XL.—The System: Ethyl Ether-Water-Potassium Iodide-Mercuric Iodide. Part I. The Underlying Three-Component Systems.

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THE formation of three partly miscible liquids in a four-component system has been observed from time to time, but has never been studied quantitatively with a view to elucidate the conditions of equilibrium underlying such a phenomenon.

The most convenient system for the purposes of such a study appeared to the author to be the system ethyl ether-water-potassium iodide-mercuric iodide, in which three liquid layers were observed by Marsh (T., 1910, **97**, 2297), who, however, made no attempt to investigate the question from the point of view of heterogeneous equilibrium.

Since ether has an appreciable vapour pressure at 20°, it was necessary to devise a special form of apparatus in which to agitate the mixture whilst equilibrium was being attained. This apparatus is shown in Figs. 1 and 2. It consisted of a glass tube *c*, that could be fixed into a metal clamp *d*, which was free to revolve in the jaws *ab*. The top of this tube was connected to a short shaft *gh*, which was fixed eccentrically to a pulley *m*, so that when this pulley revolved the tube was shaken violently backwards and forwards. This motion served to agitate the contents of the tube, and stir the water in the thermostat, in which it was immersed. The temperature was maintained constant to 0.1°. The tube was closed by means of an ordinary cork tied firmly with string.

The composition of the various solid phases was, where necessary, determined by the residue method described by Schreinemakers (*Zeitsch. physikal. Chem.*, 1893, **11**, 81; 1907, **59**, 641). The appearances of potassium iodide and mercuric iodide, however, are unmistakable, and it is only possible for confusion to arise between potassium mercuri-iodide and its hydrate, $\text{KHgI}_3 \cdot \text{H}_2\text{O}$, which have a similar appearance.

In analysing solutions and residues, the ether was first expelled

by the passage of a current of air previously dried by means of anhydrous calcium chloride. A special weighing bottle was therefore used, as shown in Fig. 3. The air leaving the bottle was then passed through a weighed tube containing anhydrous calcium chloride, in order to absorb any water-vapour carried over by the ether. The water was then expelled at a temperature slightly above 100° by the further passage of dried air. The potassium iodide in the solid residue was then estimated by Bray and MacKay's method (*J. Amer. Chem. Soc.*, 1910, **32**, 1193), in which the iodine is liberated by the addition of potassium permanganate in slight

FIG. 1.

FIG. 2.

FIG. 3.

Apparatus.

excess in the presence of an acid, extracted with carbon tetrachloride, and titrated with standard thiosulphate. The mercuric iodide, which is not affected by permanganate, was then obtained by difference.

The System: Potassium Iodide-Mercuric Iodide-Water.

This system has been studied at 30° as well as 20° in order to confirm the existence of potassium mercuri-iodide, KHgI_3 . The results obtained at 20° and 30° are given in tables I and II, and shown graphically in Figs. 4 and 5 respectively, and since they are alike in type, a discussion of the isotherm at 20° will also serve for that at 30° .

TABLE I.

The System: Potassium Iodide-Mercuric Iodide-Water at 20°.

No.	Percentage composition of solution.		Percentage composition of residue.		Solid phase.
	KI.	HgI ₂	KI.	HgI ₂ .	
1	59.2	—	—	—	KI
2	50.9	19.3	86.2	5.6	KI
3	47.5	25.4	85.3	7.6	KI
4	44.4	32.5	82.4	10.2	KI
5	41.3	39.6	76.2	16.4	KI
6	39.0	48.0	82.7	13.6	KI
7	38.2	51.2	83.6	13.5	KI
8	37.4	53.6	42.6	50.9	KI + KHgI ₃
9	37.8	52.6	35.1	57.4	KHgI ₃
10	35.1	52.2	32.1	60.0	KHgI ₃
11	35.5	51.2	30.3	61.1	KHgI ₃ , H ₂ O
12	26.7	50.3	17.6	74.3	KHgI ₃ , H ₂ O + HgI ₂
13	26.6	49.4	10.2	82.4	HgI ₂
14	23.7	40.2	—	—	HgI ₂
15	14.9	22.5	4.1	83.4	HgI ₂

TABLE II.

