THESIS

ON THE SOLUBILITY OF SILVER IN MERCURY

for the Degree of
Doctor of Philosophy
in the
UNIVERSITY OF EDINBURGH

by

DOUGLAS RENNIE HUDSON, B.Sc. (Wales and Lond.)
Second Lieutenant, The Royal Scots - The Royal Regiment.

INDEX.

DISCUSSION.

POSSIBLE REASONS FOR THE DISCREPANCY BETWEEN OBSERVED AND CALCULATED SOLUBILITY.

THE CONSTITUTION OF SILVER AMALGAMS.

DENSITIES OF THE SILVER AMALGAMS.

THE INTERMETALLIC COMPOUNDS.

FIGURES.

HISTORICAL.

MERCURY.

If the evidence is admissible, the presence of a small pot of mercury in a burial chamber at Kurna shows that the metal was known as early as the fifteenth century B.C. Since small drops frequently occur in the outcrop or gossan of virgin cinnabar deposits this does not pre-suppose any extensive development of process work and in view of the high standard of craftsmanship in gold and silver then existing it is not altogether surprising. In the fourth century B.C. Aristotle (Meteorology and De anima) reported the use of quicksilver in religious ceremonial, it being then obtained by grinding the ore in vinegar with a copper pestle and mortar; as early as four centuries before this it was an object of commerce among Phoenician and Carthaginian traders. Later, under the Roman Empire, Italian deposits were exploited intensively, and the technique of extraction developed apace. By this time the relatively advanced metallurgical operation of distilling the metal from an iron retort containing a mixture of cinnabar and charcoal into a sealed-on condenser, was in use; this does not differ in principle from the modern process of extraction. Owing to the apparent impossibility of/

of solidifying it, and its great mobility, mercury was regarded as the symbol of liquidity with the sign of the planet Mercury, and dedicated to Hermes the Messenger-God. It received the name ὑδράργυρος or *Argentum vivum*. The Alexandrian alchemists took particular interest in mercury as the mother of all metals. Bishop Albert (*Compositum de compositis*), Thomas Aquinas (*Secretae alchemicae*) and Geber (*Summa perfectiones magisterii*) all investigated the properties of the element and as a result great progress was made in knowledge of its compounds and amalgams. The iatrochemists held salt, sulphur, and mercury to be the three "principles" of which all matter was constituted, and Paracelsus in Switzerland achieved a great reputation by his successful treatment of disease with mercurial medicines.

If one excepts the very rare gallium, which melts at 29°C. but readily undergoes surfusion, mercury is the only metal liquid at room temperature. Its rate of oxidation in air is very slow under ordinary conditions, and not rapid even at its boiling point. (Fouling will however occur eventually even at ordinary temperature, as may be seen on mercury stored in stoneware jars for many years in fume-free cupboards, in clock pendulums, and in the leather vessels of Fortin barometers.) These facts greatly stimulated investigation into the physical properties of/

of alloys containing mercury in the period of rapid progress in science towards the end of the nineteenth century, when high-temperature technique was not so familiar to physicists as it is today. With continued use of quicksilver as a measuring liquid and the enormously increased range of scientific instruments consequent on the industrial revolution, knowledge of its exact physical constants became a matter of some importance. Mercury is easy to purify by distillation, and, as Andrade has pointed out, is the metal most easily obtained in very high purity. As a result of these considerations the most diverse physical properties of mercury have been very carefully investigated, and are known more exactly and in greater detail than those of any other element.

SILVER.

Together with gold, silver was known in Ancient Egypt, and may be traced back to the Menes period about 3400 B.C. Contemporaneous gold and silver coinages, as well as personal ornaments, and burial and temple embellishments were certainly well established in the near-East Cultures for many centuries before the Christian era. Further, in North and South America the Aztec and Inca nations reached a high indigenous standard in the working

of/

of both gold and silver at a very early period. It seems inevitable that, in the early stages at least, the extraction was confined to native "placer" metals. The recovery of silver and gold also developed in India, China and Japan.

SILVER AMALGAM.

The word "Amalgam" may be derived either from μαλάγμα or the Arabic prefix Al with μῖγμα It has been suggested that both tin- and copper-amalgams were called asem by the ancient Egyptians, and even before the Christian era the use of silver and gold amalgam for plating brass and bronze was well understood in Greece and the Roman Empire.

The property of licking up gold and silver particles which quicksilver possesses, has long been utilized in extraction of these metals. Pliny (Historia naturalis) refers to the amalgamation of gold, and very large quantities of silver were recovered from sulphide ore by a combined reduction and amalgamation process using magistral (roasted and weathered pyrites) and mercury in the patio or courtyard process developed by the lost Aztec civilization in Mexico. The method of parting by wringing the liquid in a canvas or wash-leather bag "whereby the mercury exudes like a kind of sweat" (Pliny) leaving the

pasty/

pasty amalgam from which further mercury can be distilled and condensed for re-use, persisted unchanged into the present century. An enormous quantity of gold has been extracted from the Rand in this way, but the amalgamation table is now obsolete, having been replaced by the corduroy frame in South Africa and the canvas floor in U.S.A.

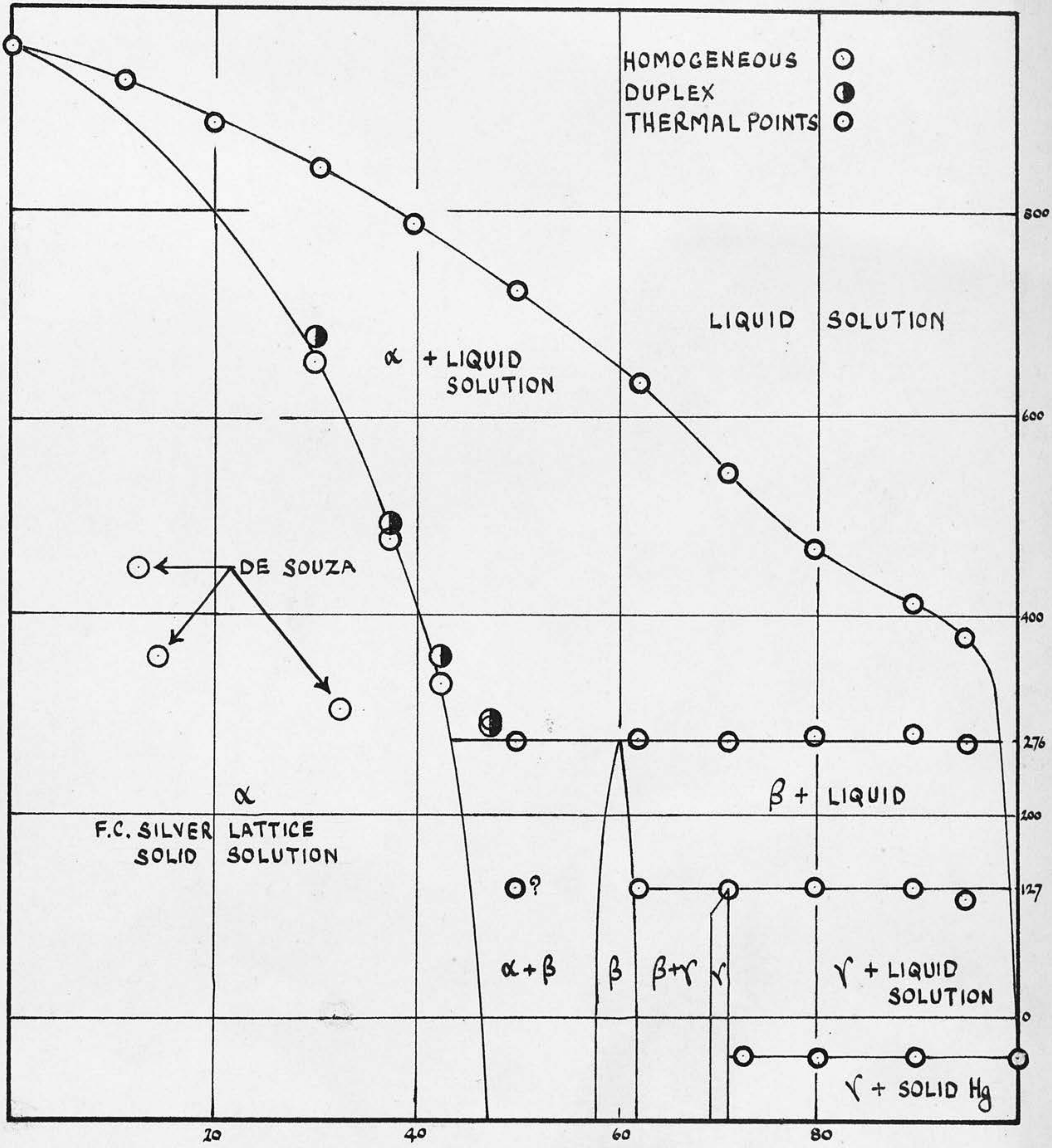
Strangely enough, in addition to its constituent elements, silver amalgam itself - possibly hydatogenetic - occurs native; it has even been discovered in rock formations remote from cinnabar deposits. Table VI gives a number of typical analyses. The names argental, amalgam, arquerite, bordosite (from Arqueros and Bordos in Chile), and kongsbergite have been given to it and at one time it was a favourite pastime of naturalists to assign definite chemical formulae to the specimens isolated. When one considers the silver-mercury equilibrium diagram it is not surprising that a whole gamut of compounds was necessary.

When mercury is immersed in silver nitrate solution simple displacement occurs and the resulting amalgam deposits long acicular or prismatic crystals on standing. This product of the reaction between silver and lunar caustic was quite familiar to the early chemists under the name of silver tree (arbor Dianae), and its distinctive form tempted them to identify/

identify it with a definite intermetallic compound. The composition however is variable, like that of native amalgams, and widely different silver contents have been reported.

One interesting point arises. In many cases of displacement reactions, e.g. silver-copper, standard potentials differ so much that the ratio of concentrations of the ion species in the final stage is so great as to be measurable only with difficulty. With silver and mercury this is not the case, the standard electrode potential at 25°C. being 0.799 V for $Hg:Hg_2^{\cdot\cdot}$ * and 0.798 V for $Ag:Ag^{\cdot}$. It is found in practice that the equilibrium can actually be attained from the side either of the mercuric or of the silver ion, in accordance with theoretical expectations for metals with such close electrode potentials.

* BUTLER The Fundamentals of Chemical Thermodynamics, London 1935, Vol. I.



PERCENTAGE OF MERCURY

FIG. 1

THEORETICAL CONSIDERATIONS.

Two methods of solubility determination are possible (a) by analysis, (b) directly. In the first, (a) a sample of saturated solution is removed at the working temperature, cooled and analysed. Theoretically this method is perfect, but in practice it has some disadvantages. In high temperature work sampling must be mechanical to be efficient. This is complicated, and if inversion of a fashioned or constricted tube is used, care must be taken to avoid hammer, which is serious with a metal as dense as mercury, despite increasing toughness of the refractory at higher temperatures. Further, unless the sample is sealed off at once there is risk that its composition may alter by distillation if any temperature gradient exists, and sealing may itself cause this through local heating. From observations made during this investigation, distillation is not marked below 200°C.

(b) In the direct method the metals are maintained in contact at the working temperature and solubility is calculated from weighings made after cooling. This method is not so well based theoretically. By a well-known principle of physical chemistry, when two components are in contact, the fields existing when equilibrium is attained are those which the isotherm cuts/

cuts on the binary equilibrium diagram. In this concept the depth of the layers (provided it exceeds a few million molecules) is unimportant, being governed by the rates of reaction and diffusion - whichever is the slower. With silver and mercury, diffusion is very rapid in the liquid phase and slow in the solid phase, so that saturation of the mercury will occur long before any large amount of mercury has diffused into the silver. Observation confirmed this deduction. It is therefore possible to obtain a system in which a core of silver into which substantially no diffusion has occurred, co-exists with a saturated solution of silver in mercury.

