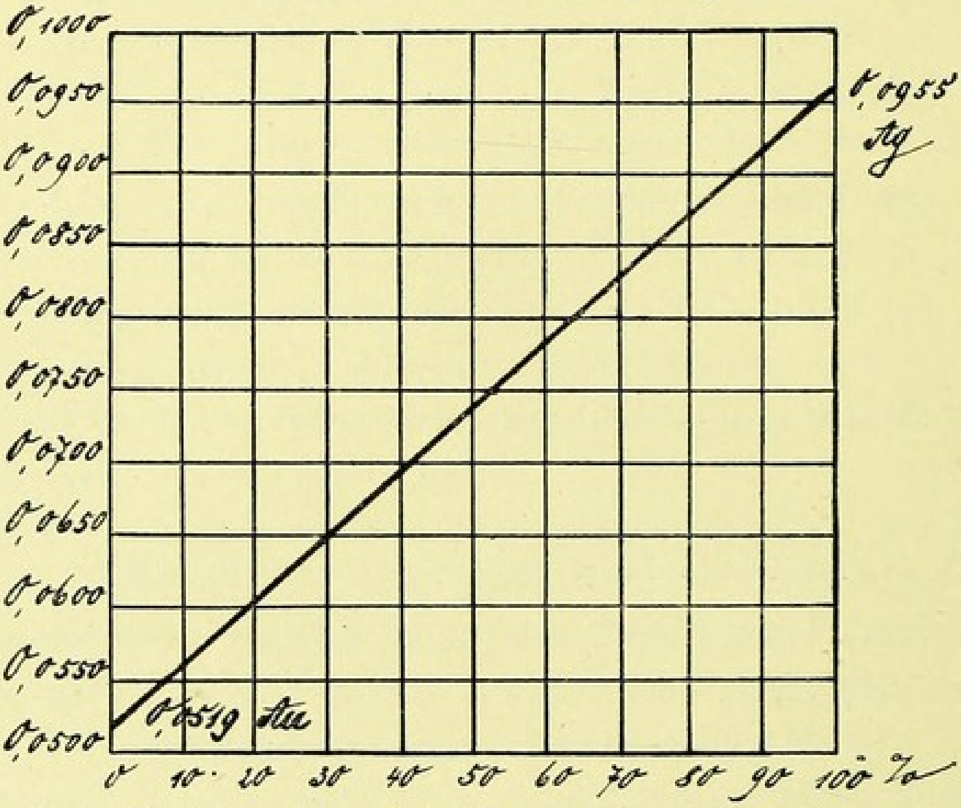

FIG. 91.—Specific volume of AuAg according to Mathiesen. Result: The specific volume is equal to the average of the components. Neither contraction nor expansion is shown.

(2) Gold—Bismuth, Au-Bi.

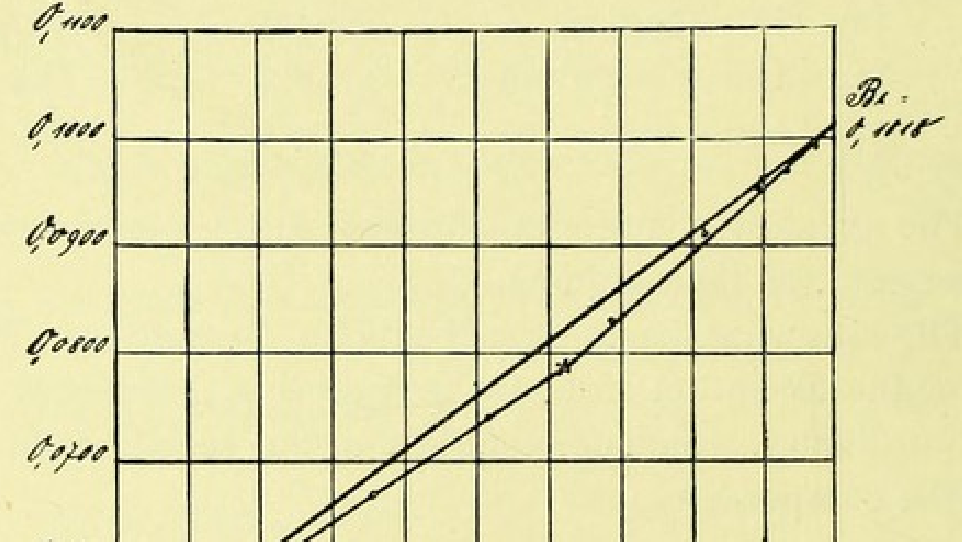

FIG. 92.—Gold-bismuth, after Maey-Mathiesen. Greatest contraction, $\frac{1}{27}$ = 3·75 per cent. with 38·8 Au.

(3) Gold—Lead, Au-Pb.

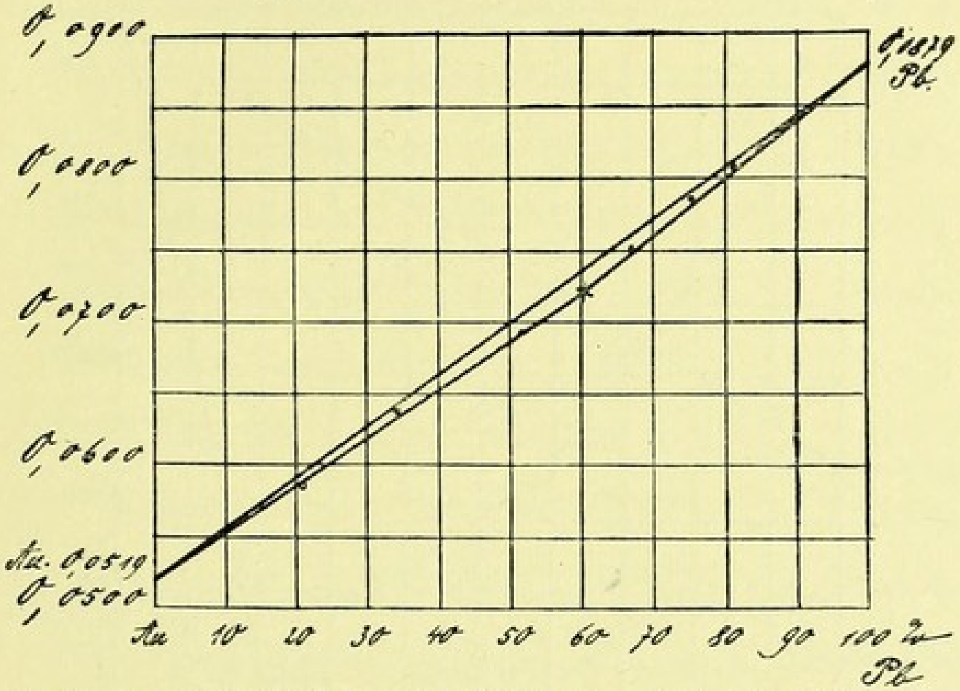

FIG. 93.—According to Maey and Mathiesen. Greatest contraction, $\frac{1}{54}$ = 1·8 per cent. with 40·5 per cent. Au.

(4) Silver—Antimony, Ag-Sb.

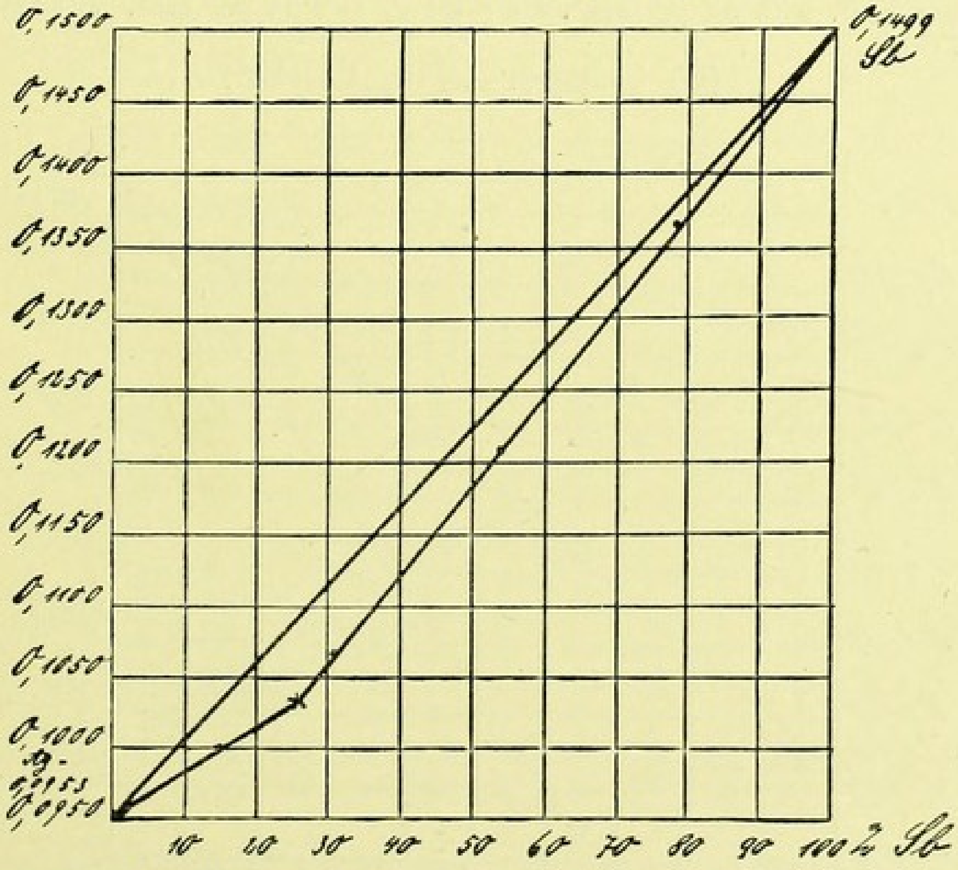

FIG. 94.—According to Maey. Greatest contraction, $\frac{1}{20}$ = 5 per cent. with 25·4 per cent. Sb.

(5) Copper—Cadmium, Cu-Cd.

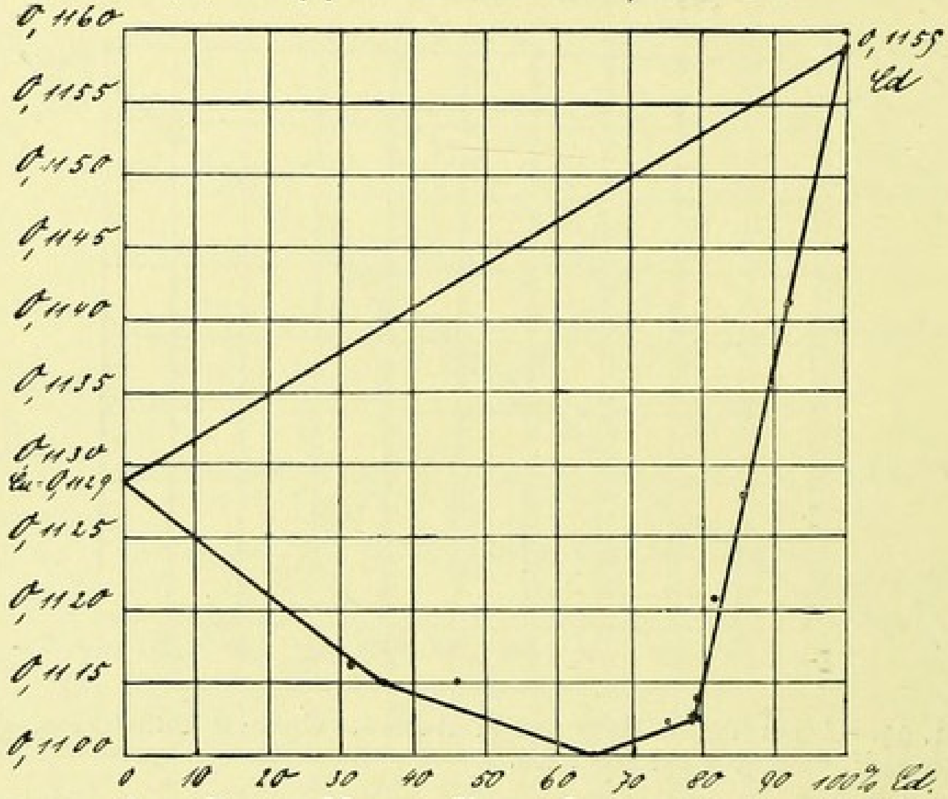

FIG. 95.—According to Maey. Shows three contractions with different percentages of Cd: (1) $\frac{1}{33}$ = 3 per cent. with 78 per cent. Cd; (2) $\frac{1}{30}$ = 3·3 per cent. with 64 per cent. Cd; (3) $\frac{1}{44}$ = 2·25 per cent. with 36 per cent. Cd.

(6) Copper—Tin, Cu-Sn.

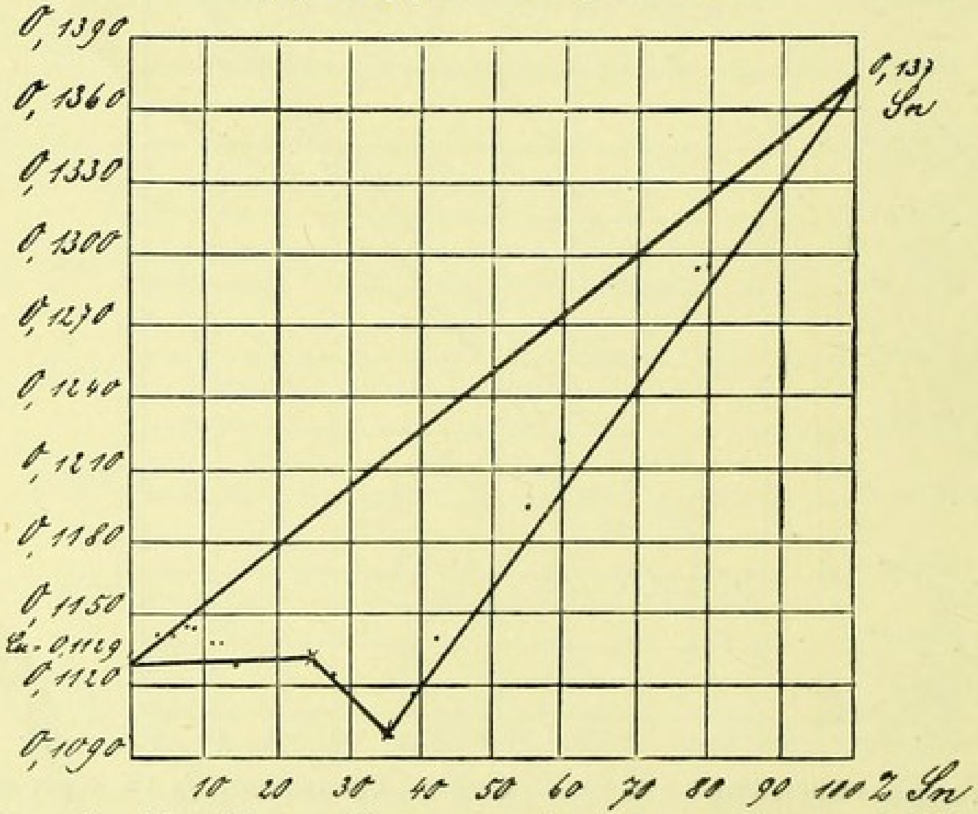

FIG. 96.—After Maey. Shows two points of contraction: (1) $\frac{1}{16}$ = 6·7 per cent. with 25 per cent. Sn; (2) $\frac{1}{10}$ = 10 per cent. with 35 per cent. Sn.

(7) Copper—Antimony, Cu-Sb.

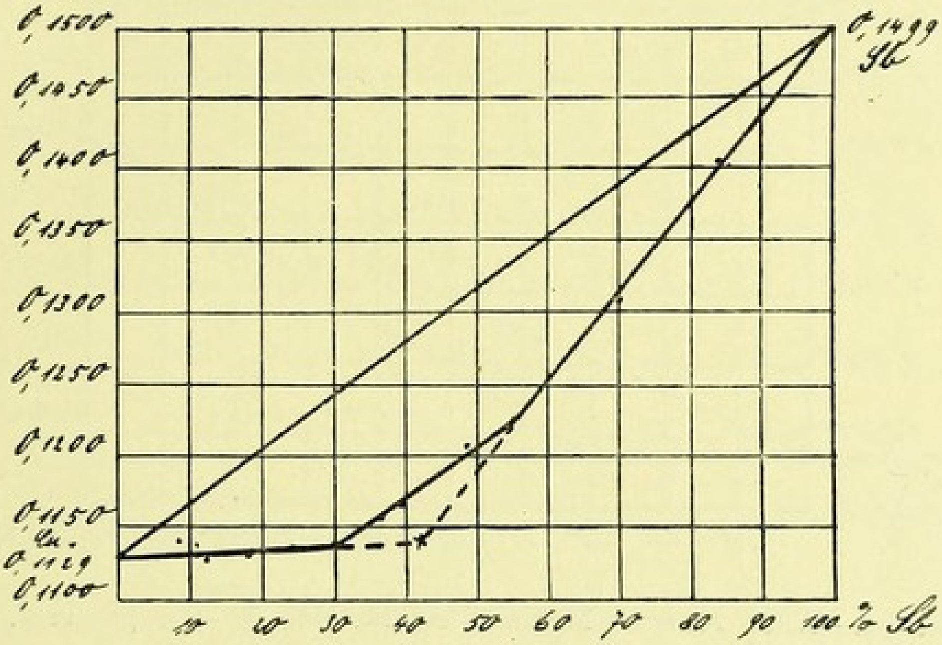

FIG. 97.—After Maey. Two maxima of contraction: (1) $\frac{1}{14} = 7$ per cent. with 31 per cent. Sb; (2) $\frac{1}{13} = 7{\cdot}5$ per cent. with 54 per cent. Sb; (3) Interpolation gives $\frac{1}{9} = 11$ per cent. with 41 per cent. Sb.

(8) Copper—Zinc, Cu-Zn.

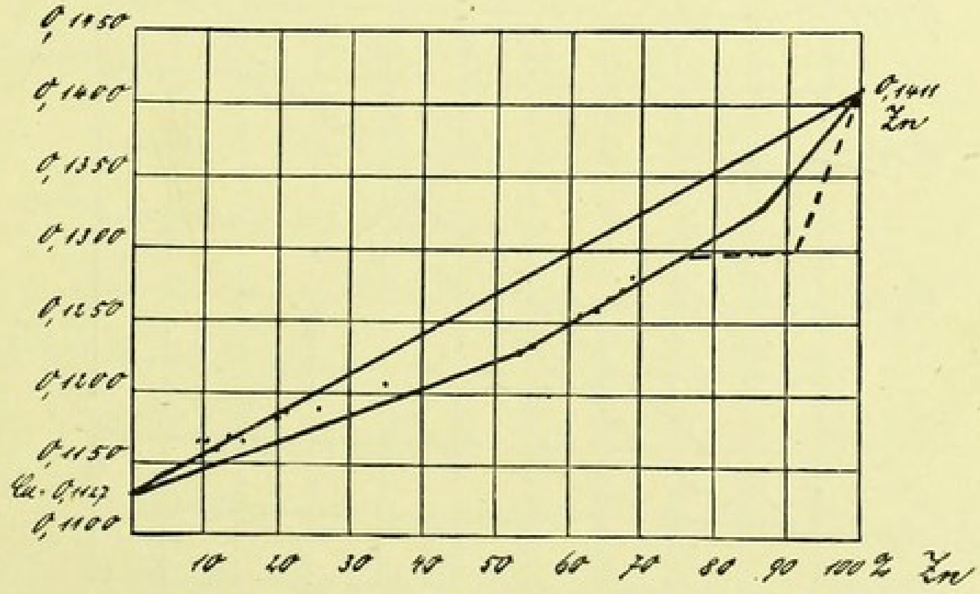

FIG. 98.—After Maey-Mathiesen. Two maxima of contraction: (1) $\frac{1}{25} =$ 4 per cent. with 52·4 per cent. Zn; (2) $\frac{1}{30} = 3{\cdot}3$ per cent. with 27 per cent. Zn.

(9) Silver—Mercury, Ag-Hg.

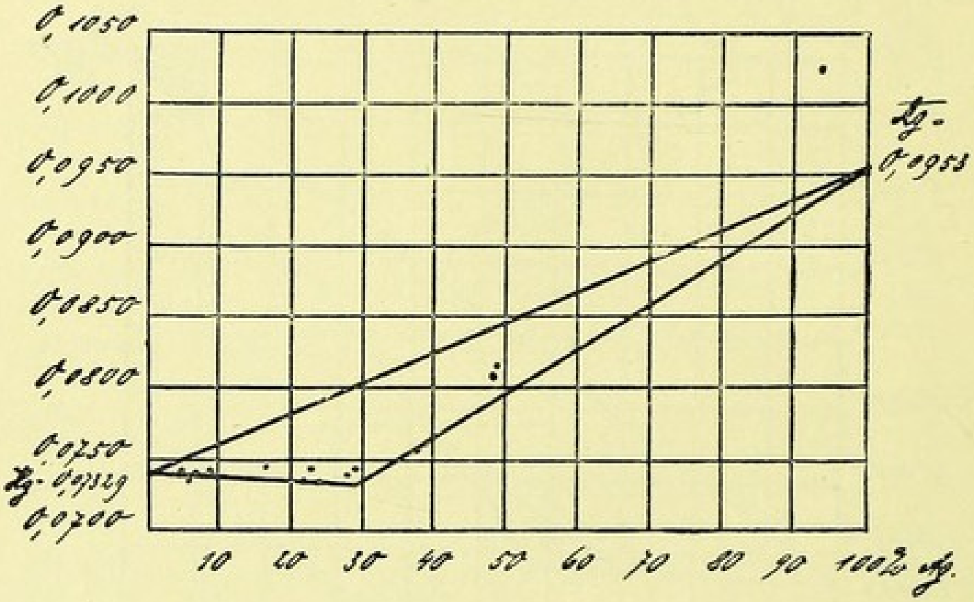

FIG. 99.—After Maey. Maximal contraction, $\frac{1}{11}$ = 9 per cent. with 29 per cent. Ag.

