

*Citation:*

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tangent, but no vertical tangents, but it may still be remarked of this melting-point line that it is the first that pursues its course undisturbed up to the melting-point of anthraquinone. The melting-point lines corresponding to higher pressures also proceed uninterruptedly from the eutectic point to the melting-point of anthraquinone, but they present a point of inflection as sole peculiarity.

Amsterdam, June 1911.

Anorg. Chem. Laboratory  
of the University.

**Chemistry.** — “On the system water-phenol.” By Prof. A. SMITS and J. MAARSE. (Communicated by Prof. A. F. HOULEMAN.)

Though the system water-phenol has already several times been the subject of investigation, and already many peculiarities of the mutual conduct of these substances have been revealed, it yet seemed worth while once more to take this system in hand, and determine the melting-point figure, the more so as we had come across a hydrate of phenol that had drawn CALVERT's<sup>1)</sup> attention already long before, but had not been met with by PATERNO and AMPOLA<sup>2)</sup> in their determination of the melting-point line of phenol in the system water-phenol.

In his paper entitled “*Ueber ein krystallisirtes Hydrat? des Phenols*” CALVERT writes as follows: “Schüttelt man 4 Theile Phenol mit 1 Theil Wasser gut durch einander und kühlt man das Gemenge auf  $4^{\circ}$  ab, so bedecken sich die Wände des Gefässes mit feinen sechsseitigen rhombischen Prismen. — Dieser neue Körper löst sich in Wasser, Alkohol und Aether und schmilzt bei  $16^{\circ}$ . Die Analyse der zwischen Fliesspapier abgepressten Krystalle führte zur Formel  $C_6H_6O_2 + HO$ ”<sup>3)</sup>).

After all CALVERT, however, seems not to have been perfectly convinced of the existence of this hydrate, for in the title he placed a note of interrogation after the word *Hydrat*. — Now it will appear from what follows, that CALVERT really had come across a hydrate of phenol and that PATERNO and AMPOLA have quite overlooked this compound in consequence of the circumstance that the formation of this hydrate very often does not take place, so that very easily metastable states

<sup>1)</sup> Zeitschr. f. Chemie 1, 530 (1865).

<sup>2)</sup> Gazz. Chim. ital. 27, 523 (1897)

<sup>3)</sup> RINKES (Thesis for the doctorate Amsterdam 1910 and Rc. 30) has availed himself of this circumstance for the preparation of perfectly pure phenol, as the homologues of phenol do not give hydrates, as far as we know.

make their appearance here. It is therefore not improbable that CALVERT's doubt finds its origin in this circumstance.

In the adjoined  $TX$ -figure the lines  $zg d_1$  and  $b_1 e_1$  represent the two parts of the melting-point line of phenol in the system *water-phenol*, which are separated by the region of non-miscibility.

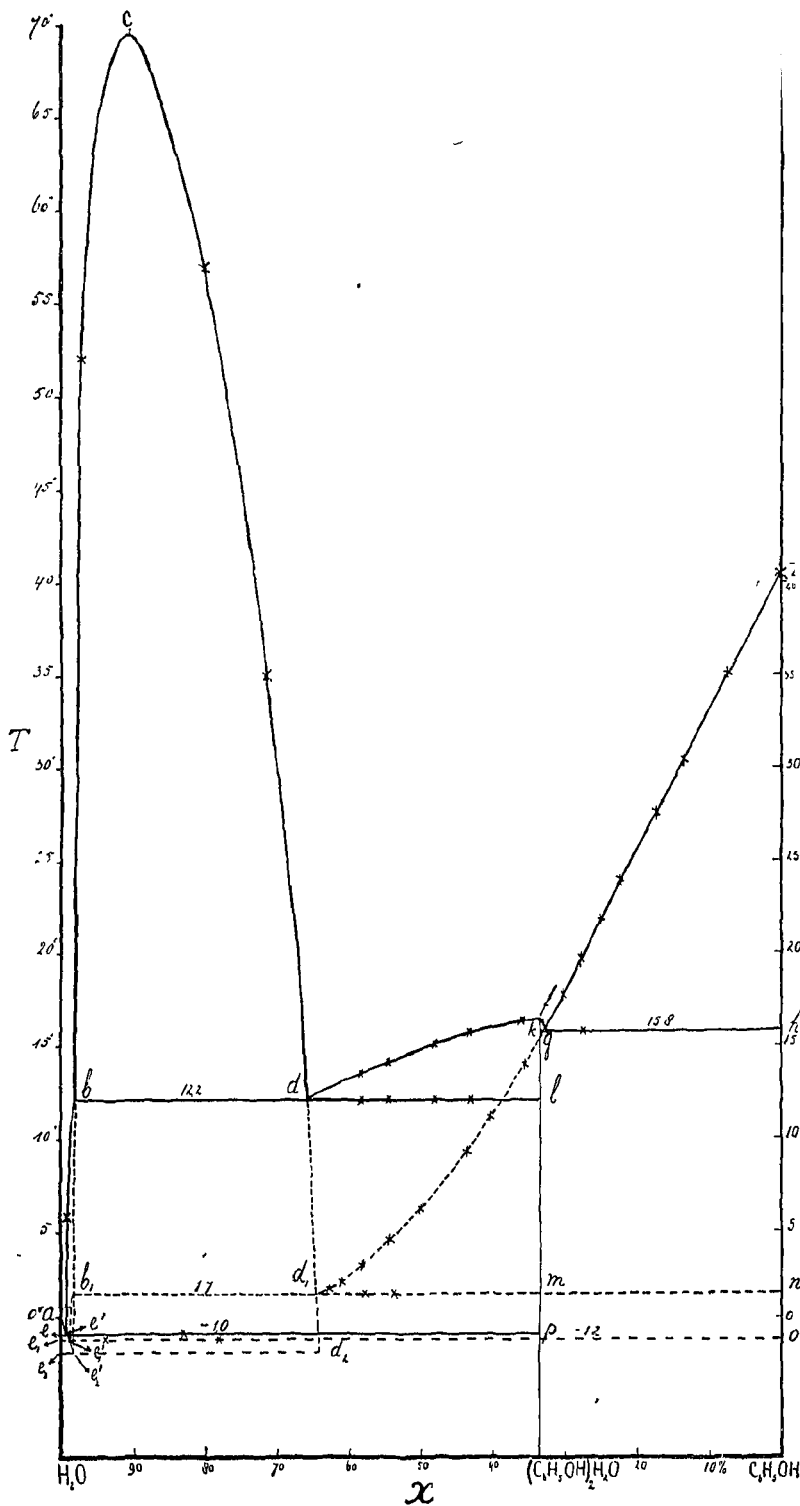
Now the most remarkable thing in the system mentioned is this that notwithstanding this part  $gd_1$  appeared to be metastable, we can just as easily determine this part as the part  $zg$ , because as a rule it is exactly points of solidification of the part  $gd_1$  that are observed when water-phenol mixtures of concentrations corresponding to this line are cooled without any precaution.

