On the Partition of Silver between Zinc and Lead.

By

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The study of the melting points of alloys has demonstrated beyond a doubt that the laws of dilute solutions apply to metallic mixtures in which one of the components greatly preponderates over the others. Consequently the law of the constant partition coefficient must also obtain for them. The experimental verification, however, has so seldom been undertaken that it may not be uninteresting to add a well defined instance. For this purpose I have at the suggestion of Prof. IKEDA, investigated the system zinc-lead-silver, because it has some additional interest in connection with PARKES' process of desilverisation of lead.

This system has already been studied by WRIGHT and THOMPSON.[1] They melted the three metals in various proportions at temperatures ranging between 750° and 850°, and allowed the melt to stand eight hours in order that the separation of the two layers might be complete. They then determined the composition of these layers by analysis. The results obtained by them are given in Table 1.

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1) Proceedings of the Royal Society of London, 48, (1890), 25-45.

TABLE 1.

Composition of the lighter layer.			Composition of the heavier layer.		
Silver.	Lead.	Zinc.	Silver.	Lead.	Zinc.
0	.0157	.9843	0	.9870	.0130
.0934	.0251	.8815	0002	.9864	.0134
.1546	.0463	.7991	.0010	.9838	.0152
.2207	.0696	.7097	.0032	.9761	.0207
.2228	.0756	.7016	.0025	.9708	.0267
.2795	.0617	.6588	.0088	.9623	.0289
.3949	.0346	.5705	.0112	.9698	.0190
.4182	.0390	.5428	.0146	.9658	.0196
.4811	.0346	.4843	.0160	.9714	.0126
.4893	.0382	.4725	.0226	.9646	.0128
.5186	.0447	.4367	.0535	.9327	.0138
.5398	.0478	.4124	.0778	.9076	.0146
.6107	.0723	.3170	.0936	.8862	.0202
.6193	.1028	.2779	.1075	.8695	.0230
.6889	.1828	.1283	—	—	—

As can readily be seen, the partition coefficient of silver between the lighter and the heavier layer varies continuously with the concentration, and this leads us to infer the existence of such molecular complexes as Ag_n or $Ag_n Zn_m$ in the former. But the concentrations of silver in the lighter layer as studied, are nearly all so high that the laws of dilute solutions can no longer be applied. Yet their results, especially in the region where the concentration of silver in the lighter phase is not too small, appear to deserve closer study. The triangular diagram shown in Fig. 1 has been drawn using WRIGHT and THOMPSON's data. The characteristic change of curvature between 10% and 40% of silver in the lighter phase, mirrowed in miniature towards the lead end of the heavier phase branch, is very interesting as
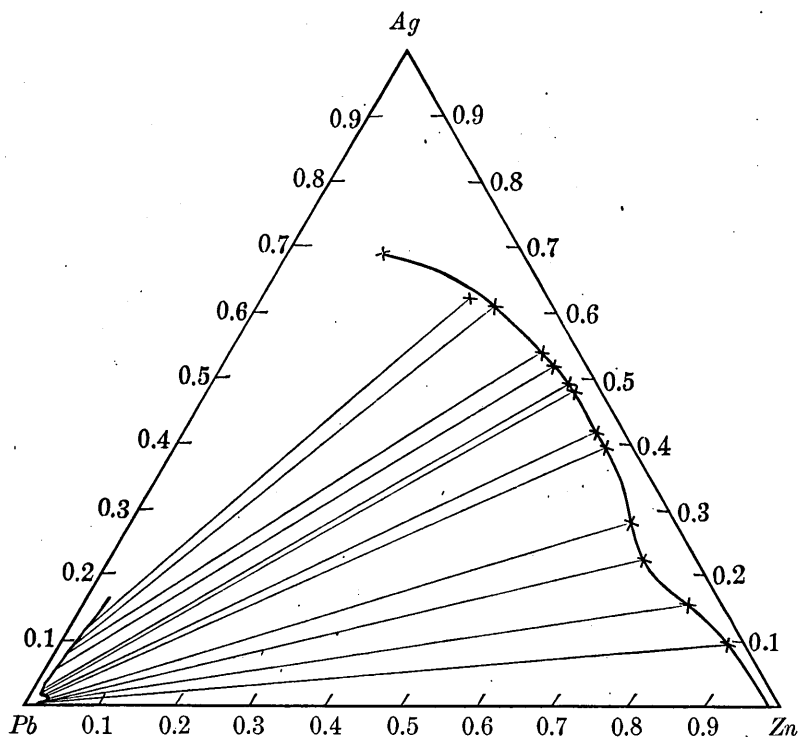
Fig. 1.

indicating the existence of a compound, perhaps $Ag_2 Zn_5$, in the solution. But as the quantitative theory of the concentrated solution has not yet been worked out, it is at present impossible to attempt to account for the course of the curve in detail.