(10) Cadmium—Mercury, Cd-Hg.

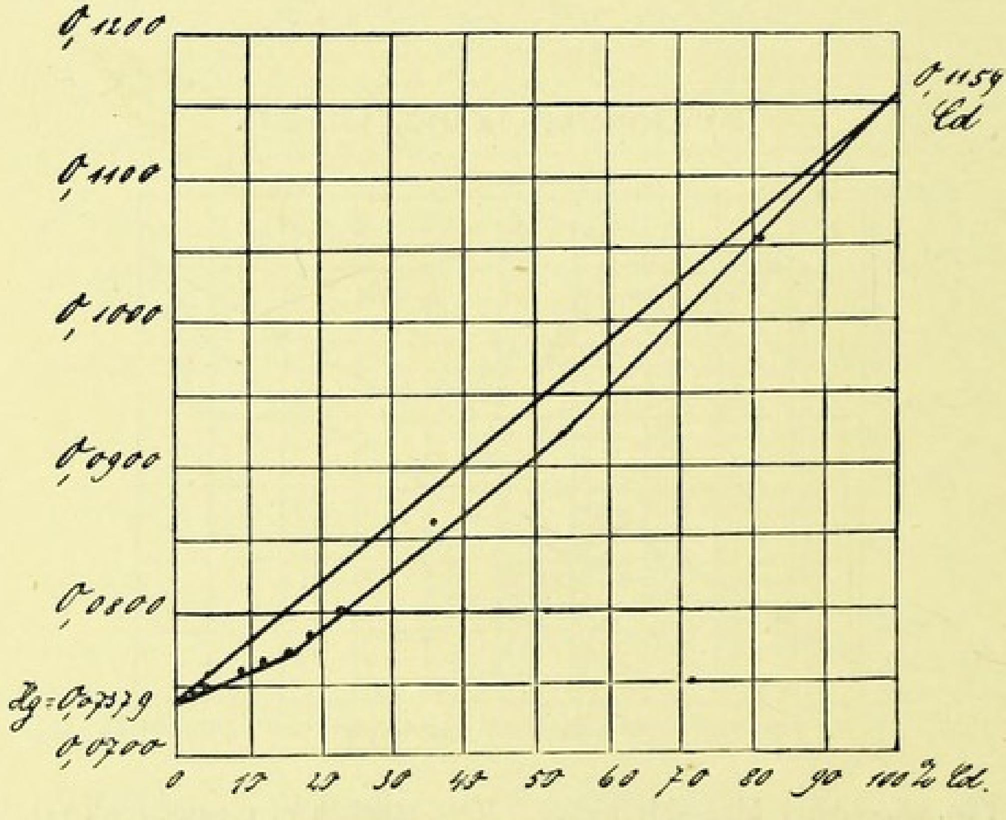

FIG. 100.—After Maey. Two maxima of contraction: (1) $\frac{1}{25}$ = 4 per cent. with 16 per cent. Cd.; (2) $\frac{1}{23}$ = 4·3 with 52 per cent. Cd.

(11) Zinc—Mercury, Zn-Hg.

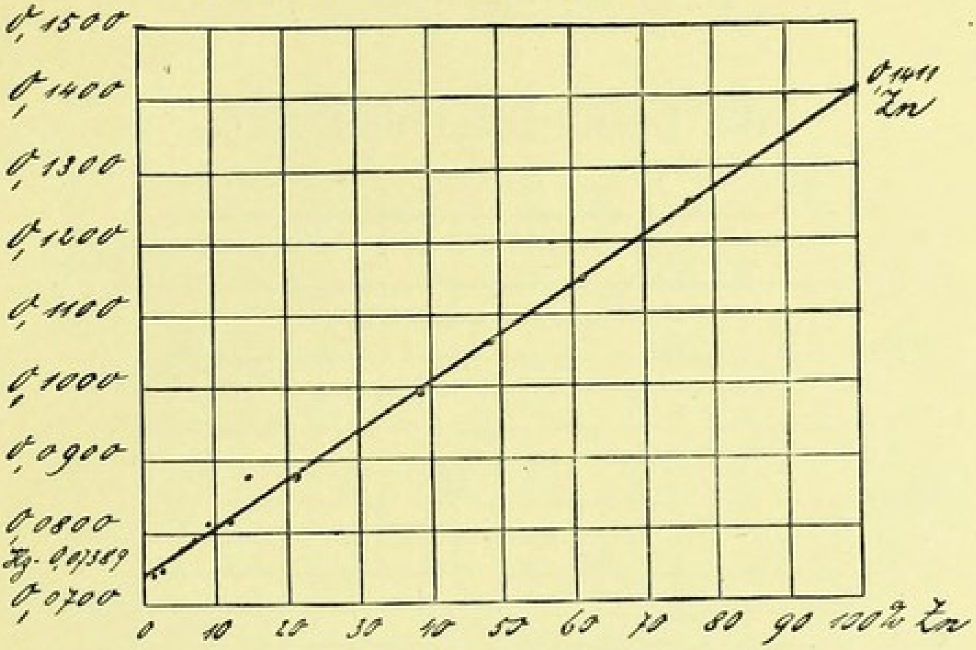

FIG. 101.—After Maey. No aberration. The specific volume corresponds to the average of the components.

(12) Tin—Mercury, Sn-Hg.

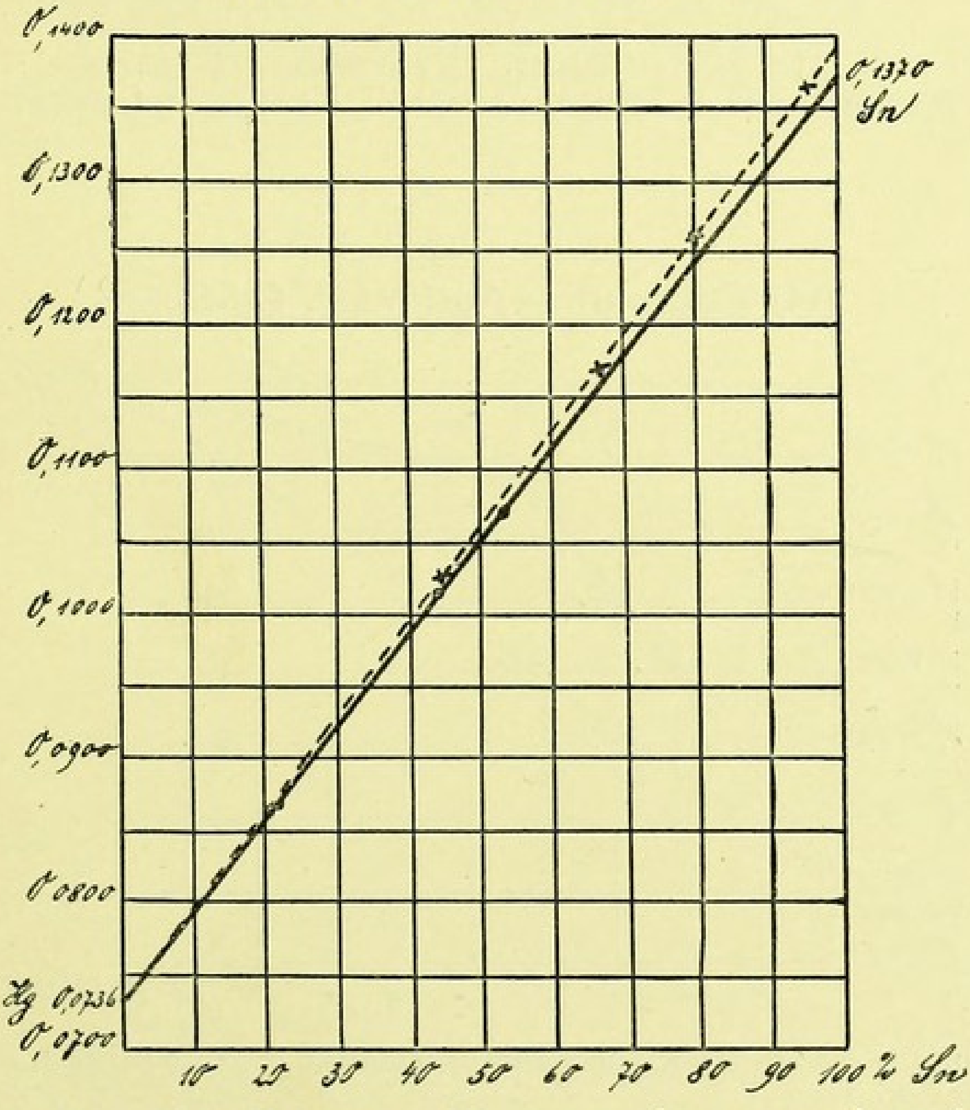

FIG. 102.—After Holzmann. My own results correspond to these. Maximum of expansion, $\frac{1}{66}$ = 1·5 per cent. with 99 per cent. tin.

(13) Lead—Bismuth, Pb-Bi.

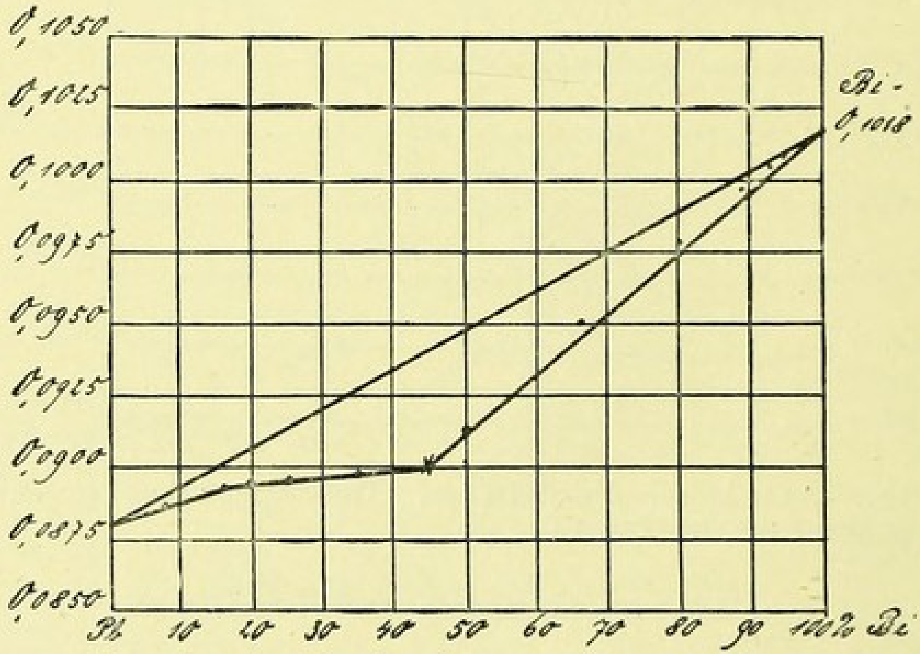

FIG. 103.—After Maey-Mathiesen. Two maxima of contraction: (1) $\frac{1}{20}$ = 5 per cent. with 45 per cent. Bi; (2) $\frac{1}{87}$ = 1·15 per cent. with 17 per cent. Bi.

(14) Cadmium—Antimony, Cd-Sb.

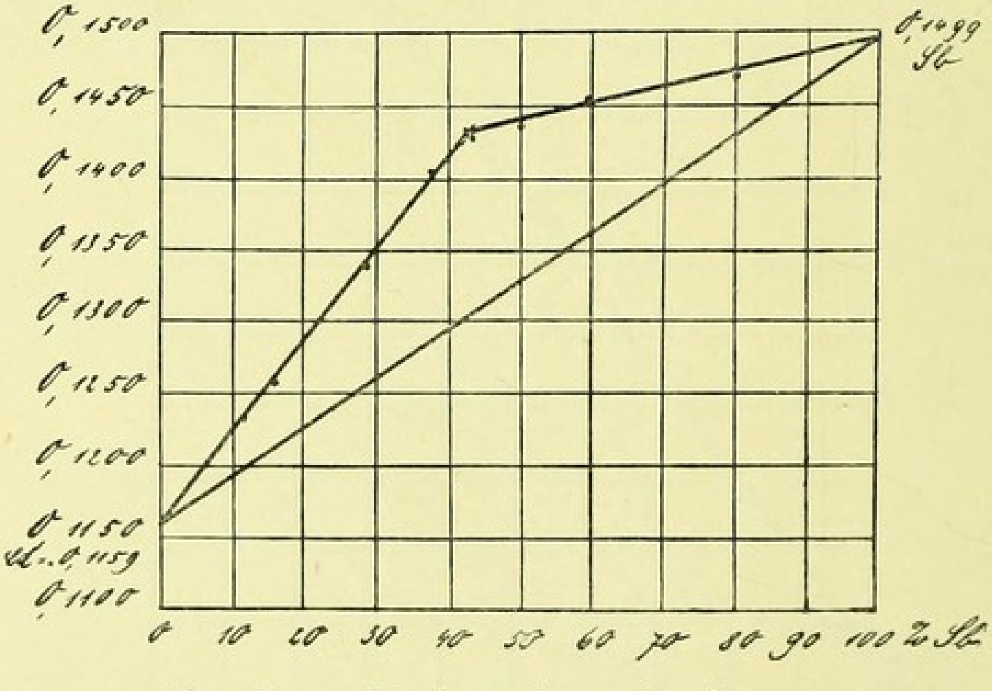

FIG. 104.—After Maey. Maximum of expansion, $\frac{1}{10}$ = 10 per cent. with 43 per cent. Sb.

(15) Zinc—Antimony, Zn-Sb.

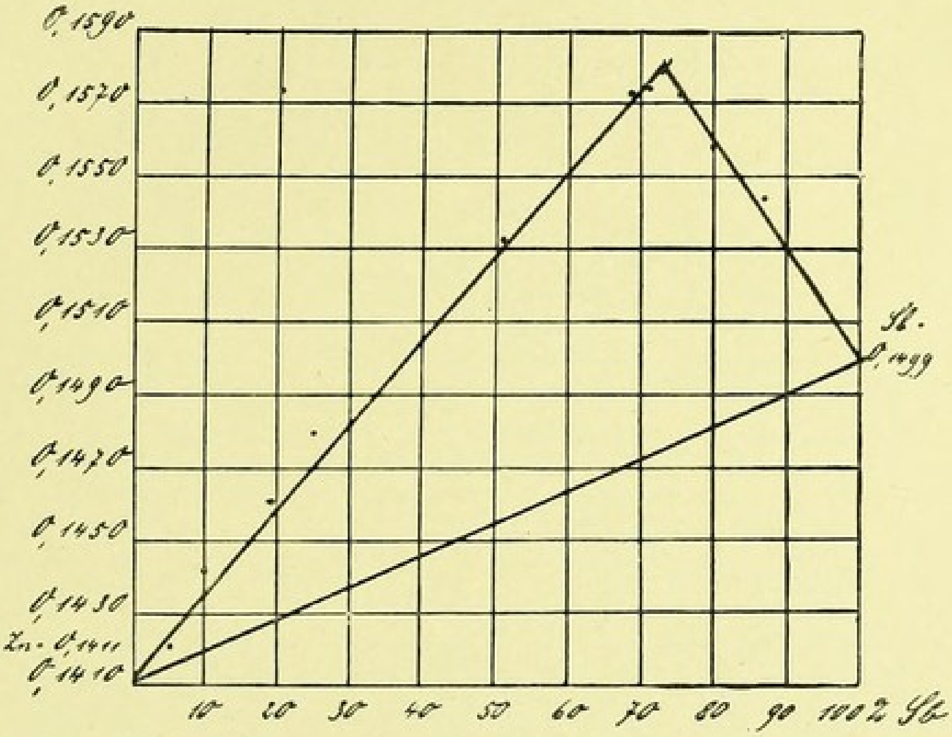

FIG. 105.—After Maey. Maximal expansion, $\frac{1}{15} = 6{\cdot}6$ per cent. with 73·5 Sb.

PRACTICAL PART.

XVI. HARD SOLDERS.

Solders and Soldering.

Soldering may be described as "the joining of two pieces of metal by a third which is melted between them." This third metal must become alloyed with the other two if the joint is expected to last.

A good solder, therefore, must have a physical or chemical affinity for the metals to be soldered, which means that it must be able to dissolve them.

The melting-point of the solder must be lower than that of the metals to be united.

Soldering is a different process from welding.

Metals to be welded are heated nearly to their melting-point and then fused together by the blows of a hammer.

This process is very similar to that used in filling teeth with gold. Here the cold gold crystals are fused together after they have been isolated by annealing. They retain sufficient latent energy to make them weld perfectly under the added force of the mallet blow.

For brazing brass, German silver and bronze, the best solder is made by using the same metal after the adding of some zinc.

Wüst gives the following approved formulæ for brass solders :—

(1) Yellow, very hard flowing brass solder : brass 10, zinc 4 (ad. tin 1).

(2) Yellow fairly hard flowing solder : brass 10, zinc 4·5 (tin 1).

(3) Light yellow solder, flows well : brass 10, zinc 5 (tin 1).

(4) Semi-white easy flowing solder : brass 10, zinc 6 (tin 1).

(5) White, very easy flowing solder : brass 10, zinc 7 to 8·5 (tin 1·5).

The addition of tin lowers the melting-point in every case.

German Silver Solders.

(1) German silver 10, brass 1, zinc 1·5.

(2) German silver 10, brass 1·5, zinc 2.

(3) German silver 10, brass 2, zinc 3.

The more zinc there is in the brass the easier the solder will run, and the more nickel there is in the German silver the harder it will be to make it fuse and run well.

It is advisable, therefore, to use the metal we wish to solder in every case as a base for making the solder.

German silver itself is a good solder for iron and steel, which it matches well in colour. Brass solders may also be used for the purpose.

Silver solders are used for soldering silver, brass, copper, German silver, and, according to Wüst, iron and steel also. For the latter purpose the silver is in my opinion detrimental, as it has neither a physical nor chemical affinity for iron.

Silver solders according to Karmant :

(1) Hardest silver solder (0·800 fine) silver 4, copper 1.

(2) Hard solder : (*a*) ·750—·580 fine : silver 4 to 9, copper 0, brass 3 ; (*b*) ·630 fine : silver 19, copper 1, brass 10 ; (*c*) ·666 fine : silver 20, copper 1, brass 9 ; (*d*) ·700 fine : silver 28, copper 2, brass 10.

(3) Soft silver solder for secondary soldering : (*a*) ·666 fine : silver 2, brass 1 ; (*b*) ·500 fine : silver 1, brass 1.

(4) Very easy flowing solder for inferior goods: ·385 fine: silver 5, brass 6, zinc 2.

(5) Kulmer reports the silver solders of Dr. Richter and Co. of Pforzheim to be composed of: (1) Silver 500, brass 400, cadmium 100. This is for the finest enamelled goods. (2) Silver 500, brass 350, cadmium 150. For fine ware not enamelled. (3) Silver 250, brass 250, copper 500. For second quality work.

XVII. GOLD SOLDERS FOR DENTAL PURPOSES AND GENERAL USE.

These are much used by dentists, and in this field they have to show much better results as regards specific resistance and retention of a good colour than in ordinary jewellers' work.

It is, therefore, very necessary for dentists to use solders which have the full carats of the gold to be soldered, but possessing at the same time lower melting points than this.

As bases for gold solders we use gold, copper, and silver, the melting points of which are lowered by additions of the following metals:—

(1) Antimony ...	Sb ...	Melting point	630° C.	Evaporating point	1437° C.
(2) Cadmium ...	Cd ...	,, ,,	316° C.	,, ,,	763° C.
(3) Bismuth ...	Bi ...	,, ,,	268° C.	,, ,,	1100° C.
(4) Zinc ...	Zn ...	,, ,,	419° C.	,, ,,	920° C.
(5) Tin	Sn ...	,, ,,	232° C.	,, ,,	1450° C.

The melting point of gold is 1062°, copper 1084°, silver 960° C.

The evaporating points are important, as they decide the order in which the metals are added when alloying the base.

If we wish to alloy cadmium and pure gold and silver we shall have to heat it above 763° C., its evaporating point, and this would make the alloy porous through partial retention of cadmium vapour. A soldered joint which has been overheated shows porosity from the same cause.

If we wish to use these base metals as constituents of solders we must lower the melting-point of the alloy before adding them to such a degree that it is not necessary to exceed their evaporating point when putting them in.

It should be stated here that an alloy of two metals or two alloys cannot be a perfect one unless the melting point of the higher of the two is reached.

We have to consider also the behaviour of the base metals with

A. *Gold* (see p. 96 ff.).

I. Antimony—Gold = SbAu.

(1) Chemical compound $AuSb_2$ = 45 per cent. gold + 55 per cent. antimony, melting-point 460° C.

(2) Eutectic : $AuSb_2$ + pure Au = 85 per cent. gold + 15 per cent. antimony, melting point 360° C.

The soldered joint, therefore, will be composed partly of $AuSb_2$ which is only 10·8 carat fine and likely to discolour, especially in the mouth.

II. Cadmium—Gold = CdAu.

(1) Chemical compound : Au_4Cd_3 = 70 per cent. gold + 30 per cent. cadmium, melting point 623° C.

