

*Citation:*

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**Chemistry.** — “*Critical phenomena of the ternary system ether-anthraquinone-naphthalene.*” By Dr. ADA PRINS. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of June 25, 1910).

In a communication to this Academy <sup>1)</sup> Prof. SMITS has pointed out what changes may be theoretically expected to occur in the system ether-anthraquinone on addition of a third component.

As an experimental study of such a ternary system was still wanting, Prof. SMITS suggested to me the research, an account of which will now be given.

As a third component we chose naphthalene, because the melting point of this substance ( $79,3^{\circ}$ ) lies considerably lower than the critical point of ether ( $193^{\circ}$ ) and its solubility in ether is pretty great, therefore the binary system naphthalene-ether will show no critical phenomena for saturate solutions, nor is this the case for the binary system naphthalene-anthraquinone, and so we may expect a similar behaviour as Prof. SMITS i.c. gave for ether-anthraquinone.

The experimental investigation has confirmed the theory perfectly. On addition of a small amount of naphthalene to the system ether-anthraquinone the two critical end-points  $p$  and  $q$  continue to exist, draw near to each other on addition of a greater percentage of naphthalene, and so have already disappeared for a quantity of  $\pm 1/2\%$  of naphthalene. So a spacial interval is formed which does not extend very far, and a projection of which in a concentration triangle has just the shape of fig. 2 in SMITS' paper. As, however,

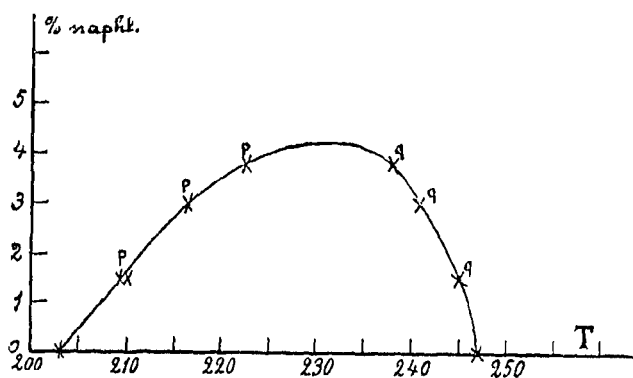


Fig. 1.

<sup>1)</sup> See the preceding paper.

I have not determined the anthraquinone concentrations of the fluid phases, the exact shape of the curve cannot be given; we can only say that the line anthraquinone —  $x_3$  takes such a course that  $x_3$  is smaller than 0.045 of naphthalene.

If, however, we think the triangle as basis of a trilateral prism, the erect side of which serves as an axis of temperature, and if we then project  $p$  and  $q$  on the side plane naphthalene-ether, we get fig. 1, from which we can also see, how the point  $p$  and  $q$  approach each other with an increasing proportion of naphthalene, and finally coincide.

Besides the temperature I also determined the pressure of the critical end-points; from this we can draw up a  $p$ - $t$ -projection of the ternary plaitpoint-curve (see fig. 2, and the table below):

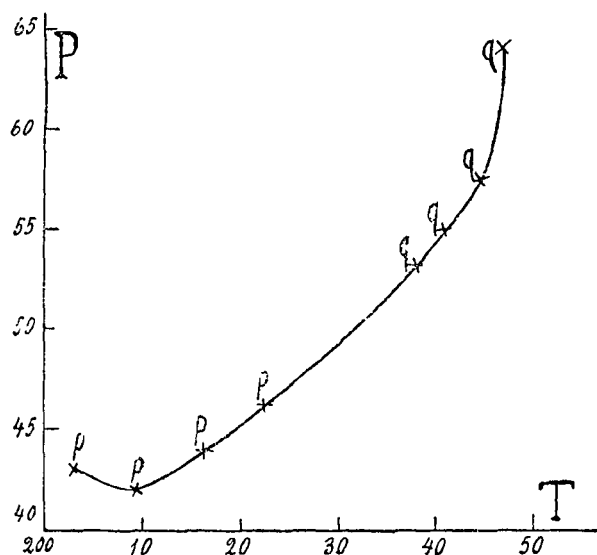


Fig. 2.