According to the equilibrium diagram (Fig. 1) the liquid solution above 276°C. is in equilibrium directly with a silver close-packed cubic lattice containing up to 45% mercury by weight in substituent positions. With falling temperature this value is little affected but liquid solubility falls sharply. The deposit resulting is identical with the silver-rich α coating down to 276°C. when a peritectic reaction occurs between it and the liquor to give the β phase (Ag_5Hg_4 lattice). Subsequent impoverishment of the liquor occurs by deposition of β , until at 127°C. a further peritectic reaction between it and the liquor gives the γ phase (Ag_5Hg_8 lattice). For cooling slow enough to allow equilibrium therefore, the/

the cross section would consist of

Ag-rich $\alpha | \alpha + \beta | \beta | \beta + \gamma | \gamma | \gamma +$ Hg-rich liquid

In view of the existence of two peritectics of low melting points and complex constitution, the chances in favour of metastability are high. Murphy points out "It appears therefore that the reaction between β and liquid, as well as that between α and liquid, is completely suppressed with the rates of cooling employed in cooling curve observations." From his data one may deduce roughly that formation of γ at 100°C. is about one tenth complete in 3 hours and about nine tenths complete in 3 days.

The following possible errors are therefore inherent in the direct method -

1. That some peritectic β or γ may remain adherent to the unchanged core.
2. That some α formed by diffusion may be removed during separation of the components.

   These would give too low and too high values respectively for solubility.
3. That diffusion of mercury within the solid silver might be rapid enough to form a deep layer of α, thus virtually removing mercury from the reacting system. This has been shown not to be the case.*

   In view of the clean-cut separation of core from amalgam occurring in practice it is not believed that the above errors can be serious.

---

* DANIELL. J. Roy. Instn. 1, 1, 1930.

SURVEY OF EXISTING DATA.

Numerous isolated determinations of the solubility of silver in mercury have been made, but with the exception of the six values for the interval 14°-163°C. published by Joyner in 1911 and the very careful and concordant results of Sunier and Hess for seven temperatures in the interval 80.2°- 198.9°C., reported in 1927, no systematic investigation has been carried out at higher temperatures.

References.

GOUY	J. Phys. 4, p.320, 1895;
HUMPHREYS	J. Chem. Soc. 69, p.243, 1896;
REINDERS	Z. phys. Chem. 27, p.285, 1898;
OGG	Z. phys. Chem. 50, p.209, 1905;
JOYNER	J. Chem. Soc. 99, p.195, 1911;
EASTMAN and HILDEBRAND	J.Amer.Chem.Soc.36, p.2020, 1914;
SUNIER and HESS	J.Amer.Chem.Soc. 50, p.662, 1928.

The values are tabulated in Table I..

The latter authors found that within the range investigated, the solubility could be expressed very accurately by the expression

$$\log N = -1074.2\ (T^{-1}) + 0.501.$$

Using the same apparatus but with greater care in analysis, Reed obtained slightly lower values for three temperatures near 200°C.

DE RIGHT J. phys. Chem. <u>37</u>, p.405, 1933, paid special attention to the attainment of equilibrium, starting from silver foil, filings, and the γ intermetallic compound with concordant results. **Using** a modification of Sunier and Hess's technique, he determined the quantity of the residual phase directly by filtration through glass wool plus a capillary — this method was found to be very satisfactory. Between 18° and 80°C. solubility is represented very closely by the equation

$$\log N = -1105.8\,(T^{-1}) + 0.5894.$$

Values obtained by filtration through chamois leather were invariably higher than those given by glass wool, in accordance with the results of RUSSELL for base metal amalgams (J. Chem. Soc. <u>32</u>, p.835, 1932).

De Right discussed in detail the meaning of solubility in terms of particle size and suggested that in view of the opacity of mercury, some optical property might be used to establish the presence of solid particles. His conclusion is that greater credence should be given to <u>lower</u> results, provided that sufficient time has been given to allow equilibrium.

MAURER J. phys. Chem. <u>42</u>, p.515, 1938, showed that de Right's formula could be extended to range 5° - 20°C., but was unable to confirm the existence of aggregates of various size in the solution below.40°C.

In this work also, residual γ was separated directly by filtration, for which a sintered glass layer was found satisfactory.

TABLE I.

VALUES OF SOLUBILITY OF SILVER IN MERCURY PREVIOUSLY RECORDED.

Observer	Temperature in ^{o}C.	$(T)^{-1}$ Absolute	Atomic % Ag.	Solubility gm.Ag/100 gm.Hg.
JOYNER	14	0.003484	0.07	0.038
	25	3356	.082	.044
	30	3300	.086	.047
	63	2976	.19	.102
	90	2755	.34	.183
	163	2294	1.13	.615
SUNIER & HESS	80.2	0.002831	0.286	0.144
	98.2	2694	.411	.221
	121.9	2535	.612	.329
	144.5	2395	.849	.456
	160.6	2306	1.057	.568
	177.9	2217	1.346	.724
	198.9	2118	1.746	.939
REED	181.8	0.002206	1.365	.739
	193.3	2144	1.573	.852
	212.7	2059	1.953	1.059
MAURER	19.24		0.0652	
	16.12		.0586	
	18.98		.0625	
	12.39		.0519	
	9.71		.0474	
	5.72		.0403	
DE RIGHT	18.17		0.0643	
	19.01		.0636	
	25.28		.0766	
	25.60		.0792	
	28.92		.0641	
	29.93		.0881	
	30.15		.0965	
	40.11		.1139	
	50.02		.1450	
	60.26		.1901	
	70.54		.2402	
	80.94		.2892	

EFFECT OF USING A SEALED VESSEL.

The bugbear of solubility determination is the volatility of mercury. In the present work this has been found not to be troublesome below 200°C. and in this connexion it is noteworthy that the highest value for solubility hitherto recorded is that at 212.7°C. (Reed). The vapour pressure of mercury, minute under ordinary conditions, increases rapidly with temperature, approximately at an exponential rate, as is shown by the following figures.

0°C.	20°C.	100°C.	200°C.	300°C.	400°C.	500°C.
1.86×10^{-5} cm.	1.2×10^{-4}	2.6×10^{-1}	1.7	25	155	315

An obvious solution of this difficulty is to measure solubility in sealed vessels. This has the additional advantage of avoiding contamination by solid or gas, but at higher temperatures (i.e. precisely where the artifice is most desirable) two marked disadvantages are evident.

1. Solubility is measured at pressure exceeding one atmosphere. The error can however be estimated by the Clausius-Clapeyron equation

$$\frac{dT}{dP} = \frac{T(V_2 - V_1)}{\lambda_f}$$

where/

where λ_f is the thermal change, in this case the latent heat of fusion. At its melting point of 961°C. (1234°K), λ_f for silver is 26 calories per gram (WÜST, MEUTHEN and DURRER, Forschungen auf Gebiet des Ingenieuerswesen, No.240, 1918), Δ is 9.46 gm. per ml. in the solid state and the change in density on melting is 4.99 per cent.

$V_1 = 1/9.46$ ml. and $V_2 = 1/9.46 \times 0.95$ and 1 calorie is equivalent to 41.4 ml. atmospheres.

$$\text{Thus } \frac{dT}{dP} = \frac{1234\left(\frac{1}{9.46 \times 0.95} - \frac{1}{9.46}\right)}{26 \times 41.4}$$

$$= 0.006 \text{ degrees centigrade per atmosphere.}$$

At boiling point of sulphur (444.5°C.) the vapour pressure of mercury is approximately 3 atmospheres. The pressure of air within the bulb may be estimated at 1½ atmospheres. From the above equation, an excess pressure of 3½ atmospheres would raise the melting point of silver by 0.021°C. As the mean atomic volume for the intermetallic compounds in the silver-mercury system does not differ greatly from that of silver, it is unlikely that the pressures resulting from the use of sealed tubes cause a discrepancy even approaching the experimental error of the determinations.

2. It is not easy to obtain a workable material which, at the working temperature is (a) refractory, (b) non-porous, (c) strong enough to withstand the internal/

internal pressure of mercury vapour and air, (d) not liable to attack or alloy with the metals, (e) endowed with a co-efficient of expansion low enough to withstand rapid sealing-off when cold.

Fig. 4: Before Tempering.

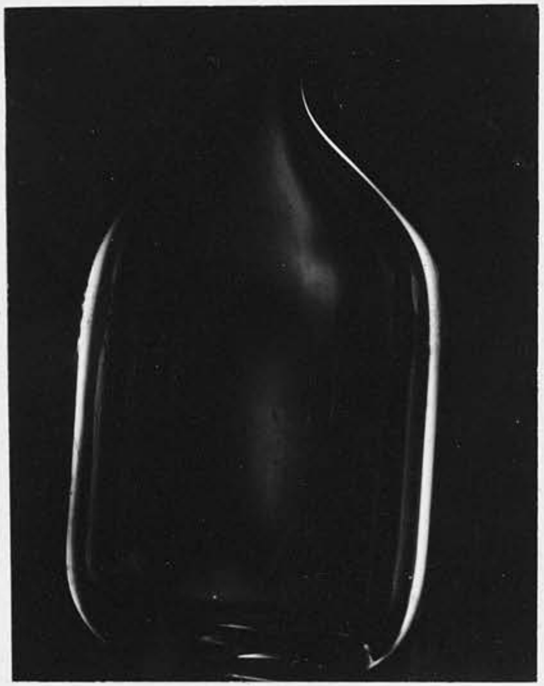


Fig. 5: After Tempering.

Radiographs

showing

Removal of Strain by Tempering.

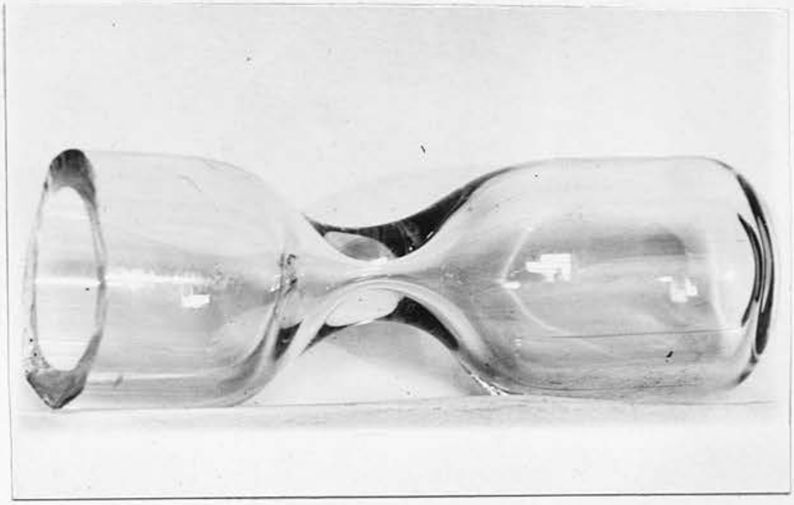


FIG. 2: GLASS BULB BEFORE FILLING.

FIG. 3: FILLED BULB SHOWING PARALLEL CRACKS.

EXPERIMENTAL.

After trial of a number of materials, the refractory boro-silicate tubing used for organic nitrogen estimations was found suitable. Following many failures a satisfactory technique was devised, it being found that success depended on a number of apparently trivial factors. Subsequently thick-walled "Carius" tubing for chloride estimations was found to be even better when new. An attempt to utilize stored tubes proved a false economy! All manipulations were carried out by orthodox glass-blowing methods, but in the oxygen-coal gas blowpipe.

1. The Carius tube was rounded, blackened and cooled. Insertion of silver into the hot tube, even when pre-heated, caused fracture.

2. A silver cube about ½ gm. in excess of that required for the particular temperature was amalgamated, and the mercury removed by heating it to about 900°C. on asbestos gauze in a Méker burner, cooled in the desiccator and weighed. (m_1). After this treatment the metal had a brilliant mat surface like white blotting paper.

