

Citation:

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0.0013 (temp. 60°.1). If a large excess of NaOH is added from the commencement, the transformation velocity again reaches the same figure as for pure water; for 10 mols. of NaOH, $k = 0.0022$.

We are dealing here with a special unknown influence of the added substances; these certainly will modify the concentration of the molecules undergoing change, [either the salt mol. or the acid ion] by the diminution of the electrolytic dissociation, but as the reaction constant is independent of the concentration, this cannot explain the fall of that constant.

In the dry state the salt is more permanent than in solution, for after heating for about 2½ hours at 60° it was not perceptibly decomposed and gave no odour of HCN. At 70° it turns darker after some time and evolves HCN; the decomposition is then evidently more complicated.

Finally, the decomposition velocity was also determined in methyl- and ethylalcohol; that in ethylalcohol is the smallest whilst methylalcohol stands between water and ethylalcohol. I found at 60° for 1% solution in water 0.0023, in absolute methylalcohol 0.0017, in 97% methylalcohol 0.0018, for a ½% solution in 97% ethylalcohol 0.001°, for 50% ethylalcohol 0.0013. Addition of water consequently accelerates the transformation.

The intensity of the colour of a solution containing the same amount of sodium salt is largest for ethylalcohol, smaller for methylalcohol and smallest for water¹⁾; this phenomenon is undoubtedly connected with the fact that the electrolytic dissociation of salts in the said solvents increases in the order indicated.

Amsterdam. Dec. 1903.

Org. Chem. Lab. Univ.

Chemistry. — Prof. H. W. BAKHUIS ROOZEBOOM presents a communication from himself and Mr. A. H. W. ATEN on: "*Abnormal solubility lines in binary mixtures owing to the existence of compounds in the solution.*"

(Communicated in the meeting of December 19, 1903).

Last year²⁾ when engaged in a research on acetaldehyde and its polymer paraldehyde, I investigated the connection between the equilibria of phases of substances which in the liquid and gaseous condition consist of mixtures of two kinds of molecules in equilibrium, and the equilibria of phases in binary mixtures.

¹⁾ The solubility of the salt in ethylalcohol is also the smallest.

²⁾ Proc. Oct. 1903, p. 283.

This investigation is capable of further extension and so we can examine the equilibria of phases in binary mixtures in which the two components form one or more compounds.

Let us limit ourselves to the first case. If an equilibrium exists the quantity of the compound in the liquid or vapour will be dependent on the proportion of the two mixed components and on the temperature and pressure.

We now consider only the equilibria between liquid and solid and this at constant pressure. If the compound is wholly undissociated, the phenomena of melting and solidifying may be represented in space by means of an equilateral triangular prism in which the height represents the temperature and points in the equilateral triangle represent the relative proportions of the components a_2 and b_2 and of the compound.

For convenience we suppose the latter to be ab . It now behaves as an independent component, as it is supposed that there is no equilibrium between ab , a_2 and b_2 . We then obtain, in space, for each of the three solid substances a melting-surface which takes a downward course from the melting point.

Should, however, the compound be in equilibrium with its components, it ceases to be an independent component and at each temperature only those relative proportions can exist in a liquid condition, which are in internal equilibrium.

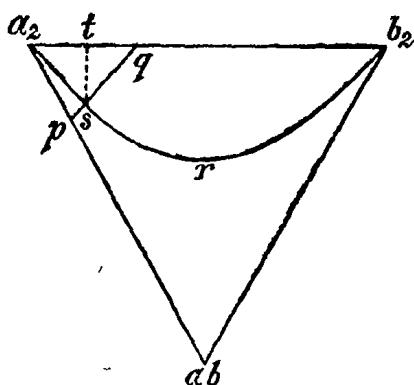


fig. 1.

The curved line $a_2 r b_2$ in the adjoining figure represents such an equilibrium line, which therefore indicates the only proportions capable of existing at a given temperature. We call this line the dissociation-isotherm.

