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The following papers were read:

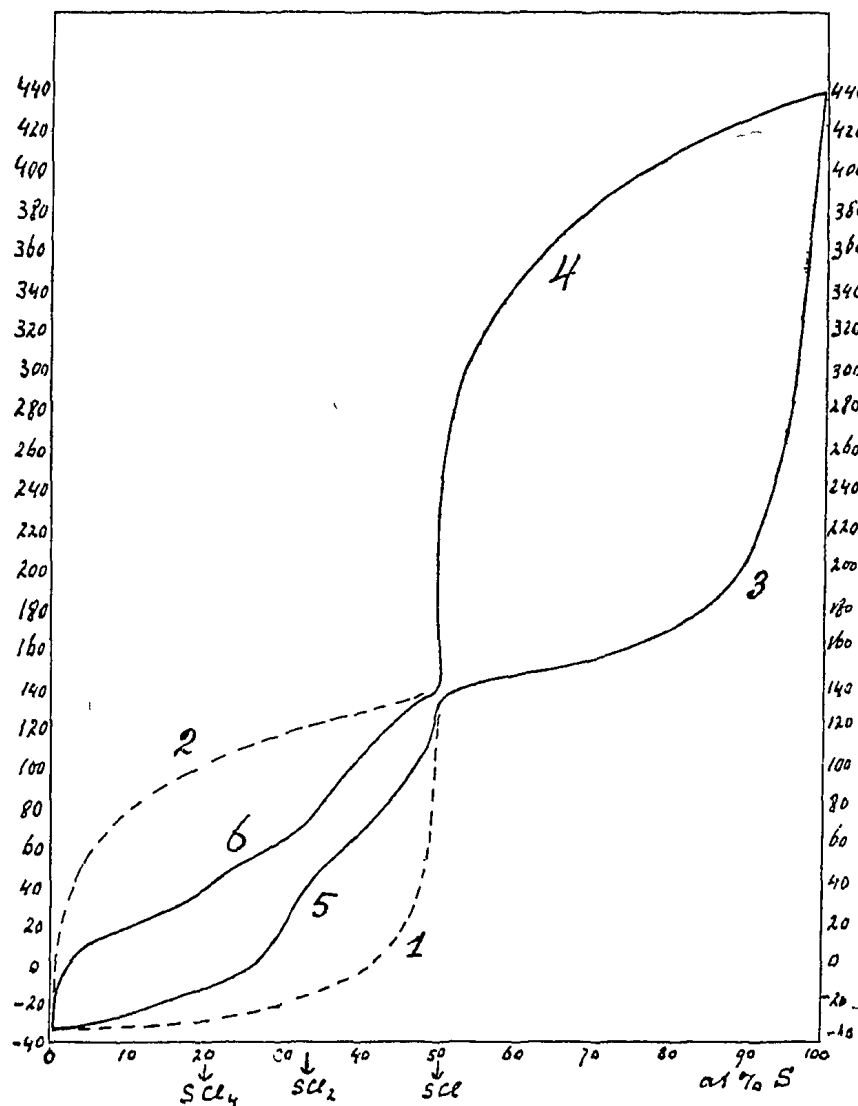
Chemistry. — "*The boiling-point curves of the system sulphur and chlorine.*" By Prof. H. W. BAKHUIS ROOZEBOOM.

(Communicated in the meeting of May 30, 1903).

Binary systems in which the formation of complex molecules may be assumed to take place in a greater or smaller degree have been frequently investigated as regards the equilibria between a liquid

phase and solid phases, but hardly ever with regard to the equilibria between liquid and vapour.

I, therefore, proposed to further investigate this relation in the case of vapour pressure- and boiling-point curves on a series of



examples in which the nature and the degree of the complex molecules varied, in order to obtain a more definite idea of the changes which these curves undergo as compared with the simple case in which the binary system consists only of two kinds of molecules.

Such an example is furnished by the system sulphur-chlorine, the boiling-point curves of which are given in the accompanying figure, which is constructed from determinations made by Mr. ATEN.

