

electrodes with different quantities of mercury may be made beforehand, and then they may be immersed in a non-aqueous solution of an aluminium salt, to determine the electric potential.

Without entering here further into the method of experimenting, we will state already now that the coexisting electrolyte is always relatively richer in aluminium than the mixed crystal, so that it could be deduced with certainty from this that the E,X-figure of the system Al-Hg belongs to the second type.

But what is remarkable is that though in virtue of the concentration of the coexisting phases it would be expected that the potential of the Aluminium in an Al-salt solution becomes less negative on addition of a little of a mercury salt, just the reverse takes place, and even to a very considerable degree.

This exceedingly remarkable phenomenon shows that, as was already pre-supposed before, the mercury dissolved in aluminium is a catalyst for the internal conversions in the aluminium. The metal magnesium, which is being examined by Mr. BECK, behaves in an analogous way, but the effects are less.

In a following communication we shall enter more deeply into the interesting phenomenon mentioned here.

*Laboratory for General and Inorganic  
Chemistry of the University.*

Amsterdam, June 1920.

**Chemistry.** — “*The Existence of Hydrates in Aqueous Solutions*”.

By Prof. A. SMITS, L. v. D. LANDE, and P. BOUMAN. (Communicated by Prof. P. ZEEMAN).

(Communicated at the meeting of December 18, 1920).

Since the research “On Retrogressive Melting-Point Lines”<sup>1)</sup>, in which an indirect proof was given for the presence of hydrated  $\text{Na}_2\text{SO}_4$  molecules in the aqueous solution, attempts have now and then been made to find other methods, which might be able to give an answer to the question whether formation of hydrates takes place in the aqueous solution, also in cases of melting-point lines with normal courses.

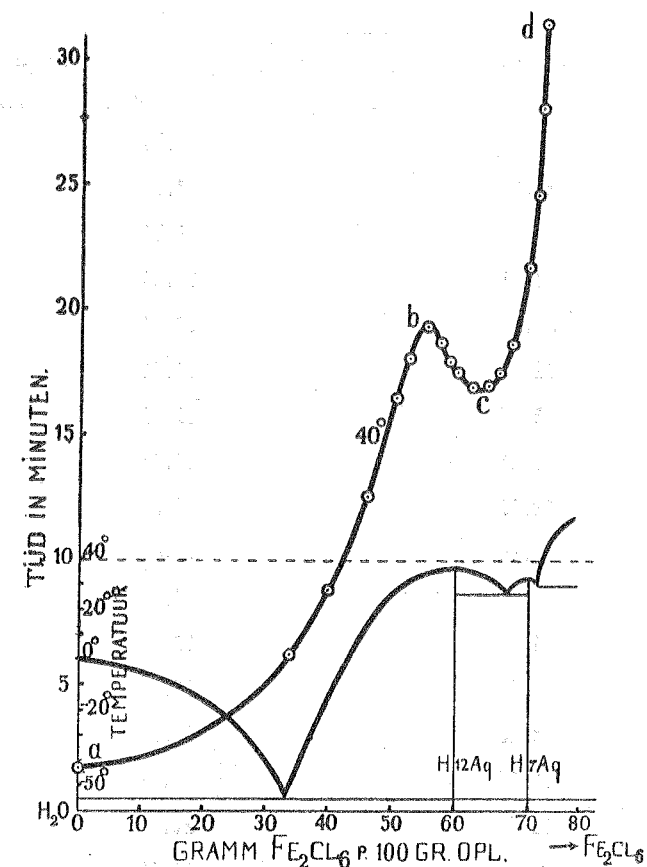


Fig. 1.

<sup>1)</sup> SMITS, These Proc. Vol. 14 p. 170 (1911).

Thus at constant temperature different properties of aqueous solutions of hydrate-forming substances, as e.g. spec. gravity, surface tension, refraction etc. were studied as function of the concentration, in which curves were obtained, which on the whole taught little or nothing of importance. Also the determination of the viscosity for a few systems yielded at first but inconclusive results; in the conviction, however, that nevertheless this method promised most on the whole for the end we had in view, the investigation was continued with the favourable result that in a few cases curves were obtained which very convincingly pleaded for the existence of hydrates in the aqueous solutions.

The system  $\text{H}_2\text{O}-\text{FeCl}_6$  was chosen, of which part of the melting-point figure, as it was studied by BAKHUIS ROOZEBOOM, has been reproduced in Fig. 1.