The same authors have also studied the system zinc-lead-tin,[1] in which the partition of tin between the two layers remains nearly constant, so long as the concentration of tin does not become too great. In this case the partition coefficient being not far from unity, the experimental determination seems to have been easier. The results are given in Table 2 and represented in the annexed diagram Fig. 2.

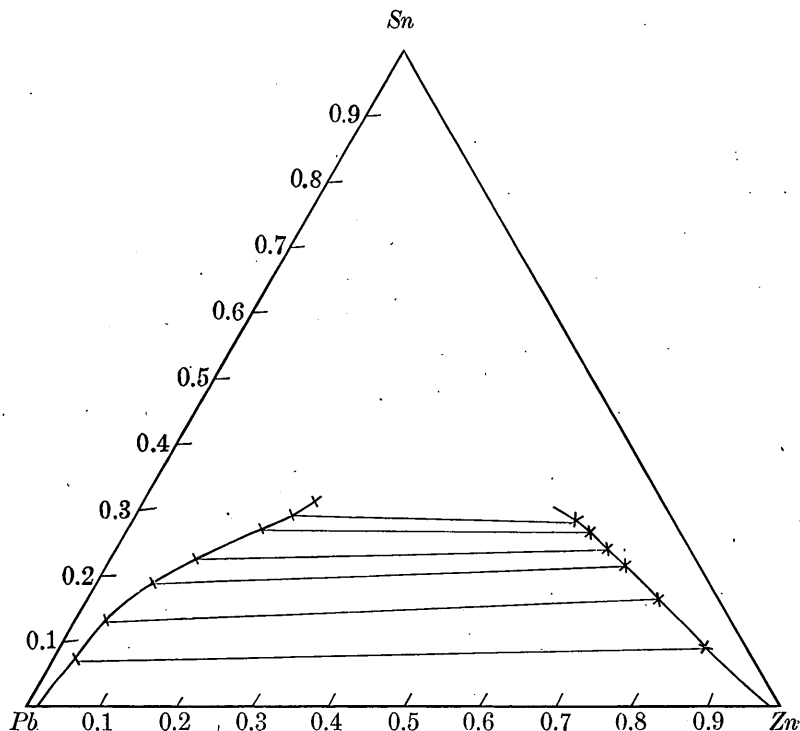1) Proceedings of the Royal Society of London, **48**, (1890), 29.

Fig. 2.

TABLE 2.

	Heavier layer.			Lighter layer.		Partition
Tin.	Lead.	Zinc.	Tin.	Lead.	Zinc.	coefficient.
0	.9870	.0130	0	.0157	.9843	—
.0701	.8987	.0312	.0928	.0539	.8533	1.324
.1277	.8298	.0425	.1636	.0800	.7564	1.281
.1929	.7317	.0754	.2156	.1004	.6840	1.118
.2284	.6580	.1136	.2394	.1139	.6467	1.048
.2712	.5490	.1790	.2662	.1213	.6125	.982
.2947	.5007	.2046	.2837	.1295	.5868	.963
.3166	.4574	.2260	—	—	—	—

In the present experiments weighed portions of lead, silver and zinc were melted in a glass tube somewhat larger than an

ordinary test-tube. This tube, being attached to an asbestos cardboard, was suspended in a larger vessel, for which the cardboard served as a lid. For this outer vessel a very big test-tube about 20 cm. in height and 4.5 cm. in diameter was found most suitable. In order to obtain a constant temperature phosphorus pentasulphide was kept boiling in this vessel.

Of the three metals used, the lead and the silver were commercially pure, the metallic impurities contained in them being in such minute quantities as not to affect the determination of the partition coefficient to any appreciable extent; the zinc was chemically pure.

