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Departm. of Agriculture, Farmers' Bulletin N°. 17, Washington 1894) are, according to the description, undoubtedly caused by a contagium fluidum, but it is still dubious whether the infection is only transferred by grafting and budding, or, — which is more probable, — also by a virus existing outside of the plant.

Chemistry. — „*On congealing- and melting-phenomena in substances showing tautomerism*". By Prof. H. W. Bakhuis Roozeboom.

The latest discoveries on tautomerism, which have shown, that tautomeric substances in the liquid state must be considered as mixtures of two kinds of molecules of different structure, have raised the problem how to explain the complicate congealing- and melting-phenomena of such substances, in case both forms or one of them can appear in the solid state.

Some remarkable investigations on this subject have of late been made by Bancroft and his disciples, which were a continuation of a theory of Duhem.

At an attempt to unravel the investigations of Claisen on this subject, the reader had come to the same conclusions, which may be united to a perfectly clear graphic sketch.

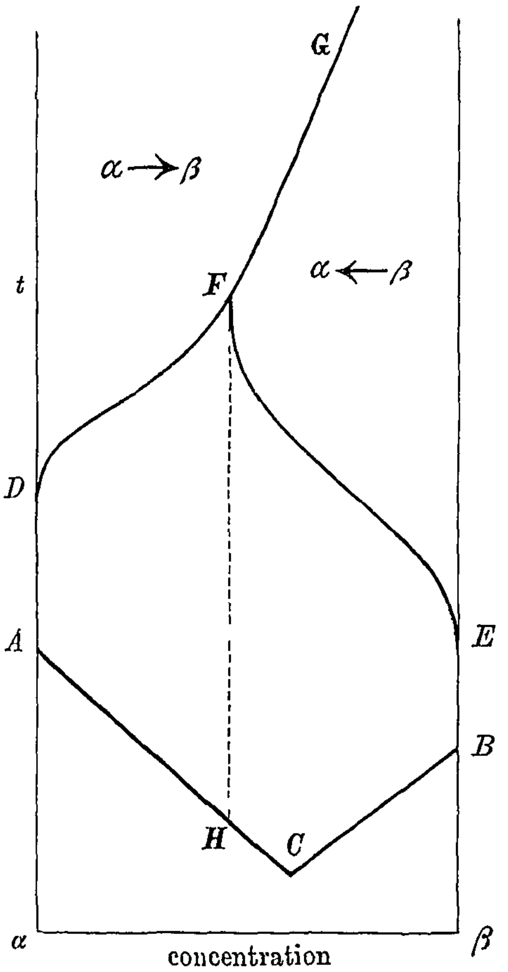
Bancroft having already published this, there would be no reason to revert to the subject, if not all examples chosen by him, referred to cases in which all the melting- and congealing-points were found in the region of temperatures in which equilibrium is still obtained between the two forms in the liquid state.

In such a case we generally have the disadvantage of there being no certainty about the mixing-proportion of the two substances at the moment of melting or congealing. Consequently it is impossible to give quantitative representations.

To arrive at a good understanding of the phenomena, it is therefore desirable to begin with a deduction of the conduct of tautomeric substances, the congealing temperatures of which are below the temperature-limit where in the liquid state transformation between two forms is still possible.

If we call the two forms α and β, we may build up a sketch in which the mixing proportion of α and β is measured on the horizontal axis of 0—100 and the temperature on the vertical axis.

According to the supposition made above, the congealing appears in the ordinary and simplest form of the congealing of mixtures of two substances i. e. starting from the melting points A and B of the two modifications, we have two melting-lines AC and BC



meeting in the point C, below which *every* liquid mixture congeals entirely to a conglomerate of α and β crystals.

We now suppose that at higher temperatures not all mixing-proportions in the liquid state are possible, but equilibrium appears, giving at each temperature a definite mixing-proportion of α and β. We represent these mixing-proportions by the line FG which is arbitrarily drawn as rising from left to right, representing the case in which the transition $\alpha \rightarrow \beta$ takes place with absorption of heat.

The reverse is also possible, or it may be a vertical line if the heat is zero.

