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Chemistry. — “*On the latent heat of mixing for associating solvents.*”
By J. J. VAN LAAR. (Communicated by Prof. H. W. BAKHUIS
ROOZEBOOM).

(Communicated in the meeting of June 25, 1904).

1. When some substance is solved in an *associating* liquid, as e.g. *water*, and we try to find an expression for the latent heat of mixing of these two substances, we shall in the first place have to take into account, besides the change of the potential energy, the heat of *ionisation* of the solved substance, if this substance is an electrolyte. The fact, however, that the state of *association* is changed by the solving, is nearly always overlooked. We are inclined to reason, that in much diluted solutions the influence of the addition of a few molecules of the solved substance must necessarily be exceedingly slight, with regard to the degree of association of the solvent; but in doing so it is overlooked that the *number* of molecules of the solvent which each undergo a very slight change in their state of association, is *very great*. For infinitely diluted solutions therefore, a value is obtained approaching to $0 \times \infty$, and I shall demonstrate in what follows, that the absorbed *heat* in consequence of the change in the state of association, approaches to a definite value, which is *finite* and even comparatively high.

2. In *diluted* solutions — which we solely have in view in the following pages — the state of equilibrium of the associating molecules of the solvent may be expressed as follows:

$$\frac{\left(\frac{(1-x)\beta}{N}\right)^2}{\frac{1/2(1-x)(1-\beta)}{N}} = K,$$

i.e.:

$$\frac{\beta^2}{1-\beta} \frac{1-x}{N} = 1/2 K \quad (1)$$

For, given $1-x$ mol. H_2O , normally reckoned, x mol. salt (calling the solved substance *salt* for convenience' sake), then there are $1/2(1-x)$ mol. H_2O , if all are double. Therefore if the degree of dissociation of these double-molecules is β , then there are:

$1/2(1-x)(1-\beta)$ double mol. ; $1/2(1-x)2\beta = (1-x)\beta$ single mol.

The total number of particles is N . If the degree of dissociation of the saltmolecules is α , then there are (in *binary* electrolytes):

$x(1 - \alpha)$ neutral mol. ; $2x\alpha$ Ions.

We have therefore :

$$N = \frac{1}{2}(1-x)(1 + \beta) + x(1 + \alpha),$$

or with $\frac{1}{2}(1+\beta) = \gamma$, $1 + \alpha = i$, where therefore i has the usual meaning, and γ is the reverse of the so-called association-coefficient:

$$N = \gamma(1 - x) + ix = \gamma(1 - x) \left[1 + \frac{i}{\gamma} \frac{x}{1-x} \right].$$

Our equation (1) becomes therefore :

$$\frac{\beta^2}{1-\beta} \frac{1}{\gamma \left[1 + \frac{i}{\gamma} \frac{x}{1-x} \right]} = \frac{1}{2} K,$$

or γ being $= \frac{1}{2}(1 + \beta)$:

$$\frac{\beta^2}{1-\beta^2} = \frac{1}{4} K \left(1 + \frac{i}{\gamma} \frac{x}{1-x} \right) \dots \dots \dots (2)$$

From this follows, putting $\frac{i}{\gamma} \frac{x}{1-x} = \sigma$:

$$\beta = \sqrt{\frac{\frac{1}{4} K (1+\sigma)}{1+\frac{1}{4} K (1+\sigma)}} = \sqrt{\frac{\frac{1}{4} K}{1+\frac{1}{4} K}} \sqrt{\frac{1+\sigma}{1 + \frac{\frac{1}{4} K}{1+\frac{1}{4} K} \sigma}}$$

Now evidently

$$\beta_0 = \sqrt{\frac{\frac{1}{4} K}{1+\frac{1}{4} K}},$$

i. e. the value of β , if x or $\sigma = 0$, so that we have got the *pure* solvent, for which the equation $\frac{\beta_0^2}{1-\beta_0^2} = \frac{1}{4} K$ holds. Therefore we obtain :

$$\beta = \beta_0 \sqrt{\frac{1+\sigma}{1+\beta_0^2 \sigma}} = \beta_0 \left(1 + \frac{1-\beta_0^2}{2} \sigma \right),$$

if, σ being very small and approaching to 0, we content ourselves with a first approximation.

Substituting for σ its value, and taking into account that $\gamma = \frac{1}{2}(1 + \beta)$, we obtain :

$$\beta = \beta_0 \left(1 + \frac{1-\beta_0^2}{2} \frac{i}{\frac{1}{2}(1+\beta)} \frac{x}{1-x} \right),$$

or with $1 + \beta = 1 + \beta_0$:

$$\beta = \beta_0 \left(1 + (1 - \beta_0) i \frac{x}{1-x} \right) \dots \dots \dots (3)$$

So this is the sought-for expression for the change in β_0 , caused by the addition of x gr.mol. salt.