The System: Potassium Iodide-Mercuric Iodide-Water at 30°.

No.	Percentage composition of solution.		Percentage composition of residue.		Solid phase.
	KI.	HgI ₂	KI.	HgI ₂ .	
16	60.6	—	—	—	KI
17	40.0	53.0	61.0	37.0	KI + KHgI ₃
18	39.6	52.7	35.1	60.7	KHgI ₃
19	40.0	52.2	33.6	62.1	KHgI ₃
20	40.2	51.2	35.9	59.2	KHgI ₃
21	39.3	50.3	33.5	60.4	KHgI ₃
22	33.7	49.8	29.5	62.7	KHgI ₃
23	33.0	52.0	30.3	61.0	KHgI ₃
24	31.4	51.7	29.1	60.6	KHgI ₃ , H ₂ O
25	29.1	52.2	25.5	67.1	KHgI ₃ , H ₂ O

At 20° the following phases are stable in equilibrium with solution: Potassium iodide, potassium mercuri-iodide, potassium mercuri-iodide hydrate (KHgI₃, H₂O), and mercuric iodide.

It has been shown by Schreinemakers (*Zeitsch. physikal. Chem.*, 1909, **65**, 553) by means of the ζ function (thermo-dynamic potential) that the type of an isotherm in a system of two solid and one liquid components, the liquid component being regarded as solute, does not alter, provided that the solute does not combine with the two solids; thus he showed that in the system silver nitrate-ammonium nitrate-alcohol-water, in which the two solid components form two compounds, these compounds persist in both the three-component systems, and right through the four-component system. By an analogous process of reasoning, one may deduce that potassium and mercuric iodides do not form mixed crystals at 20°, as there is no evidence of this in the three-component systems. This is remarkable when the great tendency of mercuric

iodide to form mixed crystals with other iodides is remembered; on the other hand, the heterogeneous area often widens rapidly below the eutectic point, and in this case may have done so to such an extent that mutual miscibility has, for practical purposes, vanished.

One may also deduce from the above that a compound, potassium mercuri-iodide, occurs in the two-component system potassium iodide-mercuric iodide, probably at all temperatures.

The isotherm under discussion presents some remarkable features

FIG. 4.

20°.

for a system in which the components are two salts and water. The restricted extent of the three-phase areas, and the great extent of the unsaturated and two-phase areas, are very unusual.

The following is a résumé of the more important features of the diagram (Fig. 4):

Point *e* represents water; *f*, potassium iodide; *g*, mercuric iodide; *m*, potassium mercuri-iodide; and *n*, potassium mercuri-iodide hydrate ($\text{KHgI}_3 \cdot \text{H}_2\text{O}$).

Line *ab* represents the range of saturated solutions co-existing with solid potassium iodide; *bc*, with solid potassium mercuri-iodide;

cd , with solid potassium mercuri-iodide hydrate ($\text{KHgI}_3 \cdot \text{H}_2\text{O}$); and de , with solid mercuric iodide.

Point b represents a saturated solution co-existing with solid potassium iodide and potassium mercuri-iodide; c , with solid potassium mercuri-iodide and its hydrate; and d , with solid potassium mercuri-iodide hydrate and mercuric iodide.

Area fab represents mixtures of saturated solutions on ab + solid potassium iodide; bcm , on bc + solid potassium mercuri-iodide; cnd , on cd + solid potassium mercuri-iodide hydrate; edg , on

FIG. 5.

30°.

de + solid mercuric iodide; fbm represents mixtures of solution b + solid potassium iodide + solid potassium mercuri-iodide; mcn , of solution c + solid potassium mercuri-iodide + solid potassium mercuri-iodide hydrate; ndg , of solution d + solid potassium mercuri-iodide hydrate + solid mercuric iodide; and mng represents solid mixtures of potassium mercuri-iodide, its hydrate, and mercuric iodide.

On attempting to prepare a saturated solution of either of the double salts, the following phenomena occur. If water is added to potassium mercuri-iodide the composition of the mixture follows the line me . When n is reached, all the salt is converted into

potassium mercuri-iodide hydrate. Further addition of water causes the formation of solution *d*, together with solid mercuric iodide, until at *p* all the double salt is decomposed, and only solution *d* and solid mercuric iodide exist. As the mixture then follows the line *pe*, the solution follows the curve *de*, more mercuric iodide being formed as the proportion of water becomes greater, until at *e* the solution is almost pure water, since the solubility of mercuric iodide is negligible.