On the left of the line FG is the region in which the transformation $\alpha \rightarrow \beta$ takes place, on the right that of the transformation $\alpha \leftarrow \beta$.

Now in case both transformations do not take place at lower temperatures, the supposition naturally occurs to us — on analogy of many other phenomena of recent date — that the transition from the region of *reciprocal equilibrium* to the region of no equilibrium is formed by two regions of *one-sided equilibrium*, as may be represented by splitting up the line GF into two lines FD and FE which end below certain temperatures on each of the axes.

If I now heat the solid modifications only a little above their melting point, they will be in a condition to congeal again at the same temperatures at which they melted. But if I heat them to a higher temperature, keeping them for some time at a temperature belonging to the region of one-sided or reciprocal equilibrium, a greater or less transformation in the liquid will take place between the two modifications, varying afterwards according to the velocity of cooling. The manner of proceeding of the congelation after return to this region will depend upon all these circumstances.

From the sketch the following conclusions may be drawn:

Case I. The substance α or β is heated for a considerable time after melting at a temperature situated *above* that of point F. Then the liquid is *slowly* cooled.

No matter what the heating-temperature was, and whether we started from α or from β, the congelation now begins in point H[1]), deposing solid α, until it is completed in C, deposing solid $\alpha + \beta$.

Case II. The substance α is heated for a considerable time after melting at a temperature situated *below* F, being afterwards *slowly* cooled.

The first melting point is now variable, always lying above H, and that the more so in proportion to the heating having taken place to a lower temperature. The first deposit is solid α, the congealing ends in C.

Starting from β, and in proportion to the heating having been lower than F, the first congealing point will be at first below H, deposing α, then falling to C, then rising along CB deposing β. C remains the final congealing point.

Case III. The substance α or β is heated for a considerable time after melting at a temperature *above* F, but afterwards *quickly* cooled.

The first congealing point is situated to the right of H, no matter whether α or β be the starting point, and this the more so in proportion to the heating having been greater and the cooling quicker.

The starting point of the congelation may even move past C, so that β becomes the substance first deposed, provided the line FG running sufficiently to the right. C remains the final congealing point.

Case IV. The substance α or β is heated for a considerable time after melting at a temperature *below* F being afterwards *quickly* cooled.

The results both for α and β are the same as in Case II.

Case V. If the heating does not last long enough to reach the final equilibrium in the liquid state, the same result as in Case II

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[1]) The point H lies vertically under F, or better still under the point of FE on which a vertical tangent may be drawn to this curve.

will be obtained in case of a quick cooling — independent of the situation of the heating-temperature.

The velocity of cooling as mentioned in Case III—V, is supposed to be such that the liquid finds no occasion to alter its mixing-proportion α/β acquired at a higher temperature. Should the velocity of cooling be less, this only results in the differences between the first acquired congealing-point and point H being smaller than in a case of very quick cooling. The deviations remain however in the same direction.

It is therefore possible to determine with perfect accuracy the apparently curious phenomena of congelation, with a knowledge of the lines GF, FD and FE. On the other hand it would be possible, from observation of the congealing temperatures, after the substance α or β having gone through a sharply defined way, to conclude to the situation of different points of these lines, consequently to determine their direction, if this were not possible along other ways.

The phenomena described here, may appear not only in tautomeric substances, but in all substances which in the liquid state, give two modifications that are apt to transformation.

Consequently many optic isomers that show equilibrium at higher temperatures, come under this head. There however the matter can often become complicated, it being possible that after the transformation of the *d* or the *l*-form, the racemic form deposes in the solid condition. It is however easy to take this into account.

Physics. — „*Variation of volume and of pressure in mixing*". By Prof. J. D. VAN DER WAALS.

The supposition of Mr. AMAGAT (C. R. 11 Juillet 1898), that in a mixture every gas can be considered to occupy the volume which it would occupy separately under the same pressure and at the same temperature, comes to the same thing as supposing, that mixing under a constant pressure does not cause variation of volume, and that there would be no question of either positive or negative contraction. As at great densities (of liquids), mixing is generally accompanied by contraction, the thesis, also in case of slight densities, can only be meant as an approximation. For slight densities this thesis can be tested by means of the characteristic equation of a mixture.