The plan was to carry out the experiment at the temperature of  $40^\circ$ , because then, passing very close over the top of the compound

conc. in weight % $\text{Fe}_2\text{Cl}_6$	(Times of outflow in minutes).
0	1.70
33.50	6.15
39.58	8.70
46.13	12.50
50.19	16.45
52.57	18.05
55.39	19.32
57.45	18.66
58.69	17.92
60.18	17.50
62.44	16.90
65.09	16.95
66.84	17.50
68.45	18.60
71.06	21.73
72.88	24.63
73.83	28.17
74.12	31.80 (This solution is supersaturate).

$\text{Fe}_2\text{Cl}_6$ , 12 aq. (melting point  $37^\circ$ ), and over that of  $\text{FeCl}_6$ , 7 aq. (melting-point  $32.5^\circ$ ) there is the greatest chance that in this neighbourhood the homogeneous solution will contain considerable hydrate concentrations. For at higher temperatures the hydrates will dissociate more strongly as a rule, hence their concentrations will decrease.

The times of outflow found at  $40^\circ$  are recorded in the table of the preceding page.

When these results are graphically represented, as has been done in Fig. 1, we get a curve of viscosity exhibiting a very pronounced maximum and minimum, lying on the left and the right of the concentration of the hydrate with 12 aq.

This peculiar shape of the viscosity curve must in my opinion be interpreted in the following way.

When no hydrates were formed in the solution, the viscosity of the solution with the  $\text{Fe}_2\text{Cl}_6$ -concentration would increase in an ever greater degree, and in the end very high values would occur, because the viscosity of supercooled liquid  $\text{Fe}_2\text{Cl}_6$  at  $40^\circ$  will be exceedingly great.

At  $b$  a decrease of the viscosity is now found here, which in my opinion must be ascribed to the increasing hydrate concentration. When only the hydrate  $\text{Fe}_2\text{Cl}_6$ , 12 aq could exist in solution, it was to be expected that the minimum would lie near the concentration of this hydrate.

At  $40^\circ$ , however, we pass not only over the top of the melting-point line of  $\text{Fe}_2\text{Cl}_6$ , 12  $\text{H}_2\text{O}$ , but also, though not at such a small distance, over that of the melting point line of  $\text{Fe}_2\text{Cl}_6$ , 7  $\text{H}_2\text{O}$ .

At the descent from  $b$  to  $c$  an appreciable increase of the concentration of the hydrate with 7  $\text{H}_2\text{O}$  will, therefore, also take place, and when this gives also rise to a decrease in viscosity, the result will be that the viscosity curve, which must finally ascend again in consequence of the increase of the  $\text{Fe}_2\text{Cl}_6$  concentration, presents a minimum, lying on the righthand side of the concentration of the hydrate with 12 aq.

After this result had been obtained, and the plan had been formed to examine also the system  $\text{HO}_2-\text{SO}_3$ , because this seemed to be particularly suitable for this purpose, it appeared that KNIETSCH<sup>1)</sup>, who studied this system from different points of view, also gives a viscosity line which presents a close resemblance with the curve discussed above and of which up to now no notice had been taken.

<sup>1)</sup> Ber. 34, 4102 (1901).

This circumstance brought, however, no change in our plan, as it was our purpose to study the influence of the temperature on the shape of the curve of viscosity in the system  $H_2O-SO_3$ .

It is seen from the subjoined  $T-X$  figure of the system  $H_2O-SO_3$ , which is not yet quite completed, that at  $15^\circ$  the tops of the compounds  $H_2SO_4 \cdot H_2O$  and  $H_2SO_4$  are passed at temperature distances of  $6.47^\circ$ , resp.  $4.65^\circ$ .