When solid mercuric iodide is added to a saturated solution of potassium iodide represented by *a*, the composition of the mixture follows the line *ag*. The first solid phase which separates is thus potassium mercuri-iodide hydrate ($\text{KHgI}_3 \cdot \text{H}_2\text{O}$).

The System: Potassium Iodide-Water-Ethyl Ether.

The results obtained in the investigation of this system at 20° are given in table III and shown diagrammatically in Fig. 6, where point *n* represents potassium iodide, *m* water, and *r* ether.

TABLE III.

The System: Potassium Iodide-Ethyl Ether-Water at 20°.

	Percentage composition of upper layer.			Percentage composition of lower layer.			Solid phase.
	KI	H ₂ O	Et ₂ O	KI	H ₂ O	Et ₂ O	
26	—	None.	—	59.2	40.8	—	KI
27	0.0	3.9	96.1	0.0	93.0	7.0	None.
28	0.4	0.4	99.2	55.6	40.7	3.7	KI
29	0.1	2.2	97.7	25.0	72.1	2.9	None.

The base line *mr* represents the heterogeneity which occurs in the system water-ether. On the addition of the third component, the limits of miscibility are naturally altered. In this case there is some indication of approaching homogeneity after saturation with potassium iodide is reached. It is therefore conceivable that at a higher temperature there would be an uninterrupted solubility curve from the solubility of potassium iodide in water to the same in ether.

The following is a brief consideration of the system.

The solubility of ether in water is represented by the point *x*, that of water in ether by the point *g*.

The solubility of potassium iodide in water is represented by the point *d*, that of potassium iodide in ether by the point *c*. This, in practice, is negligible.

The curve *da* represents the saturation curve of potassium iodide in water containing ether, *ch* that of potassium iodide in ether containing water. Further addition of ether to solution *a* in

contact with solid potassium iodide causes the separation of a second lighter layer, the composition of which is represented by h . Similarly, the addition of water to solution h in contact with solid potassium iodide causes separation of a second, denser layer, the composition of which is represented by a ; a and h are therefore invariant solutions; a is an aqueous solution saturated simultaneously with solid potassium iodide and ethereal solution h , whilst h is an ethereal solution saturated simultaneously with solid potassium iodide and aqueous solution a ; a and h are therefore

FIG. 6.

conjugate solutions in equilibrium with one another and with solid potassium iodide.

In Fig. 6 the curve ax represents aqueous solutions unsaturated with respect to solid potassium iodide, but in equilibrium with ethereal solutions represented by points on gh , whilst gh represents ethereal solutions unsaturated with respect to solid potassium iodide, but in equilibrium with aqueous solutions represented by points on the curve ax ; ax and hg are therefore conjugate curves. A solution represented by a point on one of these is in equilibrium with a solution represented by a definite point on the other. These curves, ax and hg , naturally end in the points x and g respectively.

We can now distinguish the portions into which the triangle mnr is divided.

Area dna represents mixtures of aqueous solutions on da + solid potassium iodide; chn represents mixtures of ethereal solutions on ch + solid potassium iodide; nah represents mixtures of the two conjugate solutions a and h + solid potassium iodide; $daxm$ represents unsaturated aqueous solutions; $chgr$ represents unsaturated ethereal solutions; and $axgh$ represents mixtures of two conjugate solutions (aqueous and ethereal) represented by conjugate points on ax and gh respectively.

The behaviour of a mixture of two components when the third is added to it is as follows:

If na is drawn and produced to meet mr in p , whilst nh is drawn and produced to meet mr in q , the line mr is divided into three parts, namely, mp , pq , and qr .

We will first consider a mixture of ether and water represented by a point k on mp . If, as in Fig. 6, k lies between m and x , this mixture is homogeneous, whilst if k lies between x and p , two layers, of compositions represented by x and g respectively, are formed. If now potassium iodide is added to this mixture, its composition follows the line kn . This line cuts the curve da , and enters the area dna . The addition of potassium iodide to the mixture k therefore finally gives a homogeneous saturated solution represented by a point on da . Similar considerations show that any mixture represented by a point on qr gives, on addition of potassium iodide, a saturated homogeneous solution represented by a point on ch .

