Chemistry. — *"The Apparent Contradiction between Theory and Practice in the Crystallisation of Allotropic Substances from Different Solvents".* By Prof. A. SMITS. (Communicated by Prof. J. D. VAN DER WAALS).

1. *Derivation of the equation for the connection between the saturation concentrations and those of the internal equilibrium.*

In this communication I will give in the first place the thermodynamic derivation of the equations derived in the first communication on this subject in simpler but less rigorous way.

We shall suppose for this purpose that in a homogeneous phase, a gas phase or a solution, at a definite temperature and pressure between two kinds of molecules of the same substance the following equilibrium prevails:

$$v_1 A \rightleftarrows v_2 B \qquad \qquad (1)$$

We further suppose that in two separate spaces at the same temperature the solid substances A and B are in equilibrium with their saturate vapour resp. solution, hence:

$$A_s \rightleftarrows A_G \qquad \qquad (2)$$

$$B_s \rightleftarrows B_G \qquad \qquad (3)$$

Now we shall assume that v_1 mol. of solid A by the aid of the homogeneous phase, which is a gas resp. a liquid phase, is converted into v_2 mol. of solid B

In the first process, which we shall consider now, the homogeneous phase is thought to be a gas phase, in which internal equilibrium prevails, and in the second process the homogeneous phase is thought to be a solution, in which the kinds of molecules A and B are likewise in internal equilibrium. In these two cases the increase of the molecular potential $\Sigma v\mu$ must, of course, be the same.

Before proceeding to the first process, I will first observe, that for the increase of the molecular potential or:

$$\Sigma (v\mu)_s = v_2 \mu_{s_B} - v_1 \mu_{s_A} \cdot \qquad \qquad (4)$$

may be written:

$$\Sigma(v\mu)_s = v_2\mu_{s_B} - v_1\mu_{s_A} = v_2\mu_{s_B} - v_2\mu_{G_B} + v_2\mu_{G_B} - v_1\mu_{G_A} + v_1\mu_{G_A} - v_1\mu_{s_A} (5)$$

in which μ_{G_A} and μ_{G_B} represent the molecular potentials of A and B in the saturate vapour.

For the heterogeneous equilibrium between solid A and its vapour and solid B and its vapour hold the following relations:

$$\mu_{s_B} = \mu_{G_B} \quad \text{or} \quad \nu_2 \mu_{s_B} = \nu_2 \mu_{G_B} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

and

$$\mu_{s_A} = \mu_{G_A} \quad \text{or} \quad \nu_1 \mu_{s_A} = \nu_1 \mu_{G_A} . \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

By combination of (5) with (6) and (7) we then get:

$$\Sigma \, (\nu\mu)_s = \nu_2 \mu_{G_B} - \nu_1 \mu_{G_A} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (8)$$

If we now express the internal equilibrium potentials of gaseous A and B by:

$$\mu'_{G_A} \quad \text{and} \quad \mu'_{G_B}$$

then

$$\nu_1 \mu'_{G_A} = \nu_2 \mu'_{G_B}$$

for internal equilibrium, so that instead of (8) we may also write:

$$\Sigma \, (\nu\mu)_s = \nu_2 \mu_{G_B} - \nu_2 \mu'_{G_B} + \nu_1 \mu'_{G_A} - \nu_1 \mu_{G_A} \quad \cdot \quad \cdot \quad \cdot \quad (9)$$

in which $\nu_2 \mu_{G_B} - \nu_2 \mu'_{G_B}$ represents the work done or gained when we give the equilibrium potential to ν_2 mol. of gaseous B, which possess the mol. potential of the saturate vapour, and thus

$$\nu_1 \, \mu'_{G_A} - \nu_1 \, \mu_{G_A}$$

represents the work performed or gained when ν_1 mol. of gaseous A are brought from the equilibrium potential on the potential of the saturate vapour.

These two values for the work are easy to compute.

We start from the equation:

$$d\mu = - \eta dT + vdp \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (10)$$

hence

$$(d\mu)_T = vdp \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (11)$$

or

$$(\mu)_T = \int vdp = RT \ln p + C$$

from which follows that:

$$\mu'_{G_A} = RT \ln p'_A + C$$

and

$$\mu_{G_A} = RT \ln p_A + C$$

or

$$\mu'_{G_A} - \mu_{G_A} = RT \ln \frac{p'_A}{p_A} = RT \ln \frac{C'_{A_G}}{C_{A_G}} . \quad \cdot \quad \cdot \quad \cdot \quad (12)$$

hence

$$\nu_1 \mu'_{G_A} - \nu_1 \mu_{G_A} = \nu_1 \, RT \ln \frac{C'_{A_G}}{C_{A_G}} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (13)$$