(2) Mixed crystal, saturated with 82 per cent. gold + 18 per cent. cadmium, melting point 780° C.

The only way to make a perfect alloy is to do it in a vacuum and use a surplus of cadmium to supply the loss by evaporation.

III. Bismuth—Gold.

(1) Mixed crystal α = saturated 96 per cent. gold, 4 per cent. bismuth, melting point 1050° C.

(2) Eutectic between the α crystal and pure bismuth = 18 per cent. gold + 82 per cent. bismuth. Melting point 240° C.

IV. Zinc—gold.

(1) Mixed crystal α = 84 per cent. gold + 16 per cent. zinc, melting point 700° C.

(2) Eutectic $\alpha + \beta$ = 85 per cent. gold + 15 per cent. zinc, melting point 672° C.

The direct addition of zinc to gold raises the same difficulties as in the case of cadmium.

The best way of adding Zn is the use of brass with an average of 30 per cent. Zn.

An addition of zinc to gold makes it very easy flowing and raises its specific resistance.

V. Tin—Gold.

(1) Mixed crystal α = 96 per cent. gold + 4 per cent. tin, melting point 950° C.

(2) Chemical compound AuSn = 60 per cent. gold, 40 per cent. Sn, melting point 418° C.

This alloy is as hard as glass, has a light yellow colour, and is very resistant to acids, and is probably the best one to use as a base for cast inlays.

(3) Eutectic between crystal α and AuSn = 81 per cent. gold, 19 per cent. tin = 19·5 carats, melting point 280° C.

These alloys seem to me to be the best means of lowering the melting point of a solder without the disadvantage of having a low evaporating point and consequent porosity.

A little zinc makes it run more easily. The melting must be done with every care and precaution, as badly made solders containing free tin will destroy the gold to be soldered.

B. *Silver.*

I. Antimony—silver.

(1) Mixed crystal a saturated with 85 per cent. Ag, 15 per cent. Sb, melting point 760° C.

(2) Chemical compound Ag_3Sb = 74 per cent. silver, 26 per cent. antimony, melting point 560° C.

The compound (2) may be used as an addition to solder.

II. Cadmium—silver.

(1) Mixed crystal a = 80 per cent. Ag, 20 per cent. Cd, melting point 880° C. (up to 100 per cent. Ag).

They probably form a complete series of mixed crystals down to 0 per cent. Ag, also a true chemical compound in Ag_4Cd. Information on this point is not certain.

Every 10 per cent. addition of cadmium lowers the melting point by about 50° C. The same precautions must be taken with this alloy as with cadmium—gold.

III. Bismuth—silver.

For gold solders only the a crystal is of importance; it consists of 96 per cent. Ag, 4 Bi to 100 per cent. Ag, which means that 0—4 Bi may be added to silver.

All other alloys crystallize as a + Bi. They may be used as additions to gold, but only in small quantities, so that the free Bi may take up the free gold and combine with it.

IV. Zinc—silver.

The mixed crystal is the only one of importance here. It consists of 78 per cent. Ag, 22 Zn — 100 per cent. Ag.

All other alloys show allotropic conditions. If zinc and copper are added to a solder it is preferable to introduce them together in the form of "brass."

This alloy makes a very good silver solder, the melting point of which may be considerably lowered by adding either tin (Ag_3Sn) or the AgBi α crystal, or the chemical compound Ag_3Sb.

V. Tin—Silver.

(1) The chemical compound Ag_3Sn = 73 per cent. Ag, 27 per cent. Sn, melting point 730° C.

(2) A complete series of mixed crystals, 73 per cent. Ag—100 per cent. Ag.

Both of these may be used for lowering the melting point of gold instead of pure tin (see Gold—Silver), so as to avoid making it too low, as a surplus of pure tin would do.

C. *Copper.*

I. Antimony—Copper.

(1) Chemical compound Cu_3Sb = 62 per cent. Cu, 38 per cent. Sb, melting point 675° C.

(2) Mixed crystal $\gamma = 99$ per cent. Cu + 1 per cent. Sb and the mixtures between (1) and (2).

This means that all percentages between 62 to 99 per cent. Cu may be used, but great care must be exercised on account of their liability to polymorphic changes at various temperatures.

II. Cadmium—Copper.

Alloys from 100 to 55 per cent. Cu show free copper on crystallizing.

We have to consider chiefly the alloys from 30 to 55 per cent. Cu, also mixtures of the *a* crystal with the compound Cu_2Cd, and especially their eutectic, which consists of 41 per cent. Cu + 59 per cent. Cd, melting point 550° C.

III. Bismuth—Copper.

Show perfect immiscibility and have neither chemical nor physical affinity.

IV. Zinc—Copper (brass).

Mixed crystal $\delta = 70$ per cent. Cu + 30 per cent. Zn, melting point 900° C.

More copper raises the melting point, and more zinc lowers it. This alloy is an important addition for most solders, as it dissolves silver as well as gold, lowers the melting point and makes the solder more fluid.

V. Tin—Copper (bronze).

(1) Mixed crystal $a = 88$ per cent. Cu (— 100 per cent. Cu), melting point 790° C.

(2) There is one chemical compound $Cu_3Sn =$ 61·7 per cent. Cu, 38·3 per cent. Sn, melting point 710° C.

Both alloys are useful for lowering the melting point of solders.

Conclusions :—Solders should have a melting point which is at least 100—200° C. lower than that of the metal to be soldered.

The best metal to use for lowering the melting point is tin. The best one for making it run easily is zinc, and a red colour is best obtained by the use of copper.

If silver is to be added, it is best to alloy it first with tin. If we wish to add cadmium we must first lower the melting point of the alloy so that the cadmium will not evaporate.

In order to make gold solders, the following formulæ may be used. They can be altered to suit any particular purpose by following the explanations given above.

These solders may also be used for casting purposes except where very tough plates are indicated.

I. Solder 0·800 = 19·2 carats, melting point 650° C.; 80 parts gold and 4 of copper are alloyed, 12 brass and 4 tin are then added.

Instead of copper and tin, bronze may be used.

The addition of pure copper will deepen the colour, which may be darkened still further by pickling in dilute nitric acid, and then brushing and washing and pickling again in dilute hydrochloric acid.

II. Gold solder 0·750 = 18-carat gold 75, brass 21·5, tin 3·5, melting point 675° C.

III. Gold solder 0·583 = 14-carat gold 58·3, tin 3, silver 5, brass 33·7.

IV. Low-fusing solder for repairs or casting gold for inlays: 750 = 18-carat, melting point 500° C., gold 75, tin 7·5, brass 17·5. May be coloured in hydrochloric acid.

V. Very low-fusing gold solder, or light-coloured casting gold for inlays 0·750 = 18 carat, melting point 400° C., gold 75, tin 14, brass 11. Its very light colour may be darkened in hydrochloric acid.

It is difficult to make these solders and alloys satisfactorily in small quantities. The well-known firm of Dr. Richter, Pforzheim, makes them for dental work to the author's prescriptions; and the methods of melting and alloying recommended by him give true alloys instead of the metallic mixtures hitherto sold for the purpose. These methods also give solders of a better colour.

XVIII. THE LOW-FUSING ALLOYS.

SOFT SOLDERS.

The low-fusing metals are the ones chiefly used in compounding soft solders. Tin and lead are the chief ingredients of these and they have been already described.

The lowest melting soft solder is the eutectic of these two. It has 70 per cent. Sn and 30 per cent. Pb and melts at 182° C.

The addition of bismuth to these two gives a ternary eutectic melting at 96° C.

To find its composition an equilateral triangle is drawn, Bi-Sn-Pb (fig. 106).

The sides must be imagined as perpendicular planes and the lines of primary crystallization are cut out.

Thus we get a triangular tube on the sides of which a temperature scale is marked and the lowest connections of these temperatures indicate the binary eutectics E F G.

Between the corresponding melting points of the three metals dotted lines of isotherms are drawn, so to speak, in the interior of the tube, and where these intersect a ternary eutectic is indicated.

This plane surface diagram must of course be imagined as standing in relief in order to make it intelligible.

The crystallization takes place as follows :—

First of all the metal in surplus separates out, and then the binary eutectic surplus, so that there only remains the ternary liquid eutectic, which in this case consists of

18·75 per cent. Sn, 31·251 per cent. Pb, 50 per cent. Bi, melting at 96° C.

Küpper, of Bonn, prepared solders having the following composition (according to Wüst) :—

	a	*b*	*c*	*d*
Lead	88·89	88·8	83·3	78·0
Tin	3·66	3·7	6·9	15·0
Antimony	7·45	7·5	9·8	7·0

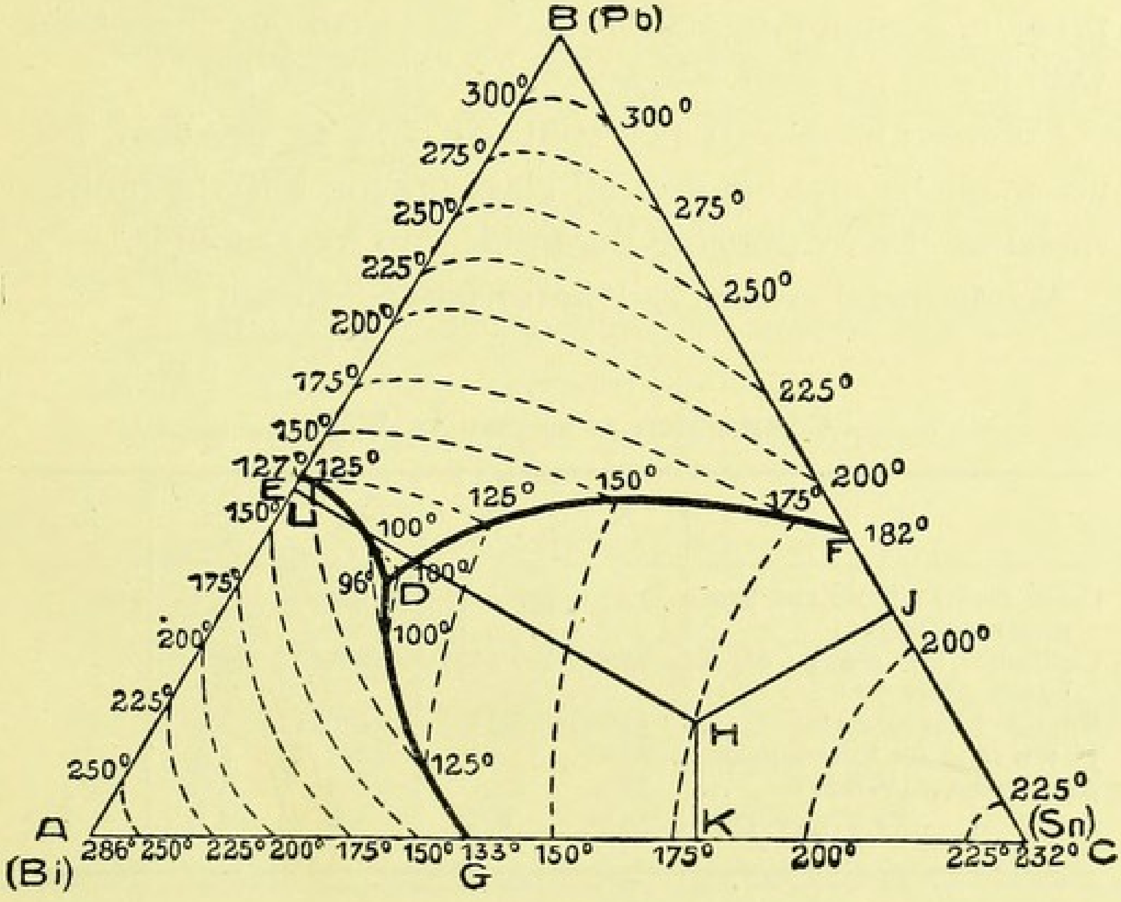

FIG. 106.—Ternary diagram of Lead, Bismuth, Tin.

The air must be excluded while melting the antimony and the tin added to the lead ; "*a*" does not melt readily and must be fused with a blowpipe, "*b*" runs more easily, "*c*" may be used with a "soldering iron," "*d*" is useful for soldering tin plate, brass and copper.

Various Fusible Alloys for other Purposes.

(1) Tin—lead alloys.

(*a*) For eating and drinking utensils. For these the lead content should not exceed 10 per cent.

(*b*) For toys, cheap finery and organ pipes the lead may be 30—50 per cent.

(2) Tin—lead with Cu and Sb (see also White Metal) 40—60 per cent. Sn.

(3) Britannia metal goods which are fashioned by pressure or stamping seldom have less than 90 per cent. Sn with 8—10 per cent. Sb, and 1—1·6 per cent. Cu.

"Tin-brilliants," 65 per cent. Sn and 35 per cent. Pb, are made by dipping ground glass prisms into the molten metal or else by pouring the metal into iron moulds.

White metal is used as "anti-friction" metal.

Composition according to Wüst.

Use	Sn	Pb	Sb	Cu	Zn
Cushions for wheels and propeller shafting	72·7	...	18·2	9·1	...
Cushions for crank of a lignite press	85·0	...	10·0	5·0	...
English friction metal ...	53·0	33·0	10·6	2·4	1·0
Piston rings for locomotives	87·0	...	12·5	6·5	...
Axle cushion (Wüst) ...	82·4	...	8·2	5·3	4·3
,, ,, for centrifuges	55·0	Ni5	5·0	35·0	...

Essential Properties of White Metals.

(1) Two components in the structure are wanted—a hard one to resist wear and avoid friction, and a soft one to support the hard one and allow for a certain amount of elasticity.

(2) The journal of the axle must not be affected by the white metal.

(3) It should be tough, that is, not liable to give way under sudden increases of stress. Tin and antimony form SbSn—a very hard metal compound with cubic crystals.

Tin and Cu form the compound $SnCu_3$, which is also very hard and even more brittle than the previous alloy, but a good deal depends on the rapidity of cooling.

The presence of both of these components makes these alloys hard and stiff, whereas tin and lead and their eutectics tend to make them soft.

Not more than 20 per cent. Sb should be used, or there will not be enough of the soft eutectic to surround the primary hard crystals.

Latterly Zn has come to be used sometimes as a substitute for Sb.

In making the alloy the copper is melted first and then the tin is added very slowly to it.

When these have been thoroughly mixed the other metals are put in.

Type Metal.—The alloys used for type must flow well and be hard and take a sharp copy.

The Sb content should not exceed 25 per cent. as in the anti-friction metal. ZnCu and Ni make it more durable.

Type metal		Pb	Sb	Cu	Bi	Zn	Sn	Ni
According to Ledebur...	Common ...	75·0	23·0	...	...	...	2·0	...
,, ,, ...	Fine	60·0	25·0	...	...	...	15·0	...
,, ,, ...	For reglets ...	80·0	20·0	...	...	...	...	...
,, ,, ...	For stereotyping	82·0	14·8	...	...	...	3·2	...
,, Krupp ...	Very suitable ...	70·0	18·0	2·0	...	...	10·0	...
,, ,, ...	,, ,, ...	59·6	17·9	4·7	1·1	...	12·0	4·7
,, Ehrhard...	Will be hard and tough	2-4	...	2-4	...	89-93	9-6	...
English types	...	64·2	19·5	1·7	...	...	9·1	...

These alloys are used also for various kinds of small castings such as statuettes, lustres, &c., and are poured into sand or oiled metal moulds. Very little finishing work is necessary after they are cast.

Zn castings are cheaper than tin.

(1) Imitation sheet silver of 91·5 per cent. Sn, 8·5 per cent. Zn can be beaten very thin.

(2) Imitation Britannia metal.

(*a*) 80 per cent. Sn, 20 per cent. Zn.

(*b*) 80 per cent. Sn, 20 per cent. Pb.

(3) Casting zinc.

Zn 95 per cent. and upwards, Sn 5 per cent. An addition of some Cu increases the hardness.

THE CADMIUM ALLOYS.

These as a class have very low melting points; they fuse even below 100° C.

When made without Bi they are tough and ductile, especially if containing 1 to 2 per cent. Ag.

They are used for solders and castings which are not likely to be subjected to high temperatures, and also for cliché blocks.

Cliché (type) metal, 50 per cent. Pb, 36 per cent. Sn, 22·5 per cent. Cd, has a lower melting point, and is harder than bismuth type metal.

	Lead	Tin	Bismuth	Cadmium
Wood metal, malleable, melting point 60-72° C.	4	2	5-8	1-2
Melting point 82° C. for soldering below water	6	...	7	1
Melting point 140° C., very soft solder fusing 42° C. below tin-lead solder	2	4	...	2
According to Lipowitz, melting point 70° C. for soldering tin, lead, &c.	8	5	15	3

Melting point Degrees C.	Tin	Lead	Bismuth	Melting point Degrees C.	Tin	Lead	Bismuth
95	3	5	8	199	4	5	—
98	3	6	8	200	2	3	—
108	3	8	8	215	4	7	—
114	1	2	2	221	8	15	—
117	3	4	4	228	1	2	—
123	1	1	1	232	1	—	—
130	4	5	4	233	8	17	—
132	2	3	2	238	4	9	—
143	7	8	4	243	2	5	—
144	2	2	1	246	4	11	—
146	3	4	2	250	1	3	—
148	9	8	4	252	4	13	—
149	1	2	1	254	2	7	—
151	5	8	4	256	4	15	—
151	5	4	2	259	1	4	—
153	12	11	4	261	4	17	—
154	6	5	2	263	2	9	—
154	3	3	1	266	1	5	—
155	11	8	4	267·5	—	—	1
155	12	9	4	268	4	21	—
158	3	2	1	269	2	11	—
159	17	16	2	270	4	23	—
160	12	13	4	271	1	6	—
160	4	4	1	272	4	25	—
160	9	8	2	273	2	13	—
161	9	16	2	274	4	27	—
162	5	4	1	275	1	7	—
164	15	16	4	276	4	29	—
166	6	7	2	277	2	15	—
167	7	8	2	278	1	8	—
169	3	2	—	279	2	17	—
170	7	4	—	281	1	9	—
171	2	1	—	282	2	19	—
172	12	15	4	283	1	10	—
173	9	4	4	284	2	21	—
175	13	16	—	286	1	11	—
176	5	2	—	287	2	23	—
177	3	4	—	288	1	12	—
178	11	4	—	288	2	25	—
178	5	4	—	289	1	13	—
180	3	1	—	290	2	27	—
182	13	4	—	291	1	14	—
183	7	2	—	291	2	29	—
184	15	4	—	292	1	15	—
186	4	1	—	292	2	31	—
187	17	4	—	292	1	16	—
188	9	2	—	292	2	33	—
189	1	1	—	292	1	17	—
191	9	4	—	292	2	35	—
192	5	1	—	292	1	25	—
193	11	2	—	322	—	1	—
194	6	1	—	—	—	—	—

Bismuth Alloys.

The low melting point of bismuth alloys was noted in the description of the ternary eutectics.

These alloys are used in stereotype work and as safety plugs in boilers (vulcanizers, &c.), also as baths for the tempering of steel, and as dies for swaging dental plates and seamless crowns.

Stereo-metal is composed of tin 48 per cent., lead 32·5 per cent., Bi 9 per cent., Sb 10·5 per cent.

Newton's metal consists of: lead 31·25 per cent., tin 18·75 per cent., bismuth 50 per cent., melting point 96° C. (ternary eutectic).

Rose's alloys, according to Fischer :—

Lead	Tin	Bismuth	Melting-point
25 per cent.	25 per cent.	50 per cent.	93·75° C.
42 ,,	16 ,,	42 ,,	79° C.

For annealing steel alloys are used according to their melting points. (See Table on preceding page, according to Fischer.)

XIX. THE THERMIC STUDY OF METALS AND ALLOYS.

The Thermic Analysis of Metals.

The technique of this work consists in obtaining accurate records of the temperatures of molten metals or alloys which are steadily cooling. The low-fusing alloys can be examined with a mercury thermometer up to 360° C. It is best to melt the metals which are to be examined in a test-tube of Jena glass (fig. 107, A), which is high fusing. The same quantities of metal must be used each time.

Instead of glass test-tubes, small crucibles may be used, either English or made of Hessian graphite.

The test-tube, or crucible itself, is prevented from irregular heating or cooling by being placed in a container, B, with sand all round it.

The thermometer, C, should not touch the inside of the tube, but be allowed to hang freely in the melted metal.

The error in the readings of the thermometer due to the projection of the mercury from the melted mass must be corrected.

With temperatures up to 100° C. an average of 0·01° C. should be added, at 200° C. add 0·02, and higher temperatures proportionately more.

For temperatures over 360° C. Le Chatelier's pyrometer is used (fig. 108).

This is a simple thermo couple, of which one element consists of a wire of pure platinum, and the other of an alloy of platinum and rhodium or iridium. These two wires are soldered or welded together at D.

The thermo couple of Heraeus, Hanau, as used at the Institute of Physical Chemistry at Göttingen, is very practical. Its wires are only 0·2 mm. in diameter, and they are isolated from one another, from the joint D upwards, by a very thin porcelain tube A, and are then passed to the bottom of the protective tube B, so as to keep the wires from the chemical influence of the molten metal.