3./

3. The silver was introduced and the tube constricted by surface tension alone to give a vessel of 2½-3½ ml. content (30-35 gm. alloy). It was found essential to maintain wall thickness equal to the original, neither thicker nor thinner. (See Fig. 2)

4. After cooling just to rigidity the wall of the bulb was heated almost to its melting point in the same flame. This process was introduced to prevent the cracking which otherwise set in sharply across the bulb, whether filled or empty, in 2-3 days.(Fig.3) Annealing did not inhibit this, and photo-elastic examination in polarized light showed a sharp bright line, normal to the axis, around the circumference at about 1 cm. from the flame constriction. Reinforcement of stresses from both constriction and seal seems ample explanation for the single or parallel cracks which occurred.(See Fig. 3) After blackening and slow cooling each bulb was examined for internal stress before use.

The difference induced by this heat treatment can be seen clearly in radiographs of treated and untreated bulbs taken between Polaroid plates in the X-Nicols position. (Fig.4,5). Before insertion of the bulb the ground is completely dark and the whitening is a measure of the internal stress in the glass.

5./

5. The bulb was filled to about four fifths of its length by the thermometer method, i.e. by pouring mercury into the cone above the constriction and coaxing it beyond by alternately cooling and warming the bulb in the palm of the hand. It was not necessary to know the exact mass of mercury at this stage. To allow for thermal expansion, a small cushion of air had to be left in the bulb.

6. Sealing was carried out in a very small and very hot flame. By careful and rapid working it could be completed without danger of cracking and with only a few degrees rise in temperature, so that the filled bulb could be held in the hand meanwhile. Owing to risk of cracking, neither annealing nor blackening was attempted, but the filled bulb was transferred to the vapour bath and heating begun forthwith.

7. After the desired time of contact (two hours at the boiling point of sulphur, about six weeks at room temperature) the bulb was allowed to cool <u>in situ</u>. When cold it was wrapped in a clean cloth and cracked by squeezing gently in a vice. After the higher temperature treatments the mush was pasty enough to separate cleanly from the silver core, but after the lower temperature treatments some mercury escaped and was caught by the cloth. The total mass of the contents was then determined (m_2)

8. The small core was separated from the mush and bounced several times in a tray to remove the final globule of mercury adhereing. After this it showed a bright amalgamated surface greasy to touch. In a supplementary experiment it was found that on a smooth rolled surface as little as 3.6 mg./cm^2. was sufficient for amalgamation. This corresponds to a thickness of less than 3 x 10^{-4} cm., and although it is improbable that removal of adherent mercury was as efficient as this, it is obvious that the amount remaining is small. The silver core was brought back to its original state by vaporization of adherent mercury as in (2), then weighed (m_3). Solubility in gm.Ag/100 gm. Hg at temperature θ is then given by 100 $(m_1 - m_3)/(m_2 - m_1)$.

CONSTANT TEMPERATURE BATH.

Constant temperatures were obtained by use of pure liquids boiling under reflux in a simple vapour bath so arranged that the tube containing the experimental vessel was, as far as possible, surrounded by vapour. A wide (bacteriological type) hard glass test-tube was inserted almost to its mouth into a cork also carrying an air or water condenser and fitted into a tall 400 ml. beaker heated on a wire gauze/

gauze. This simple arrangement gave very consistent temperatures even as high as the boiling point of sulphur (444.5°C.), the values being reproducible to ¼°C. or better, after a sufficient time (about 20 minutes) had been allowed to attain constancy.

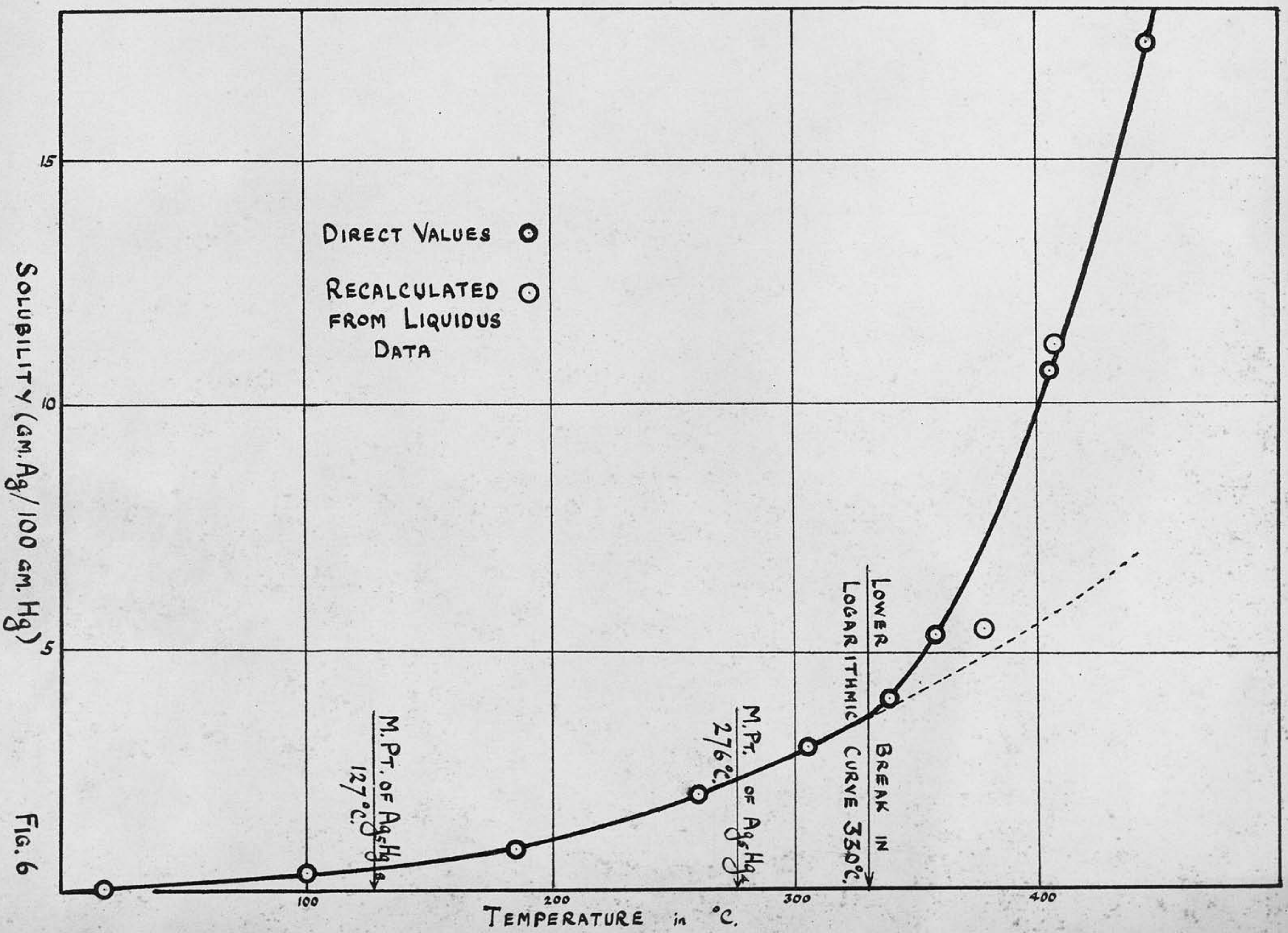
"Commercially pure" substances were found to be quite suitable without special laboratory treatment. Temperature was measured on short-range Anchütz pattern thermometers, Reichsanstalt calibrated, and the values quoted in Table II are those actually observed, not always identical with those tabulated in books of reference. Eugenol was at first tried as a vapour bath, but was replaced by amyl benzoate owing to its blunt boiling point. All the substances were found quite satisfactory for vapour baths, and remained constant during use.

MATERIALS.

Fine silver of nominal purity 99.95% and A.R. grade mercury with the following limits of impurities were used.

Non-volatile matter - 0.002 per cent.
Acid-insoluble matter - nil.
Other metals .... no reaction.

Both are standard commercial products, despite their astonishingly high purity. For subsequent work in which amalgams of definite composition were synthesized, kathode silver of purity better than 99.999 per cent was used. This was in the form of arborescent crystals ¼-4 mm. long but its remarkable standard cannot survive the melting and rolling operations required to



Direct Values ⊙
Recalculated from Liquidus Data ○
Solubility (gm. Ag/100 gm. Hg)
15
10
5
Temperature in °C.
100
200
300
400
M. Pt. of Ag_5Hg_8 127°C.
M. Pt. of Ag_5Hg_4 276°C.
Lower Break in Logarithmic Curve 330°C.

Fig. 6

TABLE II.

VALUES OF SOLUBILITY (gm. Ag/100 gm. Hg), MOLE FRACTIONS AND RECIPROCALS OF THE ABSOLUTE TEMPERATURE.

Substance	$\theta^\circ C$	$T^\circ K$	T^{-1}	S	N	$\log_{10} N$	$\log_e N$
(R.T.)	16.2	289.2	0.003458	0.030	0.000558	$\bar{4}.74663 = -3.25337$	−7.491
Water	99.6	372.6	2684	.222	.004121	$\bar{3}.6150 = -2.3850$	−5.492
Aniline	184.4	457.4	2187	.768	.014192	$\bar{2}.1520 = -1.8480$	−4.255
Amyl benzoate	260.	533.	1876	1.885	.03450	$\bar{2}.5378 = -1.4622$	−3.367
Diphenyl-:amine	306.	579.	1727	2.823	.05251	$\bar{2}.7098 = -1.2902$	−2.971
Anthracene	338.	611.	1637	3.816	.06872	$\bar{2}.7610 = -1.2390$	−2.853
Mercury	356.7	629.7	1588	5.22	.09294	$\bar{2}.9682 = -1.0318$	−2.376
Benzidine	405.	678.	1475	10.59	.18053	$\bar{1}.2566 = -0.7434$	−1.712
Sulphur	444.5	717.5	1394	17.35	.28081	$\bar{1}.4484 = -0.5516$	−1.270

RESULTS.

The solubility values obtained (expressed in gm Ag/100 gm Hg) are tabulated in Table II, and plotted in Fig. 6 . Deviation from theoretical uniformity is very difficult to appreciate on this curve, especially at the low solubilities below 100°C. but physical intuition suggests that the points above 400°C. depart from the curve that one would expect - shown dotted on the graph.

For a solution obeying Raoult's law the following equation can be derived thermodynamically

$$\log_e N^{-1} = \frac{\lambda_f}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) - \frac{(C_L - C_S)}{R}\left(\frac{T_0}{T} - 1\right) + \frac{(C_L - C_S)}{R}\log_e \frac{T_0}{T}$$

where N is the mole fraction of the solute, and λ_f its latent heat of fusion at T_0 its melting point, and C_L and C_S its specific heat in the liquid and solid states respectively. If $C_L = C_S$ which is true to a first approximation, the latent heat of solution will be the same as that of fusion, i.e. the second and third terms vanish leaving the well known expression

$$\log_e N = \frac{\lambda_f}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

i.e.

$$\log_{10} N = \frac{\lambda_f}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\Big/2{\cdot}3026$$

and the plot of $\log_e N$ or $\log_{10} N$ against T^{-1} is thus theoretically/

theoretically a single straight line cutting the horizontal axis at $1/T_0$, with a slope of λ_f/R or $\lambda_f/2.3026\ R$, according to the logarithmic base used. This line is independent of the solvent concerned, provided the solution obeys Raoult's law. RAMSAY (J. Chem. Soc. <u>55</u>, p.532, 1889) reported that a solution containing 3.22 gram atoms of silver per 100 gram atoms of mercury showed a lowering of the freezing point equivalent to an atomic weight of 112.4 for silver against the actual value of 107.9. BECKMANN and LIESCHE (Z. anorg. Chem. <u>89</u>, p.171, 1914) found that the boiling point elevation agreed with the assumption that silver is atomic in the amalgam under these conditions. EASTMAN AND HILDEBRAND (J. Amer. Chem. Soc. <u>36</u>, p.2020, 1914) found that a 1.27 per cent solution at 318°C. had a vapour pressure in agreement with Raoult's law.

