

*Citation:*

A. Smits, Some observations of the results obtained in the determination of the decrease in vapour tension and of the lowering of the freezing point of solutions, which are not very dilute, in: KNAW, Proceedings, 3, 1900-1901, Amsterdam, 1901, pp. 507-514

mol., a minimum of the molecular increase of the boiling point was, however, observed with this method and with this a minimum of  $i$ , which did not appear in the sets of measurements 1 and 2. It is very remarkable, that it was also found by the boiling point method, that solutions of  $\text{KNO}_3$  of the concentration 0.05 to 1 gram mol. make an exception to the general rule.

It is strange, that this phenomenon has not yet been brought to light by the freezing point method.

*Amsterdam, Chem. Lab. Univers. January 1901.*

**Chemistry.** — Professor H. W. BAKHUIS ROOZEBOOM presents a communication from Dr. A. SMITS entitled: "*Some observations on the results obtained in the determination of the decrease in vapour tension and of the lowering of the freezing point of solutions, which are not very dilute.*"

(Read January 26, 1901).

With the aid of the theory of the thermodynamic potential, VAN LAAR<sup>1)</sup> has calculated accurate formulae for the decrease of the vapour tension, elevation of the boiling point and lowering of the freezing point. These formulae have the advantage, that they may be applied to dilute as well as to more concentrated solutions, which renders it possible to compare quantitatively the results of investigations of solutions, which are not very dilute.

The formula for the decrease of the vapour tension is as follows:

$$\log \frac{p_0}{p} = f - \log c \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$p_0$  = vapour tension of the solvent

$p$  = " " " " solution

$c$  = concentration =  $\frac{n}{N+n}$

$f$  is a quantity which = 0 for dilute solutions.

For the elevation of the boiling point we have the equation:

$$\Delta\tau = \tau - \tau^0 = \frac{R\tau\tau^0}{W}(f - \log c) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

<sup>1)</sup> Zeitschr. Physik. Chemie 15, S. 457 (1894).

$\tau$  and  $\tau_0$  are the absolute boiling points of solvent and solution.

$W$  = molecular heat of evaporation of the solvent.

$R$  = gas-constant.

For the lowering of the freezing point we have the analogous formula

$$\Delta\tau = \tau_0 - \tau = \frac{R\tau\tau_0}{S}(f - \log e) \dots \dots (3)$$

in which  $S$  means the molecular heat of fusion of the solvent.

As the values of  $f$  in the different formulae are only comparable at the same temperature, we can for instance calculate for the temperature  $0^\circ$  the relation, which must exist between the lowering of the freezing point and the lowering of the vapour tension.

From (1) and (3) follows:

$$\log \frac{p_0}{p} = \frac{\Delta\tau}{\tau\tau_0} \cdot \frac{S}{R}.$$

or

$$\log \frac{p_0}{p} = \Delta\tau \frac{S}{R\tau_0^2} \cdot \frac{\tau_0}{\tau} \dots \dots (4)$$

In the case that water is chosen as a solvent we have:

$$\frac{S}{R\tau_0^2} = \frac{1}{1.863} \times \frac{18.016}{1000}$$

$$\frac{\tau_0}{\tau} = \frac{\tau_0}{\tau_0 - \Delta\tau} = \frac{1}{1 - \frac{\Delta\tau}{\tau_0}} = 1 + \frac{\Delta\tau}{\tau_0} + \dots \dots$$

The equation (4) therefore becomes:

$$\log \frac{p_0}{p} = \frac{\Delta\tau}{1.863} \times \frac{18.016}{1000} \left( 1 + \frac{\tau_0}{\Delta\tau} + \dots \dots \right) \dots \dots (5)$$

If, however, we neglect the powers higher than 2 then

$$\log \frac{p_0}{p} = \log \frac{p_0}{p_0 - \Delta p} = \log \frac{1}{1 - \frac{\Delta p}{p_0}} =$$

$$= -\log \left( 1 - \frac{\Delta p}{p_0} \right) = \frac{\Delta p}{p_0} + \frac{1}{2} \left( \frac{\Delta p}{p_0} \right)^2.$$

Consequently

$$\frac{\Delta p}{p_0} + \frac{1}{2} \left( \frac{\Delta p}{p_0} \right)^2 = \frac{\Delta \tau}{1.863} \left( 1 + \frac{\Delta \tau}{\tau_0} \right) \times \frac{18.016}{1000} \dots (6)$$

If we now calculate  $\frac{\Delta p}{p_0}$  from RAOULT's<sup>1)</sup> determinations of the freezing point by means of equation (6), we obtain the following figures for cane-sugar.

*Cane-sugar.*

T A B L E I.

