KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

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CONTENTS.

The following papers were read:

Chemistry. — *"A representation in space of the regions in which the solid phases, which occur, are the components, when not forming compounds."* By Prof. H. W. Bakhuis Roozeboom.

(Communicated in the meeting of September 27, 1902).

In the course of my researches, I have often made use of special kinds of graphical representations to indicate the limits of the existence of single phases or complexes of phases. It was only after the year 1896, when it could be taken for granted that the general

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character of the equilibria between liquid and vapour in binary systems had become fully understood, that efforts could be made to construct a complete graphical representation of the conditions of equilibrium in which solid phases occur.

The simplest possible case is found when only the two components of the binary system occur as solid phases. For such a case, I have since 1896 arrived at the representation in space of which photographs are given in the accompanying figures. For the case that chemical compounds or mixed crystals occur as solid phases other figures have been constructed which, however, may be deduced in a simple manner from the present ones.

In this figure the length represents the temperature, the breadth the concentrations x of the mixtures which can exist as vapour or liquid, the component A being placed at the left and the component B at the right. The height represents the pressure. The figure does not represent any particular case, but is so constructed that the different details come out plainly and the dimensions are not too great.

We start from the equilibria between liquid and vapour, which researches on the critical constants of mixtures have proved to be capable of representation by a surface of two sheets, the upper part of which represents the liquids and the lower part the vapours. The coexisting conditions of these two must have equal values of p and t and are therefore, situated on a horizontal line which is parallel to the x-axis. The said surfaces meet at the left side in the vapour-pressure line $O_A C$ of the liquid A, at the right side in the vapour-pressure line $O_B D$ of the liquid B and in front in the critical curve CD.

The points in the space between the two surfaces indicate complexes of liquid and vapour. In the representation, this space is massive, like all other spaces which represent complexes of *two* phases.

The surface of two sheets for liquid $+$ vapour is so constructed that A is the substance with the greatest vapour pressure. It has further been assumed that the liquids are miscible in all proportions and that no maxima or minima occur in the equilibrium pressure.

Descending continuously, the surface would reach the absolute zero if A or B or both did not solidify first.

The pure liquids A and B solidify in O_A and O_B; from there the vapour-pressure lines $O_A I$ and $O_B K$ of the solid substances run in the left and right vertical side-plane.