As is clearly seen from the plot of $\log_{10}N$ against T^{-1} (Fig.7), the observed values of solubility are consistently lower throughout the whole range then this relation would indicate, although near the melting point of silver the observed values approach theoretical very closely.

Where the solvent is appreciably soluble in the solid solute, the above equation assumes the modified form

$$\log_e N_L - \log_e N_s = \frac{\lambda_f}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

in which suffixes denote the liquid and solid states respectively.

Mercury atoms can enter the close-packed cubic lattice of silver in considerable amount, as is clearly shown by data obtained by metallographic methods and published by MURPHY with reserve in his study of the very difficult silver-mercury binary diagram (N.P.L. Collected Researches, 25, pp.309-327, 1935). These are well confirmed by the X-Ray determination of PRESTON, and agree fairly well with results obtained independently by DAY and MATHEWSON (Amer. Inst. Min. Met. Engg. Tech. Publn. 884, 1938); who find the solid solubility to reach a maximum at 52.4 per cent silver at 276°C., decreasing slightly with falling temperature.

These results are summarized in Table III, and values of log (N_L/N_S) obtained from them are included in Fig.7. Below about 450°C. the curve runs substantially parallel to the original for log N_L, since the solid solubility varies little below that temperature. Above it however the new curve approaches the ideal straight line much more closely, and eventually becomes coincident with it.

TABLE III - SOLID SOLUBILITY OF MERCURY in SILVER.

Temperature	°C. Weight per cent Hg	Observer	Method
655	30	MURPHY	Microscopical
485	37.5	"	"
345	42.5	"	"
276	(max.) 52.4	DAY & MATHEWSON	X-Radiology
100	51.6	"	"
R.T.	46 ±2	PRESTON	"

It is only fair to point out that the above solidus data are in sharp conflict with older figures obtained by heating silver amalgams in constant temperature baths. At the boiling points of sulphur, 444.5°C. mercury, 357°C. and diphenylamine 306°C., DE SOUZA (Berichte, <u>9</u>, p.1050, 1876) found the residues to contain products corresponding to 12.5, 14.4 and 32 per cent of mercury. By prolonged heating at the boiling points of sulphur and diphenylamine, MERZ and WEITH (ibid, <u>14</u>, p.1440, 1881), obtained even lower values, 1.24 and 5.4 per cent. In such work there is always the possibility that equilibrium may be disturbed by removal of some vapour, leading to erroneous results.

Values of the solubility derived from liquidus determinations are given in Table IV, and the corresponding points plotted in Fig. 7 . While these cannot compare in accuracy with direct determinations, they demonstrate clearly the gradual approach of the log N curve to the ideal as the melting point of silver is approached.

TABLE IV.

MOLE FRACTIONS AND RECIPROCALS OF ABSOLUTE TEMPERATURE OBTAINED FROM LIQUIDUS DETERMINATIONS.

Per Cent Ag	θ °C.	$T^{o}K$	T^{-1}	N	$\log_{10}N$	$\log_{e}N$
5.00	378	651	0.001536	0.08916	$\bar{2}.9502 = -1.0498$	-2.4174
10.03	407	680	1471	.1718	$\bar{1}.2250 = -0.7750$	-1.7846
20.08	465	738	1355	.3185	$\bar{1}.5031 = -0.4969$	-1.1441
28.86	541	814	1228	.4300	$\bar{1}.6335 = -0.3665$	-0.8438
37.72	630	903	1107	.5298	$\bar{1}.7241 = -0.2759$	-0.6353
49.96	721	994	1006	.6500	$\bar{1}.8129 = -0.1871$	-0.4308
60.23	786	1059	944	.7380	$\bar{1}.8681 = -0.1319$	-0.3038
69.60	843	1116	896	.8098	$\bar{1}.9084 = -0.0916$	-0.2110
80.08	886	1159	863	.8802	$\bar{1}.9445 = -0.0555$	-0.1278
88.97	928	1201	833	.9375	$\bar{1}.9720 = -0.0280$	-0.0645
100	961	1234	810	1.0000	Zero	Zero

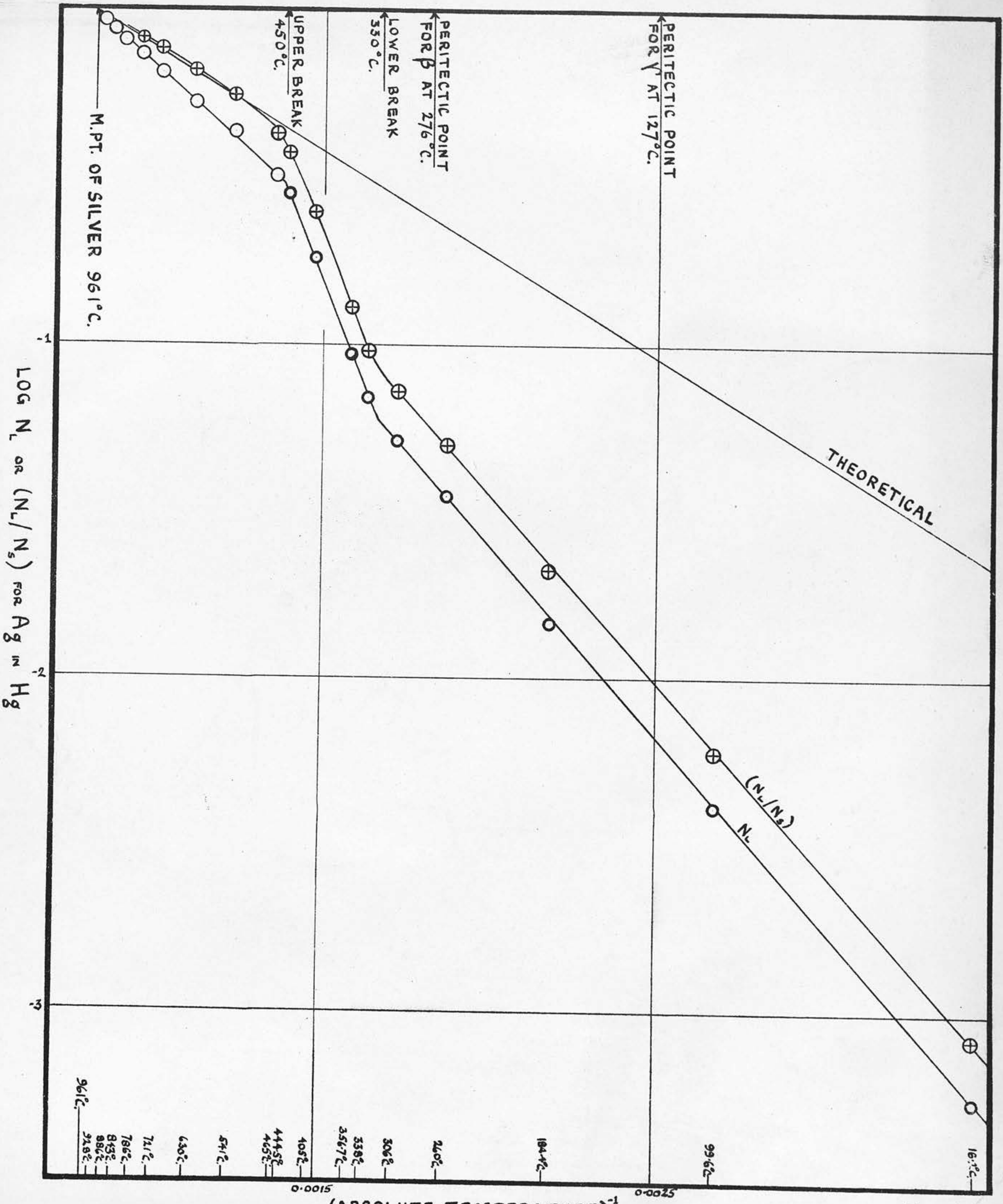

M.PT. OF SILVER 961°C.
UPPER BREAK 450°C.
LOWER BREAK 330°C.
PERITECTIC POINT FOR β AT 276°C.
PERITECTIC POINT FOR γ AT 127°C.
THEORETICAL
(N_L/N_S)
N_L
-1
-2
-3
LOG N_L OR (N_L/N_S) FOR Ag IN Hg
961°C.
928°C.
886°C.
843°C.
786°C.
721°C.
630°C.
541°C.
465°C.
444.5°C.
405°C.
356.7°C.
338°C.
306°C.
260°C.
184.4°C.
99.6°C.
16.1°C.
0.0015
0.0025
(ABSOLUTE TEMPERATURE)$^{-1}$

FIG. 7

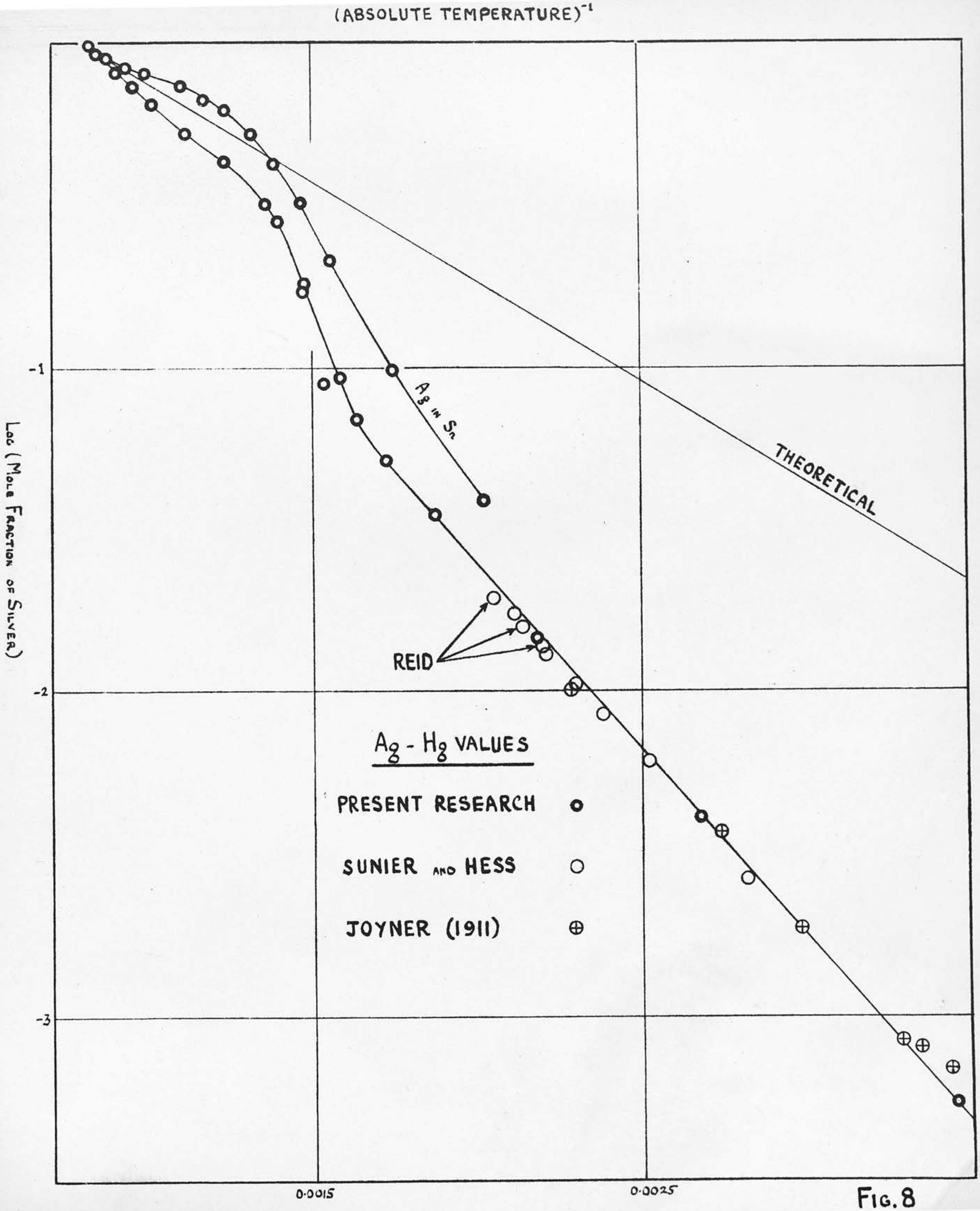

(ABSOLUTE TEMPERATURE)$^{-1}$
Log (Mole Fraction of Silver)
-1
-2
-3
0·0015
0·0025
Ag in Sn
THEORETICAL
REID
Ag - Hg VALUES
PRESENT RESEARCH
SUNIER AND HESS
JOYNER (1911)

FIG. 8

DISCUSSION.