It will further be observed that if k lies between m and x it is possible for the line kn to cut the curve xa in two places, e and f . When this is the case, the addition of potassium iodide causes the separation of an ethereal layer at e , which disappears again at f , where the mixture becomes homogeneous. This ethereal layer is, of course, very small in amount.

Any mixture of ether and water represented by a point j between p and g exists throughout as two layers. These are first represented by x and g , and as potassium iodide is added, they follow the curves xa and gh until, when the mixture reaches b , they have compositions represented by a and h respectively. Further addition of potassium iodide leaves these layers unchanged.

The phenomena occurring when potassium iodide is added to an ether-water mixture lying between g and q can be seen at once from the figure.

When ether is added to an unsaturated solution of potassium iodide in water, such as that represented by t , the composition of

the mixture follows the line tr . At v an upper or ethereal layer commences to separate. If the line tr coincides with the conjugation line through v , as in Fig. 6, the composition of this upper layer is represented by w . As the mixture moves along vw the compositions of the two layers remain unchanged, but the relative amount of w increases. At any point y the ratio of the two liquids is given by the relationship:

$$\frac{\text{amount of } v}{\text{amount of } w} = \frac{\text{length of } wy}{\text{length of } vy}.$$

When w is reached all the lower layer v has disappeared. The solution then remains homogeneous on further addition of ether.

In most cases, however, tr does not coincide with a conjugation line, but cuts through a number of them. This means that the composition, as well as the ratio of the two liquids, changes as ether is added. Since, however, in reality the curve hg is very short, the line tr always approximates to a conjugation line, and the compositions of the two layers vary only slightly.

The addition of water to a mixture of ether and potassium iodide represented by z almost immediately (at u) causes a separation into two layers, represented by a and h , in contact with solid potassium iodide. At b all the potassium iodide just dissolves, the solutions still being represented by a and h . As the mixture then moves from b to s , these solutions follow the curves ax and hg , whilst the relative amount of the ethereal solution decreases. At s the ethereal solution just disappears, and the aqueous solution remains homogeneous on further addition of water.

The System: Ethyl Ether-Potassium Iodide-Mercuric Iodide.

The equilibrium obtained in this system is of a remarkable character. The results are given in table IV and shown diagrammatically in Fig. 7, and the more important features of this diagram may first be briefly considered.

Point a represents potassium iodide; s , ethyl ether; c , mercuric iodide; and j potassium mercuri-iodide.

TABLE IV.

The System: Potassium Iodide-Mercuric Iodide-Ethyl Ether at 20°.

	Percentage composition of upper layer.		Percentage composition of lower layer.		Percentage composition of residue.		Solid phase.
	KI.	HgI ₂ .	KI.	HgI ₂ .	KI.	HgI ₂ .	
30	1.1	2.8	None.		51.0	41.9	KI + KHgI ₃
31	1.1	2.4	17.6	53.2	25.6	67.4	KHgI ₃
32	0.8	2.5	16.5	56.1	—	—	HgI ₂
33	None.		17.0	58.2	18.3	71.6	KHgI ₃ + HgI ₂

Point *e* represents a saturated solution co-existing with solid potassium iodide and solid potassium mercuri-iodide; points *f* and *h* represent two conjugate solutions co-existing with solid potassium mercuri-iodide; *g* and *m*, with solid mercuric iodide; point *k* repre-

[illegible]

Area *defgb* represents unsaturated solutions containing a small proportion of dissolved salts; *hkm* represents unsaturated solutions containing a large proportion of dissolved salts; *ade* represents mixtures of solutions on *de* + solid potassium iodide; *efj*, on *ef* + solid potassium mercuri-iodide; *fmg* represents mixtures of two conjugate solutions on *fg* and *hm* respectively; *bgc* represents mixtures of solutions on *bg* + solid mercuric iodide; *hjk*, on *hk* + solid potassium mercuri-iodide; *kmc*, on *mk* + solid mercuric iodide; *aej* represents mixtures of solution *e* + solid potassium iodide + solid

potassium mercuri-iodide; fjh , f and h + solid potassium mercuri-iodide; gmc , g and m + solid mercuric iodide; and $jk c$, k + solid potassium mercuri-iodide + solid mercuric iodide.