The method of procedure was as follows. Zinc rods and pieces of lead were first filed to remove any oxide that might have been formed on them. The lead was melted in a porcelain crucible and the silver added to it. When the latter was completely dissolved, the mass was allowed to solidify, and cut in pieces of proper size. These together with pieces of zinc were introduced into the melting tube, care being taken to have the zinc pieces at the bottom. The tube was then fitted in the outer vessel in which powdered phosphorus pentasulphide had been put. At first a rapid current of carbon dioxide gas, purified and dried by being passed through sodium bicarbonate solution and concentrated sulphuric acid, was introduced into the inner tube to displace all the air, and then

Fig. 3.

a very slow and steady current of the gas was kept up all through the experiment in order to reduce the loss of the metals by oxidation. The outer vessel was heated by the
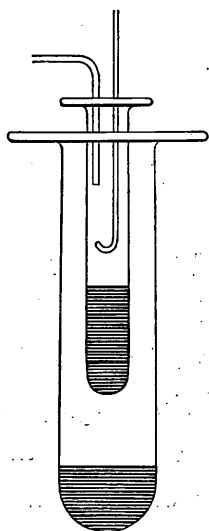
strong flame of a ring burner, the upper part of the tube being covered with asbestos paper to diminish the loss of heat by radiation. The height of the flame was so regulated that the dark brown vapour of the phosphorus pentasulphide reached to within a few centimeters of the top of the vessel and remained nearly constant the whole time. The metals in the inner tube lay well below the upper limit of the vapour so that all danger of cooling from above was excluded. Within a short time the metals became melted, and the mass was thoroughly stirred three times at intervals of five minutes. For this purpose a thin glass rod bent at one end was used. Finally the mass was kept in the melted condition for about five hours and a half, in order to secure a complete separation of the two layers. At the end of this period the flame was removed and the whole allowed to cool as rapidly as possible, so that the layers might not be disturbed and the alloys might solidify without a redistribution of the components.

The solidified lump of the metals consisted of two layers, the lighter in which zinc predominated and the heavier in which lead preponderated, each containing a small percentage of the other metal and the silver being unequally divided between them. These layers were cut in pieces with a saw parallel to the line of demarcation and the silver contents of the pieces were separately determined, VOLHARD's method of titration being employed. For the pieces from the lighter layer, which contained the greater portion of the silver, a decinormal solution of ammonium thiocyanate was used; while for the pieces from the heavier layer a twentieth to fiftieth normal solution was employed according to the amount of the silver contents.

The calculation of the ratio of the silver contents of the

two layers from the results of analysis gave very fluctuating values. Thus in some cases this ratio, or the partition co-efficient of silver between zinc and lead, was found to be as low as 45, while in others it was something like 150 or more. Not only was this discrepancy to be found with different samples, but pieces from the same lump cut at different distances from the line of demarcation gave different percentages of silver. Thus it was found in the lighter layer that the pieces nearer the line were richer in silver than those much removed from the same; while, the heavier layer showed an utter irregularity of distribution. After many trials in the case of the heavier layer it was found that the alloy was much contaminated with particles of zinc, especially on the surface, and that at some points the contamination had penetrated to some extent into the mass of the alloy. This may have happened owing to the particles of zinc oxide, already existing in the metal used or formed during the process of heating, persistently adhering to the sides of the glass tube and helping to retain particles of zinc, which would thus refuse to rise to the layer above even after vigorous stirring. The discrepancies in the zinc layer may have been due to the formation of minute crystals of a silver-zinc compound which tended to accumulate in the lower part of the layer even during the short time required for the mass to solidify.

To remove these irregularities the zinc layer was analysed as a whole mass. The whole of the lighter layer and a small part of the heavier layer next to it was cut with a saw, dissolved in nitric acid and titrated for silver as usual. In the solution the lead was determined as peroxide deposited electrolytically. The amount of zinc in the mass was determined by difference.

Previous to making these determinations, the solubility of

lead in zinc, and that of zinc in lead were separately esti-mated. For this purpose about 30 grammes of zinc and about 45 grammes of lead were kept fused in a tube under exactly similar conditions. After the mass had become cool, the per-centage of lead dissolved in the zinc was determined electrolyt-ically. For the determination of zinc in the lead the latter metal was removed as sulphate, and then the zinc was precipitated as sulphide and finally determined as oxide. From six deter-minations, the mean value found for the solubility of lead in the zinc at about 540°, the temperature of boiling phosphorus penta-sulphide, was 1.35 percent, and for that of zinc in the lead, 1.33 percent.

