

Citation:

A. Smits, On the Influence of the Solvent on the Situation of the Homogeneous Equilibrium. I, in: KNAW, Proceedings, 19 I, 1917, Amsterdam, 1917, pp. 708-712

of which the first has only been mentioned as yet. The second differs from the first only in this that the melting-point diagram possesses a eutectic point.

Fig. 3 represents in this case the T, x -projection of the three-phase regions of the pseudo system with the two phase regions of the unary system lying in them.

This figure, which does not call for any further elucidation, also represents a case not considered up to now, for which the solid phase lies between the two others on one three-phase region for $S + L + G$, the situation on the other three-phase region being the usual one. At present there is no reason to prefer one representation (Fig. 2) to the other (Fig. 3).

In conclusion it may still be pointed out that as is known, HgI_2 at high temperatures begins to split up appreciably into Hg_2I_2 and I_2 . This splitting up is disregarded here, because evidently it is not essential here for the phenomenon of allotropy.

SUMMARY:

On the ground of new researches a modification was applied to the representation of the system mercuriodide, which has entirely obviated all the former difficulties and in consequence of which an altogether satisfactory concordance with the observed phenomena was obtained.

Anorg. Chem. Lab. of the University.

Amsterdam, Sept. 1916.

Chemistry. — “*On the Influence of the Solvent on the Situation of the Homogeneous Equilibrium*”. I. By Prof. A. SMITS. (Communicated by Prof. F. A. H. SCHREINEMAKERS).

(Communicated in the meeting of October 28, 1916).

1. It is universally known that the solvent frequently greatly influences the situation of the homogeneous equilibrium. This has appeared, for instance in the determination of the equilibria of the *triazol carbonic acid esters* in different solvents, carried out by DIMROTH ¹⁾, and from VON HALBAN's ²⁾ researches on the conversion

¹⁾ Lieb. Ann. **377**, 133 (1910).

²⁾ Zeitschr. f. phys. Chem. **67**, 129 (1909).

of *para* bromine phenyldimethyl allyl ammonium bromide, besides from the study of the equilibria between the keto- and enol forms of the acetyl acetic ester made by KURT MEIJER¹⁾. In spite of various attempts the explanation of this phenomenon has not yet been found. Yet it seems to me that the solution might be given in the following way.

For this purpose we start from the equation:

$$Z = E - TH + PV \quad \dots \quad (1)$$

When with constant P and T we now differentiate with respect to \bar{n}_1 , we get:

$$\left(\frac{dZ}{dn_1}\right)_{P,T} = \left(\frac{dE}{dn_1}\right)_{P,T} - T \left(\frac{dH}{dn_1}\right)_{P,T} + P \left(\frac{dV}{dn_1}\right)_{P,T} \quad \dots \quad (2)$$

Now

$$\left(\frac{dZ}{dn_1}\right)_{P,T} = \mu_1 \quad \dots \quad (3)$$

It should further be noticed that as we consider solutions here, $\left(\frac{dV}{dn_1}\right)_{P,T}$ is very small.

With regard to P it may be said that when the solvent has a slight vapour tension and the experiment is made in vacuum, this quantity is very small too. But also when an open vessel is used, and P is 1 atm., the term $P \left(\frac{dV}{dn_1}\right)_{P,T}$ is so small, that we may safely neglect it by the side of the others.

Just as in general the entropy may be split up into a concentration entropy and a concentration term, we can write here for the entropy increase when 1 gr. mol. is added reversibly:

$$\left(\frac{dH}{dn_1}\right)_{P,T} = \left(\frac{dH}{dn}\right)_{P,T, C=1} - R \ln C_1 \quad \dots \quad (4)$$

so that we get:

$$\mu_1 = \left(\frac{dE}{dn_1}\right)_{P,T} - T \left(\frac{dH}{dn_1}\right)_{P,T, C=1} + RT \ln C_1 \quad \dots \quad (5)$$

Now on summation over all reacting components, we get:

$$\sum \nu \mu = \sum \nu \left(\frac{dE}{dn_1}\right)_{P,T} - T \sum \nu \left(\frac{dH}{dn_1}\right)_{P,T, C=1} + RT \sum \nu \ln C_1 \quad \dots \quad (6)$$

If we now put:

$$\left(\frac{dE}{dn_1}\right)_{P,T} = E_1 \quad \text{and} \quad \left(\frac{dH}{dn_1}\right)_{P,T, C=1} = H_1 \quad C=1$$

¹⁾ Ber. 47. 832 (1914),

we get

$$\Sigma v_i \mu = \Sigma v_i E_i - T \Sigma v_i H_{i,C=1} + RT \Sigma v_i \ln C_i \quad (7)$$

If we now bear in mind that in the state of equilibrium:

$$\Sigma v_i \mu = 0 \quad \text{and that} \quad RT \Sigma v_i \ln C_i = RT \ln K_C$$

it follows from (7) that:

$$RT \ln K_C = - \Sigma v_i E_i + T \Sigma v_i H_{i,C=1}$$

or

$$\ln K_C = - \frac{\Sigma v_i E_i}{RT} + \frac{\Sigma v_i H_{i,C=1}}{R} \quad (8)$$

Before we proceed it should be pointed out that $\Sigma v_i E_i$, which quantity denotes the change of energy at the temperature of observation, is practically independent of the temperature, and may, therefore, be considered as a constant; because the sum of the specific heats of the second member of the equation of reaction diminished with the sum of the specific heats of the first member yields a quantity perfectly negligible here as was lately fully demonstrated by Dr. SCHEFFER¹⁾.

