

Citation:

A. Smits, On the System Mercury-Iodide, in:
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of this appears in the tables. In the tables of the 3^d kind also, where it would have been quite possible to apply a different periodicity to the time-intervals and to the synodic arcs, this has not been done; they run practically parallel, differing only by an unimportant computational quantity; and the method of calculation which is used in the tables of the first and second kind excludes any possibility of taking into account the varying velocity of the sun.

Chemistry. — "*On the System Mercury-Iodide.*" By Prof. A. SMITS.
(Communicated by Prof. P. ZEEMAN.)

(Communicated in the meeting of September 27, 1916.)

As was already discussed more at length before mercury iodide exhibits a very peculiar phenomenon on being heated, which phenomenon consists in this that after the red phase has been converted to the yellow phase at 127°, the substance remains yellow up to about 188°, but then gradually assumes a more and more pronounced red colour, and finally melts to a dark red liquid at $\pm 255^{\circ},5$. This, combined with the fact that the vapour is colourless or light yellow, tells us that as far as the composition is concerned the solid phase lies between the vapour and the liquid at the three-phase-equilibrium solid-liquid-gas. In virtue of these data a pseudo figure was derived that took these above facts into account, and gave, moreover, an exceedingly simple explanation of the fact that on sudden cooling of the vapour the yellow modification always makes its appearance first.

Yet this figure had a drawback, which was felt by me and also by others, and which gave an indication that the view would still have to be modified somewhat. This drawback consisted in this that it was assumed that above the point of transition the yellow rhombic mixed crystals would continuously pass into red tetragonal ones.

As was communicated in the last paper on this subject, Dr. A. L. W. E. VAN DER VEEN had at my request undertaken the crystallographic study of mercury iodide in the hope that this research would bring the problem nearer its solution. This has actually been the case. By making use of a special sublimation arrangement Dr. v. D. VEEN ¹⁾ has succeeded in making crystals of yellow mercury iodide, 2 cm. long above 127°.2, and in studying them accurately microscopically at different higher temperatures. It then appeared that the originally yellow crystal begins to gradually assume an

¹⁾ Verslag van de gewone vergaderingen der wis- en nat. afd. Kon. Akademie, Vol. XXIV (1916) p. 1557.

orange tint above 200°, which becomes more and more distinct but does not pass into red as formerly seemed to follow from the investigation of a large quantity of powdery HgI_2 . The distinctly orange coloured crystal was converted to a dark red liquid drop at the melting temperature. In this it could be ascertained with perfect