Considering now the liquid-mixtures with an increasing amount of B, solid A can only be deposited at temperatures lower than O_A. At each temperature there is a definite liquid and a definite vapour
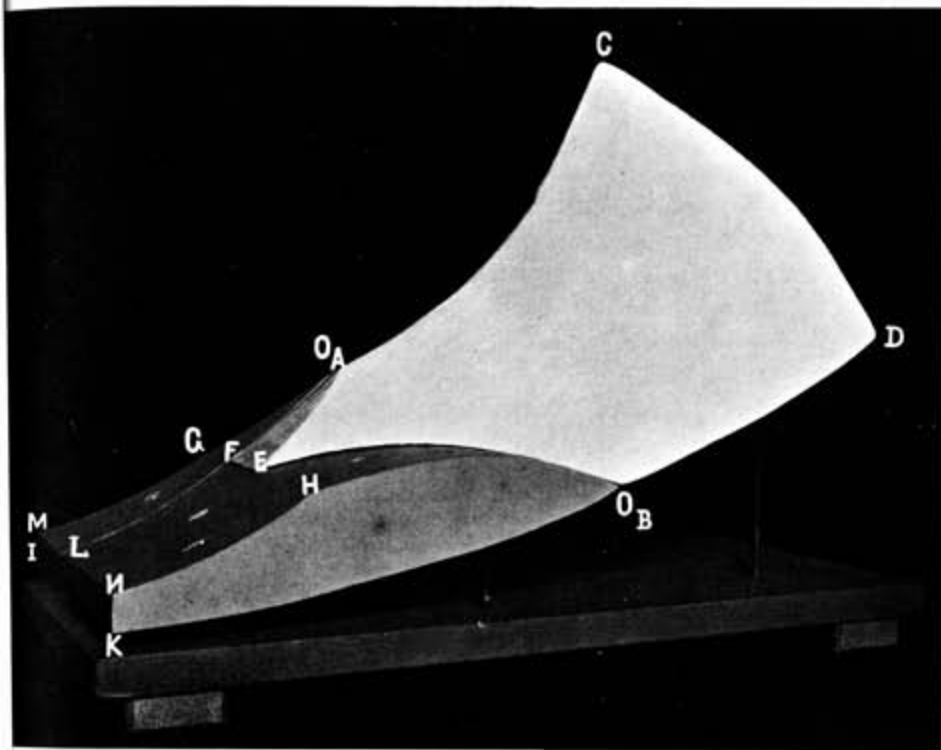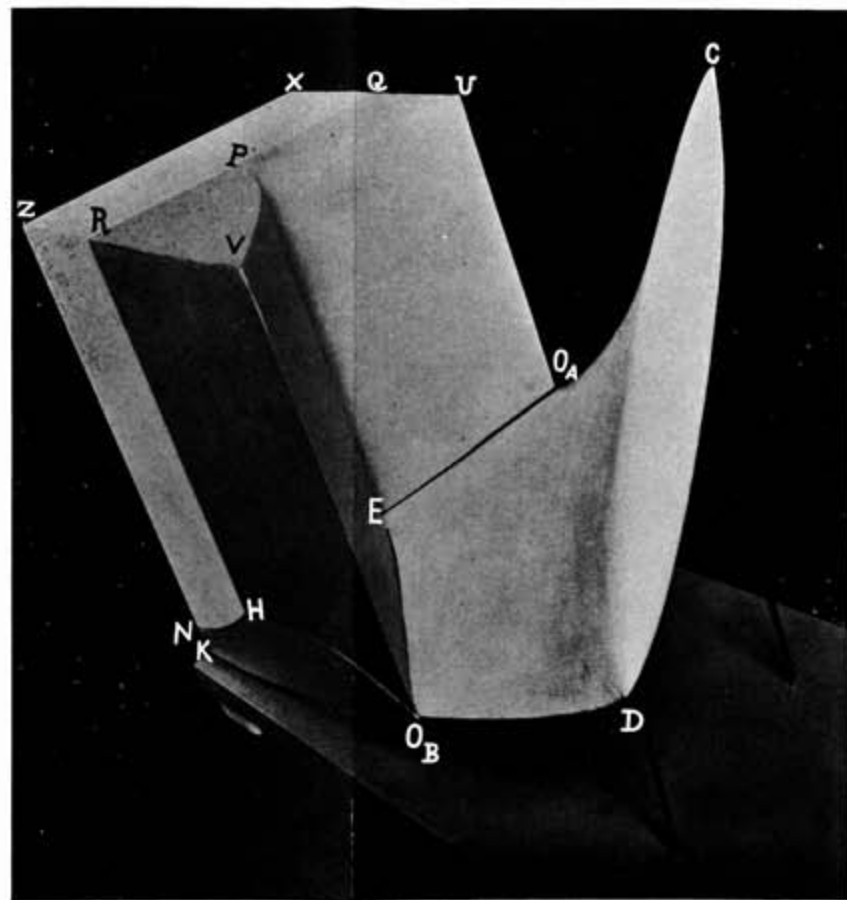
Fig. 1.

Fig. 2.

which coexist with the solid phase A at a definite pressure which is larger than the vapour-pressure of solid A alone, but the same for each of them. The three coexisting phases are represented by the lines $O_A G$, $O_A F$, $O_A E$ respectively standing for solid, gas and liquid. They are situated together on a cylindrical surface, because for equal t, also p is equal. The part $F O_A E$ is also a limitation of the surface of two sheets.

In the same manner we have for the equilibrium of solid B with liquid and vapour the three lines $O_B H$, $O_B E$, $O_B F$, for solid, liquid and gas respectively, again situated on a cylindrical surface, while the part $E O_B F$ thereof forms below a second limitation of the surface of two sheets. This cylindrical surface first rises from O_B but afterwards falls again.

The surface of two sheets terminates, as far as the liquid-surface is concerned, finally in E, the gas-surface in F. This liquid and this vapour may exist in contact with solid A (point G) and also with solid B (point H). As the points G, F, E, H belong to the same values of p and t, they are situated on a horizontal line and represent the only possible complex of four phases.

To the gas-line $O_A F$ a second gas-surface joins, representing the vapours capable of coexisting with solid A, when the quantity of B in the vapour increases; also to $O_B F$ the gas-surface for the vapours in equilibrium with solid B with increasing amounts of A. From the melting points of the pure substances down to the temperature of the quadruple-point $G F E H$ these two gas-surfaces are not in contact with each other, but each of them singly is in contact with the gas-surface of the surface of two sheets.

Below that temperature they intersect each other immediately, forming the line FL which represents the vapours capable of coexisting with solid A + solid B. To this belong the lines GM for solid A and HN for solid B which are again situated on a cylindrical surface.