If the compound did *not* form an equilibrium with its components and if the chosen temperature was situated below the melting point of a_2 a line $p q$ would then be the solubility-isotherm for the solid substance a_2 and in the case of an ideal course of the melting-surface of this component a_2 p would be equal to $a_2 q$ and the line $p q$ would be straight. The points of the line $p q$ then indicate the solutions which can be in equilibrium with solid a_2 at the temperature in question.

If, however, $a_2 r b_2$ is the equilibrium line of the liquid phase, the point s will be the only point of the line $p q$ which can exist

simultaneously with solid a_2 and be also in internal equilibrium.

But if that internal condition of equilibrium is not known we can only determine the gross composition of the liquid as a mixture of a_2 and b_2 and in this way we find the point t which is the projection of s .

Acting in the same manner we should obtain for all temperatures the actual composition of the solutions which at various temperatures are in equilibrium with solid a_2 and also their gross composition if we look upon them as binary mixtures built up from a_2 and b_2 .

The same might be determined in regard to the liquids in equilibrium with solid b_2 or solid ab . This shows that the equilibria of binary mixtures in which a dissociating compound may be formed from the components, must really be looked upon as ternary mixtures with a limiting clause, implied in the dissociation equilibrium in the liquid.

For this reason the form of the solubility-lines which we obtain in the system, considered as a binary mixture, is totally dependent on the manner in which the dissociation in the liquid phase and the melting-surfaces of the components change with a change of temperature.

Guided by these ideas, Mr. ATEN has worked out different theoretically-possible cases which can partly explain abnormal solubility-lines and which point, in addition, to phenomena as yet undiscovered.

Let us first suppose that the compound ab in the liquid condition is exothermic.

In such a case the dissociation of the compound at first increases but little as the temperature rises, then very much and afterwards again but little. If we draw, in the triangle, a series of dissociation isotherms for equal temperature intervals, these will at elevated temperatures lie close to the side a_2b_2 and will differ but little. Afterwards they will diverge greatly and finally come close together and approach the sides a_2ab and b_2ab . In Fig 2, nine such isotherms are shown.

Let us now draw for the same series of temperature the solubility-isotherms of a_2 and assume as the most normal case that they come closer together as the temperature falls (from 9 to 1).

The locus of the intersections of the dissociation- and solubility-isotherms is the projection of the spacial melting-point-curve for a_2 .

By projection on the side a_2b_2 we get the gross composition expressed in a_2 and b_2 and by now plotting temperatures as ordinates we obtain the solubility line $ABCDEF$ commencing at the melting point A . The line thus drawn exhibits three portions EF , FC and CBA which, particularly in the case of many salts, have been

repeatedly met with in different combinations and of which the middle part is particularly interesting because here the solubility of the component a_2 decreases with an increase of temperature.

