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F.A.H. Schreinemakers & Milikan, J., On a few oxyhaloids, in: KNAW, Proceedings, 15 I, 1912, 1912, pp. 52-54

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$$h(A-B) = 1,$$
 $2k(C-C') = 0,$ $\frac{k^3}{h}(D-E) = 0$
 $-k(A+B) = 0,$ $-2h(C+C') = v,$ $-\frac{h^3}{k}(D+E) = v$

which may be satisfied by

$$A + B = 0, \quad D - E = 0, \quad C - C' = 0$$

or

 $2a' = i(a-2b'+c), \quad 2c' = i(a+2b'+c), \quad 2b = i(a-c).$

Thus (5) belongs to class III.

In the same way it is seen that

- (6) is a special case of class II
- (8) belongs to class IV
- (10) is a special case of class III.

The eleven equations given by DULAC are therefore contained in the preceding 7 classes.

Chemistry. — "On a few oxyhaloids." By Prof. F. A. H. SCHREINE-MAKERS and Mr. J. MILIKAN.

Of the chlorides, bromides, and iodides of the alkaline earths several oxy-salts have already been described; in order to further investigate the occurrence or non-occurrence of these salts, to determine the limits of concentration between which they exist and, if possible, to find other oxyhaloids, different isotherms have now been determined and by means of the "residue method"¹) the compositions of the solid phases have been deduced therefrom. Here, we will discuss only the solid substances that can be in equilibrium with solution.

The system $CaCl_2 - CaO - H_2O$.

Temperature 10° and 25° . At both these temperatures occur, besides CaCl₂. 6 H₂O and Ca (OH)₂, as solid phases the oxychlorides:

CaCl₂. 3 CaO. 16 H₂O and CaCl₂. CaO. 2 H₂O

the composition of the second salt may be expressed also as:

$$Ca \left\langle \begin{array}{c} Cl\\ OH \end{array} \right\rangle \cdot \frac{1}{2}H_{s}O$$

This latter oxychloride has already been found previously by a determination of the isotherm of $25^{\circ 2}$; the first one was then

¹) F. A. H. SCHREINEMAKERS. Die heterogenen Gleichgewichte von H. W. BAKHUIS ROOZEBOOM. III^a 149.

²) F. A. H. SCHREINEMAKERS and TH. FIGEE, Chem. Weekbl. 683 (1911).

already known¹). From their determinations, SCHREINEMAKERS and FIGEE thought they might conclude that the other oxy-salt should have the composition

As the region of existence of this salt at 25° was, however, still but very small, a slight error in the determination of this composition was still possible.

Temperature 50°. At this temperature occur, besides $CaCl_2 \cdot 2H_2O$ and $Ca(OH)_2$, also the two oxychlorides:

$$Ca < Cl OH \cdot H_2O$$
 and $Ca < Cl OH \cdot 2H_2O$

as solid substances in proximity to their saturated solutions. The first one already exists at 10° and 25° , the last one had not been described, as yet.

The system: $CaBr_{\bullet}-CaO-H_{\bullet}O$.

In this system, only the isotherm of 25° has been determined; as solid phases occur, besides CaBr₂. 6 H₂O and Ca (OH)₂, the oxybromides:

CaBr₃. 3 CaO. 16 H₂O and 3 CaBr₂. 4 CaO. 16 H₂O

The latter salt was not known up to the present; the first one has been described previously. 2)

The system: $BaCl_{a}$ —BaO— $H_{a}O$.

In this system the isotherm of 30° has been determined³); as solid phase occurs here, besides Ba Cl₂ . $2\dot{H}_2O$ and Ba $(OH)_2$. $8H_2O$, the oxychloride:

Ba Cl₂. BaO. 5H₂O or Ba
$$\begin{pmatrix} Cl \\ OH \end{pmatrix}$$
. 2H₂O

This salt had already been prepared and described previously "); the two oxychlorides:

Ba Cl (OH). 3¹/, H,O and Ba Cl (OH). 2Ba Cl,

also described previously, were not found at 30°.

The system: Ba Br_{1} -Ba O-H₂O.

In this system the isotherm of 25° has been determined; as solid

¹) Rose, Schweigers Journ. 29, 155.

DITTE. Compt. rend. 91, 576.

ANDRÉ, Compt. rend. 92, 1452.

²) E. TASSILLY. Compt. rend. 119, 371.

Ann. Chim. et Phys. [7] 17, 38.

⁸) F. A. H. SCHREINEMAKERS. Zeitschr. f. Phys. Chem. 68 88 (1909).

⁵) BECKMANN, Ber. 14 2151 (1881)

André. Compt. rend. 93, 58; 98, 572.

phase occurs, besides Ba Br, 2H₂O and Ba (OH)₃. 8H₂O, the oxybromide:

Ba Br, BaO ,
$$5H_2O$$
 or Ba $\begin{pmatrix} Br \\ OH \end{pmatrix}$, $2H_2O$

This salt has already been described previously ¹); the other oxybromide:

Ba Br(OH) . 3H,O

which has also been described ') was not found at 25°.

The system: $Ba I_2 - Ba O - H_2 O$.

In this system also, the isotherm of 25° has been determined; in addition to Ba I₂. 7H₂O, Ba I₃. 2H₂O and Ba (OH)₃. 8H₂O the oxy-iodide:

Ba I₂ . BaO . 9H₂O or Ba
$$\begin{pmatrix} I \\ OH \end{pmatrix}$$
 . 4H₂O

also described previously, occurs as solid phase.²)

Besides the above systems, various other ones are now being investigated; the results of this research will be communicated later.

Physics. — "Accidental deviations of density in mixtures". By Dr. L. S. ORNSTEIN (Communicated by Prof. H. A. LORENTZ).

The theory of accidental deviations of density in mixtures does not differ, as for the principles, from that of the deviations of density in systems containing only one kind of molecules. To calculate these deviations I shall apply the canonical ensembles of GIBBS³).

1. Let us suppose a mixture of k substances to be in a volume v, n_1 being the number of molecules of the kind 1, n_z that of the kind z, and n_k that of the kind k. Besides the coordinates and moments of the centres of gravity, a number of internal coordinates and moments can be used to characterize the state of the molecules. Let us imagine a canonical ensemble built up of those systems. We shall denote by $x_{11}, y_{11}, z_{11}, \ldots, z_{1n1}$ the coordinates of the centres of gravity for the molecules of the first kind, those of the z-molecules will be represented by x_{z1}, \ldots, z_{znz} .

In order further to characterize the system, we shall introduce

¹) BECKMANN, J. f. prakt. Chem. N. F, 27 132 (1883).

²) BECKMANN. Ber. 14, 2156.

E. TASSILLY, Compt. rend. 120, 1338.

³) I shall confine myself to a single phase, the coexistence of phases offering no particular difficulties. I dealt with this question in my dissertation (comp. p. 114).