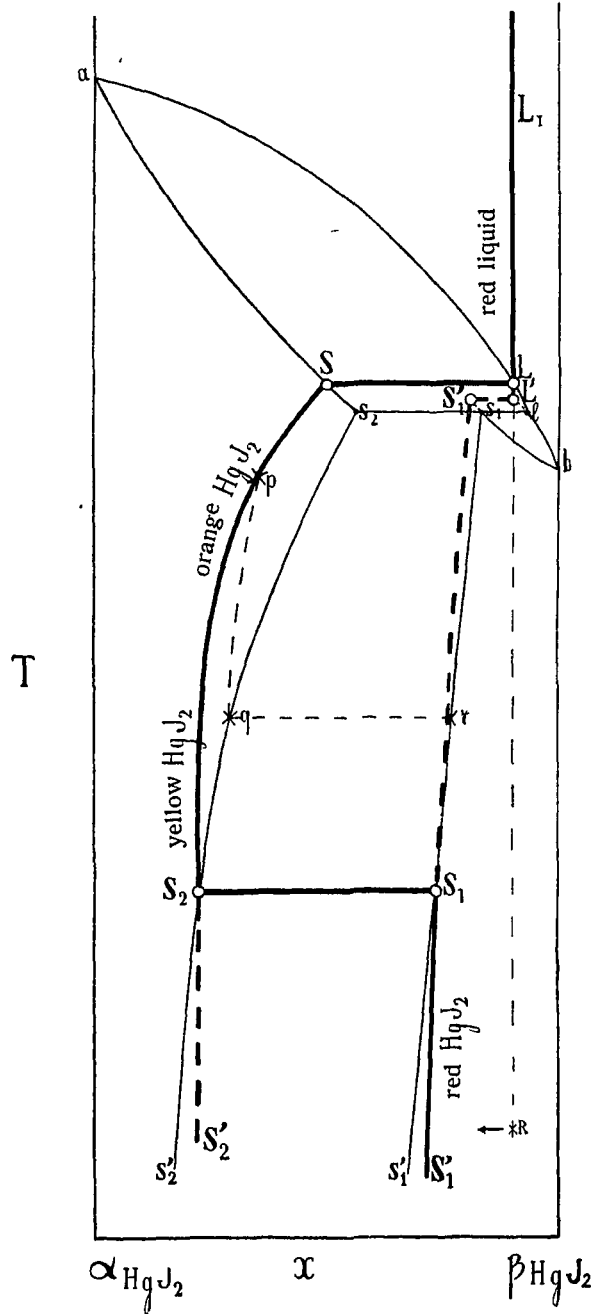


Fig. 1.

certainty that the change of colour from yellow to orange is perfectly continuous, and is not attended with a change in crystalline form, so that the assumption of a continuous transition from rhombic into tetragonal between 127° and 255.5° must be abandoned. It follows therefore from Dr. v. D. VEEN's investigation that: (see p. 703)

1. between 127° and 255.5° the internal equilibrium very perceptibly shifts to the side of the β -component, but the colour proves already that this shifting is not so considerable that the composition of the red modification is reached.

2. this shifting of the internal equilibrium, which is accompanied with a change of colour, is not attended with a change of crystalline form.

These new data rendered it necessary to modify the designed figures of the pseudo- and of the unary system somewhat. Led in this way to reconsider the problem mercury-iodide, I found that the solution was after all exceedingly simple.

One of the particularities presented by the system HgI_2 , is this that as has been stated, the concentration of the solid substance at the triple point solid-liquid-vapour lies between that of the vapour, and the liquid is richest in that component that in the solid red modification is represented in the greater quantity. This is a situation to which we are not accustomed, though it undoubtedly occurs now and then, and it is to be attributed to this that another solution was not immediately thought of, which possesses all the advantages of the former solution, while the objections advanced against the former solution are entirely removed here.

If we begin with the simplest representation, we take the T_x -section of the spacial figures corresponding to a constant pressure, and that such a pressure that equilibria with vapour cannot occur. Now there are two difficulties. The first that I will discuss here is this that the T_x -section has the shape of the figure indicated in thin lines in fig. 1. The pseudo components αHgI_2 and βHgI_2 , therefore, give mixed crystals, but the mixing is limited, hence a continuous transition between mixed crystals of a different crystalline system takes nowhere place. The situation of the unary system in this section has been indicated by thick lines, so that the connection between the pseudo binary and the unary system is at once clear.

The internal equilibrium in the tetragonal red modification is indicated by the line $S_1'S_1$ below the transition point. The internal equilibrium in rhombic modification, which continuously passes from yellow into orange between 127° and 255.5° , is indicated by the line S_2S . Comparatively near below the melting-point this line bends

very perceptibly to the right, which means that the unary mixed crystal becomes richer in the β -pseudo component on rise of temperature. At the moment that the mercury iodide melts, it lies in composition between that of the yellow and of the red modification at the transition temperature.

The liquid L formed is very rich in the β -component, which is in harmony with the fact that the liquid is dark red. The internal equilibrium in the liquid phase above the melting point is indicated by the line LL_1 . What direction this line has cannot be ascertained with any certainty.

The possibility of the occurrence of red mixed crystals *above* the transition point by sudden cooling of HgI_2 from e.g. 240° to 130° is also immediately to be seen from this figure, just as the direct formation of the red modification by sudden cooling of molten HgI_2 in a mixture of carbon dioxide and alcohol.

This is sufficient to show that this figure perfectly accounts for the observed phenomena. To be able also to explain the phenomena that can present themselves in the presence of gaseous HgI_2 , we should also indicate the T_2x -projection of the three-phase regions of the pseudo-system, and then the somewhat unusual situation of the system HgI_2 is apparent.