Percentage of naphth. with regard to ether	$T$	$P$ in atm.
$1\frac{1}{2}$	$p$ 210.0	42.0
$1\frac{1}{2}$	$p$ 209.4	41.8
	$q$ 244.7	57.4
3	$p$ 216.3	43.8
	$q$ 240.8	54.9
3.8	$p$ 222.5	46.2
	$q$ 238.0	53.3

Then this curve indicates the temperatures and pressures at which ternary liquids and vapours become critical in the presence of solid anthraquinone. This line too connects the two critical points *p* and *q* of the binary system ether-anthraquinone continuously. The pressure of the point *p* does not rise at once; on the addition of very little naphthalene (1 %) it falls somewhat, so that the curve shows a minimum lying near *p*.

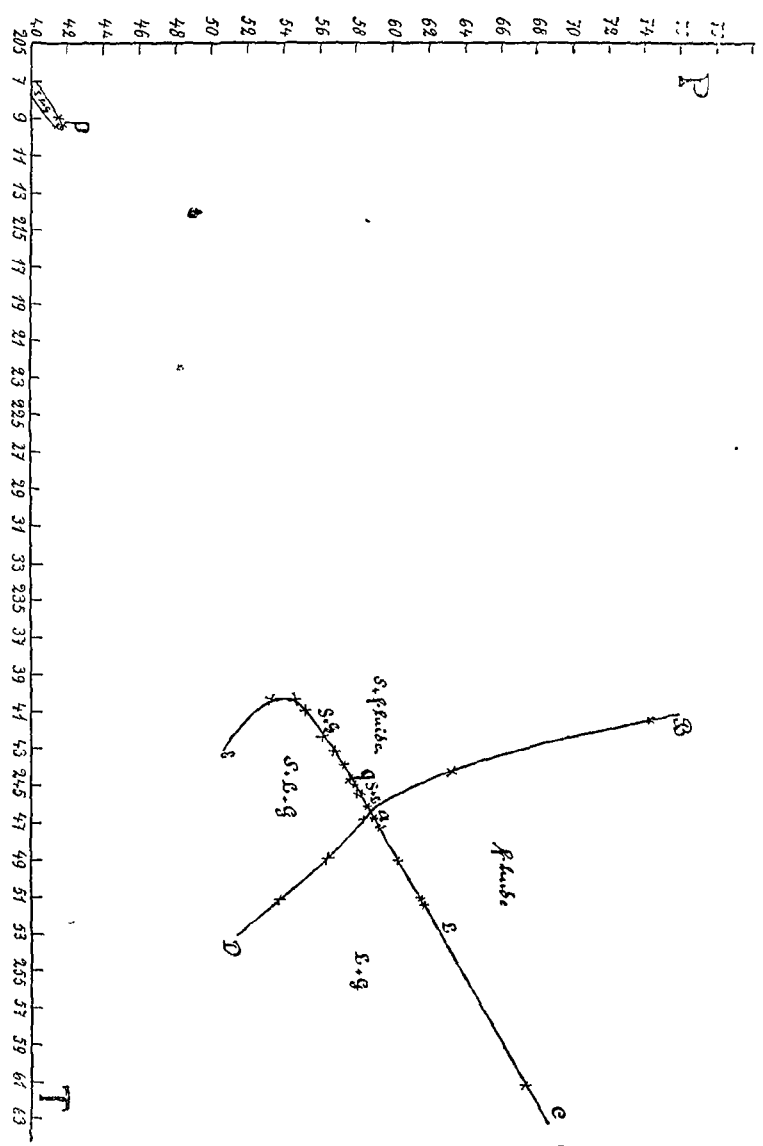


Fig. 8

The different points of these two curves were found by determining the  $P$ - $T$ -sections of mixtures with different quantities of naphthalene. These  $P$ - $T$ -sections will in general present a shape as drawn in fig. 16 in Prof. SMITS' paper. It is noteworthy that  $K$ , i. e. the critical point  $L + G \rightarrow$  fluid moves more to the right on increase of the quantity of anthraquinone. On the left of  $K$  the meniscus disappears in the top of the tube, i. e. the gas-phase becomes smaller and smaller, whereas on the right of  $K$  the meniscus disappears at the bottom, because the quantity of liquid phase decreases here. On the other hand on the right of the critical endpoint  $q$  at the transition  $S + L + G \rightarrow S +$  fluid we shall see the meniscus disappear at the top, on its left at the bottom in the tube.

