CCCXLIX.—*The Influence of Intensive Drying on Inner Equilibria. Part II.*

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THE theory of allotropy assumes that every phase of the allotropic substance is composed of different molecular species which are in inner equilibrium when the behaviour of the system is unary, *i.e.*

when it behaves as a one-component system. In certain circumstances, the establishment of the inner equilibrium is very slow or even stopped and the substance then behaves as a poly-component system.

This theory enabled the author (*Z. physikal. Chem.*, 1922, **100**, 477) to give an explanation of the influence of intensive drying on the boiling points of nitrogen trioxide and nitrogen tetroxide as found by H. B. Baker and Mrs. Baker.

The view was that by intensive drying the inner transformations in a unary phase are stopped, *i.e.*, the inner equilibrium is fixed. In 1923, this phenomenon was discussed once more (" Theory of Allotropy," p. 316) in the light of Baker's new experiments (J., 1922, **121**, 568) and the original explanation was supplemented by
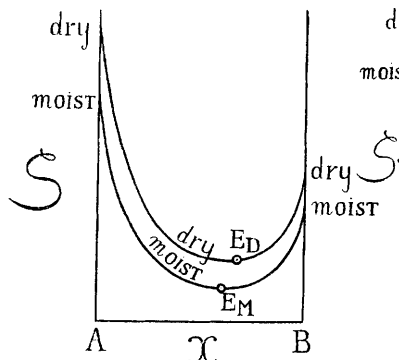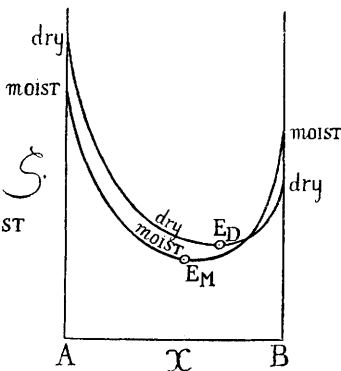
FIG. 1.   FIG. 2.

the assumption that the inner equilibrium is first displaced and then fixed (see also J., 1924, **125**, 1068).

Assuming that the so-called single substance exists in two molecular species α and β, three different cases may be considered :

A. It is possible that both α and β are more stable in the moist state than in the intensively dried state. In this case we obtain two curves for the values of the thermodynamic potential as a function of the composition x at constant pressure and temperature, one corresponding with the moist and the other with the intensively dried mixture. The curve for the more stable, moist mixture will have a lower value as indicated in Fig. 1. The inner equilibrium is always situated at the minimum point (see " Theory of Allotropy," p. 6), and from this graphical method we see clearly (1) that it would be quite fortuitous if the compositions of the dry and the moist inner equilibria were the same, and (2) that the composition

of the dry inner equilibrium may be situated either to the left or to the right of that of the moist inner equilibrium.

B. Another possibility is that α is stable in the moist and β in the intensely dry state. In this case we obtain Fig. 2, and the conclusions are the same as in the first case.

C. Finally, we have the possibility that the intensive drying has no influence at all on the stability of the pseudo-components. It is evident that in this case the ζ-x curves for the intensely dry and the moist mixtures coincide completely, and consequently the compositions of the dry and moist inner equilibria are also identical.

From these considerations, it follows that, if intensive drying has any influence on the stability of the pseudo-components, we may, in general, expect a displacement of the inner equilibrium by intensively drying a substance, but the direction of this displacement cannot be predicted. Thus the inner equilibrium may be shifted by intensive drying in one case in the direction of the more volatile pseudo-component α and in another case in that of the less volatile pseudo-component β. In the limiting case, this displacement may take place practically along the axis of one of the pseudo-components.

As regards the velocity with which inner equilibrium is established, the results obtained by H. B. Baker, Mrs. Baker, and myself show that the influence of intensive drying on the velocity of inner transformation may be very large; in several cases it appears that these inner transformations have ultimately stopped completely. In all probability this effect will not be so strong in every case, the final state depending on the individual properties of the substance, the state of aggregation, and the temperature.