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Now we shall seek the position of the 6 bivariant regions. From curve (1) = 2 + 3 + 4 the regions 23, 24 and 34 are starting. The region 23 extends itself between the curves (1) and (4); it is indicated in fig. 2 by 23. The region 24 is situated between the curves (1) and (3); the region 34 is situated between the curves (1) and (2) and therefore, extends itself over curve (2) [fig. 2]. [We keep in mind with this that each region-angle is smaller than  $180^\circ$ .]

When we act in the same way with the regions which start from the curves (2), (3) and (4) we find a partition of the regions as in fig. 2.

Previously we have deduced: each region, which extends itself over the stable or metastable part of curve ( $F_p$ ) contains the phase  $F_p$ . We see the confirmation of this rule in fig. 2. The metastable part of curve (1) intersects the region 14, the stable part of this curve the region 12; both the regions contain the phase 1. The metastable part of curve (2) intersects the regions 12 and 24, which contain both the phase 2; the metastable part of curve (3) intersects the regions 13 and 34 which contain both the phase 3. The metastable part of curve (4) intersects the region 14, the stable part of this curve is covered by the region 34; both the regions contain the phase 4.

The following is apparent from the preceding considerations. In all binary systems the partition and the position of the curves and the regions will respect to one another starting from a quadruple-point, is always the same; it can be represented by fig. 2.

(To be continued).

**Chemistry.** — “*Compounds of the Arsenious Oxide.*” II. By Prof. F. A. H. SCHREINEMAKERS and Miss W. C. DE BAAT.

*a. Introduction.*

By RÜDORFF<sup>1)</sup> and others compounds are prepared of the  $As_2O_3$  with halogenides of potassium, sodium and ammonium.

These compounds were obtained by treating solutions of arsenites (viz. solutions of  $As_2O_3$  in a base) with the corresponding halogenides.

RÜDORFF describes the compound  $As_2O_3 \cdot NH_4Cl$ , which we have found also; he also describes the compound  $(As_2O_3)_2 \cdot KCl$ , which we have not found.

In order to obtain these compounds, we have, however, worked in quite another manner; for this we have brought together water,

<sup>1)</sup> FR. RÜDORFF. Ber. 19 2668 (1886), 21 3051 (1888).

$As_2O_3$  and the halogenide, consequently without first dissolving  $As_2O_3$  in a base. Therefore, we had to deal with equilibria in the ternary systems: water- $As_2O_3$ -halogenide.

Of course we have to bear in mind in judging the results, that the possibility is never excluded that besides the compounds which have shown themselves, others might exist, that even the compounds found might be metastable.

b. The system  $H_2O - As_2O_3 - KCl$  at  $30^\circ$ .

In this system at  $30^\circ$  the two components  $As_2O_3$  and  $KCl$  occur as solid phases and further a compound, which we shall call  $D$ . The composition of this compound is defined with the aid of the rest-method, but is not known exactly. It is sure, however, that it has not the composition  $(As_2O_3)_2(KCl)$ ; it is about  $(As_2O_3)_6(KCl)_5$  or  $(As_2O_3)_6(KCl)_4$ ; we shall refer to this further.

In fig. 1 in which the point  $Z$  indicates the component  $KCl$  the isotherm of  $30^\circ$  is represented schematically, this isotherm consists of three branches,

$ab$	represents the solutions, saturated with $As_2O_3$
$bc$	" " " " " " $D$
$cd$	" " " " " " $KCl$ .

The composition of the solution  $b$ , which is saturated with  $As_2O_3 + D$ , has not been defined. It is apparent from table 1 that its percentage of  $KCl$  will be between 10.37 and 11.22 % and that its percentage of  $As_2O_3$  will be somewhat higher than 2.46 %. Further it is apparent from table 1 that the solubility of  $As_2O_3$  with increasing percentage of  $KCl$  of the solution increases a little, viz. from 2.26 % to a little over 2.46 %; consequently the point  $b$  is situated somewhat

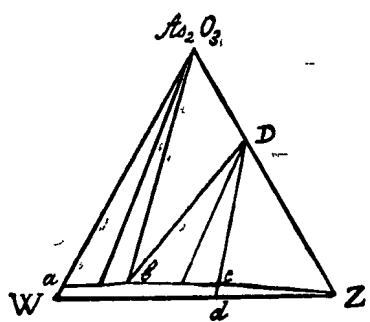


Fig. 1.  
a little by adding  $KCl$ , until the compound  $D$  is separated, after which the solubility decreases. [from 2.26 % in pure water (point  $a$ ) towards 0.78 % in a solution saturated with  $KCl$  (point  $c$ )].

No other points besides both the terminating points *c* and *d* have been defined of curve *cd*, which represents the solutions saturated with *KCl*.