In the same way we get for:

$$v_2 \mu_{G_B} - v_2 \mu'_{G_B} = v_2 \, RT ln \, \frac{C_{B_G}}{C'_{B_G}} \quad . \quad . \quad . \quad (14)$$

so that equation (9) now assumes the following form:

$$\Sigma \, (v\mu)_S = v_2 \, RT ln \, \frac{C_{B_G}}{C'_{B_G}} + v_1 \, RT ln \, \frac{C'_{A_G}}{C_{A_G}} \quad . \quad . \quad . \quad (15)$$

Now we can apply the same considerations for the case that the homogeneous phase, in which there is internal equilibrium, is a solution (second process); then we get instead of equation (15):

$$\Sigma \, (v\mu)_S = v_2 \, RT ln \, \frac{C_{B_L}}{C'_{B_L}} + v_1 \, RT ln \, \frac{C'_{A_L}}{C_{A_L}} \quad . \quad . \quad . \quad (16)$$

As $\Sigma \, (v\mu)_S$ has the same value in the two cases, the second member of equation (15) will be equal to the second member of equation (16).

Then follows from equation (15) and (16), that:

$$\frac{C'^{v_1}_{A_L}}{C'^{v_2}_{B_L}} = \frac{C^{v_1}_{A_L}}{C^{v_2}_{B_L}} \cdot \frac{C'^{v_1}_{A_g}}{C'^{v_2}_{B_g}} : \frac{C^{v_1}_{A_g}}{C^{v_2}_{B_g}} \quad . \quad . \quad . \quad . \quad . \quad (17)$$

The concentrations provided with accents indicate the internal equilibrium concentrations, and those without accents the saturation concentrations.

Let us suppose that we have to do with isomers, then:

$$v_1 = v_2 = 1,$$

hence:

$$\frac{C'_{A_L}}{C'_{B_L}} = \frac{C_{A_L}}{C_{B_L}} \cdot \frac{C'_{A_g}}{C'_{B_g}} : \frac{C_{A_g}}{C_{B_g}} \cdot \quad . \quad . \quad . \quad . \quad . \quad (18)$$

This equation is the same as equation (16) in the first communication. [1])

If we have the case of polymery, and if e.g.

$$v_1 = 2 \quad \text{and} \quad v_2 = 1$$

the general equation (17) passes into:

$$\frac{C'^2_{A_L}}{C'_{B_L}} = \frac{C^2_{A_L}}{C_{B_L}} \cdot \frac{C'^2_{A_g}}{C'_{B_g}} : \frac{C^2_{A_q}}{C_{B_g}} \cdot \quad . \quad . \quad . \quad . \quad . \quad (19)$$

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[1]) See preceding communication p. 361.

This equation is again the same as equation (20) in the first communication.

2. *Apparent contradiction between theory and practice.*

DIMROTH [1]), who wrote equation (18) as follows:

$$\frac{C'_{A_L}}{C'_{B_L}} = \frac{C_{A_L}}{C_{B_L}} G \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

has pointed out that, the direction of the isomeration being exclusively dependent on the factor G, this must be *independent* of the nature of the solvent.

Experience, says DIMROTH, is in contradiction with this, for it is known that isomers can be transformed into each other by treatment with different solvents.

In this connection I must point out in the first place that there can be question of a test of formula (20) only when we start from a solution saturate with respect to A and B *in contact* with the two solid phases. Only in one case there will then come no change in this state, viz. when the temperature of the system is exactly the transition temperature of the two solid phases. In all other cases a transformation will take place *independent* of the solvent, in which the metastable solid modification disappears, and the stable one remains. For some systems this transformation will proceed slowly, but then we must try to accelerate the process catalytically.

When, working in *this way*, we find deviations, it will no doubt have to be ascribed to this that equation (20) is applied to *non-ideal* cases, or to the case of *polymers.* That practice is really in agreement with theory, can be demonstrated in such a case in a simple way by application of the *universally holding* equation (6) of the preceding communication :

$$\frac{x_L}{y_L} = f_1 \frac{X_L}{Y_L}$$

in the way indicated there.

That isomers can be converted into each other by treatment with different solvents is an entirely different phenomenon. By this we understand namely that when e.g. the α-form is dissolved in a certain solvent, and we then bring the' solution to crystallisation in some way or other, the β-form appears.

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[1]) Lieb. Ann. **377**, 127 (1910).

We should, however, bear in mind that the formulae discussed here refer to *equilibria*, whereas the last mentioned phenomenon is a question of *number of nuclei* and *spontaneous crystallisation*.