All complexes of the solid phase A and of the coexisting vapours are situated within the space formed by the gas-surface $I O_A F L$, the surface of the solid phase $I O_A G M$ and the two cylindrical surfaces $G O_A F$ and $M G F L$. All complexes of the solid phase B and the vapours which can exist in contact with it, are situated in the space bounded by the gas-surface $K O_B F L$, the surface of the solid phase $K O_B H N$ and the cylindrical surfaces $H O_B F$ and $N H F L$.

Both spaces extend to the absolute zero if no new phases are formed.

The three surfaces representing the equilibria of gas with liquid, with

solid A and with solid B meet each other in the point F. In the same way, two other liquid-surfaces must join in the point E at which the liquid surface coming from higher temperatures ends, namely those which indicate the p, t, x values of the liquids which can coexist with solid A or solid B. The lower limits of these surfaces are the lines $O_A E$ and $O_B E$ which represent the equilibrium of solid and vapour. Setting out from these lines the vapour disappears when the pressure is increased. On account of the small changes which the composition of the liquid undergoes with an increase of pressure, the liquid-surfaces $O_A EPU$ and $O_B EPV$ will rise almost vertically. They terminate to the left and the right in the melting point lines $O_A V$ and $O_B V$ of the solid substances A and B, whilst they intersect each other in the line EP which indicates the liquids which at different p, t values can coexist with solid A and B. To this line belong the p, t lines GQ and HR for the solid phases, which again form a cylindrical surface with EP.

In this way we arrive for the complexes of solid A + liquid at the space included between the liquid-surface, the surface of the solid A, $O_A UQG$ and the cylindrical surfaces $GO_A E$ and $GEPQ$. A similar space includes, at the right, the complexes for solid B + liquid.

Finally, the region of the complexes of solid A + solid B is situated behind the cylindrical surface $GHRQ$ and above the cylindrical surface $NHGM$.

The spaces last described terminate in the figures at the back at an arbitrary temperature and above at an arbitrary pressure. One must suppose that, in reality they continue their course.

The remaining space outside the massive parts constitutes the regions of homogeneous liquids and vapours which pass into each other beyond the critical curve. The other six massive parts represent complexes of two phases, the states of matter forming the complex being represented by two side surfaces.

They further are connected with each other by four cylindrical surfaces on which three lines are always situated representing the systems of three coexisting phases and these cylindrical surfaces intersect each other in one straight line on which is situated the only possible complex of four phases.

If for any system of two substances the figure described were studied completely, it would enable us for each mixture at each temperature and each pressure to read off, of what phases it has been built up and as far as liquid and vapour are concerned it would also show their separate composition.

For the complexes of *two* phases, the relative proportions may also be read off in the figure; for those of *three* or *four* phases it would be necessary to also know the relation of the volumes.

The figure also makes it possible to ascertain what changes a mixture will undergo, when the temperature, pressure[1]) or concentration are changed.

Chemistry. — "*Equilibria of phases in the system acetaldehyde +*
paraldehyde with and without molecular transformation". By
Prof. H. W. Bakhuis Roozeboom.

(Communicated in the meeting of September 27, 1902).

The character of the equilibria of phases is exclusively determined by the number of independently variable constituents — components — of which the system is built up.

Sometimes this is equal to the number of the different kinds of molecules. It may also be smaller, if there are among the molecules those which may pass into each other as in the case of associating, ionizing or isomeric substances. If these molecular changes proceed more rapidly than the equilibria of the phases, they exercise no influence on them.

Although water, for example, is a mixture of at least two kinds of molecules, its freezing point is quite as sharply defined as that of a single substance.

If however, the velocity of the molecular change is small, the system on being treated rapidly will behave like one with more components than it shows if treated more slowly. The effect of this on the phenomena of solidification has already been mentioned by Bancroft in 1898 and by myself in 1899. So far, however, no suitable example has been found which would enable us to consider

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[1]) It demonstrates, for instance, in a simple manner that on compressing vapour mixtures with a sufficient amount of A, the component B first deposits in the solid state in increasing quantity but then again completely disappears at a certain pressure to make room for a liquid phase.

This phenomenon has recently been observed by Kuenen (Phil. Mag. July 1902) with solid CO_2 mixed with C_2H_6

It must always show itself with the component which in the liquid mixtures is the least volatile: in this case B. When however, the liquid-surface has a maximum pressure as in the instance cited by Kuenen, the phenomenon will be noticed with both components. If the surface has a minimum pressure it can only occur with one of the two.