The mixtures with a ratio of  $1\frac{1}{2}$ , 3, 3.8, and 5% of naphthalene with regard to the quantity of ether were studied, and gave rise to the graphical representations drawn in the figs. 3, 4, 5, and 6.

None of them have been completed, as the trouble required for this would be too great in comparison with the increase of knowledge it would yield us; for the essential part of the problem is perfectly represented by the determined curves.

Fig. 3 gives the  $P$ - $T$ -projection of a section with  $1\frac{1}{2}$ % of naphthalene. The quantity of anthraquinone is so great that the point  $q$  can be realized, viz. 25% of the total quantity of the mixture taken.

The region of coexistence  $S + L + G$  is bounded by the regions  $S +$  fluid, and  $L + G$ . On the upper loop-line  $S + L + G \rightarrow S +$  fluid lies the point  $q$ . So at this temperature and pressure the meniscus disappears just in the middle of the tube, solid substance being present. The line  $AB$  indicates the transition  $S +$  fluid  $\rightarrow$  fluid; the line  $AC$  the transition  $L + G \rightarrow$  fluid. So when this figure is completed the line  $AC$  would have to meet the continuation of  $AD$ , and the loop  $AE$  would have to terminate at the same point. Fig. 4 represents the behaviour of a mixture of the same ratio of ether and naphthalene, but with a smaller content of anthraquinone. This content, viz. 20% is too small to reach the point  $q$ . I succeeded for this mixture to demonstrate the point  $K$  in a supersaturated solution.

Figs. 5 and 6 give the confirmation of the possibility mentioned by SMITS that there exist still two critical end-points without the  $P$ - $T$ -figure showing a hiatus (see fig. 18 in the cited paper).

For the mixture with 3.8% of naphthalene (fig. 6)  $p$  and  $q$  approach each other more than in the 3% mixture, though their distance apart remains comparatively great; the  $S + L + G$  region for the first-mentioned mixture is wider than for the last-mentioned, and in both the minimum and the two maxima are to be observed,