We find united in table 1 the results of the different analyses; all the small bottles have been shaken in a thermostat during from three to five weeks. Although the  $As_2O_3$  and the compound *D* formed both an extremely fine powder, the eye could easily distinguish them by their different behaviour on sinking.

TABLE 1.

Composition in percentages by weight at 30°					
of the solution			of the rest		
Nº.	% $As_2O_3$	% <i>KCl</i>	% $As_2O_3$	% <i>KCl</i>	solid phase
1	2.26	0	—	—	$As_2O_3$
2	2.40	6.58	84.05	1.05	"
3	2.46	10.37	82.48	2.13	"
4	2.10	11.22	36.84	17.07	<i>D</i>
5	1.77	13.59	18.74	15.88	"
6	1.52	15.89	37.45	20.06	"
7	1.34	17.72	32.81	20.62	"
8	1.10	20.67	19.73	21.75	"
9	0.995	22.38	23.53	22.31	"
10	0.898	22.92	11.36	23.12	"
11	0.841	25.23	26.93	24.70	"
12	0.783	26.96	12.23	28.16	<i>D</i> + <i>KCl</i>
13	0.777	27.11	(8)	(32)	<i>D</i> + <i>KCl</i>
14	0	27.2	—	—	<i>KCl</i>

The solubility of *KCl* in pure water (nº. 14 of table 1) has not been determined but has been taken from the tables of LANDOLT-BÖRNSTEIN.

As table I shows, besides the compositions of several solutions, also the rests belonging to them, are determined; the numbers placed between parentheses in nº. 13 indicate however the composition of the complex. In order to examine if in the determinations errors might have occurred by analysis or anything else, several complexes were

weighed accurately; this complex must then be situated on a straight line with the solution and the rest formed from this. This was always the case in this examination.

When in fig. 1 we draw the conjugationlines, which unite the solutions of branch  $bc$  with the corresponding rests, those do not go, as is drawn in fig. 1, through the same point  $D$ . When we call the percentages of  $As_2O_3$  and water of a solution  $Y_l$  and  $W_l$ , those of the corresponding rest  $Y_r$  and  $W_r$ , and when we call  $Y_f$  the percentage of  $As_2O_3$  of the point  $D$  (the point of intersection of the line liquid-rest with the side  $As_2O_3-W$ ) then we find:

$$Y_f = Y_r + \frac{Y_r - Y_l}{W_l - W_r} \times W_r.$$

When we calculate with the aid of this formula  $Y_f$  for the determinations 4—11 of table 1, we find

76.29; 76.35; 75.52; 75.45; 75.04; 77.86; 75.65; 76.30.

As the compound  $As_2O_3 \cdot KCl$  contains 72.6%  $As_2O_3$  and the compound  $(As_2O_3)_2 \cdot KCl$  contains 84.1%  $As_2O_3$ , the point  $D$ , therefore cannot represent this compound, it is more probably  $(As_2O_3)_6 \cdot (KCl)_5$ , which contains 76.1%  $As_2O_3$  or  $(As_2O_3)_5 \cdot (KCl)_4$ , which contains 76.9%  $As_2O_3$ . When we take the average of the eight determinations, then we find 76.08%  $As_2O_3$ , which is in accordance with the composition of  $(As_2O_3)_6 \cdot (KCl)_5$ .

When we draw in fig. 1 the line  $WD$ , we see that this does not intersect the saturationcurve of  $D$ , but that of the  $As_2O_3$ . Consequently the compound is not soluble in water without decomposition, but is decomposed with separation of  $As_2O_3$ .

c. The system:  $H_2O-As_2O_3-NH_4Cl$  at  $30^\circ$ .

In this system both the components  $As_2O_3$  and  $NH_4Cl$  and further a compound  $D$  occur at  $30^\circ$ . We found for the composition of this compound, which is determined with the aid of the rest-method,  $As_2O_3 \cdot NH_4Cl$

We may represent the isotherm of  $30^\circ$  in this system again schematically, by fig. 1; the anglepoint  $Z$  represents then the  $NH_4Cl$  and the point  $D$  the compound  $As_2O_3 \cdot NH_4Cl$ . Consequently the isotherm consists again of three branches, viz.:

$ab$ , the saturationcurve of  $As_2O_3$   
 $bc$ , „ „ „ „  $As_2O_3 \cdot NH_4Cl = D$   
 $cd$ , „ „ „ „  $NH_4Cl$ .