By the aid of these values it was possible to estimate the amount of the heavier layer which accompanied the lighter layer taken for analysis. The actual amount of the lighter layer analysed being thus known, the percentage of silver in it could be readily calculated.

To remove the discrepancies in the heavier layer there was no other way than to remove the zinc particles, which was done with a file and a knife. This was tedious work and it took many hours before the contamination was completely removed. The presence of zinc particles was discernible by the different hardness of the two metals, and also by etching with dilute nitric acid, by which the presence of the zinc particles was clearly depicted by the darkening in colour due to the in-numerable small particles of silver disseminated in them.

The amount of zinc taken for a single fusion was either 20 or 30 grammes ; that of lead either 45 or 60 grammes ; while the amount of silver varied from 0.2 to a little above 2 grammes. The results obtained are contained in the following table.

TABLE 3.

No.	Percentage of silver in the lighter layer.	Percentage of silver in the heavier layer.	Partition coefficient.
1.	0.75	0.0030	250
2.	0.99	0.0037	267
3.	2.14	0.0096	223
4.	2.31	0.0069	334
5.	3.16	0.0099	319
6.	3.64	0.0110	330
7.	3.65	0.0112	326
8.	3.92	0.0199	197
9.	4.43	0.0198	226
10.	5.24	0.0192	273
11.	5.42	0.0169	320
12.	5.45	0.0194	281
13.	5.54	0.0144	384
14.	6.26	0.0197	317

These results leave much to be desired. But the accurate determination of small quantities of silver contained in large amounts of the heavier layer is particularly difficult, and a tolerably wide range of error must be allowed even on this head alone. In the table the results are arranged in the order of the increasing percentage of silver in the lighter layer, and the partition coefficient does not show any tendency to rise or fall with the same. Hence we must conclude that it is actually constant at least for the more dilute solutions of silver in zinc and lead. This proves beyond doubt that whatever compounds of silver and zinc may occur in the lighter phase, other than those corresponding to the molecular formula $Ag\,Zn_m$ must be in such minute quantities that they do not influence the partition coefficient materially.

As to the numerical value of the partition coefficient the general mean of all the results obtained was 289. This is perhaps too low, because even a small amount of the lighter phase contaminating the heavier tends to decrease the observed partition coefficient, and as we have seen this source of error is particularly difficult to eliminate. If we omit the three lowest values (Nos. 3, 8, and 9) the average is raised to 309, which may not be very far from the truth. We may therefore affirm that at about 540° silver is about three hundred times more soluble in zinc than in lead.

The principal feature of PARKES' process of desilverisation is the partition of silver between solid zinc and liquid lead. In the first place argentiferous lead is melted and heated to a little above the melting point of zinc when a certain amount of the latter metal is added and the mixture stirred. The melt is then allowed to cool slowly. Scum consisting principally of zinc and containing silver (together with gold, copper, etc.) rises to the surface and is continually skimmed off. The temperature is allowed to fall nearly to the melting point of lead. Usually a second and sometimes a third or farther addition of zinc is made, the temperature being raised each time. In this way the desilverisation may be made practically complete.

The amount of zinc remaining in the desilvered lead depends upon the temperature at which the process is brought to an end; because the solubility of solid zinc varies considerably with the temperature. The following diagram will serve to make the matter clear. It is purposely not drawn to the scale, in order to bring out the essential features more clearly. A and F are respectively the melting point of lead and zinc. B and E are eutectic points, while C represents the temperature and the com-