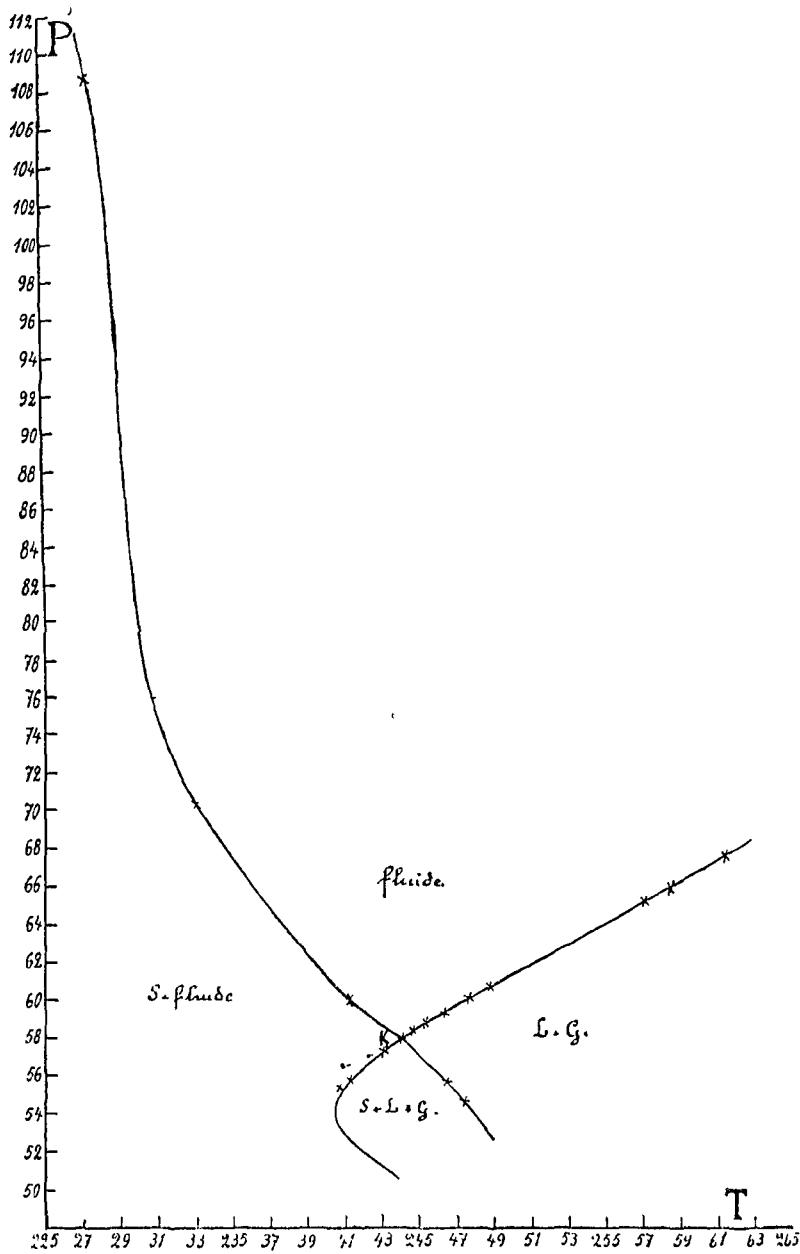


Fig. 4.

though faintly, in the continuous  $S + L + G \rightarrow S + \text{fluid}$  curve between the points  $p$  and  $q$ .

It appeared convincingly from the observations of the 5% mixture, that the critical end-points have already disappeared here, so that a graphical representation would present nothing particular.

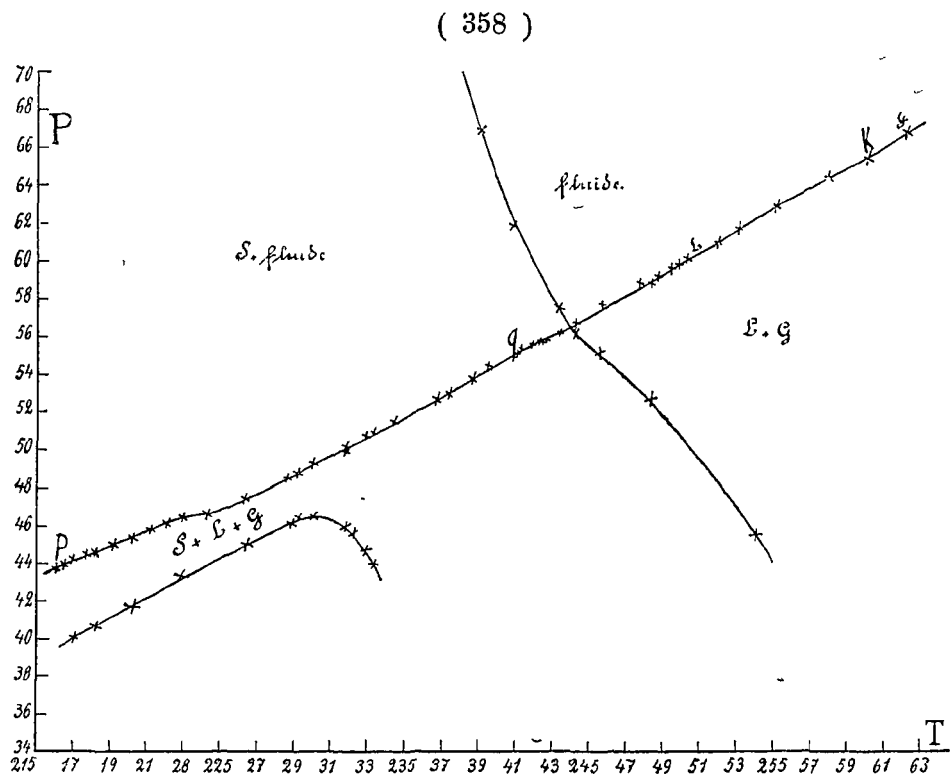


Fig. 5.