MORTIMER'S RULE.

From Fig. 7 it is evident that MORTIMER'S relation, that the logarithm of the mole fraction of solute in solution is approximately proportional to the reciprocal of the absolute temperature (J.Amer.Chem. Soc. 44, p.1416, 1922; 45, p.633, 1933) is valid qualitatively for the silver amalgams.

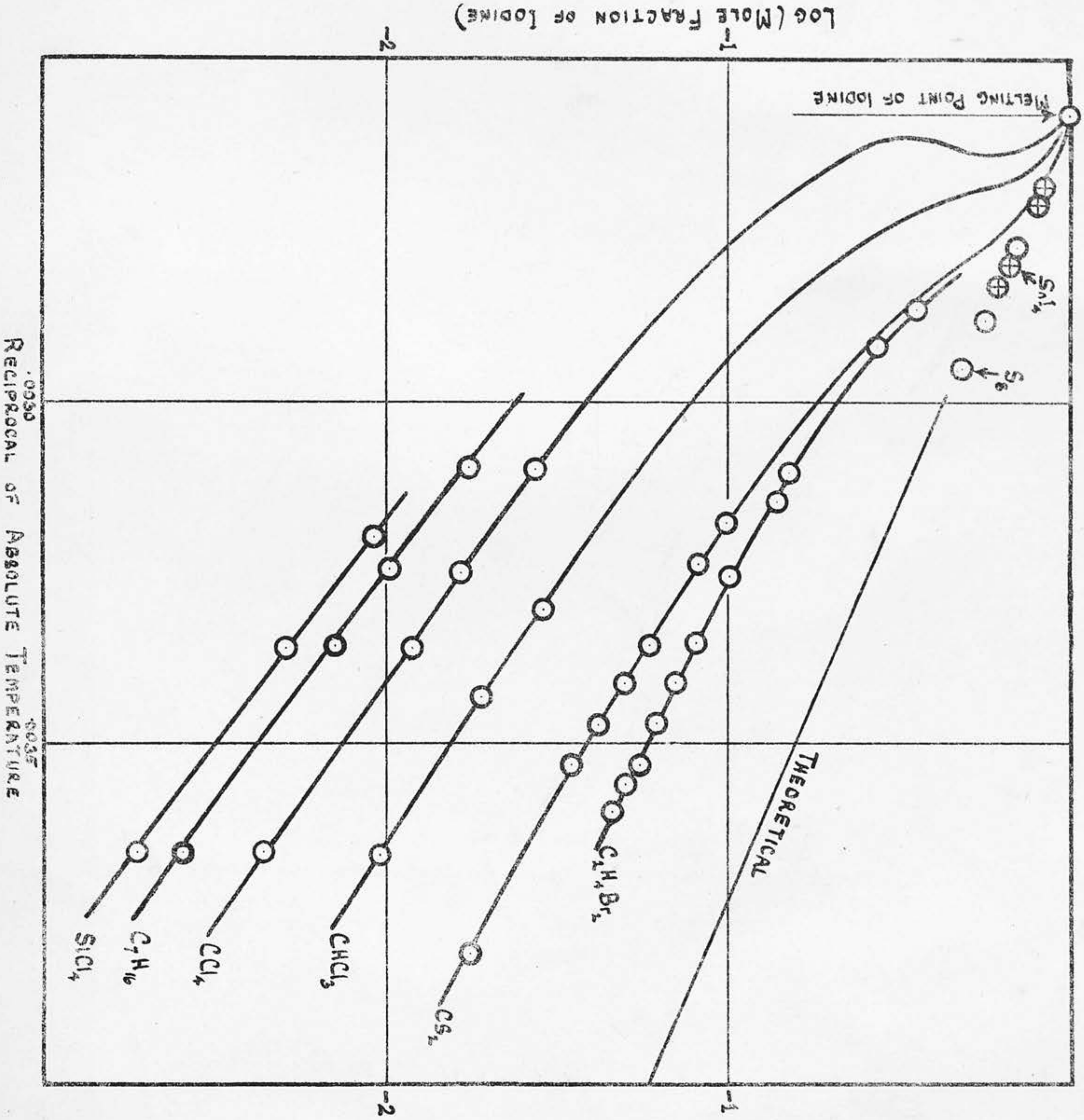
FORMULAE. The results obtained in the present investigation, together with values recalculated from the binary equilibrium diagram and the lower temperature solubilities previously determined, can be represented on the graph very accurately by three straight lines, the equations for which are

$\log_{10} N = 0.67035 - 1134.7/T$ ... up to 330°C.

$\log_{10} N = 2.9065 - 2481.8/T$ ... 330°- 450°C.

$\log_{10} N = 0.7441 - 918.2/T$ ... 450° to the melting point of silver

These intersect at or very near $T^{-1} =$ 0.001383 and 0.001660, i.e. 450° and 330°C. On first examination it appeared an attractive possibility to correlate these breaks with the melting points, or more strictly the peritectic dissociation points, of the β and γ phases. A careful check of determinations showed quite definitely that this would/



FAMILY OF SOLUBILITY CURVES FOR IODINE IN ORGANIC SOLVENTS SHOWING PROGRESSIVE DETERIORATION FROM THE IDEAL STRAIGHT LINE

FIG. 9

would not hold. Nor can there be any doubt of the peritectic values, as the following figures, quoted from the original memoir, show -

Percentage of Silver		0	5	10	20	28.9	37.7	50.0	60.2	MEAN
Peritectics on Heating	β	-	272	282	280	274	276	274	-	276
In degrees C.	γ	-	116	127	129	127	127	127	-	127

So far as can be seen the presence of these two intermetallic compounds in the system is in no way visible in the solubility curve. In Fig. 8 the values obtained by SUNIER and HESS, by REED, and by JOYNER are plotted. They agree well amongst themselves, and with those determined in the present work, but there is no suggestion of any departure from a smooth curve. In the thermal investigation no heat evolution was observed at or near these temperatures, the only "rogue" point being at about 100°C.

On consideration, the absence of any visible effect of the two phases Ag_5Hg_4 and $Ag_5 Hg_8$ on the log N plot against T^{-1} is not so astonishing. On account of the slowness of the peritectic reactions the system is highly metastable, and until some solid intermetallic compound is actually present, the solution must be regarded as in equilibrium with the silver-rich α solid solution.

It/

It is not, of course, certain that the breaks are sharp, and numerous determinations very near the points would be required to clear up this question. The data may be represented equally well by a distorted S curve as shown in Fig. 8 . Fig. 9 reproduced from data given by HILDEBRAND (Solubility of Non-Electrolytes, Amer. Chem. Soc. Monograph Series, Chap. X, 1936) shows very clearly the gradual development of this by progressive deterioration from the ideal solubility relation, for iodine dissolved in widely different liquids. The resemblance of Fig. 8 to the curve for iodine in chloroform, is very striking.

Data for the solubility of silver in gallium, a metal resembling mercury in physical properties, might throw light on the question whether the breaks are sharp, but unfortunately such values are not available. The next suitable metal for which data exist is tin, but unfortunately the range is much curtailed by its relatively high melting point of 232°C. against - 39°C. for mercury. Mole fraction values recalculated from the well-established silver-tin equilibrium diagram are plotted in Fig. 8 . Despite the lower accuracy of such derived figures, it is clear that in tin as solvent, deterioration from the ideal is much more irregular than the highly consistent deviations in the silver amalgams, and the relation between log N and T^{-1} is not even linear. This again may be

connected/

connected with the existence of tin in several crystal lattices of varying parameter but the values are neither close nor accurate enough to show up minor irregularities. In this connexion it may be noted that the mean atomic volume of Ag_3 Sn the intermetallic compound found in this system, which possesses an orthorhombic (pseudo-hexagonal) structure, is 18.4 Å³ against 19.3 Å³ for Ag_5 Hg_8.

TABLE V.

STOICHIOMETRIC DATA FOR THE PHASES CONSIDERED.

	I.		II.			III.	
Parameter	Half of nearest-neighbour distance in Å (approximate only)		Atomic reading in Å Goldschmidt (empirical)	Pauling (theoretical)		Mean atomic volume in Å³	
Ag	1.44	(1)	1.13	1.26	(4)	16.9	
Hg	1.6	(1)	1.12	1.10	(4)	24.5	
Ag_5Hg_4	-					18.4	(2)
Ag_5Hg_8	-					19.3	(2)
Sn	1.65	(1)	0.74	0.71	(4)	26.9	
Ag_3Sn	-					18.4	(3)

References.

1. SEITZ, The Modern Theory of Solids, International Series in Physics, New York, 1940.
2. PRESTON, loc. cit.
3. NIAL, ALMIN, and WESTGREN, Z. phys. Chem. 14, p.81, 1931.
4. GOLDSCHMIDT, Trans. Faraday Soc. 25, p.253, 1929.

VOLUME OF THE PHASES.

Following extensive investigations of the alloys of copper-, silver-, and magnesium-, HUME-ROTHERY has emphasized the importance of what he terms "size factor", i.e. the ratio of the atomic radii of solvent and solute, in governing the extent of solid solution field. Where this differs from unity by a definite amount, which he estimates at one seventh, it is unfavourable, and extensive solid solubility does not occur. The rule is based on the conception of atoms as rigid spheres, in serious conflict with modern views, and there is also the question which parameter should be used - (1) half of the interatomic distance, (2) the Goldschmidt radius, (3) the cube root of the atomic volume, (4) the unit cell. Nevertheless the rule is valuable for semi-quantitative work. In liquid solution one would expect *a priori* that structural or lattice considerations would be of less importance, and that consequently the rule would apply more closely than in the solid state. The following are the data for the phases concerned in the mercury-silver system with those of the tin-silver system added for comparison. (See Table V). It is evident that under Column III the criterion is not favourable, while under Columns I,IIa or IIb, it is very favourable.

POSSIBLE REASONS FOR THE DISCREPANCY BETWEEN OBSERVED AND CALCULATED SOLUBILITY.

It has been shown that the deviation between observed and ideal solubilities is considerable, and possible explanations of this may be investigated.

1. Use of the approximate thermodynamical equation.

The straight line marked "theoretical" in Figs. 7 and 8 represents the equation

$$\log N = (0.4343)\,\frac{\lambda}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)$$

derived on the assumption that λ is equal to the latent heat of fusion, i.e. that the specific heat of silver is equal in the liquid and solid states and is thus independent of temperature. The correct equation (p. 22) may be written -

$$\log N = (0.4343)\,\frac{\lambda_f}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)+(0.4343)\frac{(C_L-C_s)}{R}\left(\frac{T_0}{T}-1\right)-\frac{(C_L-C_s)}{R}\log\frac{T_0}{T}$$

where the second and third terms can be regarded as refinements of the original approximation.

These can be estimated with some certainty, since remarkably concordant data exist for silver (I.C.T., 5, p.92 and 94; et al.)

$C_s = 25.11 + 6.03 \times 10^{-3}(\theta)$ in joules per mole

and $C_L = 0.0748$ cals./gm. = 8.07 cals./mole. (EUCKEN)

Now/

Now the deviation between the observed and theoretical solubility widens rapidly as temperature falls (scissors), it is therefore desirable to investigate the correction at the lowest temperature concerned.

At 16.2°C. $C_S = 6.02$ cals./mole, so that $(C_L - C_S)/R = 1.03$

and $T_0/T = 1234/289.2 = 4.27$

The corrections applicable are therefore

$$(0.4343)(1.03)(4.27-1) - (1.03) \log 4.27$$

$$= 1.463 \qquad - .649$$

Total correction = + 0.814.