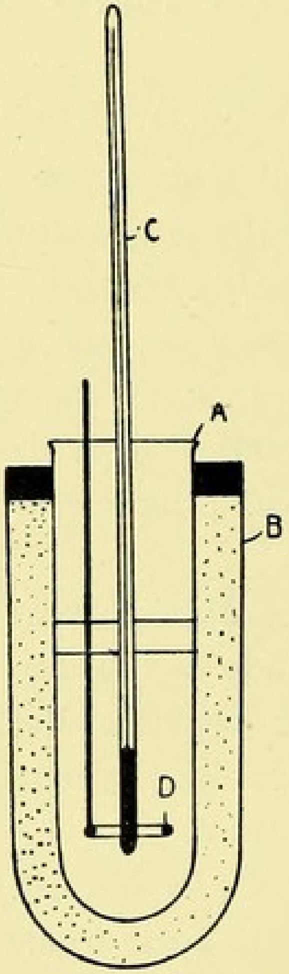

FIG. 107.—Arrangement for thermic analysis of metals melting below 360° C. A, tube of Jena glass. B, protection (iron-tube with sand lining to get a regular heating and cooling). C, mercury thermometer hanging free in the molten metal (best with nitrogen above the mercury), the so-called nitrogen-thermometer.

They are then led to the two poles of a galvanometer, which are immersed in a beaker of water of known temperature (fig. 108, E).

This milli-voltmeter is arranged to give readings both on the electric current and the temperature.

The *modus operandi* is as follows :—

When the test metal is heated up and the pyrometer placed in it a current is generated where the wires are jointed. The tension between the ends of the wires in E can be measured with the galvanometer and increases as the temperature rises.

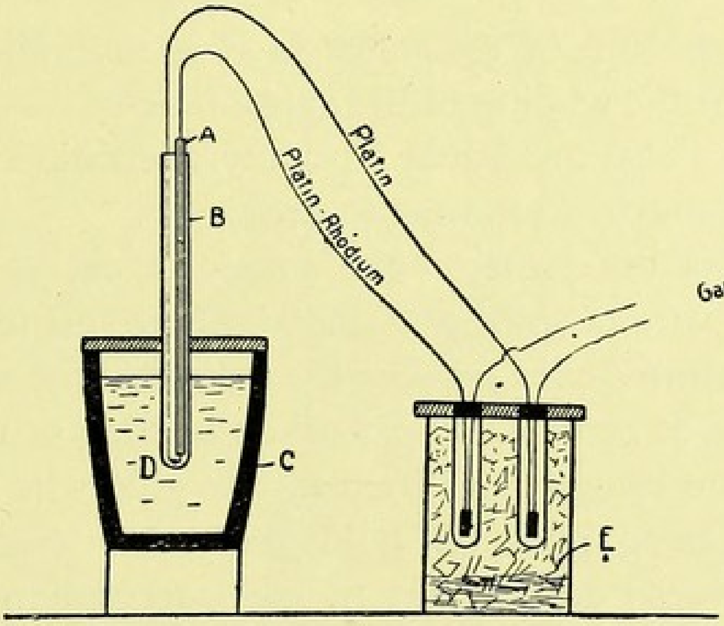

FIG. 108.—Thermo couple after Le Chatelier. A, isolating sheath for the wires inside the protective-tube. B, protective-tube for the element. C, crucible. D, the molten metal (at D the wires of the thermic element are soldered or welded). E, beaker containing water to keep the ends of the element at a constant known temperature.

When the water in the beaker is kept at 0° C., the readings are correct, but otherwise allowances must be made for error.

According to Vogel, the temperature of the water in E must be taken, and the following corrections made :—

Temperature as indicated by the galvanometer		ρ
0	...	1
100	...	·89
200	...	·76
300	...	·65
400	...	·59
500	...	·56
600	...	·54
700	...	·52
800	...	·51
900	...	·50
1,000	...	·49

The temperature of the water in E is multiplied by ρ and added to the reading of the galvanometer.

Voltmeters also are liable to many aberrations which require adjustment from time to time.

To do this the joint on the couple is cut at D and a short thin wire of some pure metal, whose melting point is known, is introduced between the cut ends : for example, gold melting at 1064° C. or palladium melting at 1541° C. After this, the element is heated till the gold wire melts.

At the fusing point of gold the galvanometer will suddenly relapse on account of the interruption of the current which takes place exactly at 1064° C.

If the galvanometer does not register 1064° C. then we know how much to add or subtract at about 1000° in order to make a correct reading.

In the proving for lower temperatures, simpler methods can be used on account of the cheapness of the metals.

Thus a quantity of antimony (630·6° C.) can be melted to prove temperatures around 600° C., lead (326° C.) for those about 300° C., and tin (232° C.) for those around 200° C., and be compared with the known melting point of the metals.

The metals must of course be absolutely pure.

The level on the galvanometer enables it to be placed exactly horizontal.

Also in order to keep it in good order it should be locked after use and released before working.

In the galvanometer are two resistances, one of which is used in measuring low temperatures.

For measuring points of crystallization below the freezing point of water (such as amalgams with a big mercury content) a Dewar's flask is used (fig. 109).

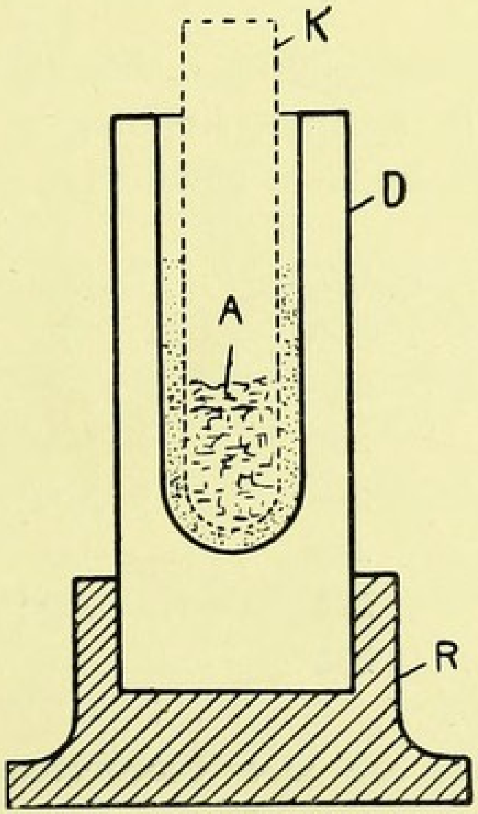

FIG. 109.—Dewar's arrangement according to Goerens. A, molten metal. K, test tube. D, glass holder, double-walled, with vacuum. R, stand.

D is a double-walled flask from between the walls of which the air has been exhausted. The test tube containing the metal to be examined is placed in this.

Compressed CO_2 from a steel cylinder is played into a woollen stocking placed over the top opening.

This forms carbonic acid snow at a very low temperature, and this can be kept in the Dewar flask long enough to crystallize a measurable quantity of the fluid metals.

The method of measurement is the same as that used with higher temperatures.

Practical Thermic Analysis.

(*For examples see p.* 9.)

Thirty gr. of tin are melted in a test tube and heated up to 300° C.

The cooling temperature is then taken by the thermometer every 10 seconds, stopping at 232° C., and by writing it down a scale is obtained as follows :—

Seconds		Centigrades	Seconds		Centigrades
0	...	300	70	...	**232**
10	...	280	80	...	**232**
20	...	265	90	...	229
30	...	250	100	...	225
40	...	240	110	...	220
50	...	**232**	120	...	215, &c.
60	...	**232**			

The numbers are now transferred to a diagram on squared paper.

Having the time as the abscissa and the temperature as ordinate, and 1 millimetre equal to 10° of heat, and 10 seconds of time. The diagram will show that a liberation of heat or energy has taken place at 232° C. and retarded the cooling for about 40 seconds.

The conclusion is that a crystallization has taken place.

Alloy 19·5 gr. Pb with 10·5 Sn = 65 per cent. Pb, 35 per cent. Sn.

Heat the metal over 326° C. (the melting point of Pb) and cool it off, taking the temperature every 10 seconds.

The scale obtained will read as follows :—

Seconds	Centigrades	Seconds	Centigrades
0	350	90	202
10	328	100	188
20	307	110	184
30	287	120	180
40	268	130	180
50	250	140	180
60	238	150	180
70	227	160	169
80	215	170	159

From this construct the diagram.

Conclusion.—(1) There has been a primary retardation of cooling, lasting from 250° C. to 180° C., and during this interval a primary crystallization has taken place. (2) The temperature remains stationary for 30 seconds at 180° C., thus indicating a second crystallization at this point.

It is a good plan to keep the regulus for microscopic study.

Alloy 9 gr. Pb with 21 gr. Sn, that is 70 per cent. by weight of Sn and 30 per cent. of Pb. Heat the metal after having been molten thoroughly before to 250° C. and take the temperature every 10 seconds while cooling.

The scale will be as follows :—

Seconds	Centigrades	Seconds	Centigrades
0	250	70	180
10	230	80	180
20	212	90	180
30	196	100	180
40	180	110	170
50	180	120	161, &c.
60	180		

Now construct the diagram.

Conclusion.—There is only one halt (60 secs.), that at 180° C. All the metal crystallizes at once. The regulus should be kept for microscopic examination.

(*c*) Alloy 25·5 gr. Sn with 4·5 gr. Pb = 15 per cent. by weight of Pb and 85 per cent. Sn. Melt and heat to 280° C. and cool as before. The scale will be as follows :—

Seconds	Centigrades	Seconds	Centigrades
0	284	80	**180**
10	263	90	**180**
20	243	100	**180**
30	224	110	169
40	206	120	159
50	195	130	150
60	185	140	141, &c.
70	**180**		

Draw the diagram.

Conclusion.—(1) A primary retardation from 206° C.—180° C. During this interval the first crystallization takes place.

(2) A stoppage of 30 seconds, or a second crystallization at 180° C. Keep the regulus.

These experiments show :—

(1) A primary crystallization beginning at 250° C. in the first case, and at 206° C. in the second.

(2) A crystallization at 180° C. in all the three alloys.

(3) In the second case there is only one crystallization at 180° C., which is considered as a secondary one in the others.

The secondary crystallization is the eutectic of the two components.

The first shows the freezing out of whichever metal is in excess. It appears also that the solvent property of the tin causes the lead, which should freeze at 326° C., not to crystallize till 250° C. is reached, and in addition the melting point of tin, of which there is a surplus, is lowered to 206° C.

Now draw the diagram showing these facts and note the following conclusions :—

(1) 70 Sn and 30 Pb crystallize at 180° C. and liberate 60 heat seconds, which is the whole melting heat.

(2) 35 Sn and 65 Pb liberate 30 heat seconds at 180° C., *i.e.*, half the melting heat.

(3) 85 Sn and 15 Pb liberate 30 heat seconds at 180° C., *i.e.*, half the melting heat.

(4) Therefore only the proportions of No. 1 constitute a balanced eutectic (60 seconds), and 2 and 3 consist of half eutectic (30 seconds) and half of pure crystals from the primary formation (surplus).

Additional Conclusions.—In examples 1 and 3, 50 per cent. of the regulus must consist of pure lead or tin and the other half of eutectic.

This is proved by the stoppage of 30 seconds for the eutectic to crystallize.

Final Conclusion.—With 70 Sn and 30 Pb the metals crystallize all at once at 180° C. with a retardation of 60 seconds.

This implies an equal structure throughout, namely, that of the eutectic (*vide* fig. 10, E).

A diagram should be made of these facts, putting the metal percentages on the abscissa and the crystallizing temperature on the ordinate.

Now draw a line 1 cm. in length from the base of the diagram at the point where the eutectic forms and shows 60 seconds of retardation. (*See* fig. 16, O P.)

Connect the end of this with the end of the abscissa. In the triangles thus formed the apices will show :—

Firstly, the duration of the retardation when the eutectic crystallizes, 1 cm. indicating 60 seconds of time.

Secondly, the amount of the fully crystallized metal which consists of eutectic.

In order to understand these methods better it will be excellent practice for the student to carry out the examples given below.

With (*e*) we note the melting of Sb and Zn, and with (*g*) that of Au and Sn. Both form chemical compounds.

These results when plotted will give a drawing consisting of several diagrams of the described kind (like fig. 12).

The melting is done under powdered wood charcoal or, better still, under hydrogen, which is easily obtained from a Kipp's apparatus.

Fuller explanations of the methods of thermic analysis are to be found in the works of Goerens and Ruer, which are recommended for that purpose.

ADDITIONAL EXAMPLES FOR PRACTICE.

(*a*) Ascertain the melting point of (about 30 gr. of) Bi, Sn, Pb, Zn, Sb, Ag, Au.

(*b*) Plot out on squared paper—

  (α) The melting points,
  (β) The freezing points

of the above metals.

(*c*) Ascertain the melting points and crystallizing periods of—

  (α) 22·5 Sn, 77·5 Bi.
  (β) 45 „ 55 „ (eutectic).
  (γ) 72·5 „ 27·5 „

The reguli should be kept for microscopic examination.

(*d*) Draw a complete diagram showing the crystallization of the metals together with the percentage composition of the mixtures.

(*e*) Ascertain the melting points and crystallizing periods of Sb, Zn.

(*a*) Sb 55, Zn 45 ($Sb_3 Zn_2$).
(*β*) Sb 97, Zn 3 (E_1).
(*γ*) Sb 80, Zn 20 (E_2).

Keep the reguli for microscopic examination.

(*f*) Make a diagram of the binary alloy SbZn together with the percentage composition of the mixture.

(*g*) Plot out the diagram and ratios for gold—tin.

(*a*) 81 per cent. Au, 19 per cent. Sn.
(*β*) 60 „ „ 40 „ „

Keep the reguli.

XX. THE MICROSCOPICAL EXAMINATION OF METALS AND ALLOYS.

Analysis by the Microscope.

Metals being opaque bodies have to be studied microscopically on their plain surfaces and hence artificial illumination is required. The simplest way of doing this is by means of a mirror, or a plane parallel glass which is introduced between the object and the objective.

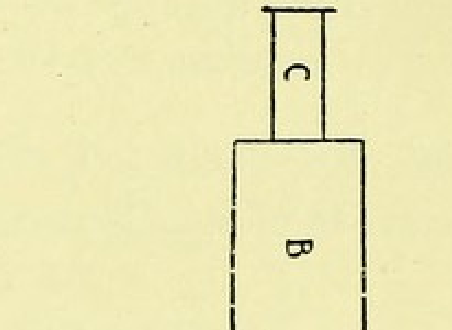

FIG. 110.—Way of rays through a vertical illumination.

The usual method of illumination is by means of a so-called vertical illumination between the eye-piece and the objective of the microscope (fig. 110).

The rays of light enter the prism G from the side and are refracted downwards by the hypotenuse to the object D.

The rays reflected from the object pass through the objective A and so into the microscope.

They then pass the prism G, which only occupies half the tube, and so into the eye-piece C to meet the eye of the observer.

The test-pieces should be polished till they show a high metallic lustre and then they are to be etched with acids to bring out the structure.

The best way to obtain a good surface is first of all to grind the object and then rub the plane surface on a sheet of fine emery paper.

That made by George Voss, of Deuben, is very useful, numbers 3 to 00 and 0 to 60 minutes.

A very fine paper No. 0000 made by Dujardin & Co., Düsseldorf, is used for the final polish.

This paper is laid on plate glass (to get a level surface) and the specimen is rubbed on it, always in the same direction, so that any scratches remaining are easily recognized as such, and also because the polygons resulting from irregular rubbing may easily be mistaken for crystals.

Alloys having components of different degrees of hardness, such as tin-silver alloys with a surplus of mercury, are best after a final polish on soft silk velvet.

This brings out the structure well without further treatment.

Specimens which do not exhibit their micro-structure without further treatment are etched with chemical reagents.

Those are selected which will colour the two components of an alloy differently, and so render the structure more conspicuous to the eye.

Various media are used for etching.

(1) Concentrated nitric acid.

(2) Nitric acid diluted with water, ethyl alcohol or other alcohols. Strength ½ to 10 per cent.

(3) Picric acid, 4 gr. to 100 ethyl alcohol, wash with pure alcohol after immersion. Chiefly used for iron carbon alloys (steels).

(4) Hydrochloric acid concentrated and diluted with water to 1:500. Tempered steels in 1 in 100 (1:100) absolute alcohol. It is used on tin-silver amalgams with 10 per cent. dilution and they are given twelve hours immersion.

(5) Tincture of iodine 5 per cent.

A large number of reagents are given in the metallographies of Goerens and Ruer, and to these the reader is referred, as space does not permit of a further development of the subject here.

The following examples may be worked up.

(*a*) Cut a regulus in two consisting of one metal only, grind the cut surface level and smooth it with emery and red Paris paper, going from the coarse to the finest till a high polish is obtained.

This must show no scratches worth mentioning under the microscope.

Soft metals are best polished on plate glass covered with the finest silk velvet.

The specimen must always be moved in one direction during the polishing process so that any remaining scratches may be recognized and not mistaken for part of the structure of the specimen as has been already explained.

Having finished the polishing process the specimen is next etched with a drop of hydrochloric or nitric acid (dilute or concentrated according to the metal) till the micro-structure appears. In addition to the above acids, iodine is used and bromine and permanganate of potash, in fact any agent which will oxidize the specimen.

A pure metal is homogeneous in structure, that is to say, it consists of crystals which are similar throughout; fig. 11 *a* and *f*, and fig. 111 (*a*) show clearly the sections of these polyhedra.

(*b*) Take a section of example (b) of the thermic analysis and treat it as before.

According to the thermic analysis this is an eutectic, and the microscope will reveal both metals on the etched surface in fine equal distribution, having a macular or striated appearance (fig. 111 (*b*), fig. 11 *d* and fig. 69).

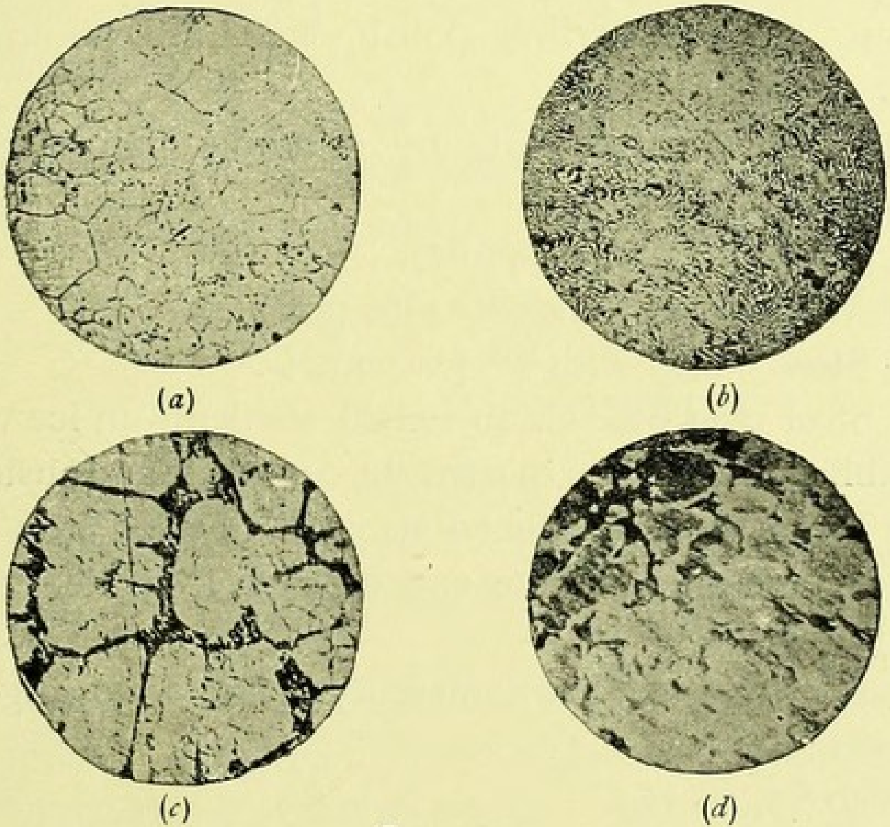
(*a*) (*b*) (*c*) (*d*)

FIG. 111.

(*c*) Take a section of example (*a*) of the thermic analysis. This should reveal a 50 per cent. excess of Pb which was thrown out before the eutectic formed. The eutectic will be found all around it.

If an etching medium is chosen which does not act on lead but on tin, then the free lead will have a light colour, and the eutectic be light and dark mixed (fig. 111 (*c*), and fig. 11 *c*).

(*d*) Now prepare and etch a specimen of (*c*) in the same way.

The section will show 50 per cent. free tin mixed with 50 per cent. eutectic.

If the free metal was light before, it will now be dark, or *vice versâ* (fig. 111 (*d*) and 11 *e*).

(*e*) A chemical compound or a mixed crystal will appear homogeneous like a pure metal. It has been agreed recently to use the term "metarals" for these homogeneous bodies.

(*f*) Cut sections of the various ingots obtained in the thermic analyses, grind, polish, etch and photograph them.

(*g*) Study the following by grinding, polishing and etching :—

(*α*) Grey iron (free graphite).

(*β*) White iron (cementite plus pearlite).

(*γ*) Steel. Iron with 1·8 per cent. C.

(*δ*) Steel over 800° C. quenched suddenly in ice water, probably martensite, or martensite, cementite and austenite.

(*ε*) Temper the quenched steel on a heated iron plate to see cementite, pearlite and perhaps troostite (*cf.* figs. 68-75).

(*h*) Now melt tin with mercury in the following proportions :—

(*α*) 50 Sn, 50 Hg.

(*β*) 70 Sn, 30 Hg.

(*γ*) 80·6 Sn, 19·4 Hg.

(*δ*) 90 Sn, 10 Hg.

Cut and etch and observe by the formation the chemical affinity from 81 per cent. Sn and upwards.

(*i*) Note the eutectic and chemical relationship under the microscope of the gold-tin alloys (*α*) with 81·5 per cent. Au (*β*) with 60 per cent. Au.