It will be noticed at once that the saturation curve of potassium mercuri-iodide is divided into the two parts cf and hk , whilst that of mercuric iodide is divided into the two parts bg and mk . These two saturation curves intersect at k , which thus represents a solution saturated with both solids. Both these saturation curves are divided into two portions by a binodal curve, k_1xfgk_2mhy , which cuts across them. Only the parts fg and hm , representing two series of conjugate solutions, are stable. The metastable parts, both of the binodal curve and of the saturation curves, are indicated by dotted lines.

Unfortunately, the actual range of all the curves is exceedingly small, but the form of the isotherm as shown in Fig. 7 is deduced from the experimental evidence given below.

There is no formation of two liquid layers in any of the three two-component systems from which the three-component system is built up.

Both potassium iodide and mercuric iodide are practically insoluble in ether, so that in the ordinary way it might be expected that the addition of a small quantity of mercuric iodide to a solution already saturated with potassium iodide, and containing a considerable quantity of that salt as solid phase, would merely cause the solution to become saturated with respect to potassium iodide and potassium mercuri-iodide; the formation of the double salt can be premised on the law of corresponding isotherms. The actual course of events, however, is different from the above scheme.

The experiment described above causes the separation of a heavy liquid rich in potassium iodide and mercuric iodide, which, on continued shaking, disappears, and leaves the solution saturated with respect to potassium iodide and potassium mercuri-iodide.

The transitory formation of this heavy liquid may be readily explained by reference to the diagram, in which the whole of the binodal curve is shown, the stable part by complete lines, the metastable part by dotted lines. A consideration of the ζ surfaces shows us that if the metastable prolongation of the saturation curve of potassium iodide cuts the metastable portion of the binodal curve, we can obtain two liquid layers in equilibrium with solid potassium iodide. The conditions for such a metastable equilibrium are shown in the diagram by the area axy , in which x and y represent the two liquid layers. This area is divided up into two stable areas representing the following equilibria: (1) potassium

iodide + potassium mercuri-iodide + solution *e*, and (2) potassium mercuri-iodide + solutions on *ef*.

Since we started with a solution containing a considerable excess of solid potassium iodide, it is evident that the ultimate stable equilibrium will be potassium iodide + potassium mercuri-iodide + solution *e*.

If we take some of solution *e* saturated with potassium iodide and potassium mercuri-iodide, but containing only potassium mercuri-iodide as solid phase, and add mercuric iodide to it, a second liquid layer is formed almost at once, which does not disappear on continued shaking. This means that we rapidly traverse the small range of solutions on *ef* saturated with potassium mercuri-iodide, and arrive in the complex area, *fjh*, which represents mixtures of potassium mercuri-iodide with solutions *f* and *h*.

If a complex consisting of a small quantity of solution *f* and a large quantity of solid potassium mercuri-iodide and solution *h* is now taken, and solid mercuric iodide added to it, the solution *f* disappears, and if sufficient mercuric iodide is added, we obtain a solution saturated with respect to two solid phases, namely, potassium mercuri-iodide and mercuric iodide. This means that the complex of solid and solution has entered the area *jk*.

If, on the other hand, the two solutions *f* and *h* saturated with potassium mercuri-iodide and containing this salt in slight excess are treated with small quantities of solid mercuric iodide, the solid phases disappear, and we enter a two liquid region. This is shown in the diagram by *fhmg*.

The addition of a large excess of mercuric iodide causes the formation of two liquid layers saturated with respect to mercuric iodide. This equilibrium is also attained when potassium iodide is added to a saturated solution of mercuric iodide in ether, containing an excess of that salt. It is represented by the area *gmc*.

The author is carrying out a further series of observations on this system at other temperatures.

The System: Mercuric Iodide-Water-Ethyl Ether.

Since mercuric iodide is practically insoluble in ethyl ether and water, and in all mixtures of these two components, no points have been determined in this system, which is similar in type to the system potassium iodide-water-ethyl ether.

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