position of the heavier liquid phase, which is in equilibrium
with the lighter liquid phase and solid zinc. *BC* is the curve
of solubility of solid zinc in
lead, and the curve *CDE*
shows the mutual solubility
of liquid zinc and lead in
each other. The curve *CDE*
and a point on the curve
BC have been determined
by SPRING and ROMANOFF,[1]
but their results agree nei-
ther with the determinations
of WRIGHT and THOMPSON
nor with my own, nor with
the experience of practical
metallurgists. I prefer
therefore to rely on the data
of WRIGHT and THOMPSON
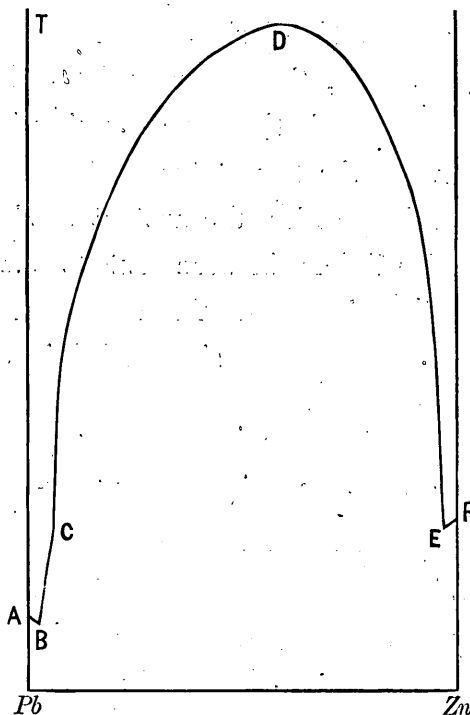and my own, though they
are rather meagre. From

Fig. 4.

these it appears that the curve *CD* proceeds upwards nearly
perpendicularly and by extrapolation the composition of the
point *C* is estimated at 1.2 percent zinc, the temperature being
that of the eutectic point *E*, which is only slightly below 420°
the melting point of pure zinc. Working at the temperature
of boiling mercury, that is about 358°, and employing the ap-

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1) Zeits. anorg. Chem., **13**, (1897), 29—35. That they have taken the liquid phases a
such, and not the solidified layers is much in their favour; but they did not wait long
enough before taking the samples for analysis. At lower temperatures the separation of the
two layers may have been incomplete, and so vitiated their results.

paratus described above, I found the solubility of solid zinc in melted lead to be 0.55%. Assuming the curve BC to be a straight line the composition of the point B is estimated at about 0.2% of zinc, the temperature being but very slightly below 325°, the melting point of lead.

Hence if the last scumming in PARKES' process takes place between the temperatures 325° and 360° as it appears to be the case in practice, the amount of zinc remaining in the desilvered lead will lie between 0.2 to 0.6%. That this amount is so small is important for the economical success of the process. The quantites of zinc added in excess of this are available for the extraction of silver.

The recent exhaustive study of zinc-silver alloy by PETRENKO[1] in TAMMANN's laboratory has shown the existence of a series of compounds and solid solutions. But in the temperature range which comes into consideration in PARKES' process none of the compounds has a realm of independent existence, so that we shall have a series of surfaces of solubility of zinc-silver solid solutions in lead, provided no ternary solid phase is formed. Hence it is clear that the partition coefficient must vary with the concentration, and the variation itself must show sudden changes at certain points. Yet for very dilute solid solutions the partition coefficient must be practically constant; for the law of dilute solutions also applies to solid solutions.

I have tried to test this conclusion experimentally, but without success. The temperature chosen was 358°, the boiling point of mercury. The three metals were melted together in a bath of sulphur vapour, then transferred into one of mercury vapour

1) Zeits. anorg. Chem., 48, (1906), 347.

and kept in it for about one hour, when most of the zinc separated out as scum. The scum was separated by filtering off the melted mass through closely packed glass wool under the pressure of about ten inches of mercury. The scum and the filtrate were analysed separately. The former contained most of the silver, and not a small quantity of lead which adhered to the particles of zinc-silver alloy. The latter contained such minute quantities of silver that its exact determination was difficult. This was accomplished by dissolving the mass in nitric acid and concentrating the solution (when the greater part of the lead separated out as nitrate and was removed) and then titrating it with a dilute solution of thiocyanate.

In three experiments the concentration of silver in solid zinc varied from 0.171 to 0.233% and the partition coefficient from 1300 to 5700. The discrepancy is no doubt due to the contamination of the liquid phase by solid particles which passed through the glass wool. But whether the highest value be near the truth or not can not be decided; for in this case the determination of the silver retained in the melted lead is very uncertain. Yet it is quite clear that the partition coefficient of silver between solid zinc and liquid lead is enormously large, and this fact explains the practical completeness with which the lead is desilverised in practice.

I very much regret that I must leave this investigation in this unsatisfactory form; for the time at my disposal is nearly over, and I can neither repeat nor extend the determinations.