The use of this the more exact theoretical equation will therefore increase the deviation.

2. LE VERRIER'S Anomaly in Specific Heats.

From his experimental determinations, LE VERRIER has suggested that there is a sudden drop in the specific heat of silver at about 260°C.

Temperature Range	Mean Specific Heats in cal./gm.
0 - 260°C.	0.0565
260° - 660°C.	0.075
660° - 900°C.	0.076

The discontinuities in the log N —— T^{-1} curve are however found at 330° and 450°C., and moreover le Verrier's results are not confirmed by other workers.

3. Value of λ_f.

Obviously the slope of the straight line representing the theoretical solubility is directly proportional to the thermal change. At room tempera-

ture/

temperature the calculated value of log N is almost exactly half the observed value. It is clear that if the actual heat of solution at room temperature were twice the latent heat of fusion determined experimentally at the melting point of silver, theoretical and experimental values for solubility would agree much better. It is noteworthy that even for the upper straight line in Fig. 7, i.e. for observed values near the melting point, the slope is greater than that obtained by use of λ_f in the theoretical curve. Further, values obtained by different observers for the latent heat of fusion are in fair agreement.

4. Polymorphous Transformation in Silver.

Examination of Fig. 7 shows that the upper and lower straight lines have roughly the same slope, while that of the central portion is two to three times as great. The existence of silver in a crystalline modification stable between 330° and 450°C. might account closely for this. Such an example is well-established in the case of iron, which exists in two lattices, body-centered and face-centered cubic. The latter close-packed variety is stable only between about 725° and 1405°C. There is however no crystallographic, radiological, or thermal evidence for such a lattice transformation in silver, for which the only structure reported is the face-centered cube.

5./

5. Übergitter.

Copper and gold closely resemble silver in physical properties, and the three lattices are almost identical - not unexpectedly since the three atoms have a structure identical in many shells. Formerly copper and gold were considered to form a continuous solid solution, in accordance with liquidus/solidus determinations, but within the last fifteen years feeble unexplained thermal evolutions in the solid state stimulated interest in the system. X-Ray investigation showed the existence of an order-disorder transformation within the solid solution with the formation of an "Übergitter". Such changes were also discovered in other systems, *e.g.* the phenomenon cleared up a long unexplained thermal evolution in the β phase of the copper-zinc system, which is unaccompanied by microscopical change.

Though not so similar as the copper-gold pair, silver and mercury closely resemble each other, as the large substituent solid solubility of mercury in the silver lattice shows. It is quite conceivable that a superlattice may exist within this α constituent; very careful radiological measurement would be required to decide this point. Certainly no thermal points have been reported, but in general the energy change in superlattice formation is small and protracted, and any heat evolution will consequently

be/

be feeble and blunt; even with fairly slow rates of cooling it may easily pass unrecognised unless specially sought for. It is not impossible therefore that a super-lattice may exist within the α field.

References.

HAUGHTON and PAYNE. J. Inst. Met. 46, p.457, 1931;
KURNAKOW and AGEEW ibid p.481.

THE USE OF MERCURY IN SILVER MINING.

It is evident that the licking up of silver and gold does not depend on great solubility, that of silver at room temperature being 0.03 per cent. Nor does it depend on cleanliness of surface since platinum is not amalgamated although it solders readily without a flux, nor on ability to form alloys. The governing factor seems to be the angle of contact, i.e. the ability of mercury to "wet" the surface of the metal, together with the high surface tension of mercury and its recessive contact ($\theta = 140^\circ$) with non-metallic materials. From consideration of Neumann's triangle, the ability of mercury to pick up silver and gold is at once understood.

TABLE VI.

NATURAL SILVER AMALGAMS.

Locality	Ag %	Hg%	Phase	Lattice Parameter in Å	Density	Reported by	
Arqueros-Chile	99.35	-	α			Heide 1937	Compact
Almeria-Spain	92.79	-	α			"	Fine plates
Milagro- "	91.64	-	α			"	" "
Ems-Germany	54.95	-	α			"	Arborescent
Stahlberg-Germany	50.60	-	α	4.176		"	Polycrystalline films
Sala-Sweden	29.98	-	γ			"	Compact
Landsberg-Germany	28.44	-	γ	10.015 ±.003		"	Compact
" - "	27.13	-	γ		13.78 ±.04 (actual)	"	Loose crystals
Kongsberg-Norway	92.45	7.2				Flight	
" - "	75.9	23.1				"	
California-U.S.A.	(61.0) (to) (58.4)	(39.0) (to) (41.6)				Ure	
Ems-Germany	57.6	43.3				Weiss	
Sala-Sweden	46.3	51.1				Nordström	
Landsberg-Germany	25.0	73.3				Heyer	
New Grenada -	5.0	57.4				Schneider	Contains 34.8% Au
Landsberg-Germany	27.04	72.94	γ	10.1 Space Group Im3m	13.48 (actual)	Goyner 1938	Silvery. Brittle with Conchoidal fracture
Calanches-Frace	27.5	72.5	γ			Cordier 1802	
Sala-Sweden	26.48	73.44			13.71 (actual)	Sjögren 1900	Crystalline
" "	29.91	70.44				" "	Massive
Landsberg-Germany	36.					Klaproth 1892	

THE CONSTITUTION OF SILVER AMALGAMS.

In the past, considerable controversy has arisen regarding the constitution of silver amalgams and a variety of intermetallic compounds has been identified - sometimes on rather slender evidence. For example, JONES (J. Chem. Soc. 97, p.336, 1910) reported no less than eight products, of composition $Hg_{31}Ag$, $Hg_{15}Ag$, $Hg_{11}Ag$, Hg_7Ag, Hg_5Ag, Hg_3Ag, Hg_2Ag and $HgAg$. Even investigators who have deduced the presence of a chemical individual from a well established break or interruption of some precise physical property measured for a whole series of alloys, have reported contradictory results. The following is a brief summary of data existing.

1. CHEMICAL EQUILIBRIA.

MÜLLER and HONIG (Z. anorg. Chem. 121, p.344, 1922) obtained acicular Ag_3Hg_2 by contact between metallic mercury and silver nitrate dissolved in pyridine in the absence of water, provided a little cuprous iodide is added.

By reaction between either metal and the other ion, REINDERS (Z. phys. Chem. 54, p.627, 1906) obtained evidence for the existence of Ag_3Hg_4 (bluish) and/

and Ag_3Hg_2 (reddish). This was confirmed by measurements of e.m.f. for silver amalgams against solutions containing both silver and mercurous ions. There was some evidence for Ag_3Hg but none for Ag Hg.

OGG (Z. phys. Chem. 27, p.285, 1898) had previously concluded that the solid amalgam in contact with excess silver had the formula Ag_3Hg_4.

2. VAPOUR PRESSURE.

OGG reported that the vapour pressure /composition curve showed breaks corresponding to Ag_3Hg_4 and Ag Hg. This was confirmed by Loebich (J.Inst.Met.46, p.532,1931).DE SOUZA found that after heating at the boiling points of sulphur, mercury and diphenylamine the residue contained respectively $Ag_{12}Hg$, $Ag_{11}Hg$ and Ag_4Hg. (See p. 25)

RAMSAY reported that amalgams had the composition Ag Hg after heating to "dark redness".

Loebich suggested that the reaction $Ag_3Hg_4 + Hg \rightleftarrows AgHg$ occurs between 110° and 115°C.

3. DENSITY.

The first systematic investigation of density in the silver amalgams was made by JOULE (J. Chem. Soc., 1, p.378, 1863) but his results were somewhat erratic.

From careful determinations on a series of amalgams MAEY (Z. phys. Chem. 50, p.200, 1905) reported a break corresponding closely to Ag Hg, See Table VIII.

4. CHEMICAL COMPOSITION OF SYNTHESIZED AMALGAMS.

Arbor Dianae the well-formed crystalline amalgam known for many centuries has long been identified with $Ag_4\ Hg_3$, to which composition it often corresponds closely. In view of accepted uncertainty attaching to the analytical composition of any phase obtained by separation, it seems impossible to differentiate between $Ag_4\ Hg_3$ at 41.8 and $Ag_5\ Hg_4$ at 40.2 per cent silver. The latter compares with the composition of 40 per cent silver assigned to β by direct microscopical examination.

CROOCKEWIT (Specimen chemicum de conjunctionibus chemicis metallorum: Amsterdam 1848) synthesized products corresponding to Ag Hg, $Ag_2\ Hg_3$, $Ag_5\ Hg_8$, and $Ag\ Hg_2$.

5. ANALYSES OF MINERALS.

Mineral amalgam specimens often correspond to the Hg/Ag ratio of 3/2. One of the earliest found at Sala (Sweden) in 1660 was found to be a composition equivalent to the empirical composition $Ag_5\ Hg_6$ and density 11.56.

Recently, under stimulus of X-Ray analysis, there has been marked recrudescence of interest in native amalgam. In none of several specimens of the mineral investigated was HEIDE (Naturwissenschaft, No.40, p.651, 1937) able to identify any β constituent. Citing the rarity of compositions within the heterogeneous/

heterogeneousfield (50-70 per cent silver) he has suggested that the native alloys are composed either of α or γ. Further, finding that copper, tin, lead, and barium (but not gold) were invariably present in native amalgam, sometimes to the extent of ½ per cent, he concluded that it can be regarded as a binary silver-mercury alloy only as a first approximation.

For arquerite the formula $Ag_{12}Hg$ has been suggested by various research workers, but BERMAN and HARCOURT (Amer. Mineralogist 23, p.761, 1938) have pointed out that, together with bordosite and kongsberite, it should actually be classified as native silver with mercury in solution. They also proposed that the name moschellandsbergite should be extended to all mineral amalgams with γ structure.

References.

SCHREIBER, J. Phys. 36, p.353, 1790.

HEYER, Crelles Ann. ii, 36, 1790.

CORDIER, Jour. Mines, 12, p.1, 1802.

BERTHIER, Comptes Rendus, 14, p.567, 1842.

DOMEYKO, Mineralojia: Santiago 1879.

LACROIX, Bull. Soc. Min., 20, p.233, 1879.

SJÖGREN, Geol. För. Förh. Stockholm, 20, p.183, 1896.

Typical analyses of native minerals are included in Table VI.

6./

TABLE VII.

DATA FOR THE GAMMA PHASE.

OBSERVER	COMPOSITION.			X-RAY DATA. UNIT CELL			DENSITY		PROPOSED SPECIES.		ORIGIN	DATE
	Hg %	Ag %	Ag/Hg Empirical	a in Å	No. of atoms.	Space Group	Calc.	Obs.	Formula	Ag%		
WERYHA				10.09	28				(Ag_3Hg_4)	28.74	Synthetic Radiological	1926
WESTGREN				10.	52	γ-brass					Synthetic Radiological	1931
(MURPHY	70.5	29.5	1/1.285						?		Metallographic)	1931
(PRESTON	70.5	29.5	1/1.285	10.0	46 or 52	(γ-brass ((	13.1 or 12.		?		Radiological)	
STENBECK	74	26	1/1.530	10.024	52	γ-brass			Ag_5Hg_8	25.15	Synthetic Radiological	1933
TROIANO	<75	>25	<1/1.600	10.032 to 10.014	-				Ag_5Hg_8 Ag_3Hg_4	25.15 28.74	Trituration Radiological	1938
DUMAS	72.6	27.4	1/1.425	-	-	-	-	-			Synthetic 17 years' contact	1869
DE RIGHT			3/4 approx.	-	-	-	-	-	Ag_3Hg_4	28.74	Synthetic 3 years' contact	1933
HEIDE		28.44		10.015	52						Mineral (Landsberg)	1937
HEIDE		27.13			52			13.78 ± .04	Ag_5Hg_8 ?	25.15	Mineral (Landsberg)	1937
GOYNER	72.94	27.04	1/1.453	10.1	50	Im3m		13.48	$Ag_{20}Hg_{30}$	26.4	Mineral (Landsberg)	1938
BERMAN and HARCOURT	73.44 (MAUZE	26.48 LIUS	1/1.492 ANALYST)	10.1	50 or 52	Im3m	13.49 or 13.73	13.71	$Ag_{20}Hg_{30}$ or Ag_5Hg_8	26.4	Mineral (Sala)	1938
GOLDSCHMIDT						$4/m3\bar{2}/m$					Mineral (Landsberg)	1913

6. MICROSCOPICAL EXAMINATION.

Owing to the fact that at standard pressure mercury boils much below the melting point of silver, investigation by metallographic methods is out of question. Even with the use of a special freezing technique devised by MURPHY, microscopical examination and interpretation is very difficult. Fortunately the diagram itself is not complicated:- The α phase contains about 50 per cent of mercury in solid solution at room temperature, two other phases show peritectic melting points, β with sixty per cent mercury at 276°C. and γ with 30 per cent at 127°C.; the rate of formation of these peritectics is slow. In each case the range of composition is small. (See page 8) There is no trace of the individual $AgHg$ (35 per cent silver) suggested by examination of some physical properties, confirming the conclusions of FEODOROW (Chem. Z. 36, p.220, 1912) after ad hoc investigation of cooling curves for this amalgam.