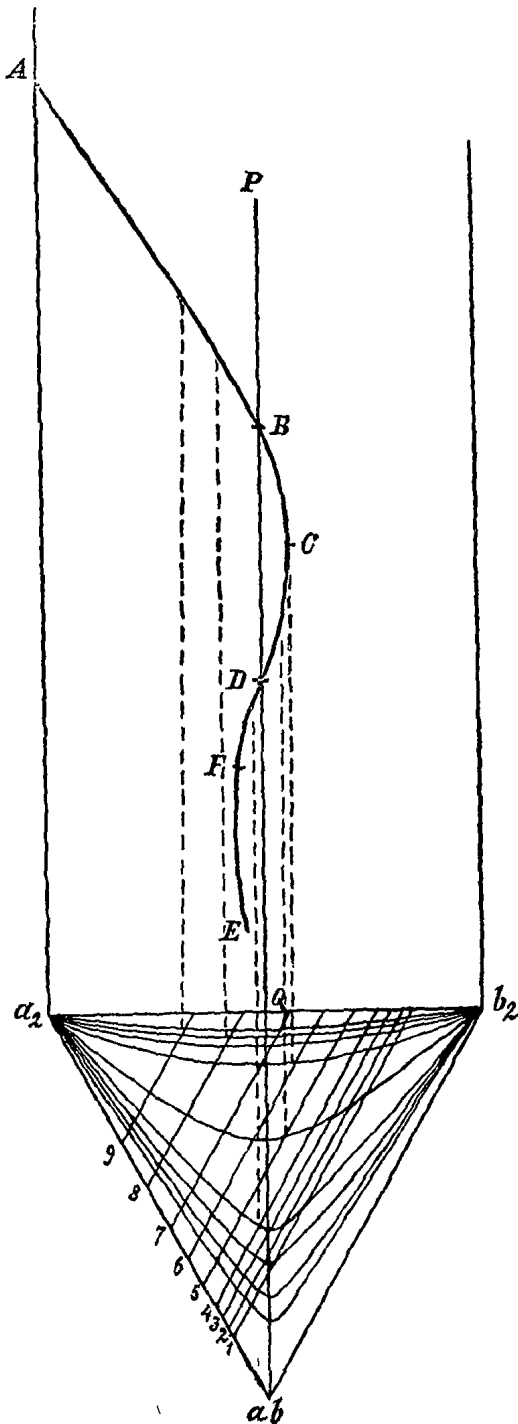


Fig. 2.

The heat of solution is here thermochemically positive; and zero in F and C . The explanation is now as follows:

The dissolution of the solid substance a considered by itself will be accompanied by absorption of heat; the formation of the compound, this being exothermic, with development of heat. In that region of temperature in which the formation of the compound chiefly takes place, it may, therefore, happen that the heat of formation of the compound exceeds that which is absorbed during the dissolution. This is the case from F to C , between which temperatures, as seen in the triangle, the dissociation isotherms are the most divergent and the quantity of the compound formed, therefore, increases most rapidly with a decreasing temperature.

The solubility-isotherms for a_2 will, at a sufficiently low temperature, approach to the side $b_2 ab$. If at a lower temperature the combination is complete, the intersection of the dissociation- and melting-isotherm will finally come very close to the angular point of the compound and the projected melting point line will, therefore, become an asymptote to the straight line PQ which indicates the composition of the compound. It is also possible that the melting point curve does not intersect the straight line PQ for the second time but remains to the right of PQ .

When a larger quantity of the compound is already present at a higher temperature, the bend is shifted further to the left, so that it may happen that the melting point line is not intersected by PQ .

If the formation of the compound takes place over a larger temperature interval, the bend $BCDF$ may disappear from the line and there may only remain a more strongly inclined part.

In a similar manner the solubility line for the compound ab or for the component b_2 may be determined. The different forms which these lines assume either wholly or in those parts which, owing to their mutual interference, are alone capable of existence, are again entirely dependent on the manner in which the solution-isotherms shift in regard to the dissociation-isotherms.

In this way all the known cases of the meeting of the lines of the components with those of the compound may be deduced. It also is shown how it is possible that the compound which exists partly in the liquid *cannot* separate in the solid condition and must, therefore, again be decomposed when the components solidify.

Another case, as yet unknown, may also be possible namely that after the solidification of the two components by *cooling* a liquid is again formed from which on further cooling the compound is depo-

sited (Fig. 3). This case is possible when the lines of the components have the shape of Fig. 2 and meet above C .

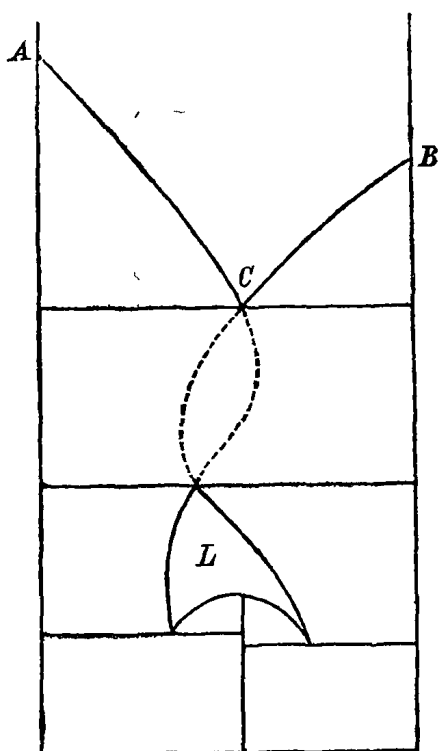


Fig. 3.

curve with two vertical lines in points where the heat of solution is zero, and two melting points.