XXI. THE DETERMINATION OF SPECIFIC VOLUME AND SPECIFIC GRAVITY.

Volumetric Investigation. (*See also Chapter IV* (*e*).)

The specific volume of a metal or an alloy is obtained by first determining the specific gravity and from that calculating the volume.

The formula for doing this has been already given and also the reason why the volume rather than the specific gravity is used for diagrams.

$$\frac{1}{\text{Sp. gravity}} = \text{Sp. volume.}$$

$$\frac{1}{\text{Sp. volume}} = \text{Sp. gravity.}$$

To determine the specific gravity a specific gravity balance is used. This allows the object to be suspended in water at 4° C. by means of a thread or wire of known weight.

Having previously found the normal or dry weight of the object, the weight in water will be less (in proportion to the weight) of water displaced.

This gives its specific volume.

1 grm. of water is 1 cc. in volume, and therefore the normal weight divided by the weight of water displaced gives the specific gravity.

Example.—A block of metal is found to weigh 6 grm. in air and only 5·5 grm. in water. There it has displaced ·5 grm. of water.

The specific gravity then is $\frac{6}{0·5} = 12$; or 1 c.c. of the metal weighs 12 grm., 1 c.dcm. = 12 kg., 1 cb.m. = 12,000 kg. and so on.

The specific volume is therefore $\frac{1}{12} = \cdot 08\dot{3}$. Another method of determining the specific volume is by means of a pycnometer or specific gravity bottle.

This is a glass flask having a ground stopper. The stopper is perforated by a fine hole, the flask is filled with boiled water at 4° C., and the stopper pressed in so that the surplus water escapes through the hole.

The flask is carefully dried outside with alcohol and weighed (weighing I.)

The specimen of metal is now carefully weighed (weighing II.) and put into the pycnometer and the stopper replaced.

The water which the specimen displaces will obviously have the same volume as the specimen itself.

The flask is again carefully dried and weighed (weighing III.).

Weighings I. and II. are added together and III. is subtracted. We will call the result IV.

Then II. is divided by IV. thus : $\frac{\text{II.}}{\text{IV.}}$ and this gives the specific gravity of the specimen.

Example.—Weighing I. (full pycnometer) = 8 grm., weighing II. (metal) = 6 grm., I. + II. = 14 grm., weighing III. (metal in pycnometer) = 13 grm., I. + II. (14 grm.) − III. (13 gr.) = IV. (1 grm.).

$$\text{II. (6 gr.) : IV. (1 gr.)} = 6, \text{ or } \frac{\text{II.}}{\text{IV.}} = 6 \text{ sp. gr.}$$

That is, the specific gravity = 6.

Therefore the specific volume = $\frac{1}{6}$ = ·166.

In the case of porous metals some fluid lighter than water is generally used, in order to displace the air in the metal which would otherwise increase its volume.

The fluid most favoured for this purpose is petroleum (sp. gr. ·8) because it contains no oxygen and hence will not attack the specimens weighed in it.

When a specific gravity is found by using petroleum it is obviously the weight of the displaced petroleum, and the same quantity of water would give the real specific gravity if divided by the specific gravity (·8) of petroleum.

Supposing that, by weighing or using a pycnometer with petroleum, 12 grm. have been displaced by 1 cm.^{3} of the metal to be researched, then the real specific gravity will be $\frac{12}{\cdot 8} = 15$.

The specific volume then is $\frac{1}{15}$ — $\cdot 0\dot{6}\dot{6}$.

The specific volume of alloys is ascertained in this way from 10 to 10 per cent.

When the results are plotted out on a diagram the ordinate or vertical line will show the specific volume and the abscissa the percentage of one of the components of an alloy.

By this means it is possible to see at a glance variations from the average specific gravity, and to note at once any expansions or contractions which have taken place. The signification of the curves has been fully explained already (see Chap. XV, p. 169).

Exercises :—

(*a*) Ascertain the specific weight and volume of—

- (α) Silver.
- (β) Tin.
- (γ) 73 per cent. Ag, 27 per cent. Sn.
- (δ) 48 per cent. Ag + 52 per cent. Sn.
- (ε) 80·6 per cent. Sn + 19·4 per cent. Hg.

(*b*) Draw complete diagrams of the specific volume of these alloys, and show by means of it the points of maximum contraction.

XXII. CHEMICAL RESEARCH OF METALS AND ALLOYS.

PRELIMINARIES.

(For the preparation of sulphuretted hydrogen (H_2S) and sulphuretted hydrogen water ($H_2S + H_2O$) and sulphate of ammonia, see end of chapter.)

I. HEATING IN GLASS TUBE.—A piece about ¼ to ⅛ of a pea in size is slowly heated to redness in a glass tube 6 cm. length and ·6 cm. in diameter. Observe the distillate, sublimate or smell.

(1) *Sublimate :—*

(*a*) *White.*—(*a*) Oxide of antimony volatilizes with difficulty, melts on heating ; (*β*) arsenious trioxide, volatilizes easily, does not melt on heating ; (*γ*) ammonium chloride or ammonium carbonate ; these three sublimates do not change colour when tested with sodium hydrate (NaHO) ; (*δ*) mercurochloride (HgCl) blackens under sodium hydrate ; (*ε*) mercurichloride ($HgCl_2$) reddens with sodium hydrate.

(*b*) *Grey.*—(*a*) Mercury, globules easily recognized ; (*β*) cadmium.

(*c*) *Brownish-yellow.*—(*a*) Sulphur, globules remain fluid a short time ; (*β*) trisulphide of arsenic.

(*d*) *Yellow.*—(*a*) Trisulphide of arsenic ; (*β*) Iodide of mercury (HgI2).

(*e*) *Black.*—(*a*) Sulphide of mercury ; (*β*) iodine (violet vapour) ; (*γ*) arsenic (soluble in hypochloride of soda).

(2) *Vapours*:—

(*a*) Violet = iodine.

(*b*) Brown = bromine.

(*c*) Colourless and odourless oxygen (viz., from oxides of precious metals) will cause a glowing match to flare up again.

(*d*) Colourless, but with marked odour. ~~Sulphide~~ Sulphur. dioxide from metallic sulphides and sulphates, also sulphuretted hydrogen from wet sulphides.

(3) Change of colour: White turning to yellow, zinc oxide, and oxide of tin, which will become white again on cooling. Permanent yellow indicates lead carbonate or mercuric oxide (HgO.)

(4) Formation of regulus indicates the presence of metallic dust or compounds which have been reduced.

(5) When the substance seems to volatilize completely, heat a little on platinum foil. If it really vaporizes then mercury is indicated, or ammonium, arsenic, or antimony.

Speaking generally, a play of colour suggests the presence of one of the heavy metals.

II. BLOWPIPE TESTING.—A small piece of the specimen to be tested is pressed into a block of charcoal and heated in the reducing flame of a blowpipe.

(1) Odour of garlic indicates arsenic.

(2) Efflorescence.

(*a*) White (α) zinc—yellow under the flame; (β) ammonium, arsenic, both volatile; (γ) antimony, volatilizes with difficulty. Other sublimates are not characteristic, as they can be produced by various salts, &c.

(*b*) Yellow: bismuth, lead.

(*c*) Brown: cadmium.

(3) A metallic globula may be tin, lead (both soft, the latter will mark paper). Bismuth, antimony (both brittle).

Copper (not as a globule, but as a loose, spongy mass of red metal). Silver (not brittle, but considerably harder than lead).

(4) If a white unfused residue is left it is moistened with a trace of a very dilute solution of nitrate of cobalt and again strongly heated. The residue may now appear coloured.

- (*a*) Blue: indicates Al (but not with certainty and it should be controlled.)
- (*b*) Green = zinc.
- (*c*) Pink = magnesium.
- (*d*) Grey = alkaline earths metals.

III. Flame Test.—A loop of platinum wire is heated to a white heat, and then a little of the substance to be tested is moistened with HCl and heated on it.

It then is moistened again with HCl and heated intensely. If the flame shows

- (*a*) Green = barium, copper (bluish green), perhaps also phosphoric acid.
- (*b*) Deep red = lithium, strontium (appear bluish red through a dark blue glass), calcium orange red (appears colourless or faint green through dark blue glass).
- (*c*) Blue = tin, copper.
- (*d*) Yellow tinge indicates sodium, but as this is always present it cannot be considered as characteristic.

IV. Phosphor Salt Bead.—A little sodium ammonium phosphate is melted on a platinum loop and some of the substance heated on it till it fuses.

- (*a*) A yellow to brownish red colour (hot), and almost colourless when cold, indicates iron nickel.
- (*b*) Green = chronium, uranium (which becomes yellow in the oxidizing flame).

(*c*) Blue = copper cobalt.

(*d*) Violet, in the oxidizing flame, manganese (colourless in the reducing flame).

(*e*) Dark red (sealing wax) in the reducing flame = Cu.

V. TESTS FOR ARSENIC, ANTIMONY AND MERCURY.—A little of the dry substance is mixed with double the same quantity of a finely powdered mixture consisting of dry sodium carbonate and calcium cyanide (of which a small quantity is kept in a closed bottle), and the mass is then thoroughly heated in a small glass tube, which is closed at one end (see above). If a metallic mirror-like deposit appears on the side of the tube :—

(*a*) Brown (uniform) indicates arsenic, which is soluble in hypochlorite of soda.

(*b*) Black (uniform) indicates antimony, insoluble in hypochlorite of soda.

(*c*) Grey (showing globules), mercury.

This test is not absolutely necessary, and is dangerous if the blowpipe test has caused the substance to detonate or crackle. This would indicate the probable presence of nitrate or chlorates which would explode violently on heating with potassium cyanide, therefore the open end of the tube should always be held away from the face.

REACTIONS OF THE PURE METALS.

Group I.—Aluminium, Nickel, Zinc.

Aluminium—Al.

(1) Melt a piece of Al on a block of charcoal (660° C.). A thick crust of oxide of Al will form on the surface and prevent further oxidation.

(2) Dissolve a little aluminium in dilute HCl to which a little concentrated HCl has been added. The Al will dissolve with a liberation of H.

(3) Dissolve a little aluminium chloride and add to the $Al\ Cl_3$ solution a few drops of a concentrated soda hydrate solution (NaHO). Oxyhydrate of aluminium will be precipitated in flaky gelatinous masses ($Al(OH)_3$), which will lose water on exposure to the air and change to : $2Al(OH)_3 = Al_2O_3 + 3H_2O$.

$2AlCl_3 + 6NaOH = Al_2O_3 + 3H_2O + 6NaCl$.

A further addition of NaOH dissolves the oxyhydrate of aluminium, and it becomes an aluminate of soda $_3AlO_3$ ~~$Al(OH)_2$~~. CO_2 or chloride of ammonia precipitates oxyhydrate of aluminium again.

The oxyhydrate of aluminium may be filtered out, washed with water, and heated on a platinum wire or charcoal block. When moistened with cobalt solution and again heated, a blue colouring (Thénard's blue) appears.

Nickel—Ni.

(1) Take a damp platinum loop and put on it some nickel salt ($NiSO_4$), and sodium ammonium phosphate.

The phosphorus salt bead appears brownish when hot, but becomes lighter on cooling.

(2) Dissolve nickel in nitric acid and add soda hydroxide solution (NaHO). A light green hydroxide of nickel appears.

$Ni(NO_3)2 + 2NaOH = Ni(OH)_2 + 2NaNO_3$.

An addition of bromide solution forms a brownish black hydrate of nickel oxide $Ni(OH)_2 + 2Br + 2NaOH = NiO_2 + NaBr + 2H_2O$.

(3) A few drops of ammonia precipitate a light green salt, soluble in excess of the reagent, to a dark blue colour showing a tinge of red.

(4) Add to (2) some ammonia and ammonium sulph~~ate~~ide. Dense black precipitate indicates Ni.

Zinc—Zn.

(1) Heat a piece of zinc on charcoal with the fine oxidizing flame of a blowpipe.

When overheated it will burn with a bluish-white flame. A yellow deposit appears on the charcoal, which becomes white on cooling.

(2) A salt of zinc heated on charcoal or platinum foil with a little soda (Na_2Cl_3), nitrate of cobalt is added. A dark green colour (Rinman's) indicates Zn.

(3) Dissolve in concentrated HCl and neutralize with NH_3. Add sulphuretted hydrogen (H_2S).

There is no precipitate from a neutral or slight acid solution.

Now add an alkaline acetate (ammonium, sodium or potassium) (K). There is a white precipitate of sulphide of Zn.

(4) To a solution of zinc salt add a little of sodium hydroxide (solution of NaOH).

A flaky gelatinous precipitate of hydroxide of Zn appears, which is soluble in excess of the reagent.

(5) Sulphide of ammonia precipitates white sulphide of Zn as in (3).

$ZnCl_2 + (NH_4)_2S = ZnS + 2(NH_4)Cl.$

Group II.—Tin, antimony, arsenic, bismuth, cadmium, copper and platinum.

Tin—Sn.

(1) Dissolve tin in 50 per cent. hydrochloric acid and a solution of chloride of tin is obtained, $SnCl_2$.

(2) Dilute the solution: If there is a precipitate of SnOHCl, add more HCl till it disolves. Now add sulphuretted hydrogen, H_2S. A yellow spot of sulphide of tin appears. This spot is soluble in sulphate of ammonia $(NH_4)_2S$.

(3) Dilute solution No. 1 and add diluted KHO or NaHO potassium or sodium hydrate.

A gelatinous precipitate soluble in excess of KHO indicates the presence of tin.

(4) Add chloride of mercury ($HgCl_2$) to solution (1). $SnCl_2 + HgCl_2$ forms $SnCl_4$. ~~Pure mercury~~ Mercurous Chloride comes down as a white precipitate which, however, soon turns grey.

$SnCl_2 + 2HgCl_2 = 2HgCl + SnCl_4$.

$2HgCl + SnCl_2 = 2Hg + SnCl_4$.

(5) Zinc will precipitate metallic tin as a spongy, glistening, finely crystalline mass.

(6) Add a drop of diluted chloride of gold: A rich purple colouring results, called purple of cassius (see Gold).

Antimony—Sb.

(1) Dissolve in concentrated HNO_3. It will be oxidized into Sb_2O_3.

(2) Now add concentrated HCl to the solution, and the dissolved Sb_2O_3 will be changed to $SbCl_3$.

Dilute thoroughly till a slight turbidity appears, and then warm and introduce sulphuretted hydrogen (H_2S). An orange red pentasulphide of antimony (Sb_2S_5) is precipitated. This is dissolved in ammonium sulphide $(NH_4)_2S$, giving a solution of a sulpho salt.

Now add concentrated H_2SO_4: A yellow precipitate of Sb_2S_5 reappears.

(3) Evaporate a part of solution (1) and dissolve the precipitated Sb_2O_3 in a drop or two of dilute HCl. Place the solution on platinum foil and introduce into it a bit of zinc. A black precipitate appears on the platinum.

Bismuth—Bi. Dissolve in concentrated nitric acid (HNO_3). It is insoluble in hydrochloric acid (HCl).

(1) Evaporate the solution to dryness and dissolve the residuum in dilute HCl, or nitric acid (HNO_3). Now add sulphuretted hydrogen (H_2S), a black precipitate of trisulphide of bismuth appears. This is soluble in con-

centrated nitric acid (HNO_3), but insoluble in sulph~~ate~~ide of ammonia.

(2) Take part of the solution made with concentrated HNO_3, warm it, and add water drop by drop by pouring or filtering it in. There is no turbidity at first, but the addition of water in excess brings down a precipitate of basic nitrate of bismuth.

$Bi(NO_3)_3 + 2H_2O = Bi(OH)_2, NO_3 + 2HNO_3$.

(3) Add sodium hydrate ($NaOH$) to a little of the clear, slightly diluted solution (2).

Hydroxide of bismuth is precipitated, which does not dissolve in excess of sodium hydrate.

Hydrogen peroxide colours the precipitate a light brown.

Cadmium—Cd.

(1) Take a little cadmium chloride and mix it with soda (Na_2CO_3 carbonate of soda), and fuse with the reducing flame of the blowpipe. A brown deposit appears on the charcoal.

(2) Dissolve a little cadmium in hydrochloric acid (HCl). This gives a solution of cadmium chloride. Pass sulphuretted hydrogen through it.

If the solution is strongly acid there is no precipitate. If however the solution is alkaline, or only slightly acid, a yellow precipitate of cadmium sulphide appears, which is insoluble in sulphate of ammonia.

(3) To solution of chloride of cadmium is added potassium, or sodium hydrate. A precipitate of white cadmium hydroxide appears.

$CdCl_2 + 2KOH = Cd(OH)_2 + 2KCl$.

(4) Add potassium cyanide to a solution of cadmium chloride, $CdCl_2 + 2KCN = Cd(CN)_2 + 2KCl$.

A white precipitate of cadmium cyanide appears which is, however, redissolved in excess of the cyanide of potash.

It is not precipitated by sodium or potassium hydrate, but by H_2S (yellow deposit).

Copper—Cu.

(1) Melt on a platinum loop a little phosphorus salt (sodium ammonium phosphate) or borax, till a clear bead is obtained. Moisten this with sulphate of copper $CuSO_4$ (blue vitriol) in solution. The bead shows a dark red colour in the reducing and blue in the oxidizing flame.

(2) Mix a little copper salt with soda (Na_2CO_3) and fuse with the blowpipe. The flame is coloured a greenish blue, and after thorough fusing particles of metallic copper remain.

(3) Dissolve copper sulphate $CuSO_4$ and add sodium hydrate (NaOH) to the solution.

A greenish-blue precipitate of hydroxide of copper is deposited, which on boiling turns brown at first and then black. Add a little ammonia to the solution (3).

Hydroxide of copper is precipitated as before. Excess of ammonia will re-dissolve the precipitate, giving a deep blue solution.

(4) Sulphuretted hydrogen or ammonium sulphide brings down a brown-black precipitate of sulphide of Cu. This should be filtered quickly, because it easily becomes colloidal and escapes through the filter.

(5) Polished iron is moistened with a copper salt solution. Copper is deposited which can be easily wiped off.

Platinum—Pt. Dissolve a little platinum in aqua regia. Evaporate to dryness and dissolve the residue in water.

(1) Pass H_2S through part of the solution. A brown precipitate of sulphide of platinum is formed.

(2) Add a little metallic zinc and some HCl to the rest of the solution of (1). Black metallic platinum is precipitated.

Group III.—Silver, gold, mercury.

Silver—Ag.

(1) Mix about ·1 grm. of nitrate of silver with the same amount of carbonate of soda and fuse with the blowpipe. A bead of pure silver will be formed.

(2) Dissolve the bead in concentrated nitric acid HNO_3; this gives a solution of silver nitrate $AgNo_3$.

(3) Dilute HCl is now added and a white precipitate of chloride of silver appears.

$AgNO_3 + HCl = AgCl + HNO_3$.

This is filtered and the precipitate is put into two different test tubes.

(*a*) Nitric acid is added to the first and no change takes place, as the precipitate is insoluble in HNO_3.

(*b*) Ammonia (NH_3) is added to the second and this dissolves the precipitate.

The dissolved precipitate ($AgNH_3Cl$) can be again brought down by adding HNO_3 as $AgCl + NH_4NO_3$.

Gold—Au.

Take three parts of hydrochloric acid (HCl) and one part nitric (HNO_3). This is called aqua regia.

Dissolve a little fine gold in this and evaporate to dryness. Add a little more HCl and evaporate again, and dissolve the dry gold chloride $AuCl_3$ in water.

Divide the yellow solution into five parts.

(1) Sulphuretted hydrogen is passed through and this causes a precipitate of black sulphide of gold. Filter. The precipitate is insoluble in all acids except aqua regia. It will also dissolve in sulphide of ammonia $(NH_4)_2S$.

(2) Add a solution of chloride of tin ($SnCl_2$) and warm it. A deep purple colouring (almost violet) appears. It is called purple of cassius (see Tin).

(3) To this add sulphate of iron $FeSO_4$. The gold is precipitated in the form of a brown, finely divided

metallic powder. $3FeSO_4 + AuCl_3 = Fe_2(SO_4)_3 + FeCl_3 + Au$.

(4) Add oxalic acid. Gold is precipitated in the form of finely divided brown metallic particles.

(5) Add peroxide of hydrogen H_2O_2 and then concentrated sodium hydrate (NaHO) solution. The gold precipitates in thick flaky masses which are easy to work.

This is the best method of precipitation.

Mercury—Hg.

Dissolve a little mercury in concentrated nitric acid. A solution of nitrate of mercury $HgNO_3$ is obtained or in the presence of excess of acid $Hg(NO_3)2$.

Sulphuretted hydrogen is passed through. This brings down a black precipitate of sulphide of mercury HgS.

Test for HgS.

The black sulphide is insoluble in (*a*) hydrochloric acid (HCl), (*b*) nitric acid HNO_3. It is only soluble in aqua regia.

The HgS dissolved in aqua regia is there as a chloride $HgCl_2$.

Add chloride of tin $SnCl_2$. A white precipitate appears which soon becomes grey. This is mercury in a ~~colloidal~~ finely divide state.

ANALYTICAL PROCESSES.

The chemical analysis of an alloy containing the metals: Mercury, platinum, gold, silver, tin, cadmium, copper, zinc (amalgams).

(1) Take 1 gram of the amalgam to be analysed, and heat it (under hydrogen) to a bright red.

The escaping mercury vapour is caught in a receiver, condensed and weighed.