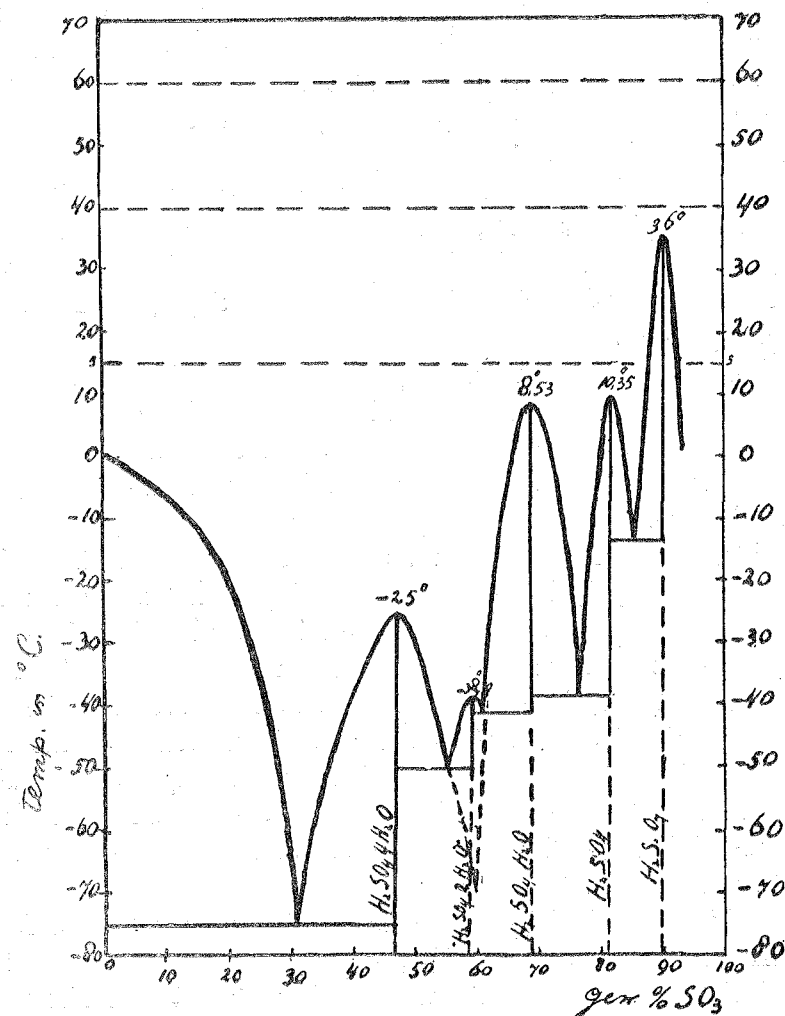


Fig. 2.

The compounds  $H_2SO_4 \cdot 2 H_2O$  and  $H_2SO_4 \cdot 4 H_2O$  are, indeed, also passed, but the melting-points of these compounds lie so far below  $15^\circ$  ( $-38.9^\circ$  resp.  $-25^\circ$ ) that it is not to be expected that the

curve of viscosity will still give any information about these hydrates at  $15^\circ$ .

Also with a view to this the concentrations were examined between 61 and 83 weight %  $SO_3$ .

The investigation was carried out at three different temperatures, viz.  $15^\circ$ ,  $40^\circ$ , and  $60^\circ$  with the following result:

weight % $SO_3$	Time of outflow at $15^\circ$	Time of outflow at $40^\circ$	Time of outflow at $60^\circ$
88,84	5 min. $27\frac{1}{5}$ sec.	2 min. $21\frac{1}{5}$ sec.	1 min. $20\frac{4}{5}$ sec.
82,13		2 " $15\frac{3}{5}$ "	1 " $18\frac{4}{5}$ "
81,72	4 " $6\frac{1}{5}$ "		
81,55	4 " $4\frac{2}{5}$ "	2 " $10\frac{2}{5}$ "	1 " $18\frac{1}{5}$ "
81,42	3 " $56\frac{4}{5}$ "		
80,53	3 " $56\frac{4}{5}$ "	2 " $\frac{2}{5}$ "	1 " $15\frac{3}{5}$ "
77,55		1 " $41\frac{3}{5}$ "	1 " $7\frac{2}{5}$ "
76,27	4 " $1\frac{2}{5}$ "		
75,72		1 " $51\frac{2}{5}$ "	1 " $7\frac{4}{5}$ "
75,33	4 " $8\frac{3}{5}$ "		
75,19	4 " $14\frac{2}{5}$ "		
75,03		1 " 56 "	1 " $10\frac{1}{5}$ "
73,96		1 " $57\frac{1}{5}$ "	1 " $10\frac{3}{5}$ "
72,69		1 " $57\frac{1}{5}$ "	1 " $10\frac{4}{5}$ "
72,08	4 " $42\frac{2}{5}$ "		
69,72		2 " $1\frac{2}{5}$ "	1 " $10\frac{2}{5}$ "
69,60	4 " 35 "		
64,78		1 " $43\frac{3}{5}$ "	1 " $2\frac{3}{5}$ "
63,76	3 " $27\frac{3}{5}$ "		
63,28		1 " 36 "	$59\frac{1}{5}$ "

Fig. 3 represents these results graphically. It shows that the curve of viscosity at  $15^\circ$  really has the same shape as that of the system  $H_2O-Fe_2Cl_6$  at  $40^\circ$ . The curves found at  $40^\circ$  and  $60^\circ$  show further that the peculiar character of the shape of the curve of viscosity

becomes less and less pronounced at higher temperature, which can be accounted for by the increasing dissociation of the hydrates on increase of temperature.