The vapour coexisting in the triple point with the orange solid phase and the dark red liquid, has a light yellow colour. The vapour is, therefore, richest in the pseudo component αHgI_2 ; consequently the vapour lines in the pseudo system lie as they are indicated in fig. 2. This is, indeed, an unusual situation, which however, will undoubtedly occur now and then. The vapour lines of the unary system are, just as the lines for the solid phases and those for the liquid, indicated by thick lines. What the direction is of the vapour lines and of the liquid line in the unary system, cannot be stated with certainty as yet, but it is of very little importance here ¹⁾.

If we knew that βHgI_2 is a polymer of αHgI_2 , the line for the internal equilibrium in the vapour would run towards higher temperature to the left, but that this case should present itself does not seem very probable, because, as has been said, the liquid at the triple point temperature is richer in the β -component than the coexisting solid phase. The assumption of isomerism, therefore, seems

¹⁾ The vapour lines ag and bg of the pseudo system must intersect in g in such a way that the metastable prolongations do not lie inside each other, as is drawn here, but outside each other. In this case the point G' will also lie exactly on the prolongation of the line G_1G .

to be more likely. This, however, is a question, which cannot be settled until later on. For the present we may be contented to have found a view which explains the observed phenomena in an exceedingly simple and plausible way.

I have pointed out in this paper that there are two possibilities,

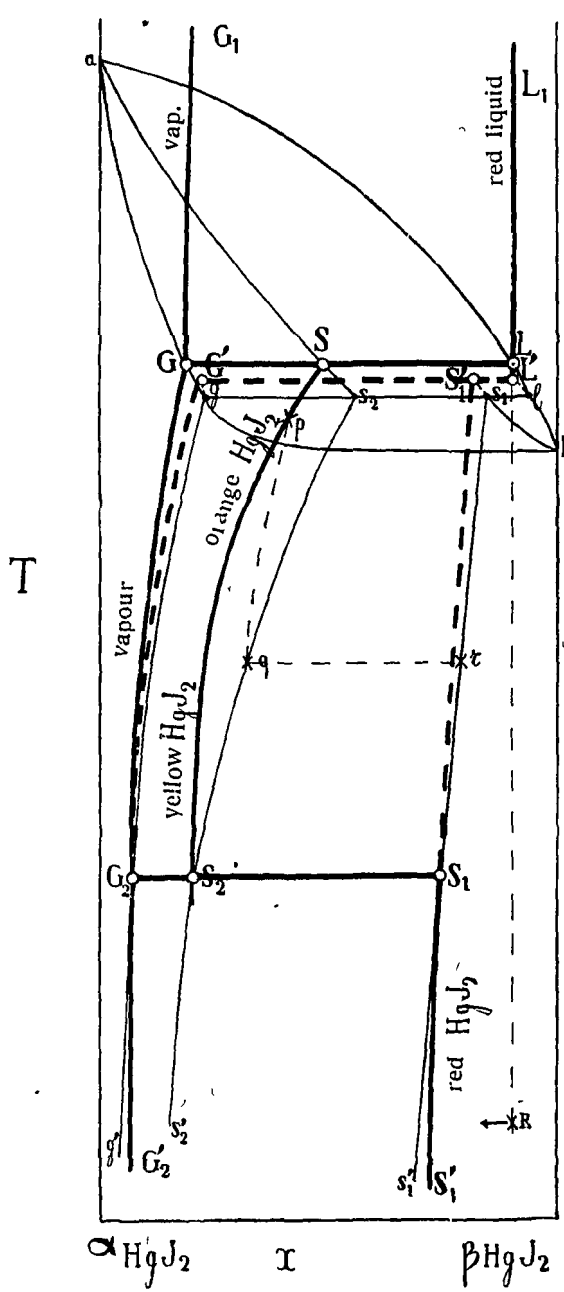


Fig. 2.