The amalgam is now weighed, and the loss represents the evaporated mercury, the weight of which can be compared with it if it (Hg) has been carefully dealt with. An apparent excess of weight might be due to evaporated cadmium or zinc.[1]

(2) Powder the residue and dissolve in concentrated nitric acid, and evaporate to dryness over a water bath.

Dissolve the nitrates thus obtained in water.

The insoluble residue will be gold, platinum, and tin.

(3) Now filter.

On the filter the insoluble metals, gold, platinum, and tin will be found. The other metals will be in the filtrate and traces of the platinum also, if much is present.

Keep the filter for further treatment.

(4) To the filtrate add a little HCl. This brings down the silver in flaky masses as a chloride (AgCl), and any remaining mercury as HgCl. Warm for five or ten minutes so that the precipitate may be thoroughly settled.

(5) Filter: The silver and mercury remain on the filter. Now add ammonia (NH_3) to the silver and mercury. The silver chloride will be converted into $Ag(NH)_3Cl$ and dissolved. Filter again. The mercur~~ic~~ous chloride now remains on the filter and is dried and weighed. Nitric acid is added to the filtrate and this precipitates AgCl again.

Filter off the deposit and dry it. Then place it carefully with the aid of a camel-hair pencil on to black glazed paper and burn in a weighed porcelain crucible till free from carbon.

Heat the remainder carefully with the precipitate till it fuses and weigh: Silver.

All the other metals are in the filtrate.

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[1] For the purpose of accurate quantitative determinations it is better to omit the heating and sublimation, and to estimate the mercury by wet methods, as shown later.

(6) Neutralize the filtrate from (5) with ammonia and acidify it slightly with dilute HCl.

This is done firstly because cadmium will not precipitate from a strongly acid solution, and secondly, because zinc would be precipitated from an alkaline solution.

(7) Now pass sulphuretted hydrogen through the solution. This precipitates the cadmium and copper as sulphides. Filter. The sulphides remain on the filter and the zinc in the filtrate.

(8) Dissolve the sulphides on the filter in concentrated nitric acid and evaporate to dryness.

Dissolve the nitrates with water and add a little potassium cyanide and ammonia till the solution is alkaline.

(9) Again pass H_2S through the solution. The CdS is precipitated.

The CuS remains in the solution because of the presence of potassium cyanide.

Filter through a dried and weighed filter.

The CdS remains on the filter. Dry it for an hour at 105° C. and weigh. It is CdS. The copper remains in the filtrate.

(10) Acidify the Cu solution of 9, and boil till all odour of cyanides ceases. (N.B.—Poison! The warning previously given to hold the test-tube away from the face should be remembered.)

Now pass H_2S through the solution. This brings down the Cu as a sulphide.

Filter, roast the filter, and weigh as CuO. (Roasting converts the CuS into CuO.)

(11) Make the filtrate from (7) alkaline with NH_3 and pass H_2S through it. Let it stand twelve hours. White sulphide of zinc is precipitated ZnS. Filter, dry, roast, and weigh as ZnO (as with CuO).

(12) The filter of No. 3 containing gold, tin and platinum

is thoroughly roasted and placed in a platinum crucible with some carbonate of soda and fused, and the fused mass taken up with water. The tin dissolves as stannate of soda (Na_2SnO_3). Filter, and add H_2SO_4 to the filtrate. This precipitates the tin as SnO_2. Filter, roast and weigh. This disposes of the tin, leaving the gold and platinum on the previous filter.

(13) Dissolve the precipitate containing the gold and platinum in aqua regia, and evaporate to dryness over a water bath. Shake up with water and add a few drops of chloride of tin ($SnCl_2$). This brings down the gold in the form of a brown finely divided precipitate.

It is, however, better to use peroxide of hydrogen and concentrated sodium hydrate ($H_2O_2 + NaHO$). The gold obtained as a black precipitate becomes brown on boiling (see p. 229, under Gold).

Oxalic acid will also precipitate, but it must be given a longer time to settle, because of the tendency of the gold to cling to the sides of the vessel. Filter, roast, and weigh the gold.

(14) The filtrate now contains platinum. The chloride, which was yellow $PtCl_4$, has changed into the lower chlorid ~~a chlorate~~ ($PtCl_2$) which is dark brown. Add to this a little metallic zinc and some HCl and warm till no more gas is evolved. Black metallic platinum is precipitated.

Remarks.—Use filter papers of a known dry weight and ash weight, as the latter has always to be subtracted from the total weight.

Sulphide of cadmium is very volatile, as is the metal itself, and therefore should not be roasted.

Cadmium sublimes at 760° C. and the loss during evaporation of the mercury should not be overlooked.

A longer treatment at a lower temperature (say 600 to 700° C.) is better, as otherwise the Hg may be retained—chiefly by the gold, silver and tin.

One might even omit the evaporation of the Hg and estimate it afterwards by wet methods.

In either case the mercury will come down with the silver in the HCl precipitation as described above (see p. 231 (4)).

The precipitated salts may be estimated as follows :—

HgCl	contains	Hg	82·24	per cent.
AgCl	,,	Ag	75·27	,,
CuO	,,	Cu	79·80	,,
Cu_2S	,,	Cu	79·80	,,
CdS	,,	Cd	77·74	,,
ZnS	,,	Zn	66·97	,,
ZnO	,,	Zn	80·3	,,
SnO_2	,,	Sn	78·60	,,
Au	,,	Au	100	,,
Pt	,,	Pt	100	,,

Instead of passing H_2S through the solution by means of a Kipp's apparatus, the sulphuretted hydrogen water may be used for the preliminary reactions.

Put a little iron sulphide into a flask and pour dilute HCl over it, and to this add a few drops of concentrated HCl and warm till the gas (H_2S) begins to come off.

(A simpler way of making H_2S is heating of sulphur with vaseline.)

This may be led into water by means of a glass tube and absorbed to saturation.

By dissolving it in ammonia (NH_3) one obtains sulphide of ammonia $(NH_4)_2S$.

Analytical Methods for Estimating Gold, Silver, and Platinum with Silver at more than 25 per cent.

If tin or a large quantity of other base metal is present then treat a weighed mass of the alloy with warm HCl for some hours till all the soluble metal has been taken up.

The remainder is fused with soda in a Pt crucible and then boiled with water. Then filter.

In the filtrate will be found all the tin and perhaps also a part of the other base metals as chlorides. Wash thoroughly and dry the filter and add litharge (PbO[illegible]) freely and then as much silver as will make 25 per cent. at least of the mixture.

Fuse on an earthenware saucer till the metallic mixture disappears and the mass is covered with lead dross.

Cool, break out the regulus, and place it in a cupel of suitable size, together with some of the dross and a sufficient quantity of metallic lead.[1]

Fuse till the dross is completely absorbed by the cupel and the surface of the molten metal gives off no more vapour or appears agitated at all.

At a temperature of less than 960° C. the white sheen of the silver will appear.

Cool and weigh, and roll out thin. Roll up the thin sheet and boil in nitric acid (sp. gr. 1·2—1·3) free from chlorine, till all the silver is dissolved. No more brown vapour will appear.

A roll of fine gold will remain, together with platinum, if such is present. If no platinum is present melt the gold.

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[1] When there is no tin present and only gold is to be determined, pure lead is to be put in at once, For a test of each ·5 grm. of alloy more lead is used in proportion, as there is less gold present.

Fineness of test blow on	Lead required for ·5 grm.
1·000	4 grm.
·900	8 ,,
·800	12 ,,
·700	16 ,,
·600	20 ,,
·500	24 ,, &c.

For each additional 100 parts of impurities 4 grm. more.

If platinum is present dissolve in aqua regia and treat as previously described.

The filtrate contains silver nitrate ($AgNO_3$) which can be precipitated as a chloride by means of HCl or NaCl. Filter. Weigh as AgCl or shake up the filter with diluted H_2SO_4 and separate the silver by inserting strips of metallic zinc.

Boil with hydrochloric acid to remove the zinc impurities. Filter, wash and fuse—a pure silver regulus is thus obtained.

The electrolytic separation of silver from the chloride is, however, simpler :—

Take a glass jar holding about 5 litres and place in it a long earthenware cell and put in this an iron plate. Fasten a copper wire to the iron plate.

Now suspend a sheet of silver 5 cm. in width from the side of the glass jar so that it reaches to the bottom and partly covers it, also encircles the earthenware cell and extends along the wall of the outer jar.

The copper wire attached to the iron plate is now connected with the silver sheet.

Now pour in the silver chloride and then 10 per cent. H_2SO_4 till the iron plate is almost covered.

This generates a current between the silver sheet and the iron and causes a deposit of pure silver to form on the silver plate. This can be easily removed and melted.

XXIII. ELECTROLYSIS.

ELECTRICAL UNITS.

Definitions of the International Congress of Electricians, Chicago, 1893, *according to the proposals of the Imperial Chemico-technical Institute. Officially adopted in Germany by the law of June,* 1908.

(1) The official units for the measurement of currents are the "ohm," *i.e.*, the resistance of the conducting medium to the passage of a current; the ampere = the amount or quantity of the current passing, and the volt, which is the pressure or tension of the current.[1]

(2) The (so-called international) ohm is the unit of resistance and represents the obstruction offered to a current by a column of mercury at 0°C., the length of which is 106·3 cm. and the cross-section equal to 1 mm., and the weight 14·4521 grm.

(3) The ampere is the unit of quantity. It is that amount of a direct current required to precipitate in one second of time ·001118 grm. of silver from a watery solution of silver nitrate.

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[1] The best illustration of these units may be taken from a water-pipe. The volt represents the pressure in the pipe, which may vary according to the height of the water tower.

The amperage corresponds to the diameter of the pipe, that is the same thing as the amount of water running through it. The ohm may be said to represent the condition of the pipes inside, as a rough or obstructed surface will obviously cause more resistance to the flow of water than a smooth one, and, moreover, the longer the pipe, the greater the resistance. Also the higher the tap is, so much less is the pressure. The difference in tension between the two ends of a conductor is also a measure of the electromotive force.

(4) The volt is the unit of the pressure. It is the pressure required to generate a current of 1 ampere against a resistance of 1 ohm.

OTHER ELECTRICAL TERMS.

A watt is the work done in one second by a current of 1 ampere in a conductor, whose ends show a difference in tension amounting to 1 volt.

One h.p. (horse-power) = 746 watt (= 75 metre kg. per second).[1]

A coulomb is the quantity of electricity at 1 ampère which passes through a conductor in one second; 96,540 coulomb = 1 grm. equivalent or the quantity of electricity necessary to develop 1 grm. of hydrogen.

A "Farad" is the capacity of a condenser which is charged by an amount of 1 coulomb from a current showing a difference of 1 volt.

Meg = the quantity 1,000,000 times.
Kilo = " 1,000 "
Milli = " $\frac{1}{1000}$ "
Micr(o) = " $\frac{1}{1000000}$ of the unit.

These various units have a fixed relationship to one another, which is explained by using as before the analogy of running water.

If water runs without resistance through a rubber tube then everyone knows that if the end be squeezed, which means resistance offered, the water will spurt out in a fine stream, but with more force (pressure). By increasing the resistance we raise, therefore, the pressure.

It is the same when dealing with an electric current.

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[1] A metre kilogram is the work done in raising 1 kg. through 1 metre. One h.p., therefore, is the work done in raising 75 kg. through 1 metre in one second of time or 1 kg. in one second through 75 metres.

The greater the resistance (ohm) to the current (ampere), the greater will be the electromotive force (voltage).

From this we can deduce a rule for finding the relationship of the three units thus :—

The quantity (ampere) × the resistance (ohm) = the electromotive force or ampere × ohm = voltage.

Another relationship would be—

$$\text{(C) Ampere} = \frac{\text{volt (E)}}{\text{ohm (R)}} \text{ or (R) ohm} = \frac{\text{volt (E)}}{\text{ampere (C)}}$$

To understand the nature of electrolysis, we must recall certain facts which have been previously dealt with, viz., the structure of metals (p. 4 ff.) and the nature of chemical compounds (p. 6).

We have there seen graphically that the smallest particle of matter that can have a free existence is called a molecule, and it is made up of one or more atoms.

Modern thought has carried this theory much farther, and we must now consider one or two of the more recent theories in this connection.

Whilst still thinking of the molecules as infinitely small particles of matter, we must imagine that they do not touch each other, but are separated by a space of greater bulk than the molecules. The molecules are therefore free to move. This explains the so-called theory of solid solutions (mixed crystals) and polymorphic changes, which take place in the solid state (*see* p. 24 ff.).

Secondly, we must consider those special cases of the electrolysis of acids, bases and salts. Such substances in aqueous solution are conductors, and the solution of them is called an electrolyte.

The compound in solution is not entirely represented by molecules, but partly broken down, in the case of salts, into metal (acids give hydrogen) and the residue or acid radicle (*e.g.*,—$CuSO_4$ gives $Cu + SO_4$). The former (Cu or H) is called the Cation and the latter the Anion.

These ions (or free atoms or radicles) carry a charge of electricity, by virtue of which they move freely across the liquid. Atoms in the "ionic state" possess quite different properties from the normal or non-electrified condition. Thus sodium, a metal that reacts with water with great energy to form sodium hydroxide, can exist as sodium ions in an aqueous electrolyte without such a result.

Ions (Greek—the wanderers) are obviously charged negatively (—) or positively (+). We find that the metallic or hydrogen portion of the dissociated molecule always carries a positive (+) charge and the acid radicle (or residue) of the original molecule has a negative (—) charge.

It will be shown that these charges of electricity carried by the ions are neutralized by a charge of opposite sign at one or other of the electrodes.

The metallic surfaces (generally platinum plates) by which an electric current enters or leaves the solution are called the electrodes.

Following the direction of the flow of the current, we call that electrode at which the current enters the solution the positive electrode. The current flows across the solution, passing a chain of electrically-charged ions, and returns to the generator by passing up the negative electrode. The ions thus touched by the current, as their name implies, begin "to wander," but their wandering is in a definite direction. All the positive ions or cations tend to move to the negative electrode (kathode), and the negative ions (or an-ions) to move to the positive electrode (anode).

On reaching the oppositely charged electrode the charge on the ions is neutralized, and they once more become the ordinary type of atom, with their original chemical and physical metallic properties.

It may be emphasized besides that the work of the current is confined to the carrying of the ions to the electrodes.

This tendency to change from the electrified to the neutral atomic condition or state constitutes the so-called theory of osmotic pressure of solutions.

This osmotic pressure is equated by the tendency of the solution to replace the free ions, which have been deposited on the cathode, by others as long as atoms of the metal are present in the solution, thus enabling the continuance of the change. This we call the electrolytic pressure of solution.

This latter makes it possible to deposit the metal completely from the solution, for without it the deposition would cease as soon as the initial number of ions had transferred their electrical charge to the electrodes.

If, therefore, it is desired to effect electrolytic separation of metals from their solution, the object on which they are to be deposited must be connected with the negative pole of the electrical generator.

Observance of this rule must be made whether the purpose be electro-chemical analysis, the production of electrotypes, or the commercial application to gilding, coppering, &c. In the latter cases, a sheet of the same metal as it is intended to deposit constitutes the other (+) electrode.

We have now to consider briefly the relation of the weight of the deposited metal to the area of the cathode and the strength of the current.

According to Faraday's laws, which in the present treatise it is impossible to touch upon at any length, the weight of the deposited metals is a definite quantity depending on—

(*a*) The electro-chemical equivalent of the metal.

(*b*) The strength of the current expressed in amperes.

(*c*) The time during which the current flows, expressed in seconds.

The electro-chemical equivalent is found by dividing the atomic weight of the metal by its valency × 96,540 which is the grm. equivalent of it.

This means that 96,540 coulombs of electricity deposit the atomic weight of any metal expressed in grammes divided by the valency.

Thus, since the atomic weight of copper = 63·6 and its valency II[1] (see table, p. 36), 96,540 coulombs of electricity will deposit $\frac{63·6}{2}$ grm. of copper.

One coulomb therefore deposits—

$$\frac{63·6}{2·96540} = 0·0003294 \text{ gr. Cu.}$$

This is called the E.C.E. (electro-chemical equivalent) of copper. It means that if a current of 1 ampere flows for 1 second 0·0003294 grm. (= 0·3294 mgrm.) of copper is deposited—or in 1 hour, 1·18584 grm.

The following table (after Neumann) shows the atomic

---

[1] Valency is the term used to express the combining value of a metal as compared with hydrogen. Thus, the valency of hydrogen being 1 and that of oxygen being 2, we find that water is composed of 2 atoms of hydrogen united with 1 atom of oxygen. Oxygen would, therefore, seem to have two bonds to satisfy, and the symbol for water is H_2O or $H + O + H$.

Similarly iron (Fe) in ferric salts is trivalent (or has a triple hydrogen value), and since chlorine (Cl) is only monovalent, we find that it takes 3 chlorine atoms to satisfy 1 atom of iron, thus :—

$$\mathrm{Fe}\begin{cases} + \mathrm{Cl} \\ + \mathrm{Cl} \text{ or } \mathrm{Fe\,Cl_3} \\ + \mathrm{Cl} \end{cases}$$

Some metals (*e.g.*, Cu) can have more than one valency (Fe, &c., *see* table on p. 36).

weights, valencies, and electrochemical equivalents of twenty of the commoner metals.

		Valency	Atomic weight[1]	Electrochemical equivalent depositing by 1 ampère	
				1 second mgm.	1 hour gr.
1	Aluminium, Al ...	III	27·04	0·0938	0·3377
2	Antimony, Sb ...	III	119·6	0·4151	1·494
3	Lead, Pb	II	206·4	1·0744	3·868
4	Cadmium, Cd ...	II	111·7	0·5814	2·093
5	Gold, Au	III	196·7	0·6827	2·458
6	Copper[2], Cu ...	I	63.18	0·6578	2·368
7	,, ,, ...	II	63·18	0·3289	1·184
8	Nickel[2], Ni ...	II	58·6	0·3050	1·098
9	,, ,, ...	III	58·6	0·2033	0·732
10	Platinum, Pt ...	IV	194·3	0·5078	1·1828
11	Mercury[2], Hg ...	I	199·8	2·080	7·488
12	,, ,, ...	II	199·8	1·040	3·744
13	Silver, Ag	I	107·66	1·1183	4·026
19	Zinc, Zn	II	61·5	0·3389	1·220
20	Zinn, Sn	II	118·8	0·6184	2·226

The numbers given in the columns under "electrochemical equivalent" are for a current of 1 ampere acting for 1 second or 1 hour as stated.

The microscopical structure varies very largely with the relative strength of the current (in amperes) to the area of the surface receiving the deposit. It is usual to state it as so many amperes per 100 sq. cm., and is termed the Current Density (contracted to C.D. 100).

If in any particular case it is desired to use a C.D. of two amperes per 100 sq. cm., the area of the article must be approximately determined, and if, say, it be 200 sq. cm., then the ammeter must show a reading of 4 amperes passing through the solution. Similarly if the area of the object be less than 100 sq. cm. the current must be proportionately less.

---

[1] Neumann's atomic weights are slightly different from those now accepted, but the error in the E.C.E. will be very small (see pp. 36, 37).

[2] Various metals have different valencies in different compounds, *e.g.*, Cu in $CuCl_2$ is divalent, whilst Cu in CuCl is monovalent.

We have hitherto only spoken of current. It will be obvious that besides large and small currents we can have currents of different tension. This tension or electromotive force (E.M.F.) is measured by a unit called the volt, just as ~~amount~~ rate of flow or volume of current is measured by amperes. It will also be apparent that the E.M.F., *i.e.*, the force necessary to drive the current, varies widely with different electrolytes and from different causes. Thus the resistance of electrolytes varies very much, and until this is overcome and a certain current actually passes round the circuit, no deposit can take place.

Another cause that operates against the flow of the current is that due to polarisation, that is, a current is generated, *opposite in direction* to the main current, which of course lessens or even totally prevents the passage of electricity in the direction required.

It is therefore essential that the tension (or E.M.F.) of the current used shall be such as to overcome these opposing influences.

The following data by Classen show the composition of the electroplating solutions of gold, silver, nickel and copper according to various workers' formulæ, together with details of the best current density (ampere per 100 sq. cm.), the voltage necessary, and the weight of deposit secured.

As stated before, the current (C.D. 100) must be proportional to the area of cathode surface.

The temperature of the electrolyte is also a matter requiring consideration, since the conductance of a solution is increased by raising its temperature.

In other words the resistance of the solution to the passage of the current is lessened by raising its temperature. Hence a current of lower tension (E.M.F.) would be required.

Similarly various acids, bases and salts added to the solution effect the same result, since they are good conductors and form as it were a ladder for the current. They must, however, be of such a character that they will not react with the metallic salt it is sought to electrolyse.

The usual substances used for this purpose are oxalic acid or potassium cyanide, according to circumstances.

I. *Gold.*

Electrolyte.—Dissolve 0·5 grm. of neutral gold chloride (gold salts) in aqueous solution of 120 grm. of potass. cyanide. Add 3 grm. of cyanide in excess for so-called "free cyanide."

(1) The bath should be worked at a temperature of 50—60° C. (at ordinary temperatures there are brown deposits).

(2) Current density (C.D. 100) = 0·3—0·8 ampere.

(3) E.M.F. = 2·7—4·0 volts.

(4) Rate of deposition (*a*) 0·3 ampere = 0·374 grm. per hour; 0·8 ampere = 1·0 grm. per hour.

N.B.—Use only pure cyanide salt in the preparation (KCN).

Langbein's formula for gold bath :—

(1) Cold solution.