I discussed this question already fully on an earlier occasion [1]), so that I will only say a few words about it here.

Suppose that at a definite temperature and pressure, the situation of the solubility isotherms aL and bL and that of the line for the internal equilibrium in the liquid phase is as is indicated in fig. 1;
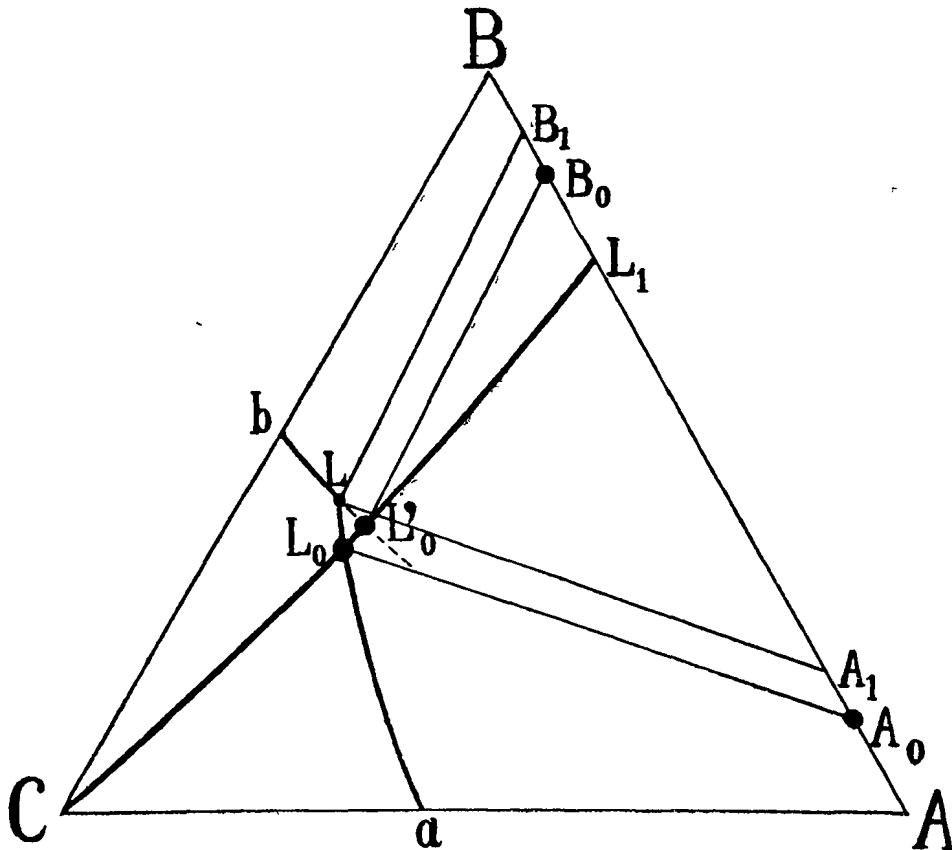

Fig. 1.

then we see immediately that from an supersaturate solution, in which A^- and B are in internal equilibrium, the stable modification A_0 or the metastable modification B_0 can deposit. The liquid L_0 is namely the stable saturate solution coexisting with A_0, L'_0 indicating the metastable saturate solution, which is in equilibrium with B_0. If the solutions L_0 and L'_0 lie under the point L, i. e. if L'_0 and L_0 contain more of the pseudo-component A than L, and if these points,

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[1]) Zeitschr. f. phys. Chem. 84 (1913).

as in fig. 1, lie pretty much on the B-side, it may occur that in
consequence of the greater concentration of B than of A, the number
of nuclei for the metastable modification B_0 reaches that value first,
at which spontaneous crystallisation sets in. In this case, therefore,
the metastable modification deposits from the supersaturate solution,
and if under the given circumstances the velocity of conversion is
small, the metastable modification that has crystallized out, con-
tinues to exist.

If, therefore, the situation is as Fig. 1 indicates, it is very well
possible that when the stable modification A_0 is dissolved in C at
higher temperature, i.e. at such a temperature that the internal
equilibrium is entirely or almost entirely established, the metastable
form is deposited when the solution is cooled.