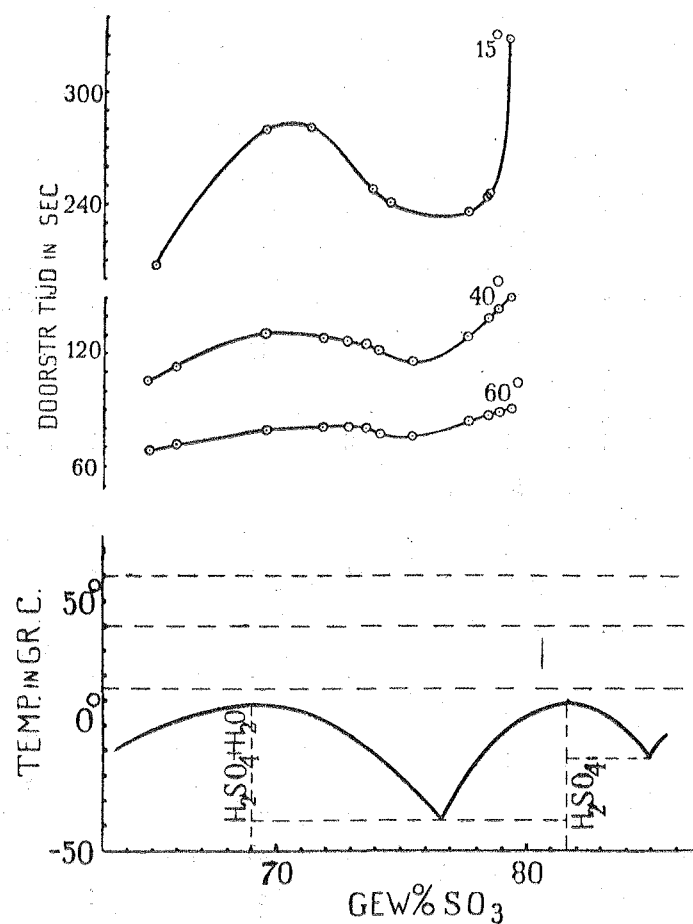


Fig. 3.

Laboratory of General and Inorganic  
Chemistry of the University.

Amsterdam, December 1920.

**Chemistry.** — “*The Electromotive Behaviour of Magnesium*”. I.

By Prof. A. SMITS and R. PH. BECK. (Communicated by Prof. P. ZEEMAN.)

(Communicated at the meeting of Dec. 18, 1920).

As was stated before magnesium closely resembles aluminium in its electromotive behaviour. Also the pure magnesium is as a rule a state disturbed in a noble direction, which reaches internal equilibrium by the absorption of small quantities of mercury; but in this case with magnesium these phenomena are weaker than with aluminium.

Our purpose was to examine the electromotive behaviour of mixtures of magnesium and mercury of different concentration in order to be able to set forth still more clearly the particular influence of small quantities of mercury.

Before proceeding to this research, it was desirable to determine the melting-point diagram of the system Mg—Hg, which investigation was attended with several difficulties, which we will, however, not discuss here. The result to which this research led, is represented in the adjoined  $T, X$ -figure. It must be pointed out here that this system had already been examined on the Hg-side by L. CAMBI and G. SPERONI<sup>1)</sup>, but that this research had been discontinued at the very point where the difficulties set in, and the system becomes most interesting.

We see from our diagram, which represents the situation of the melting-point lines under the varying vapour pressure, that the system Mg—Hg is very complicated, and contains several compounds.

In order to ascertain what corrections must be applied in the concentration, in connection with the mercury in the vapour phase, the determination of the vapour tension of the different mixtures was undertaken, in which use was made of a glass spring indicator. This investigation, which is now being continued with the mixtures rich in mercury, however, yielded the result that for mixtures from 0 to 50 at. %, Hg the vapour tensions are very small, even up to the final temperatures of fusion.

<sup>1)</sup> Atti della R. Accad. dei Lincei 24, 734 (1915).