7. RADIOLOGY.

Of all methods employed for investigation X-Ray analysis has been most fruitful of results, and in view of the difficulty of this binary system this is quite understandable.

The β phase was first examined by GOLDSCHMIDT (Z. phys. Chem. 133, p.409, 1928) and subsequently by/

by PRESTON who proposed a close-packed hexagonal unit with $a = 2.98$ Å and $c/a = 1.62$, analogous with a close-packed hexagonal phase approximately $AgCd_3$ with $a = 3.06$ Å and $c/a = 1.57$. From these dimensions the theoretical density of the phase is a little over 12 gm./cm^3.

For the γ phase contradictory conclusions have been reached. There is general agreement on the dimension of 10 Å for the unit cube reported by WERYHA (Comptes Rendus Société Polonaise Phys. **7**, p.57, 1926) but several suggestions have been put forward as to the number of atoms it contains, and the problem is complicated by conflicting chemical and metallographic data.

TABLE VIII.

PREVIOUS DETERMINATIONS OF DENSITY OF SYNTHESIZED AMALGAMS.

Per cent Ag.	Density.	$(\text{Density})^{-1}$	Observer
34.5	14.68	0.0681	JOULE
51.6	12.49	800	"
53.5	13.25	755	"
60.9	12.34	810	"
72.3	11.42	876	"
74.6	12.54	797	"
0.	13.552	0.07379	MAEY
0.13	.552	379	"
1.0	.558	376	"
1.5	.548	381	"
5.1	.526	393	"
6.1	.582	363	"
6.9	.541	385	"
9.3	.567	371	"
17.2	.449	336	"
20.5	.643	330	"
22.0	.489	414	"
22.6	.640	331	"
27.8	.572	368	"
29.5	.503	406	"
37.9	13.197	0.0758) $v = 0.0577 + 0.000477(w)$	"
39.1	13.164	760)	"
47.9	12.359	809)	"
48.4	12.267	815)	"
64.0	10.818	924)	"
94.0	9.715	0.1025)	"

DENSITIES OF THE SILVER AMALGAMS.

In view of the divergent X-Ray data for the γ phase, and doubt as to its chemical composition, it was considered desirable to redetermine with care the density of a number of silver amalgams.

PREVIOUS VALUES FOR Δ.

Results previously reported (see p. 38) are tabulated in Table VIII. MAEY concluded that for a silver content up to 30 per cent by weight, the density differed little from that of pure mercury at 13.6, and with increasing silver content fell to 9.715 at 94 per cent, against 10.5 for pure silver. Between 38 and 94 per cent the reciprocal of density could be represented very well by the straight line

$$v = 0.0577 + 0.000477(w)$$

where w is the percentage of silver. These results and the correponding line are plotted in Fig. 10. Maey deduced that a break occurred at 34 per cent which he decided was connected with the presence of a compound Ag Hg (35 per cent silver). Amalgams of varying compositions were obtained by expressing liquid from a mushy amalgam in an iron press, and no time seems to have been allowed for standing. Amalgams richer in silver were obtained by vaporization of mercury on heating.

In/

In view of the slowness of the β + liquid → γ peritectic (see p. 55) it is unlikely that equilibrium was even approached. In these circumstances the constant densities in the range 0-30 per cent silver probably do not represent those of amalgams at equilibrium, i.e. amalgams free from β .

The densities of a number of natural amalgams have also been reported.

EXPERIMENTAL.

All amalgams were prepared by synthesis from A.R. mercury and fine arborescent kathode silver crystals, weighed quantities being introduced into a previously-formed bulb, similar to that used for determination of solubility, shown in Fig. 2. After heating to equilibrium the contents were removed and put aside to allow completion of peritectic action. Density was then determined directly without alteration of composition by removal of any phase. Either the specific gravity bottle or the Archimedes method was used as was best suited to the physical conditions of the alloy. Results showing the crude densities obtained, as well as values corrected for buoyancy, are shown in Table IX , and plotted in Fig. 10. Together with MAEY'S data, the reciprocals and the corresponding X-Ray parameters for the unit cell are included for comparison.

DENSITIES DETERMINED.

In the interval 0-30 per cent silver, in which MAEY found that density did not vary much from that of pure mercury, the present values show a slight but consistent drop which continues in a smooth curve to 12.76 at 44.64 per cent silver (Ag/Hg = 3/2). It is right to point out that amalgams within this range are generally porous, and therefore the results are likely to be low rather than high. To combat this possibility, two methods were used to ensure that the specimen was completely "waterlogged" before the second weighing

(a) by boiling and cooling,

(b) by evacuation of air from a vessel,

these gave concordent results.

For the Ag_3Hg_2 amalgam quoted above a figure of 12.756 was obtained by the Specific Gravity Bottle and 12.762 by Archimedes' method on a separately prepared alloy.

Densities actually found for amalgams corresponding to definite atomic ratios are as follow -

Ag_5Hg_8	13.174	25.15 per cent silver
Ag_3Hg_4	13.171	28.74 " " "
Ag_5Hg_4	12.971	40.20 " " "

and there is certainly no discontinuity apparent in the immediate neighbourhood of any of these; so far as can be seen neither β nor γ reveals its presence by/

by any break in the density/composition plot.

In the α field, density appears to vary almost linearly with composition from 10.499 for pure silver to about 10.9 at the boundary, and MAEY'S value of 10.818 at 64 per cent fits the present curve much better than his own straight line for Δ^{-1}. In fact, apart from the slight discrepancy at 25 - 30 per cent silver, all his results agree well with the author's, except for one value - 9.715 at 94 per cent, which appears quite inexplicable. Further, from the additional points now available, it is clear that his proposed relation $\Delta^{-1} = 0.0577 + 0.000477\,w$, is, to say the least, not valid for the whole range claimed, i.e. 30-94 per cent silver. It has been suggested already (p. 46) that MAEY'S amalgams may not have attained equilibrium, while in the present case they were allowed to stand about two years before measurement. There is however a sharp discontinuity in density at the boundary of the silver-rich solid solution, i.e. when the β phase makes its appearance.

THEORETICAL DENSITIES.

On the basis of X-Ray parameters PRESTON has calculated a theoretical density of "about 12" for β, 13.1 for $(Ag_5Hg_8)_4$ and about 12 for a phase with 29-30 per cent silver and 46 atoms in the unit cell - an interpretation tacitly favoured. The calculated/

calculated density of β is about 1 unit too low according to all determinations, while the author's value for Ag_5Hg_4 is 13.174, and for 30 per cent silver about 13.1. BERMAN and HARCOURT however have calculated 13.49 for $Ag_{20}Hg_{30}$ which composition they preferred, or 13.73 for $(Ag_5Hg_8)_4$. For natural amalgams with 26.48 and 27.04 per cent silver they found densities of 13.71 and 13.48 respectively, these check HEIDE'S value of 13.78 for a 27.13 per cent amalgam, very well. These densities exceed even the highest published by MAEY - 13.643 at 20.5 per cent silver - and it is evident that mineral amalgam has a density considerably greater than the laboratory product, although in lattice structure they are identical. The fact that palladium and gold - which have lower atomic volumes than silver, are frequently present as impurities, may account for this to some extent.

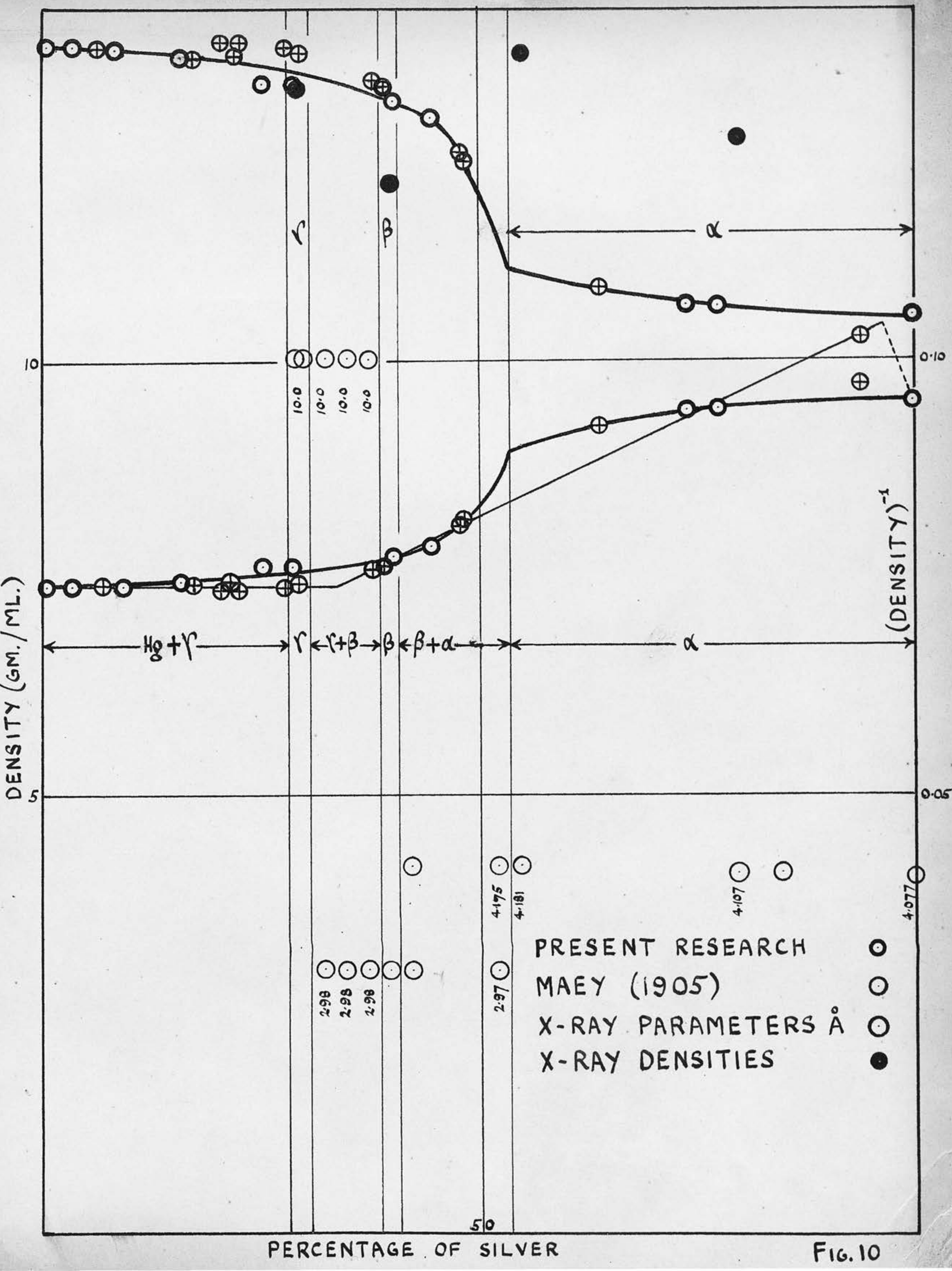

DENSITY (GM./ML.)
10
5
0·10
0·05
(DENSITY)⁻¹
γ
β
α
Hg+γ
γ
γ+β
β
β+α
α
10.0
10.0
10.0
10.0
4·175
4·181
4·107
4·077
2·98
2·98
2·98
2·97
PRESENT RESEARCH
MAEY (1905)
X-RAY PARAMETERS Å
X-RAY DENSITIES
50
PERCENTAGE OF SILVER

FIG. 10

TABLE IX.