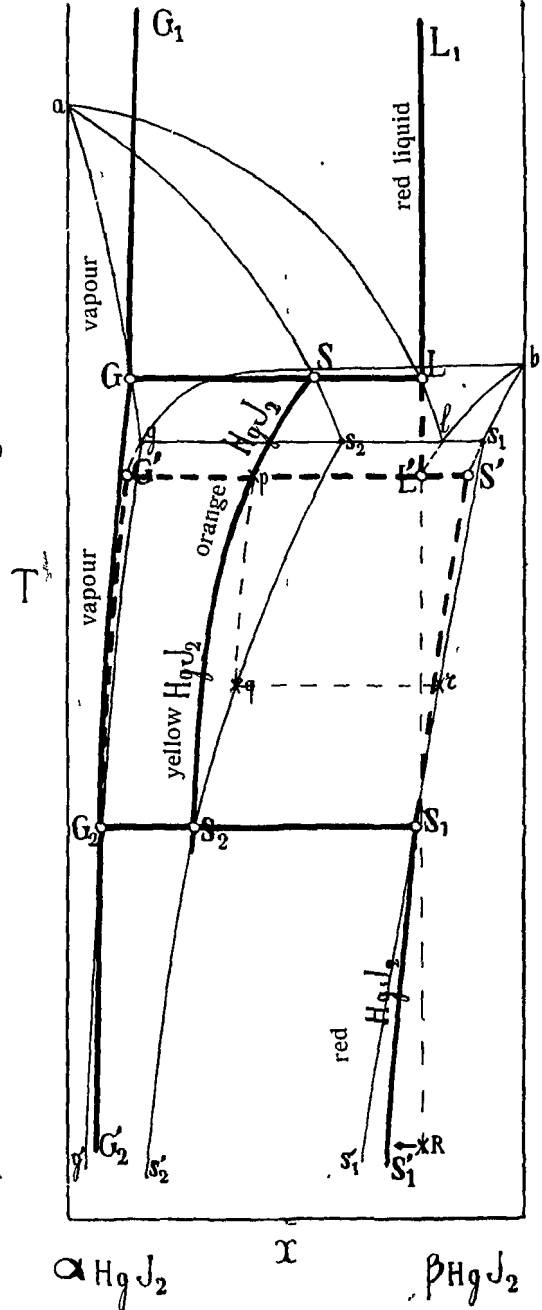


Fig. 3.
45°

of which the first has only been mentioned as yet. The second differs from the first only in this that the melting-point diagram possesses a eutectic point.

Fig. 3 represents in this case the T, x -projection of the three-phase regions of the pseudo system with the two phase regions of the unary system lying in them.

This figure, which does not call for any further elucidation, also represents a case not considered up to now, for which the solid phase lies between the two others on one three-phase region for $S + L + G$, the situation on the other three-phase region being the usual one. At present there is no reason to prefer one representation (Fig. 2) to the other (Fig. 3).

In conclusion it may still be pointed out that as is known, HgI_2 at high temperatures begins to split up appreciably into Hg_2I_2 and I_2 . This splitting up is disregarded here, because evidently it is not essential here for the phenomenon of allotropy.

SUMMARY:

On the ground of new researches a modification was applied to the representation of the system mercuriodide, which has entirely obviated all the former difficulties and in consequence of which an altogether satisfactory concordance with the observed phenomena was obtained.

Anorg. Chem. Lab. of the University.

Amsterdam, Sept. 1916.

Chemistry. — “*On the Influence of the Solvent on the Situation of the Homogeneous Equilibrium*”. I. By Prof. A. SMITS. (Communicated by Prof. F. A. H. SCHREINEMAKERS).

(Communicated in the meeting of October 28, 1916).

1. It is universally known that the solvent frequently greatly influences the situation of the homogeneous equilibrium. This has appeared, for instance in the determination of the equilibria of the *triazol carbonic acid esters* in different solvents, carried out by DIMROTH ¹⁾, and from VON HALBAN's ²⁾ researches on the conversion

¹⁾ Lieb. Ann. **377**, 133 (1910).

²⁾ Zeitschr. f. phys. Chem. **67**, 129 (1909).