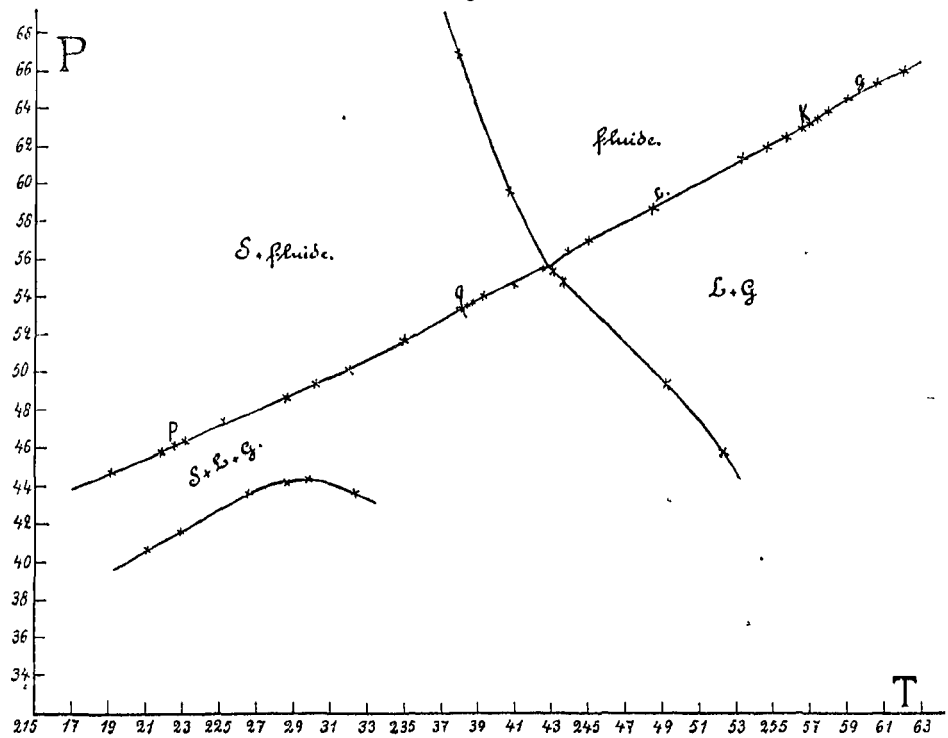


Fig. 6.

Mixture 5% of naphthalene		
<i>T</i>	<i>P</i>	
241°	45.6	<i>S + L + G</i>
237°	43.7	<i>S + L + G</i>
cooled down to 200°	~	remains <i>S + L + G</i>

The experiments were arranged in the well-known way <sup>1)</sup>. The pressures were read on a manometer of SCHÄFFER and BUDENBERG, and provided with the required correction. The heating was brought about by means of  $\alpha$ -monobromonaphthalene boiling under low pressure.

Anorg. Chem. Labor. of the University.

Amsterdam June 23, 1910.

**Chemistry.** — "*Investigations on the radium content of rocks.*" I.

By Dr. E. H. BÜCHNER. (Communicated by Prof. A. F. HOLLEMAN.)

(Communicated in the meeting of June 25, 1910)

*Introduction.* The fact that everywhere in the atmosphere radio-active emanations are found, in connection with the observation — at different places of the surface of the earth — of a very penetrating radiation, suggest very clearly that radio-active substances are found everywhere in the earth's crust. As far as radium is concerned this conclusion was experimentally confirmed for the first time by STRUTT <sup>2)</sup>, who by means of the new methods of radium-determination could ascertain not only that a number of typical rocks contain radium, but even succeeded in measuring how great the content of radium was. The quantitative character of his results gave a still greater significance to his investigation in another respect, namely with reference to the question whether radio-active processes can be the cause of the internal heat of the earth. It was already known — from calculations by RUTHERFORD — that the presence of a quantity of radium of  $4.6 \times 10^{-14}$  gr. per gramme of the earth would be sufficient to keep the surface of the earth at a constant temperature, in other words to maintain the thermal equilibrium of the earth. And now STRUTT arrived at the surprising result, that on an average about  $1.5 \times 10^{-12}$  gr. of radium is present per gramme of rock, considerably more than the quantity calculated by RUTHERFORD. It appears

<sup>1)</sup> See SMITS, Z. phys. Chem. LII, p. 587.

<sup>2)</sup> Proc. Roy. Soc. A 77, 472 (1906) and 78, 150 (1906).