In the space indicated by L there exist again unsaturated solutions all situated below the eutectic point C of $a + b$.

When the compound is endothermic the order of the dissociation isotherms is the reverse of that indicated in Fig. 2. Without entering into all the peculiarities which the solubility-lines may then exhibit, attention must be called to two as yet quite unknown types of melting point lines which may occur (Figs. 4 and 5).

In the first figure we have the remarkable fact that the compound forms with the component a a eutectic point C as well as a transition point D . In the second figure, the melting point line of the compound occurs as a closed

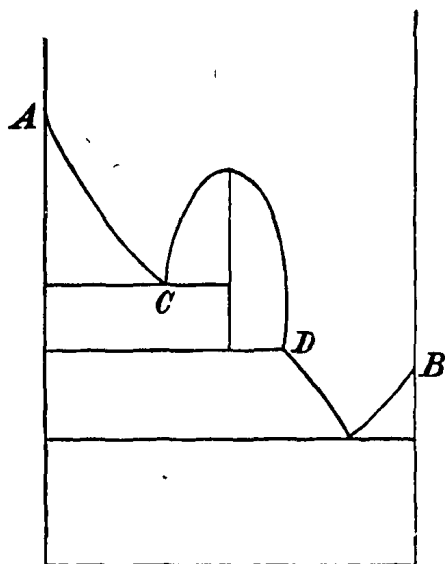


Fig. 4

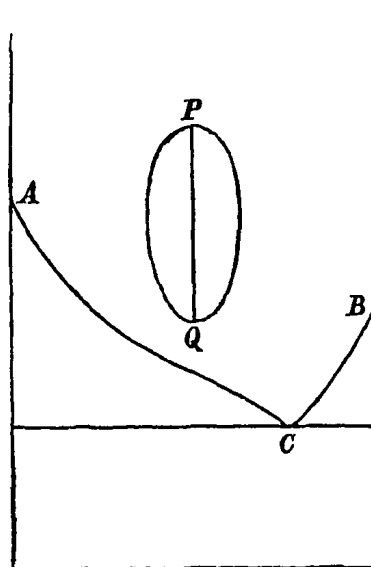


Fig. 5.

In the upper point P the compound passes into the liquid state, heat being absorbed. This absorption consists of two parts, the ordinary heat of fusion and the heat evolved when a part of the liquid (endothermic) compound decomposes until the equilibrium in the liquid is reached. As at higher temperatures the quantity of the compound in the liquid is large, the second quantity of heat will be small in comparison with the first and the melting will cause absorption of heat.

At Q it is, however, just the reverse because at a low temperature there exists but little compound in the liquid and the dissociation of a large proportion of the liquid compound may evolve so much heat that this exceeds the actual heat of fusion of the solid compound. The total fusion therefore produces heat and consequently the liquid field is situated below Q .

Up to the present, however, no endothermic compounds are known in the liquid state.

Microbiology. — Professor BEIJERINCK presents a paper from himself and Mr. A. VAN DELDEN: “*On the bacteria which are active in flax-rotting*”.

(Communicated in the meeting of December 19, 1903).

1. *How far flax-rotting should go.*

The object of flax-rotting is the partly solving and softening of the rind of the flax-stalk to remove the *pectose*, in consequence of which the bast-bundles are freed so that later, after drying, the fibres may easily be separated from the wood by breaking and scutching. Pectose (*pt* Fig. 1) is the substance of which the young cell-walls consist, as also the outer layers of the old cell-walls; these walls are further built up from *cellulose*, which in a good rotting does not undergo any change¹⁾.

By the rotting also the middle-lamellae, by which the fibres in the bast-bundles stick together, may go into solution and consequently the bast-bundles would be decomposed into the fibres proper. This is not desirable as in this case no large coherent “lints” would be got in scutching, but only loose fibres, of about 2 cm. in length.

The fibres of the bast-bundles, however, separate with much greater

¹⁾ For the microbes which affect the cellulose proper see OMELJANSKY, Centralb. f. Bacteriol. 2 Abt. Bd. 8 p. 193, 1901, and G. VAN IERSON. These Proceedings 24 April 1903.