3. Now on 1 saltmol. there are $\frac{1-x}{x}$ gr.mol. H_2O (normally reckoned), among which there are evidently $\frac{1}{2} \left(\frac{1-x}{x} \right) 2\beta = \frac{1-x}{x} \beta$ single mol. In consequence of the fact, that the state of dissociation of the watermolecules is changed by the solved substance, this number according to (3) will amount to

$$\frac{1-x}{x} \beta = \frac{1-x}{x} \beta_0 + \frac{1-x}{x} \times \beta_0 (1-\beta_0) i \frac{x}{1-x},$$

that is to say an *increase* of

$$\frac{1-x}{x} \times \beta_0 (1-\beta_0) i \frac{x}{1-x}.$$

And now it is clear that, as was already observed above, the one factor of this product, viz. $\frac{1-x}{x}$, approaches to ∞ , while the other factor, viz. $\beta_0 (1-\beta_0) i \frac{x}{1-x}$, approaches to 0. The product however is evidently *finite*, viz.:

$$\Delta = \beta_0 (1-\beta_0) i \dots \dots \dots (4)$$

Now if Q is the heat, absorbed when 1 gr.mol. (18 Gr.) H_2O changes from the state of double molecules to that of single molecules, then the heat, absorbed in consequence of the state of association being changed by 1 mol. of the solved substance, is:

$$W = \beta_0 (1-\beta_0) i Q. \dots \dots \dots (5)$$

And *this* heat it is, which we have to take into account for *associating* solvents.

For H_2O at 18° $\beta = 0,21$ ¹⁾, so that the factor $\beta_0 (1-\beta_0)$ becomes $= 0,17$. Further Q (as I calculated some time ago ²⁾) $= \pm 1920$ gramcalories, so for water (at 18°) will be:

$$W = 326 i \dots \dots \dots (5a)$$

If the solved substance is *no electrolyte*, then $i = 1$, so for much diluted solutions about 325 gr.cal are absorbed with *every* concentration, if 1 gr.mol. is solved in the water, only in consequence of the change in the degree of association of the water; for salts, acids

¹⁾ Zeitschr. für Phys. Ch., **31**, p. 4 (1899); Lehrbuch der math. Chemie, p. 36 (1901).

²⁾ Z. f. Ph. Ch., **31**, p. 5 (1899); Lehrb. der math. Chem., p. 37 (1901).

and bases, where $i =$ nearly 2, this number becomes 650 gr. cal.

So e. g. for KCl, of which the heat of ionisation of 1 gr.mol. = -720 gr. cal.¹⁾, the total heat of mixing with much H₂O, (excluded the change in potential energy) will therefore be not -720 gr. cal., but only $-720 + 650 = -70$ gr. cal.

So it is seen, that the order of magnitude of the heat to be expected, can be totally modified, and that in general a great mistake would be committed, when we neglected the above calculated $326 i$ gr. cal. in the calculation of the heat of mixing.

Therefore, with *diluted* solutions of *non-electrolytes* in *associating* solvents, 325 gr. cal. on each gr. mol. of the solved substance must always be subtracted from the absorbed heat determined by experiment, in order to calculate the *pure* (absorbed) heat of mixing, that is to say that heat, which is caused solely by the change in potential energy.

Physics. — Prof. BAKHUIS ROOZEBOOM, in the name of Dr. A. SMITS, presents a paper, entitled: "*On the phenomena appearing when in a binary system the plaitpointcurve meets the solubility curve.*" (Third communication).²⁾

(Communicated in the Meeting of June 25. 1904).

The previous qualitative examination of the binary system ether-anthraquinone showed that a good survey of the whole could only be obtained by continuing the examination in quantitative direction with the aid of the pump of CAILLETET.

Some difficulties were to be foreseen; the investigation would have to be extended over a range of temperature from $\pm 170^\circ$ to $\pm 300^\circ$, in which the pressure might be expected to reach a pretty considerable amount -- and the combination of high temperature and high pressure being exactly the thing against which glass is but seldom proof, it seemed at first that we should meet with great experimental difficulties in the quantitative examination. The experiment however showed that the pressures were not exceedingly high; it appeared a maximum pressure of 100 atm. would suffice, and this pressure Jena-glass could withstand up to more than 300° ³⁾.

¹⁾ Z. f. Ph. Ch., 24, p. 611 (1897); Lehrb. der math. Chem., p. 53 (1901).

²⁾ This paper is a continuation of the two preceding ones on the system ether-anthraquinone. The title chosen first seemed to me undesirable and was therefore modified.

³⁾ With pleasure I avail myself of this opportunity to thank professor KAMERLINGH ONNES for his kindness towards me in procuring the necessary information and in lending me some instruments wanted.