The solution of the problem now under discussion, is exceedingly simple, when the sum of the entropies $\Sigma v_i H_{i,C=1}$ has the same value in the different solvents, at least so little different that the deviations can be entirely neglected by the side of the sums of the energies $\Sigma v_i E_i$ ²⁾.

This case can of course only be expected when the influence of the solvent on the dissolved substance is of exclusively physical nature.

If we, therefore, apply equation (8) to the same equilibrium in two different solvents *I* and *II*, the just mentioned supposition comes to this that in the equations:

$$\ln K_I = - \frac{(\Sigma v_i E_i)_I}{RT} + C_I \quad (9)$$

and

$$\ln K_{II} = - \frac{(\Sigma v_i E_i)_{II}}{RT} + C_{II} \quad (10)$$

the relation:

$$C_I = C_{II} \quad (11)$$

¹⁾ This part of these Proceedings p. 656.

²⁾ This assumption is of the same nature as that introduced by Dr. SCHEFFER in his paper 'On the Velocity of Substitutions in the benzene nucleus'. He assumed there that the "difference in substitution entropy would be zero for the different hydrogen atoms". These Proc. Vol. XV. p. 1118.

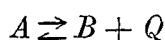
holds for the entropy constants, so that, when we put $(\sum v_i E_i)_I = Q_I^s$ and $(\sum v_i E_i)_{II} = Q_{II}$

$$\ln \frac{K_I}{K_{II}} = \frac{Q_{II} - Q_I}{RT} \dots \dots \dots (12)$$

This formula expresses that the difference in situation of the chemical equilibrium in the two different solvents must be ascribed to a difference in heat of reaction.

Now it is at once clear that a difference in thermal effect of the same reaction in different solvents is due to the difference in heat of mixing of the reacting components in the different solvents.

If we, namely, consider the simple conversion :



we can think this heat-effect split up into three factors.

1. the differential heat of unmixing of $A = -Q_{M_A}$,
2. the heat of reaction of the conversion of 1 gr. mol. of liquid A in 1 gr. mol. of liquid $B = Q_R$,
- and 3 the differential heat of mixing of $B = Q_{M_B}$;

hence

$$Q = -Q_{M_A} + Q_R + Q_{M_B}$$

We get, therefore, for the heat effects in the two solvents :

$$Q_I = -Q_{M_{A_I}} + Q_R + Q_{M_{B_I}} \dots \dots \dots (13)$$

and

$$Q_{II} = -Q_{M_{A_{II}}} + Q_R + Q_{M_{B_{II}}} \dots \dots \dots (14)$$

so that

$$Q_{II} - Q_I = (Q_{M_{A_I}} - Q_{M_{A_{II}}}) - (Q_{M_{B_I}} - Q_{M_{B_{II}}}) \dots \dots (15)$$

If we now indicate the difference in heat of mixing of A in the two solvents by $Q_{M_{A_I-II}}$, that of B by $Q_{M_{B_I-II}}$, our equation (12)

becomes

$$\ln \frac{K_I}{K_{II}} = \frac{Q_{M_{A_I-II}} - Q_{M_{B_I-II}}}{RT} \dots \dots \dots (16)$$

i. e. the influence of the solvent on the situation of the chemical equilibrium is due to the difference in heat of mixing for the reacting components in these different solvents.

To test this conclusion it will, therefore, be sufficient to determine by the side of the constants of equilibrium the heats of solution

of the reacting substances in different solvents, because the difference in heat of solution of e.g. *A* in different solvents is equal to the difference of heat of mixing.

3. Another conclusion to which the supposition made here leads, is this: It follows from equation (12) that when $K_I > K_{II}$, also $Q_{II} > Q_I$.

If we now differentiate (12) with respect to *T*, we get:

$$\frac{d \ln \frac{K_I}{K_{II}}}{dT} = \frac{Q_I - Q_{II}}{RT^2} = \text{negative.} \quad (17)$$

from which therefore follows that when $K_I > K_{II}$ the difference $\ln K_I - \ln K_{II}$ will diminish on increase of temperature, i.e. the difference in situation of the equilibria in the two different solvents will decrease at higher temperature.

4. It is almost superfluous to point out here that when the supposition $C_I = C_{II}$ is not introduced, we obtain through subtraction of equation (10) from (9) the equation:

$$\ln \frac{K_I}{K_{II}} = \frac{Q_{II} - Q_I}{RT} + C_I - C_{II} \quad (18)$$

which likewise gives

$$\frac{d \ln \frac{K_I}{K_{II}}}{dT} = \frac{Q_I - Q_{II}}{RT^2}$$

on differentiation with respect to *T*, but this equation in itself could not convey any special meaning to us. In virtue of (12) it could be concluded that when $K_I > K_{II}$, also Q_{II} must be $> Q_I$, and this gave rise to the conclusion under 3.

5. In conclusion it may be pointed out that when it should appear that the difference $C_I - C_{II}$ may not be neglected the above given consideration will lead us to the knowledge of this difference, so that at any rate a study in this direction will lead us to a deeper insight in this so important phenomenon.

*Anorg. Chem. Laboratory of the
University of Amsterdam.*

Amsterdam, 17 October.