So this must be the reason that PATERNO and AMPOLA found exactly this line, or rather that they only got deposited *solid phenol*. The melting-point curve they found, agrees, indeed, with the curve  $zg d_1$  with regard to its shape, but on the whole they found lower temperatures; at some places the difference is even  $1^\circ$ .

It is clear from the fig. that for concentrations lying between the points  $d_1$  and  $b_1$  at a certain temperature solid phenol must deposit from the two layer system, whereas the aqueous liquid layer must be formed at the same temperature for concentrations lying between  $n$  and  $d_1$ . — On cooling the conversion  $L_2 \rightarrow L_1 + S_{phenol}$  takes place on the line  $nd_1 b_1$ , so that at last the liquid layer  $L_2$ , which is richer in phenol, has quite disappeared. So long as the three phases are present the temperature remains constant, and this explains the fact that PATERNO and AMPOLA have found a somewhat oscillating temperature of solidification of  $\pm 1,74^\circ$  in a certain range of concentration. The temperature of the three-phase equilibrium  $L_1 + L_2 + S_{phenol}$  was accurately determined by us by means of the resistance thermometer, and found at  $1,7^\circ$ .

As it was expected that the eutectic point lying under it, where *ice*, *solid phenol*, and *liquid* coexist, would differ little in temperature from the just mentioned three-phase equilibrium, this point too was determined with the resistance thermometer, when the temperature of  $1,2^\circ$  was found.

As was already observed before, the melting-point line of phenol is only stable up to the point  $g$ , for it appeared in our investigation that in the stable state not the continuation  $gd_1$ , but the melting-point line  $gfd$  is found with a maximum in  $f$ , which maximum corresponds to the concentration  $(C_6 H_5 OH)_2 \cdot H_2 O$ . In this case, where mixed crystals play no part, this points to the fact that in stable state a compound of the concentration mentioned above occurs, which, as appeared to us, was easy to obtain by sudden cooling of



the liquid mixtures in a bath of solid carbon-dioxyde and alcohol.

When the solid compound had once been obtained in this way, the different points of the stable melting-point line were determined by seeding the undercooled mixtures with solid hydrate, and by determining the temperature, in which the last trace of solid substance vanishes by slow heating.

Instead of the metastable three-phase equilibrium between two liquid layers and solid phenol discussed just now, we now likewise get such a three-phase equilibrium in stable state, but now between two liquid layers and solid hydrate. For this stable three-phase equilibrium indicated by the points *ldb* the temperature  $12,2^{\circ}$  was found.

If we now go to lower temperature, we get the continuation of the melting-point line of the compound which lies very much to the side of the component, water, and ends in the eutectec point for *ice*, *liquid* and *solid hydrate*, the temperature of which appeared to lie at  $-1.0^{\circ}$ .

In conclusion we may still mention that to get perfect certainty that the top of the melting-point line of the hydrate really lies in the stable region it must be examined if there exists a eutectic point of *solid hydrate*, *liquid*, and *solid phenol*, which in this case must lie below the highest melting-point observed on the melting-point line of the hydrate. This question was settled beyond all doubt by the following procedure: we started from a mixture lying in concentration between *y* and *h*; this mixture was entirely melted, then undercooled by cooling to  $\pm 15^{\circ}$ , and then seeded with a conglomerate of the solid compound and the solid phenol. Then the temperature rose to  $15^{\circ}.8$  and remained constant there for a considerable time, from which follows that the top of the melting-point line of the hydrate really still lies just in the stable region, as has been indicated in the *T*-*x*-figure.

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**Chemistry.** — “*On the system hydrogensulphide-water.*” By Dr.

F. E. C. SCHEFFER. (Communicated by Prof. A. F. HOLLEMAN.)

1. In a previous communication<sup>1)</sup> I already mentioned the principal part of the results of my investigation on the system hydrogen sulphide-water in the neighbourhood of the quadruple point hydrate-two liquid layers-gas. From the determination of the *P-T*-projection of the four three-phase lines the behaviour of the said system could

<sup>1)</sup> These Proc. Jan. 1911.