Fulminate of gold (precaution—do not allow to get dry; substance very explosive), 3·5 grm.
Potass. cyanide (98—99 per cent.), 10—15 grm.
Water, 1 litre.

(*a*) Temperature—ordinary (room).

(*b*) C.D. 100 = 0·15 ampere (electrodes 10 cm. apart).

(*c*) E.M.F. = 1·35 volts with 10 grm. cyanide.
1·2 " " 15 " "

Preparation of bath : dissolve the neutral gold chloride n water, and add ammonia to complete precipitation (brown precipitate). Evaporate the excess of ammonia off (caution—great care). Filter and dissolve the *wet* precipitate in 1 litre of water containing the 10—15 grm potass. cyanide previously dissolved in it.

(2) Warm solution.

Fulminate of gold 1 grm. (or 2 grm. gold chloride). Prepare as cold solution, using only 5 grm. cyanide in 1 litre water.

(*a*) Temperature 60—70° C.
(*b*) C.D. 100 = 0·1 ampere (electrode 10 cm.).
(*c*) E.M.F. = 2·0 volts.

II. *Silver.*

Dissolve the silver salt in water (120 c.c.). (If insoluble, dissolve in 120 c.c. water, and just sufficient cyanide to effect solution.) Add 3 grm. purest potass. cyanide in excess.

(*a*) Temperature 20—30° C.
(*b*) C.D. 100 = 0·2—0·5 ampere.
(*c*) E.M.F. = 3·7—4·8 volts.
(*d*) Deposit: 0·2 ampere = 0·8052 grm. in 1 hour; 0·5 ampere = 2·013 grm. in one hour.

Langbein's formula for silver solution :—

(1) Special use—silvering of weights.

Take potass. cyanide (98 per cent.) 100 grm.
Cryst. double cyanide of potassium of silver, 500 grm.
Distilled water, 10 litres.
C.D. 100 = 0·3 ampere.
E.M.F. = 1 volt (electrodes 10 cm. apart).

(2) Ordinary silver solution.

Potass. cyanide (98 per cent.), 100—120 grm.
Cryst. double cyanide of silver and potassium, 200 grm.
Distilled water, 10 litres.

C.D. 100 = 0·3 ampere.

E.M.F. = 1·25 volt (electrodes 10 cm. apart).

III. *Nickel.*

Dissolve 20 grm. nickel amm. sulphate in 120 cc. liquid and add 4—5 gr. amm. oxalate, for white deposits.

(*a*) Temperature, 17—70° C.

(*b*) $C.D._{100}$ = 0·4—0·9 ampere.

(*c*) E.M.F. = 2·7—4·35 volts.

(*d*) Deposit varies with the valency of the salt used; thus: a salt having valency of II.:—

With 0·5 amp. a deposit of 0·549 gr. per hour obtained.
" 0·9 " " 0·9882 " " "

Langbein gives the following formula for nickel bath:—

Nickel-ammonium-sulphate: 500 grm.

Distilled water: 10 litres.

$C.D._{100}$ = 0·35 ampere.

E.M.F. = 1·8—2·0 volts (electrodes 10 cm. apart).

The solution must be maintained in a neutral condition by the addition of sulphuric acid or ammonia, as the case may need.

IV. *Copper.*

Solution—copper sulphate 1 grm. + ammonia oxalate 4 grm. in 120 cc. of water.

(*a*) Temperature: 80° C.

(*b*) $C.D._{100}$ = 0·35—1·0 ampere.

(*c*) E.M.F. = 2·5—3·2 volts.

(*d*) Deposit:—

(*α*) from a monovalent salt—
0·35 ampere gives 0·8288 gr. Cu in one hour.
1·0 " " 2·368 " " "

(*β*) from a divalent salt—
0·35 ampere gives 0·4144 gr. Cu in one hour.
1·0 " " 1·184 " " "

Langbein's formula for coppering solution :—

(*a*)	Copper acetate (neutral)	200 grm.
	Sodium carbonate	250 "
	Sodium bisulphate (powdered) ...	200 "
	Potassium cyanide (98-99 per cent.) ...	225 "

The sodium carbonate is dissolved in 7 litres water, and the sodium sulphate (sod. bisulphate) added in small quantities at a time. Then add the copper salt slowly and mix well.

Dissolve the potass. cyanide in 3 litres of water.

Add the latter solution to the former slowly, with continual agitation, and set aside for twelve hours.

Carefully decant from any residue.

The solution should be colourless or wine yellow.

If it is not so, add potass. cyanide in small quantities until this is effected. Working details :—

C.D._{100} = 0·35 ampere.

E.M.F. = 3 volts.

Electrodes : 10 cm. apart.

(*b*) Coppering solution for electrotype production.

Preparation : Prepare 100 litres of copper sulphate (blue vitriol) solution, containing 22 per cent. $CuSO_4$. This should have a sp. gr. of 19·5° Bé.

Add slowly, with constant stirring, 2 to 3 kg. of sulphuric acid (arsenic free) of sp. gr. 66° Bé. Working details :—

Temperature : 15° C.

Current strength : 2—3 amperes.

Those who desire further information on electrolytic separations and electro-plating will find references in the index to current works on the subject.

XXIV. VARIOUS FORMULÆ AND TABLES.

Table giving Specific Gravity (Water = 1) of various Substances.

	Substance	Specific gravity—dried in air	Specific gravity—green*
1	Maple	0·53—0·81	0·83—1·05
2	Beech...	0·51—0·77	0·8—1·09
3	Pearwood	0·61—0·73	0·96—1·07
4	Cedar	0·57	...
5	Ebony	1·26	...
6	Oak	0·69—1·03	0·93—1·28
7	Pine	0·35—0·60	0·40—1·07
8	Guaiacum wood	1·17—1·39	...
9	Cherry wood...	0·76—0·84	1·05—1·18
10	Lime	0·32—0·59	0·58—0·87
11	Mahogany	0·56—1·06	...
12	Nut-tree	0·60—0·81	0·91—0·92
13	Bones	1·7—2·0	...
14	Building sandstone (artificial)	2·03	...
15	Sandstone	2·2—2·5	...
16	Ivory	1·83—1·92	...
17	Plaster of Paris	2·306—2·331†	...
18	Wax	0·965	...
19	German silver	8·4—8·7	...
20	Argentan	8·4—8·7	...
21	Deltametal	8·6	...
22	Iron	7·85	...
23	Steel	7·86	...
24	Bell metal	8·86	...

* "Green" or freshly cut wood.

† Average 2·32.

Formula for Calculating the Weight of Metal required for a Casting in any Particular Metal, from the known Weight of the Model.

(A) = the sp. gr. of the material of which the model is made.

(B) = the sp. gr. of the metal to be used for the casting.

(C) = the specific weight of the model.

(D) = ,, ,, ,, ,, metal casting.

$$\text{Then D (the weight of the casting)} = \frac{B \times C}{A}$$

Example: Required the weight of a casting in deltametal from an oak model weighing 3 kilos.

Sp. gr. of oak = 0·75 (= (A)) Sp. gr. of deltametal = 8·6 (= (B))

$$\text{Since D} = \frac{B \times C}{A} = \frac{8{\cdot}6 \times 3}{0{\cdot}75} = 34{\cdot}4 \text{ kilograms.}$$

The amount of metal taken must therefore be 34·4 kilos plus the necessary percentage for waste by oxidation, &c.

TABLE OF COEFFICIENTS OF CUBICAL EXPANSION (LINEAR × 3)—α—OF VARIOUS *Alloys and Amalgams*, ACCORDING TO LANDOLT AND BÖRNSTEIN (pp. 202, 208).

	Composition of alloy		Temperature	Coefficient of expansion = α
	Per cent.	Per cent.	° C.	
1	36 Sn	64 Pb liquid	262—356	$0{\cdot}0_3$ 1269
2	87 ,,	13 ,, ,,	249—355	$0{\cdot}0_3$ 1123
3	35·1 Cd	64·9 ,,	0—100	$0{\cdot}0_3$ 09138
4	83·9 Sn	16·1 Zn	0—100	$0{\cdot}0_3$ 07184
5	45·5 Au	54·5 Sn	0—100	$0{\cdot}0_3$ 04233
6	68·6 Ag	31·4 Au	0—100	$0{\cdot}0_3$ 05166
7	2·0 ,,	1 Pt	0—100	$0{\cdot}0_3$ 04568
8	43·0 Sn	57 Bi liquid abt.	140	$0{\cdot}0_3$ 1217
9	68·0 ,,	32 Cd	175	$0{\cdot}0_3$ 1235
10	67·0 Bi	33 Pb	130	$0{\cdot}0_3$ 1384
11	90·0 Pb	10 Sb	250	$0{\cdot}0_3$ 1228
12	90·0 Cd	10 Zn	265	$0{\cdot}0_3$ 1531
13	22·7 Sn	77·3 Hg	242—316	$0{\cdot}0_3$ 125
14	20·0 Pb	80 Hg	199—319	$0{\cdot}0_3$ 161
15	13·9 Zn	86·1 Hg	237—323	$0{\cdot}0_3$ 184
16	1·0 Bi	1 Hg melting point 162·7	163—280	$0{\cdot}0_3$ 134

TABLE OF COEFFICIENTS OF LINEAR EXPANSION ($\frac{1}{3}$ CUBICAL) (β) OF VARIOUS ALLOYS AT ABOUT 20° C.

	Substance	Percentage composition				Coefficient of expansion
1	Brass	73·7 Cu	24·2 Zn	1·5 Sn	0·6 Pb	$0{\cdot}0_4\ 18112$
2	Bronze	81·2 ,,	8·6 ,,	9·9 ,,	0·2 ,,	$0{\cdot}0_4\ 17740$
3	Phosphorbronze	97·6 ,,	2·2 Sn	0·2 Pb	hard	$0{\cdot}0_4\ 16849$
					annealed	$0{\cdot}0_4\ 16778$
4	Constantan ...	60 ,,	40 Ni	...	...	$0{\cdot}0_4\ 16971$
5		90 Pt	10 Ir	...	...	$0{\cdot}0_4\ 08734$
6		80 ,,	20 ,,	...	...	$0{\cdot}0_4\ 08255$
7	Nickel steel ...	24 Ni	...	...	...	$0{\cdot}0_4\ 17768$
8		36 ,,	...	...	...	$0{\cdot}0_4\ 00928$
9		63·8 Bi	36·2 Sn	...	...	$0{\cdot}0_4\ 1680$
10		50·1 ,,	49·9 Pb	...	...	$0{\cdot}0_4\ 2842$

FORMULA FOR CALCULATING THE THEORETICAL SPECIFIC VOLUME (AVERAGE) OF THE *Binary Alloys.*

Let V represent the specific volume of the required alloy
and V_1 the specific volume of component metal A
V_2 ,, ,, ,, ,, B
P_1 the percentage of A in the alloy
P_2 ,, ,, B ,, ,,
Then V = (the specific volume of the required alloy)

$$V = \left(\frac{P_1 \times V_1}{100}\right) + \left(\frac{P_2 \times V_2}{100}\right)$$

Example: An alloy containing—
$(P_1) = 40$ per cent. of a metal A of specific volume $8 = (V_1)$
$(P_2) = 60$,, ,, B ,, ,, $12 = (V_2)$
Then the specific volume of the alloy =

$$\left(\frac{(40 \times 8) + (60 \times 12)}{100}\right) = \frac{1{,}040}{100} = 10{\cdot}4 = V.$$

FORMULA FOR CONVERTING WEIGHT PROPORTION INTO ATOMIC WEIGHT PROPORTION.

A = weight of metal A
B = ,, ,, B

a = atomic weight of metal A
b = ,, ,, ,, B

Then $\frac{A}{a} : \frac{B}{b}$ = atomic weight proportion A : B.

Example: An alloy containing 40 per cent. weight tin, 60 per cent. weight mercury.

Atomic weight of Sn = 120 atomic weight of Hg = 200.

$$\left.\begin{array}{l}\text{Number of atoms of tin} = \frac{40}{120} = \frac{1}{3} = \frac{A}{a}\\ \text{,,} \quad \text{,,} \quad \text{Hg} = \frac{60}{200} = \frac{3}{10} = \frac{B}{b}\end{array}\right\} \frac{1}{3} : \frac{3}{10} = 10 : 9$$

Or this alloy contains 9 atoms of mercury : 10 atoms of tin, or in 100 parts :—

$$\frac{100}{19} \times 9 = 47{\cdot}4\ \%\ \text{Hg and } \frac{100}{19} \times 10 = 52{\cdot}6\ \%\ \text{tin.}$$

FORMULA FOR CONVERTING ATOMIC WEIGHT PROPORTION INTO WEIGHT PROPORTION.

A = atomic weight per cent. metal A
B = ,, ,, B
a = ,, A
b = ,, B

Then is $\frac{A\,.\,a}{B\,.\,b}$ = ordinary weight proportion of A : B.

Example like V.

52·6 atomic weight % Sn. 47·4 atomic weight % Hg.

$$\begin{array}{l} A = 52{\cdot}6\,.\; a = 120\\ B = 47{\cdot}4\,.\; b = 200\end{array} \qquad \frac{52{\cdot}6\,.\,120}{47{\cdot}4\,.\,200} (= 52.6 : 79) = 40\ \text{Sn} : 60\ \text{Hg.}$$

CALCULATION OF SPECIFIC GRAVITY FROM SPECIFIC VOLUME.

The specific gravity indicates the relative weight of any substance compared with an equal volume of water at 4° C. The specific volume is that volume occupied by 1 grm. of the substance. (Thus 1 grm. water occupies a volume of 1 c.c. at 4° C., and specific volume is therefore 1.)

For any other substance the specific volume is found from :—

Let a = specific gravity of the substance
,, b = ,, volume required

$$\text{then } \frac{1}{a} = b \text{ and } \frac{1}{b} = a$$

i.e., the specific volume is found by dividing the specific gravity into 1.

The specific gravity is found by dividing the specific volume into 1.

STANDARD WEIGHTS OF VARIOUS COUNTRIES.

Germany :—1 tonne—20 centner.
1 centner = 50 kilograms.
1 kilogram = 1,000 grms.
1 gr. = 1,000 mgrs.

England :—

(*a*) Troy weight—
1 pound (lb.) = 12 ounces (·3) (= 0·373242 kgm.).
1 ounce = 20 pennyweights (dwts.).
1 pennyweight = 24 grains (grs.).

(*b*) Avoirdupois weight—
1 ton = 20 hundredweight (cwt.).
1 cwt. = 4 quarters (qrs.).
1 quarter = 2 stones.
1 stone = 14 pounds (lb.).
1 lb. = 16 ounces (oz.).
1 oz. = 16 drachms.
1 drachm = 3 scruples = 10 grains.

N.B.—1 lb. avoirdupois = 7,000 grains.
Troy = 0·453592 kg.

France :—

Weights equal to those given for Germany.

Japan :—

1 kwan= 3·75 kilogram.
1 kilogram = 0·267 kwan.
1 kwan = 1,000 momme = 10 fun.
1 fun = 10 rim.
1 rim = 10 mo.
Also 1 kwan = 6·25 kin.
1 kin = 160 me.

North America :—

English avoirdupois weights in use.

GOLD CARATS OF DIFFERENT COINS.

	Carat	1,000 fine
(1) Austria (*a*) Dukaten...	22	·9184
(*b*) crowns ...	21	·875
(2) Holland	23	·9584
(3) Gold dollars, U.S.A....	21	·875
(4) England	22	·9167
(5) Russia	22	·9167
(6) Germany	21·6	·900

LITERATURE.

All references to literature are confined to the more important works, and are registered alphabetically according to the subjects.

The literature of amalgams is registered in a double way, once alphabetically according to the authors' names, and secondly alphabetically according to the names of metals which are alloyed with mercury. Thus repetition of references is avoided, as most works treat a number of different amalgams.

The abbreviations signify :—

Roman capitals—I., II. = series, &c.
Arabic figures before the parentheses—1 ( ) = volume.
Arabic figures in parentheses (1910) = year.
Arabic figures after parentheses—( ) 1 = page.
Berzel. = *Jahresberichte von Berzelius.*
JB. = *Jahresberichte für Fortschritte der Chemie von Liebig u. Kopp bezw. Fittica.*
CB. = *Chemisches Centralblatt.*
Beibl. = *Beiblatter zu Wiedemanns Annalen.*
C. r. = *Comptes rendus de l'Académie française.*
Z. = *Zeitschrift.*
Ztg. = *Zeitung.*
Ann. = *Annalen.*
Bull. = *Bulletin.*
Arch. = *Archiv.*
Trans. = *Transactions.*
Proc. = *Proceedings.*
Mem. = *Memoires.*
Rend. = *Rendiconti.*
Drudes Ann. = Continuation of *Wiedemanns Annalen.*

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Roberts Austen. *Phil. Transact.*, 187 A (1896); JB. (1896), p. 23.

Roberts Austen and Kirke Rose. *Proc. Roy. Soc. Lond.*, 71 (1903), p. 161; CB. I (1903), p. 278.

Roberts Austen and Kirke Rose. *Chem. News*, I (1903), p. 154.

(3) **Silver—Bismuth** = AgBi.

Alexejeff. Beibl., 10, 387.

Heycock and Neville. *Chem. News*, 62, p. 280; CB. I (1891), p. 129.

Idem. *Journ. Chem. Soc.*, 61 (1892), p. 888; CB. II (1892), p. 1061.

Idem. "Ternäre Vbdgn.," *Journ. Chem. Soc.*, 65 (1894), p. 65; CB. I (1894), p. 410.

Le Chatelier. "Contrib. à l'étude des alliages' (1901), p. 441; Beibl., 19, p. 754.

MARX. "Über ein merkwürdiges Verhalten des Wismuts beim Erstarren," *Schweigg. Journ.*, 58 (1830), p. 454; Berzel. (1832), p. 134.

PETRENKO. *Z. an. Ch.* (1906), p. 136.

(4) **Silver—Cadmium** = AgCd.

GAUTIER. *Bull. Soc. d'Encour.* (1905), pp. 1, 1315 (1896), "Contrib. à l'étude des alliages" (1901), p. 93.

KIRKE ROSE. *Proc. Roy. Soc.*, 74 (1905), p. 218.

(5) **Silver—Copper** = AgCu.

FRIEDRICH UND LEROUX. "Metallurgie," 4 (1907), p. 297.

HEYCOCK and NEVILLE. *Phil. Trans.*, 189 A (1897); CB. I (1897), p. 786.

LEPKOWSKI. *Z. an. Ch.*, 59 (1908), p. 285.

(6) **Silver—Mercury** = AgHg, *vide* "Amalgams" VIII.

(7) **Silver—Magnesium** = AgMg.

PARKINSON. *Journ. Chem. Soc.*, 20 (1867), p. 117; *Journ. Pract. Ch.*, 101 JB.; (1867), pp. 196, 375.

ZEMCZUZNY. *Z. an. Chem.*, 49 (1906), p. 400.

(8) **Silver—Nickel** = AgNi.

PETRENKO. *Z. an. Ch.*, 53 (1907), p. 212.

(9) **Silver—Lead** = AgPb.

FRIEDRICH. "Metallurgie," 3 (1906), p. 396.

HEYCOCK and NEVILLE. *Phil. Trans.*, 189 A (1897), p. 3; CB. I (1897), p. 786.

PETRENKO. *Z. an. Ch.*, 53 (1907), p. 200.

(10) **Silver—Palladium** = AgPd.

RUER. *Z. an. Ch.*, 51 (1906), p. 315.

(11) **Silver—Platinum** = AgPt.

DOERINCKEL. *Z. an. Ch.*, 54 (1907), p. 338.

MILLER. *Journ. an. Chem. Soc.*, 28 (1906), p. 1115.

(12) **Silver—Antimony** = AgSb.

GAUTIER. *Bull. Soc. d'Encour.* (1896), pp. 1309, 1310.

HEYCOCK and NEVILLE. *Phil. Trans.*, 189 A (1897), p. 25.

PETRENKO. *Z. an. Ch.*, 50 (1906), p. 139

(13) **Silver—Tin** = AgSn.

FENCHEL. "Volumen," *Dental Cosmos*, January, 1910.

PETRENKO. *Z. an. Ch.*, 51 (1909), p. 200.

(14) **Silver—Zinc** = AgZn.

GAUTIER. *Bull. Soc. d'Encour.* (1896), p. 1315; CB. II (1896), p. 533.

HEYCOCK and NEVILLE. *Journ. Chem. Soc.*, 71 (1897), p. 40; *Z. an. Chem.*, 48 (1906), p. 347.

II. ALUMINIUM = Al.

(1) **Aluminium—Gold** = AlAu.

HEYCOCK and NEVILLE. *Phil. Trans.*, 194 A (1900), p. 201.

(2) **Aluminium—Bismuth** = AlBi.

GWYER. *Z. an. Ch.*, 49 (1906), p. 316.

HEYCOCK and NEVILLE. *Journ. Chem. Soc.*, 61 (1892), p. 888.

PECHEUX. *Compt. rend.* (1902), 138 (1904), p. 1501.

(3) **Aluminium—Cadmium** = AlCd.

GWYER, *Z. an. Ch.*, 57 (1908), p. 150.

WRIGHT. *Journ. Chem. Soc.*, 61 (1892), p. 888.

(4) **Aluminium—Copper** = AlCu.

CAMPBELL. *Journ. an. Chem. Soc.*, 24 (1902), p. 253; 26 (1904), p. 1290.

CARPENTER and EDWARDS. *Proc. Inst. Mech. Engin.*, 1—2 (1907), p. 57.

CURRY. *Journ. Phys. Chem.*, 11 (1907), p. 425.