Liquid sulphur and liquid chlorine are miscible in all proportions. If in these mixtures no compound molecules were formed, two regular boiling-point curves might be expected which would diverge very much in the centre because the boiling points of the two components lie far apart.

In these mixtures, however, a fairly stable compound S_2Cl_2 is formed. If this compound were absolutely stable, that is if a liquid and a vapour of the composition S_2Cl_2 consisted of nothing but molecules of this formula, then the liquid and vapour would at this point, have exactly the same composition. The system $S+Cl$ would then in reality be compounded of the two systems $S+S_2Cl_2$ and $S_2Cl_2+Cl_2$ which could no doubt be represented in one figure, but then the liquid- and the vapour-pressure curves would not pass continuously into each other at the composition S_2Cl_2 .

As it is known that the dissociation of the vapour of S_2Cl_2 is small it may be anticipated that, in the system $S+Cl$, the connection at the composition $S Cl$ might become continuous, but in such a way that the vapour and liquid curves nearly coincide at this point.

This state of affairs was now confirmed and is indicated in the figure by the liquid curve 1,3 and by the vapour curve 2,4. It will be seen that the curves 1 and 2 and 3 and 4 nearly meet in a point situated near the composition $S Cl$, but in reality we have here continuity, from which it appears that S_2Cl_2 is not absolutely stable either in the form of liquid or vapour. The difference however, is so small that this type really exhibits one of the smallest forms of deviation.

In the case of binary mixtures where the compound formed is more strongly dissociated the divergence of the two curves at the point representing the compound will be much greater. The liquid curve and the vapour curve of the entire system will then more and more assume the form which in the figure belongs to both halves.

The investigation however, showed a further peculiarity in the lower half. The boiling-point curves 1 and 2 for the mixtures whose composition lies between Cl and $S Cl$ only relate to mixtures which are freshly prepared from liquid S_2Cl_2 and liquid chlorine.

These mixtures at temperatures below 0° retain for a very long time their yellow colour and then exhibit the boiling point lines indicated at 1 and 2. At higher temperatures, and very quickly above 30° , the colour becomes darker and finally blood red, chiefly in the case of mixtures approaching the composition $S Cl_4$.

The boiling points then rise, sometimes very considerably, to a maximum amount of about 70° so that the line 5 is found for the

5*

definite boiling points of liquids which have reached their final equilibrium, which occurs after some hours at the ordinary temperature.

At the same time we get, in place of the vapour curve 2, the new vapour curve 6. As the velocity of reaction above 40° becomes very great, the lines 1 and 2 cannot be accurately determined above this temperature. For 1 this causes no inconvenience as its further course must be almost vertical, but the upper part of 2 becomes rather uncertain.

The final boiling-point curves 5 and 6 are situated much closer together than the first named one and have moreover an exceedingly irregular shape. It cannot as yet be decided whether this is solely attributable to the formation of SCl_4 molecules in the mixtures, or whether other compound molecules are formed.

The formation of compound molecules may be noticed not only from the change of colour, but also from a diminution of the volume and will if possible, be studied quantitatively.

The important question in what manner the melting-point curve of solid SCl_4 is modified by the presence of more or less compound molecules in the liquid phase is still the subject of investigation.

Chemistry. — “*The velocity of transformation of carbon monoxide II*”.

By DR. A. SMITS and L. K. WOLFF. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Communicated in the meeting of May 30, 1903).

In our previous paper on the above subject¹⁾ we communicated results obtained at the temperatures 256° , 310° and 340° , from which we concluded that at these temperatures the transformation of CO into CO_2 and C is unimolecular.

Our present paper contains the results obtained at 445° . This communication appears to us to be of importance for the following reasons. Three months after our first paper a communication appeared from SCHENCK and ZIMMERMANN²⁾ from which it appeared that they had also studied the transformation of CO into CO_2 and C and had arrived at the result that the reaction at temperatures from 310° and 360° was a unimolecular one, thus confirming our experiments, but that at 445° the reaction became bimolecular.

On continuing our investigation we found, however, that the

¹⁾ Proc. 8 Jan. 1903.

²⁾ Ber. 36. p. 1231.