It is apparent from table 2 that the solubility of the  $As_2O_3$  remains invariable within the errors of analysis on increasing percentage of  $NH_4Cl$  of the solutions. The solution (point *b*) which contains 7.08%  $NH_4Cl$ , contains 2.28%  $As_2O_3$ , while the aqueous saturated solution (point *a*) contains 2.26%  $As_2O_3$ . Further it appears from table 2 that the solubility of the compound decreases on increasing percentage of  $NH_4Cl$  of the solutions; in point *b* (N<sup>o</sup>. 3 in table 2) the solution contains still 2.28%  $As_2O_3$ , in the solution, saturated with  $NH_4Cl + D$  (point *c*; N<sup>o</sup>. 9 in table 2) the percentage of  $As_2O_3$  is however lowered to 0.291%. Consequently the  $As_2O_3$  is less soluble in a solution, saturated with  $NH_4Cl$  than in a saturated solution of  $KCl$ .

Only the terminatingpoints *c* and *d* of curve *cd*, which represents the solutions saturated with  $NH_4Cl$ , have been determined.

In table 2 the results of the determinations are united; all the small bottles have been shaken during 3 to 5 weeks in a thermostat. Also here, although the  $As_2O_3$  and the compound are both an extremely fine powder, the eye could easily distinguish them by their different behaviour on sinking.

TABLE 2.

Composition in percentages by weight at 30°					
of the solution			of the rest		
N <sup>o</sup> .	% $As_2O_3$	% $NH_4Cl$	% $As_2O_3$	% $NH_4Cl$	solid phase
1	2.26	0	—	—	$As_2O_3$
2	2.29	3.86	82.55	0.34	"
3	2.28	7.08	73.09	6.67	$As_2O_3 + As_2O_3 \cdot NH_4Cl$
4	1.31	9.08	44.59	15.90	$As_2O_3 \cdot NH_4Cl$
5	0.993	11.76	48.35	17.09	"
6	0.490	21.09	27.43	20.93	"
7	0.432	24.61	47.11	22.14	"
8	0.398	27.18	39.13	23.81	"
9	0.291	29.52	(8)	(35)	$As_2O_3 \cdot NH_4Cl + NH_4Cl$
10	0	29.3	—	—	$NH_4Cl$

The solubility of the  $NH_4Cl$  in pure water (N<sup>o</sup>. 10 of table 2) is not determined, but taken from the tables of LANDOLT-BÖRNSTEIN, the

numbers placed between parentheses do not indicate the composition of the rest but that of the complex.

When we draw in fig. 1 the line  $WD$ , then we see that it does intersect curve  $ab$ , but not  $bc$ . The compound  $As_2O_3 \cdot NH_4Cl$  is, consequently decomposed by water with separation of  $As_2O_3$ .

d. *The system  $H_2O-As_2O_3-NaCl$ .*

In this system at  $30^\circ$  only the two components  $As_2O_3$  and  $NaCl$  occur as solid phases, we have not found a compound.

We may represent the isotherm schematically by fig. 2; then the anglepoint  $Z$  represents the  $NaCl$ . Consequently the isotherm consists of two branches, viz.:

$ab$  the saturation curve of  $As_2O_3$   
 $bc$  " " " "  $NaCl$ .

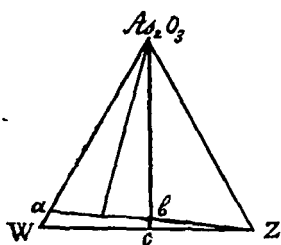


Fig. 2.

It is apparent from table 3 that the solubility of  $As_2O_3$  decreases with increasing percentage of  $NaCl$  of the solutions. The saturated aqueous solution of  $As_2O_3$  contains viz. 2.26%  $As_2O_3$ , the solution saturated with  $NaCl + As_2O_3$  contains only 1.58%  $As_2O_3$ . As a saturated solution of  $KCl$  contains 0.78%  $As_2O_3$  and a solution saturated with  $NH_4Cl$  0.291%  $As_2O_3$ , it is apparent

that  $As_2O_3$  is expelled least by  $NaCl$  and the most by  $NH_4Cl$  from its solution.

T A B L E 3.

Composition in percentages by weight at $30^\circ$					
of the solution			of the rest		
No.	% $As_2O_3$	% $NaCl$	% $As_2O_3$	% $NaCl$	solid phase
1	2.26	0	—	—	$As_2O_3$
2	2.18	5.93	(5)	(16)	"
3	2.04	11.49	(10)	(14)	"
4	1.88	16.86	(15)	(12)	"
5	1.71	22.06	74.12	5.90	"
6	1.58	26.17	(30)	(5)	$As_2O_3 + NaCl$
7	0	26.5	—	—	$NaCl$

In table 3 the results of the determinations are united, all the small bottles have been shaken during three to five weeks in a thermostat.

The solubility of the  $NaCl$  in pure water (N<sup>o</sup>. 7 of table 3) is taken from the tables of LANDOLT-BÖRNSTEIN; the numbers placed between parentheses indicate again the compositions of the complexes (consequently not of rests).

*(To be continued).*

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**(July 13, 1915).**

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