GUILLET. *Rev. de Métallurgie* (1905), p. 568; C. r. 141 (1905), p. 464.

GWYER. *Z. an. Ch.*, 57 (1908), p. 114.

LE CHATELIER. "Contr. à l'étude des alliages" (1901), p. 421.

(5) **Aluminium—Magnesium** = AlMg.

BOUDOUARD. C. r. 132, p. 1325; 133, p. 1003.

GOERENS. "Metallographie," p. 79.

GRUBE. *Z. an. Ch.*, 45 (1905), p. 225.

(6) **Aluminium—Mercury** = AlHg, *vide* "Amalgams" VIII. and XII.

(7) **Aluminium—Nickel** = AlNi.

BRUNCK. *Ber. Deutsch. chem. Ges.* (1902), 34 (1901), p. 2733.

GUILLET. *Génie civil*, 41 (1902), pp. 170, 394.

GWYER. *Z. an. Ch.*, 57 (1908).

(8) **Aluminium—Lead** = AlPb.

GWYER. *Z. an. Ch.*, 57 (1908), p. 147.

HYCOCK and NEVILLE. *Journ. Chem. Soc.*, 61 (1892), p. 88.

PÉCHEUX. C. r. (1902) 138 (1904), p. 1042.

WRIGHT. *Journ. Soc., Chem. Ind.*, 11 (1892), p. 442; 13 (1894), p. 1014.

(9) **Aluminium—Antimony** = AlSb.

CAMPBELL and MATTHEWS. *Journ. Am. Soc.*, 24 (1902), p. 259.

Gautier. "Contr. à l'étude des alliages" (1901), p. 112.
Roche. *Monit. scient.* (1904), 7 (1893), p. 269.
Tammann. *Z. an. Ch.*, 48 (1905), p. 53.
Wright. *Journ Soc. Chem. Ind.* (1892), p 493.

(10) **Aluminium—Tin** = $AlSn$.

Campbell and Matthews. *Journ. Am. Chem. Soc.*, 24 (1902), p. 253.
Gautier. *Bull. Soc. d'Encour.* (1905), 1 (1896), p. 1293.
Gwyer. *Z. an. Ch.*, 49 (1906), p. 311.
Heycock and Neville. *Journ. Chem. Soc.*, 57 (1890), p. 376.
Shepherd. *Journ. Phys. Chem.*, 8 (1904), p. 233.

(11) **Aluminium—Zinc** = $AlZn$.

Charpy. *Bull. Soc. d Encour.* (1897). "Contr. à l'étude des alls.," p. 13.
Heycock and Neville. *Journ. Chem. Soc.*, 71 (1897), p. 383.
Shepherd. *Journ. Phys. Chem.*, 9 (1905), p. 504. "Métallurgie" (1905), p. 86.

III. GOLD = Au.

(1) **Gold—Bismuth** = $AuBi$.

Heycock and Neville. *Journ. Chem. Soc.*, 61 (1892), p. 888.
MacIvor. *Chem. News*, 55 (1887), 191.
Maey. *Z. phys. Ch.*, 38 (1901), p. 297.
Mathiesen. *Pogg. Ann.*, 110 (1860), pp. 30—35.
Osmond and Roberts Austen. *Phil. Trans.*, 179 (1884), p. 339.
Rössler. *Z. an. Chem.*, 9 (1895).
Vogel. "Inaug. Diss.," Göttingen (1906), p. 60

(2) **Gold—Cadmium** = $AuCd$.

Heycock and Neville. *Journ. Chem. Soc.*, 61 (1892), p. 888 (Au_3 Au Cd.)
Idem. *Journ. Chem. Soc.*, 61 (1892), p. 914.
Mylius u. Fromm. *Ber. d. deutsch. chem. Ges.*, Berlin, XXVII, 1 (94), p. 636.
Vogel. "Inaug. Diss.," Göttingen (1906), p. 47

(3) **Gold—Copper** = $AuCu$.

Kirke Rose. *Proc. Roy. Soc.*, 23, pp. 349, 481.
Kurnakow and Zemczuzny. *Z. an. Chem.* 54 (1907), p. 159
Mathiesen. *Pogg. Ann.*, 110 (1860), p. 190 (*Elektr. Conductivity*).

(4) **Gold—Mercury** = AuHg, *vide* "Amalgams," VIII. and XII.

(5) **Gold—Nickel** = AuNi.
LEVIN. *Z. an. Chem.*, 45 (1905), p. 238.

(6) **Gold—Lead** = AuPb.
VOGEL. "Inaug. Diss.," Göttingen (1906), p. 6.

(7) **Gold—Palladium** = AuPd.
RUER. *Z. an. Chem.*, 51 (1906), p. 391.

(8) **Gold—Platinum** = AuPt.
DOERINCKEL. *Z. an. Chem.*, 54 (1907), p. 345.

(9) **Gold—Antimony** = AuSb.
ROBERTS AUSTEN. *Phil. Trans.*, 179 (1888), p. 339.
RÖSSLER. *Z. an. Chem.*, 9 (1895), p. 70.
VOGEL. "Inaug. Diss.," Göttingen (1906), p. 65.

(10) **Gold—Tin** = AuSn.
LAURIE. *Phil. Mag.* (1905), 33 (1892), p. 94.
MATHIESEN. *Pogg. Ann.*, 110 (1860), 190, pp. 30-35.
VOGEL. "Inaug. Diss.," Göttingen (1906), p. 20.

(11) **Gold—Zinc** = AuZn.
HEYCOCK and NEVILLE. *Journ. Chem. Soc.*, 71 (1897), p. 419.
VOGEL. "Inaug. Diss.," Göttingen (1906), p. 34.

IV. BISMUTH = Bi.

(1) **Bismuth—Cadmium** = BiCd.
DREWITZ. "Diss.," Rostock (1902), mit Pb und Sn.
v. HAUER. Jahresber. (1865), 236, mit Pb und Sn.
HEYCOCK and NEVILLE. *Journ. Chem. Soc.*, 61 (1892), p. 892.
KAPP. "Diss." Königsberg (1901).
MAEY. *Z. phys. Chem.*, 38 (1901), p. 295.
MATHIESEN. *Pogg. Ann.*, 110 (1860), p. 32.

(2) **Bismuth—Copper** = BiCu.
GAUTIER. "Contrib. à l'ét. des all." (1901), p. 110.
HIORNS. *Journ. Chem. Soc. Ind.*, 25 (1906), p. 616.
JERIOMIN. *Z. an. Ch.*, 55 (1907), p. 412.
ROLAND GOSSELIN. *Bull. Soc. d'Encour.* (1905), 1 (1896), p. 1310.

(3) **Bismuth—Mercury** = BiHg, *vide* "Amalgams," VIII. and XII.

(4) **Bismuth—Magnesium** = BiMg.
GRUBE. *Z. an. Chem.*, 49 (1906), p. 83.
MASING. "Diss.," Göttingen (1909).

(5) **Bismuth—Nickel** = BiNi.
RÖSSLER. *Z. an. Chem.*, 9 (1895), p. 31.
VOSS. *Z. an. Ch.*, 57 (1908), p. 52.

(6) **Bismuth—Lead** = BiPb.

Charpy. "Contrib. à l'ét. des. all." (1901), p. 203 (BiPbSn).

Kapp. "Diss.," Königsberg (1901).

Sahmen und v. Vegesack. *Z. phys. Chem.*, 59 (1907), p. 257.

Stoffel. *Z. an. Chem.*, 53 (1907), p. 57 (BiSnPb).

(7) **Bismuth—Palladium** = BiPd.

Heycock and Neville. *Journ. Chem. Soc.*, 61 (1892), p. 892.

Idem in Landolt und Börnstein. *Chem. Phys. Tabellen*, 7, S. 111 (1904).

(8) **Bismuth—Platinum** = Bi—Pt.

Heycock and Neville. *Journ. Chem. Soc.*, 61 (1890), p. 892.

Idem in Landolt und Börnstein. *Chem. Phys. Tabellen*, 7, S. 111 (1904).

(9) **Bismuth—Antimony** = BiSb.

Charpy. "Contrib. à l'ét. des all." (1901), p. 20 ff.

Gautier. *Ibid.* (1901), p. 114.

Heycock and Neville. *Journ. Chem. Soc.*, 61 (1892). p. 896.

Hüttner und Tammann. *Z. an. Chem.*, 44 (1905), p. 131.

(10) **Bismuth—Tin** = BiSn.

Campbell. *Journ. Frankl. Inst.*, 154, 1 (1902), pp. 131, 201.

Charpy. *Bull. Soc. d'Encour.*, 2 (1905) (1897), p. 384.

Kapp. "Diss.," Königsberg (1901).

Le Chatelier. "Contrib. à l'ét. des all."

Lepkowski. *Z. an. Chem.*, 59 (1908), p. 286.

Maey. *Z. phys. Chem.*, 38 (1901), p. 292.

Shepherd. *Journ. phys. Chem.*, 38 (1901), p. 292.

(11) **Antimony—Zinc** = SbZn.

Heycock and Neville. *Journ. Chem. Soc.*, 71 (1897), p. 394.

Mönckemeyer. *Z. an. Chem.*, 43 (1905), p. 182.

Roland-Gosselin in Gautier. "Contrib. à l'ét. des all." (1901), p. 101.

V. **CADMIUM** = Cd.

(1) **Cadmium—Copper** = CdCu.

Mylius and Fromm. *Ber. d. chem. Ges.*, 27 I (1894), p. 630.

Sahmen. *Z. an. Chem.*, 49 (1906), p. 301.

(2) **Cadmium—Mercury** = CdHg, *vide* "Amalgams," VIII. and XII.

(3) **Cadmium—Nickel** = CdNi.

Voss. *Z. an. Chem.*, 57 (1908), p. 69.

(4) **Cadmium—Lead** = CdPb.
Holzmann. *Pogg. Ann.*, 110 (1860), p. 33.
Kapp. "Diss.," Königsberg (1901).
Maey. *Z. phys. Chem.*, 38 (1901), p. 295.

(5) **Cadmium—Antimony** = CdSd.
Alder Wright. *Journ. Chem. Soc. Ind.*, 13 (1894), pp. 1014—1020.
Heycock and Neville. *Proc. Chem. Soc.*, 6 (1890), p. 158.
Kurnakow and Konstantinow. *Russ. phys. chem. Ges.*, 37 (1905), p. 580.
Treitschke. *Z. an. Chem.*, 50 (1906), p. 217.

(6) **Cadmium—Tin** = CdSn.
Heycock and Neville. *Journ. Chem. Soc.*, 57 (1890), p. 376.
Kapp. "Diss.," Königsberg (1901).
Maey. *Z. phys. Chem.*, 38 (1001), p. 295.
Matthiessen. *Pogg. Ann.*, 110 (1860), p. 28.

(7) **Cadmium—Zinc** = CdZn.
Heycock and Neville. *Journ. Chem. Soc.*, 71 (1897), p. 383.

VI. **COPPER** = Cu.

(1) **Copper—Mercury** = CuHg. *vide* "Amalgams," VIII. and XII.

(2) **Copper—Magnesium** = CuMg.
Sahmen. *Z. an. Chem.*, 57 (1908), p. 218 ($\mathrm{Cu_2Mg}$, CuMg).

(3) **Copper—Manganese** = CuMn.
Lewis. *Journ. Soc. Chem. Ind.*, 21 (1902), p. 842.
Sahmen. *Z. an. Chem.*, 57 (1908), p. 20.
Wologdine. *Rev. de Metallurgie*, 4, I (1907), p. 25.
Zemczuzny, Urasow, Rykowskow. *Z. an. Chem.*, 57 (1908), p. 253.

(4) **Copper—Nickel** = CuNi.
Gautier. C. r. 123 (1896), p. 172.
Gürtler and Tammann. *Z. an. Chem.*, 52 (1907), p. 25.
Heycock and Neville. *Phil. Trans.*, 189 A (1897), p. 25.
Kurnakow und Zemczuzny. *Z. an. Chem.*, 54 (1907), p. 151.
Tafel. *Metallurgie*, 5 (1908), p. 348.

(5) **Copper—Palladium** = CuPd.
Ruer. *Z. an. Chem.*, 51 (1906), p. 223.

Copper—Lead = CuPb.
Doerinckel. *Z. an. Chem.* (1907), p. 335.

(7) **Copper—Antimony** = CuSb.
BAYKOW. *Bull. Soc. d'Encour.*, I (1903), p. 626.
HIORNS. *Journ. Soc. Chem. Ind.*, 25 (1906), p. 616.

(8) **Copper—Tin** (Bronzes) = CuSn.
GIOLITTI and TAVANTI. *Gazz. chim. ital.*, 38, II (1908), p. 209.
HEYCOCK and NEVILLE. *Phil. Trans.*, 189 A (1897), p. 42; 202 A (1904).
ROBERTS AUSTEN. "Fourth rep. to the alloy res. committee," *Proc. Inst. Mech. Eng.* (1897), p. 67.
SHEPHERD and BLOUGH. *Journ. Phys. Chem.*, 10 (1906), p. 630.

(9) **Copper—Zinc**=CuZn.
BAKER. *Z. phys. Chem.*, 38 (1901), p. 630.
ROBERTS AUSTEN. *Proc. Inst. Mech. Eng.* (1897), p. 31.
SACKUR. *Ber. d. D. chem. Ges.*, 38 (1905), p. 2186.
SHEPHERD. *Journ. Phys. Chem.*, 8 (1904), p. 421.
TAFEL. *Metallurgie*, 5 (1908), p. 349

VII. **NICKEL** = Ni.

(1) **Nickel—Magnesium** = NiMg.
COEHN. *Z. an. Ch.*, 41 (1904), p. 299.
VOSS. *Z. an. Ch.*, 57 (1908).

(2) **Nickel—Manganese** = NiMn.
RUER. *Metallurgie* (1907), p. 173. (Zemczuzny und Durdin.)

(3) **Nickel—Lead** = NiPb.
VOSS. *Z. an. Ch.*, 57 (1908), p. 45.

(4) **Nickel—Tin** = NiSn.
CHARPY. *Bull. Soc. d'Encour.*, 5, 2 (1897), p. 384.
GAUTIER. *Bull. Soc. d'Encour.*, 5, 1 (1896), p. 1293.
HEYCOCK and NEVILLE. *Journ. Chem. Soc.*, 57 (1890), p. 376.
VOSS. *Z. an. Ch.*, 57 (1908), p. 35.

(5) **Nickel—Zinc** = NiZn.
HEYCOCK and NEVILLE. *Journ. Chem. Soc.*, 71 (1897), p. 383.
TAFEL. *Metallurgie*, 4 (1907), p. 781.
VOSS. *Z. an. Ch.*, 57 (1908), p. 67.

(6) **Nickel—Antimony** = NiSb.
LOSSOW. *Z. an. Ch.*, 49 (1906), p. 58.

VIII. **MERCURY** = Hg., Amalgam.
(1) BACHMETJEFF. *Journ. Russ. Phys. Chem. Ges.*, 25; JB. (1893), p. 108.
(2) *Idem. Russ. Phys. Chem. Ges.*, 26 (1894); *Phys. Abb.*, 2.

(3) *Idem.* und Wsharow. JB. (1893), p. 108.

(4) *Idem.* JB. (1893), p. 108.

(5) Baykow. *Journ. Russ. Phys. Ges.*, I, 32 (1900), p. 630.

(6) Bill. *Z. phys. Ch.*, 41 (1902), p. 641.

(7) Black. *Dental Cosmos* (1895-1896).

(8) Calvert and Johnson. *Phil. Mag.*, IV, 18 (1859), p. 354.

(9) Cattaneo. *Rend. R. Accad. Lincei. Roma*, IV, 7 I, p. 88.

(10) Chester. *Sill. Amer. Journ. of Science*, III, 16 (1878), p. 29; JB. (1878), p. 308 (AuHg).

(11) Cossa. *Z. f. Chemie*, II, 6 (1870), p. 380.

(12) Crookewitt. *Journ. prac. Ch.*, 45 (1887); JB. (1847-1848), p. 393.

(13) Fenchel. *Dental Cosmos* (1909-1910); *Östr. Ung. V. J. f. Z.*, 4 papers (1909-1910).

(14) Gore. *Phil. Mag.*, V, 30 (1890), p. 228; JB. (1890), p. 627.

(15) Gouy. *Journ. de phys.*, III, 4 (1895), p. 320. Beibl., 19, p. 754.

(16) Henry. *Phil. Mag.*, IV, 9 (1855), p. 458.

(17) Heteren. *Z. phys. Chem.*, 42 (1909), p. 129.

(18) Horsford. *Sill. Amer. Journ. of Science*, II, 13 (1852), p. 305.

(19) Humphreys. *Journ. Chem. Soc.*, 69 (1896), p. 243.

(20) Joule. *L'Institut*, I, 18 (1850), p. 327; JB. (1850), p. 333.

(21) Kasanzeff. *Bull. Soc. Chem.*, II, 30 (1878), p. 20; *Ber.* 11 (1878), p. 1255; JB. (1878), p. 308 (AuHg).

(22) Kerp, Böttger, Winter und Iggena. *Z. an. Ch.*, 25 (1900), p. 1; CB. II. (1900), p. 710.

(23) Knaffl. *Dingl. Polyt. Journ.*, 168 (1863), p. 282; JB. (1863), p. 288 (AuHg).

(24) Konowaloff. *Russ. Z. f. Phar.*, 35 (1896), p. 328; *Russ. Cb.*, II. (1896), p. 338 (AlHg).

Maey. *Z. phys. Ch.*, 29 (1899), p. 119; CB. II (1899), p. 6.

Maey. *Z. phys. Ch.*, 38 (1901), p. 289; CB. II (1901), p. 841.

(25) Maey. *Z. phys. Ch.*, 38 (1901), p. 292; CB. (1901), p. 841.

(26) Merz und Veith. *Ber.*, 14 (1881), p. 1438; JB. (1881), p. 29.

(27) Meyer. *Wied. Ann.* 40 (1890), p. 244; JB. (1890), p. 328.

(28) Michaelis. "Diss.," Berlin (1883); JB. 9 (1885), p. 257. Beibl. 27.

(29) Ogg. *Z. phys. Ch.*, 22 (1897), p. 536; JB. (1897), p. 327.

Ogg. "Diss.," Göttingen (1898); *Z. phys. Ch.*, 27 (1898), p. 285; CB. II, p. 1077 (AgHg).

(30) Puschin. *Z. anorg. Chem.*, 36 (1903), p. 201.

(31) Ramsay. *Journ. Chem. Soc.*, 55 (1889), p. 521.; JB. (1889), p. 140.

(32) Reinders. *Z. phys. Chem.*, 54 (1906), p. 609.

(33) Schumann. "Diss.," Erlangen (1891); *Wied. Ann.*, 43 (1891), p. 11.

(34) de Souza. Ber. 9 (1876), p. 1050; JB., p. 281.

(35) Tarugi. *Gazz. Chim. Ital.*, I, 26 (1896), p. 425.

(36) Tissier. C. r. 49 (1859), p. 54; JB., p. 143 (AlHg).

(37) Wanklyn and Chapman. *Journ. Chem. Soc.*, 19 (1866), p. 141.

(38) Wislicenus und Kaufmann. Ber. 28 (1895), p. 1323; CB. II., p. 151 (AlHg).

(39) Wood. *Chem. News*, 6 (1862), p. 135.

(40) Wünsche. "Diss.," Rostock (1902). *Drudes Ann.*, 7 (1902), p. 116 (HgNi).

IX. **LEAD** = Pb.

(1) **Lead—Antimony** = PbSb.

Charpy. "Contr. à l'ét. des all." (1901), p. 131. Paris: Chamerot et Renouard,

Roland-Gosselin. *Ibid.*, 93 (1901), p. 107.

(2) **Lead—Tin** = PbSn.

Charpy. "Contr., à l'ét. des all." (1901), p. 121

Charpy. *Ibid.*, 203 SbSnPb et SbCuSn.

Guthrie. *Phil. Magaz.*, XVII (1884), p. 462.

Roberts Austen. *Engineering*, 63 (1897).

X. **ANTIMONY** = Sb.

(1) **Antimony—Tin** = SbSn.

Charpy. "Contr. à l'ét. des all.," p. 121.

Reinders. *Z. an. Ch.*, 25 (1900), p. 113.

(2) **Antimony—Zinc** = SbZn.

Monckemeyer. *Z. an. Ch.*, 43 (1905), p. 182.

Roland-Gosselin et Gautier. "Contr. à l'ét. des all." (1901), p. 101.

XI. **Tin** = Sn.

Tin—Zinc = SnZn.

Heycock and Neville. *Journ. Chem. Soc.* (1897), p. 383.

Idem. *Ibid.*, 65 (1894), p. 31.

LITERATURE OF AMALGAMS.[1]

1. General.
   1, 2, 3, 4, 7, 13, 19, 27, 31.
2. HgAg.
   12, 13, 20, 25, 26, 29, 32.
3. HgAl.
   5-11, 24-35, 37.
4. HgAu.
   10, 12, 16, 21, 23, 26, 34.
5. HgBi.
   8, 12, 15, 26, 30.
6. HgCd.
   6, 12, 14, 15, 22, 26, 30, 38.
7. HgCu.
   20, 26, 28, 30, 34.
8. HgMg.
   33, 37.
9. HgMn.
   33.
10. HgNi.
    33, 40.
11. HgPt.
    20, 33, 35.
12. HgSn.
    8, 9, 13, 17, 18, 20, 26, 30.
13. HgZn.
    8, 9, 12, 15, 26, 30, 33.

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[1] The figures refer to Part VIII. (Mercury), 1 to 40.

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