For one solvent the situation will be as is indicated in Fig. 1,
whereas this situation will be less one-sided when another solvent
is used, and in this probably lies the explanation of the fact that
by means of one solvent from the stable form the metastable form can be
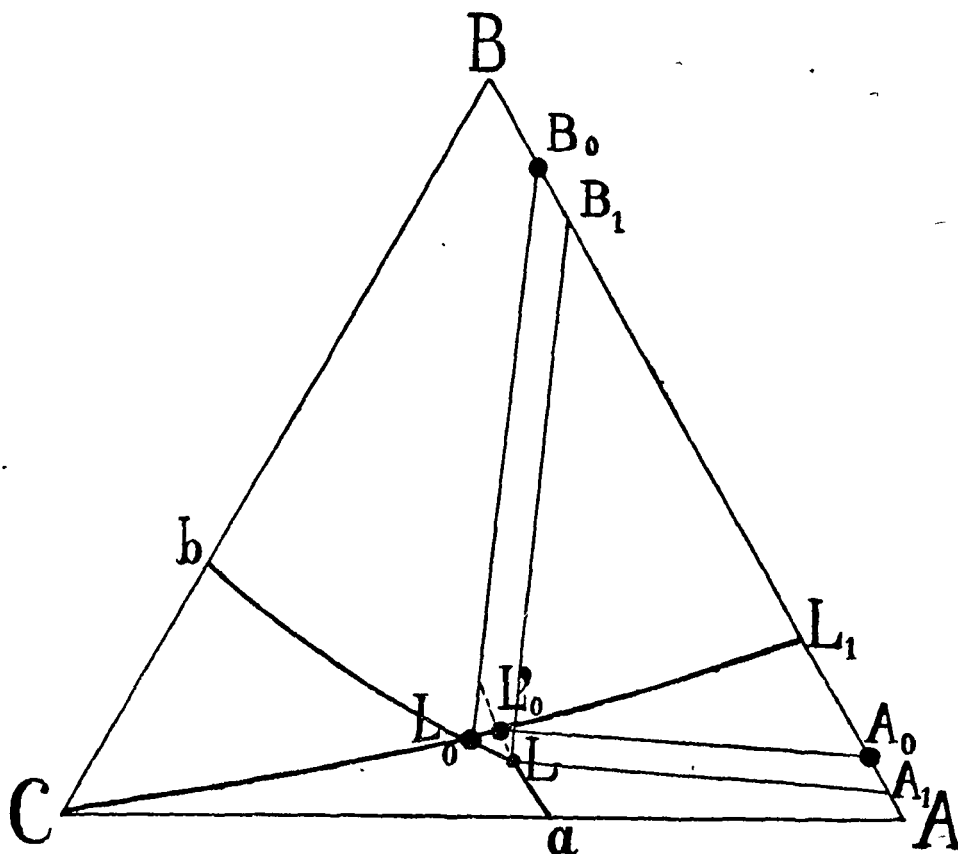

Fig. 2.

obtained, whereas another solvent always yields the stable modification.

If, therefore, the line for the internal equilibrium as Fig. 2 shows, lies above L, i.e. if at the considered temperature B_0 is stable, and L_0 and L'_0 lie greatly on the A-side, then for the same reason the *possibility* is to be expected that when B_0 is dissolved in C, the metastable modification A_0 deposits from the supersaturate solution at lower temperature.

Where this phenomenon presents itself it will be an interesting problem to determine the situation of the points L, L_0, and L'_0 at a definite temperature, to find out in this way in how far the given explanation is the true one.

Amsterdam, 24 June 1915. *Anorg. Chem. Lab. of the University.*

Chemistry. — *"Supersaturation and release of supersaturation."*
     By Devendra Nath Bhattacharyya and Nilratan Dhar.
     (Communicated by Prof. Ernst Cohen).

The older literature on supersaturation, chiefly works of Gay Lussac [1]), Schweigger [2]), Ziz [3]), Thomson [4]), Ogden [5]), and others, abounds with evidences showing that the phenomenon is rather common.

But after that, the general idea of the chemists was that only few substances could form supersaturated solutions.

But now a days chemists have recognised again that the phenomenon is common. Thus Mendeléeff [Principles of Chemistry, English translation (1905), p. 93] states that salts which separate out with water of crystallisation and form several crystallohydrates yield supersaturated solutions with the greatest ease, and the phenomenon is much more common than was previously imagined. Ostwald has studied this case very thoroughly and is of opinion that this is very common. Tutton also mentions in his book, "Crystals" (p. 238) that supersaturation is a phenomenon of frequent occurrence.

But the reminiscence of the old idea is still unconsciously present in the popular mind. For demonstration experiments, sodium acetate, or sodium sulphate, or sodium thiosulphate is invariably taken. Also

[1]) Ann. Chim. **87**, 225; Schw. **9**, 70; Ann. Chim. Phys. **11**, 301.

[2]) Schw. **9**, 79.

[3]) Schw. **15**, 160.

[4]) Ann. Phil. **19**, 169.

[5]) N. Ed. Phil. J. **13**, 309