DENSITIES OF SYNTHESIZED SILVER ANALGAMS

Composition % Ag	Empirical	Density Observed	Temperature	Method	Density corrected	Reciprocal of Density
0.0	Hg					
0.4	-	13.605	13.5°C	S.G.Bottle	13.576	0.07366
3.42	-	13.606	13.5°C	"	13.577	.07365
8.22	-	13.550	16. °C	"	13.524	.07395
15.84	-	13.490	15.9°C	Archimedes	13.464	.07425
25.15	Ag_5Hg_8	13.174	16. °C	S.G.Bottle	13.149	.07606
28.73	Ag_3Hg_4	13.171	16. °C	S.G.Bottle	13.146	.07607
40.2	Ag_5Hg_4	12.971	16. °C	S.G.Bottle	12.946	.07725
44.64	Ag_3Hg_2	(12.779) (12.785)	16. °C 15.9°C	S.G.Bottle) Archimedes)	12.756 12.762	.07847 .07836
74.02	-	10.645	15.9°C	Archimedes	10.625	.09412
77.62	-	10.629	16.1°C	Archimedes	10.609	.09426
100	Ag	10.518	16. °C	Archimedes	10.499	.09525

THE INTERMETALLIC COMPOUNDS.

THE BETA PHASE.

There is general agreement about the close-packed hexagonal β phase at about 40 per cent silver (Ag_4Hg_5 = 40.2 per cent). LOEBICH suggested 37.7 - 36.2 per cent silver from vapour pressure data.(p.38).

GOLDSCHMIDT	Z.phys.Chem.133, p.409,1928;	a = 2.987, c/a = 1.621
PRESTON	loc. cit. ;	a = 2.98 , c/a = 1.62
STENBECK	Z.anorg.Chem.214,p.16, 1933;	a = 2.987, c/a = 1.617
	At Ag boundary	a = 2.964, c/a = 1.631
LOEBICH	loc. cit.	

THE GAMMA PHASE.

For the γ phase there are small but very definite discrepancies which are clearly brought out in Table VII. It is generally agreed that the range of composition is narrow, possibly about 2 per cent, and the unit cell is a body-centered cube of side about 10 Å. This was first established by WERYHA in 1926 (10.09), and confirmed by PRESTON in 1931 (10.0), STENBECK in 1933 (10.031 falling to 10.013 with rising silver content, TROIANO in 1938 (10.032 to 10.014). All these were obtained with synthesized amalgam but investigation of minerals has yielded concordant values/

values of 10.015 (HEIDE 1937), and 10.1 (BERMAN and HARCOURT 1938). In regard to the composition of the phase there is considerable doubt. Using his ingenious liquid - CO_2 technique MURPHY suggested 29-30 per cent as the position of the homogeneous range, but emphasized the difficulty of interpreting such microstructures. His observation was confirmed by X-radiology by PRESTON who guardedly indicated an imperfect γ-brass structure with 46 atoms in the unit cell, against 52 for $(Ag_5Hg_8)_4$ as a Hume-Rothery compound with the standard electron/atom ratio of 21/13. The corresponding composition is 25.15 per cent silver, and the calculated density is 13.1.
STENBECK however found the homogeneous composition to occur at 26 per cent silver, and the structure definitely to be that of γ -brass in agreement with WESTGREN (J. Inst. Met. 46, p.532, 1931).
TROIANO (J. Inst. Met. 63, p.247, 1938) reported that the alloy at 25 per cent silver definitely contained excess mercury.

HEIDE has suggested that the β (Ag_5Hg_4) constituent does not occur in native amalgam, and that the composition Ag_5Hg_8 is not attained even in those specimens which contain free mercury, although equilibrium might be expected in a mineral if anywhere. This contention is a good agreement with the compositions for solid material which had stood in prolonged contact/

contact with mercury, viz. 27.4 per cent after seventeen years (DUMAS), and approximately Ag_3Hg_4 (i.e. 28.74 per cent) after three years (DE RIGHT). Compositions obtained by separation of a phase are notoriously deceptive, and in view of the very high surface tension of mercury there is great difficulty in removing it completely, so that the analytical result is likely to be high in that element. These considerations support the composition of MURPHY.

BERMAN and HARCOURT have pointed out that many mineral amalgams are shown by X-Ray analysis to contain or consist of γ, and suggested that the true unit cell is $Ag_{20}Hg_{20}$ (26.4 per cent silver) with 50 atoms. This composition checks the analytical composition of several amalgams from Germany and Sweden (see Tables VI and VII) also HEIDE'S analyses, and is in good agreement with STENBECK'S value of 26 per cent, also obtained radiologically.

The correlation of densities observed for synthetic and natural amalgams with that calculated theoretically, is treated on p. 48 .

On chemical evidence alone, it is impossible to decide what identity should be assigned to γ , since several compounds fall within the range of compositions suggested by various observers

Formula	Ag/Hg ratio	Per cent silver	Electron/Atom Ratio
$(Ag_5Hg_8)_4$	1/1.6	25.15	13/21 = 1.615 (Hume-Rothery)
$(Ag_{20}Hg_{30}$	1/1.5	26.4	5/8 = 1.600
Ag_3Hg_4	1/1.33	28.74	7/11 = 1.571
Ag_4Hg_5	1/1.25	30.07	9/14 = 1.556

CONCLUSIONS.

From the survey the following facts appear well established:-

1. The γ phase exists in the lattice structure of γ-brass, but it is not certain whether or no this is perfect.
2. Its chemical composition lies near 27 per cent silver - electron/atom ratio 1.592 - and its range of stability probably does not exceed one per cent in either direction.
3. This definitely excludes the composition Ag_5Hg_8 with 13/21 atom/electron ratio, from the permissible range. Such an exclusion is not unique; careful investigation by STOCKDALE (J. Inst. Met. 52, p.111, 1933) has shown that the range of the θ phase in the aluminium-copper series does not include the composition $Cu\,Al_2$, although it possesses a typical intermetallic compound structure. This was confirmed by BRADLEY (ibid, p.117).
4. The discrepancies in observed data are probably due to the great difficulty in obtaining equilibrium for a phase whose maximum temperature of existence is 127°C. The extreme slowness of reaction in alloys at ordinary temperature is well known.
5. The suggestion that the β (Ag_5Hg_4) constituent does not occur in mineral silver amalgams is well supported by radiological evidence, and may yield

a/

a solid constituent containing 27-28 per cent silver. If these minerals are to be regarded as in chemical equilibrium, a minor revision of the silver-mercury diagram proposed by Murphy is necessary. This would make the β constituent metastable at room temperature. In view of the very slow rate of reaction to which attention has been called by several workers (HUMPHREYS, MURPHY, GAYLER, TROIANO) this does not seem unreasonable.

6. The densities of the intermetallic compounds are not sufficiently different from that of mercury to allow any conclusions to be drawn from the variation of this property with composition. The densities obtained for mineral amalgams are slightly but definitely higher than those for synthetic products, and accord much better with those calculated from lattice parameters obtained by radiology.

SUMMARY AND CONCLUSIONS.

After a review of historical information regarding silver, mercury, and silver amalgam, existing data for the solubility of silver in mercury - available up to about 200°C. - are surveyed. By calculation from the Clausius-Clapeyron differential, the effect on solubility of the vapour pressure generated within a sealed vessel is shown to be negligible under the conditions of the determination. The direct method of measuring solubility is examined critically in light of the equilibrium diagram.

The solubility of silver in mercury - both metals being very pure - has been determined by using sealed refractory bulbs held at definite temperatures in vapour baths, and the various precautions required are discussed. Removal of the internal strain resulting from the glass-working was found to be essential, otherwise spontaneous cracking occurred; and to achieve this tempering at very high temperature near the softening point of the refractory glass was necessary. A simple and effective method of ascertaining whether this freedom had been attained by photo-elastic observation, is described and illustrated.

Values/

Values of solubility determined are plotted directly against temperature, yielding a curve of normal (parabolic) shape. They are in good agreement with those reported in the ranges investigated by previous authors, which are tabulated.

Results are also plotted as log N —— T^{-1} . The latter graph consists of three straight lines

$\log N = 0.67035 - 1134.7\,T^{-1}$ ...... up to 330°C.

$\log N = 2.9065 - 2481.8\,T^{-1}$ ...... 330° - 450°C.

$\log N = 0.7441 - 918.2\,T^{-1}$ ...... 450 - 961°C.

The intersections of these at 330° and 450°C. are not identical with the peritectic points of the two intermetallics formed in the system, which "melt" at 276° and 127°C. These compounds have no effect on the slope of the logarithmic curve.

A graph in which values of $\log (N_L/N_S)$ are plotted against T^{-1} (i.e. the application of a correction for the solubility of mercury in solid silver) shows no particular difference from the original.

Data for diverse physical properties showing that the silver amalgams obey Raoult's law are cited. Solubilities calculated thermodynamically on this assumption, with accepted value of the latent heat of fusion of silver at its melting point, are very much higher than those actually observed, and possible explanations of this deviation are examined. The use of a thermodynamical equation more rigid than $\log_e N = (T_0^{-1} - T^{-1})$, in which corrections are applied

for/

for the decrease with temperature of the specific heat of the solute, shows a still <u>wider</u> deviation.

Mortimer's law is found to hold approximately.

The original logarithmic solubility curve much resembles that for iodine in chloroform. Data are quoted to show how the latter distorted S shape is attained by progressive degradation from the ideal solubility of iodine realization in S_8 and SnI_4 . A comparison of the solubility of silver in mercury with that in liquid tin, the nearest similar metal for which data are available, shows that in this case the results are much less regular.

Established results regarding the physical properties of silver-mercury alloys have been examined critically with the object of correlating breaks in continuity with chemical individuals. The results point to AgHg and Ag_3Hg_4 but are somewhat conflicting.

Various chemical individuals have been suggested as occurring in silver amalgam. Since boiling-and freezing-point results are suspect owing to peritectic reactions, the best criterion is lattice structure. Results for β - a close packed hexagonal cell with a = 2.98 and c/a = 1.62 - are concordant, but those for γ are conflicting. Chemical analyses of the laboratory product agree well with those of minerals, but in such circumstances it is not possible to differentiate between species like Ag_3Hg_4 and Ag_2Hg_3.

To/

To clarify the position the densities of various silver amalgams have been determined for comparison with values calculated from X-Ray analysis. The results supplement those of Maey, with which they agree except on one single value. The β and γ phases do not manifest themselves on the density/composition curve, probably because their densities are too near those of mercury; there is a well marked discontinuity at the boundary of the α phase.

Although a period of two years was allowed for attainment of equilibrium, observed densities were found to be below those reported for native amalgams, the latter agree much better with the theoretical values calculated from X-Ray parameters.

Following a critical correlation of all available data, it is concluded that the best value for γ is at 27 per cent silver. The phase crystallises the γ - brass lattice although the composition Ag_5Hg_8 with Hume-Rothery electron/atom ratio of 21/13 does not fall within its narrow homogeneous range. Since β is absent from natural amalgams it may, in fact, be metastable; it is suggested that the slow rate of reaction at ordinary temperature may account for the general agreement on its parameters in laboratory preparations. Minor modification of the now accepted constitution diagram would be sufficient to fit these facts.