Concentration in gr. mol. per 1000 gr. H <sub>2</sub> O	$\Delta \tau$	$\frac{\Delta \tau}{1.863}$	$\frac{\Delta \tau}{1.863} \left( 1 + \frac{\Delta \tau}{\tau_0} \right)$	$\frac{\Delta p}{p_0} + \frac{1}{2} \left( \frac{\Delta p}{p_0} \right)^2$	$\frac{\Delta p}{p_0}$
1.0107	2.0897	1.122	1.130	0.02036	0.02015
0.5056	0.9892	0.5310	0.5329	0.009600	0.009554
0.2500	0.4806	0.2580	0.2585	0.004657	0.004646
0.1250	0.2372	0.1273	0.1274	0.002295	0.002292
0.0652	0.1230	0.06602	0.06605	0.001190	0.001189
0.0285	0.0532	0.02856	0.02857	0.0005147	0.0005147

By multiplying the figures in the last column by  $p_0 = 4.62$ , we obtain the decrease of the vapour tension corresponding to the lowering of the freezing point observed by RAOULT.

In order to be able to compare these figures with my latest results,

<sup>1)</sup> Zeitschr. f. Physik. Chemie 27, S. 638 (1898).

obtained with solutions of cane-sugar <sup>1)</sup>, I have calculated by interpolation the decreases of the vapour tensions for the same concentrations as used by RAOULT in his determinations. The result is as follows:

T A B L E II.

Concentration	$\Delta p$ in m.m. of Hg RAOULT.	$\Delta p$ in m.m. of Hg SMITS.	Difference	%
1.0107	0.09289	0.09090	- 0.00199	- 2.1
0.5056	0.04414	0.04446	+ 0.00032	+ 0.7
0.2500	0.02146	0.02167	+ 0.00021	+ 0.9
0.1250	0.01059	0.01072	+ 0.00013	+ 1.0
0.0652	0.00549	0.00557	+ 0.00008	+ 1.5
0.0285	0.00238	0.00240	+ 0.00002	+ 0.8

The agreement is, therefore, a very satisfactory one, the differences being within the range of the experimental errors.

If we now calculate in a similar manner the decrease of the vapour tension from the lowering of the freezing point of Na Cl-solutions observed by RAOULT and then compare these figures with those obtained by direct measurement, we find the following:

*Sodium chloride.*

T A B L E III.

Concentration	$\Delta \tau$	$\frac{1.863}{\Delta \tau}$	$\frac{\Delta \tau}{1.863} \left( 1 + \frac{\Delta \tau}{\tau^0} \right)$	$\frac{\Delta p}{p_0} + \frac{1}{2} \left( \frac{\Delta p}{p_0} \right)^2$	$\frac{\Delta p}{p_0}$
1.0000	3.4237	1.838	1.8610	0.03353	0.03297
0.4887	1.6754	0.8993	0.9048	0.01630	0.01617
0.2393	0.8211	0.4407	0.4420	0.007962	0.007930
0.1179	0.4077	0.2188	0.2191	0.003947	0.003939
0.05829	0.2073	0.1113	0.1114	0.002007	0.002005

<sup>1)</sup> Report Kon. Akad. v. Wet. 30 Sept. 1899, p. 162. It is stated there that the greatest concentration is 1.0811; this should be 1.0089.

T A B L E IV.

Concentration	$\Delta p$ in m m. of Hg RAOULT	$\Delta p$ in m m. of Hg SMITS.	Difference	%
1.0000	0.1523	0.1437	0.00860	- 5.6
0.4887	0.07470	0.06937	0.00533	- 7
0.2393	0.03664	0.03367	0.00297	- 8
0.1179	0.01820	0.01646	0.00174	- 9.5
0.0582	0.00926	0.00800	0.00126	-13.6

Here there is absolutely no question of agreement and at the same time we observe, that the difference continually increases with the dilution.

Before proceeding further I will just show, that if I had compared RAOULT's results with mine by calculating the factor  $i$ , I really would have committed an error, although as we will see presently, this error is so small that it is only revealed at the greatest concentration.

According to VAN 'T HOFF, the factor  $i$  may be calculated from the decrease of the vapour tension and the lowering of the freezing point by means of the formulae:

$$i_d = \frac{\Delta p}{p_0} \cdot \frac{N}{n} \dots \dots \dots (7)$$

and

$$i_v = \Delta \tau \frac{S}{R\tau_0^2} \cdot \frac{N}{n} \dots \dots \dots (8)$$

From this follows:

$$\frac{\Delta p}{p_0} = \Delta \tau \frac{S}{R\tau_0^2} \dots \dots \dots (9)$$

This equation is perfectly true for exceedingly diluted solutions, but it no longer applies to solutions, which are not very much diluted. For these, VAN LAAR has found indeed the relation (4) instead of the equation (9):

$$\log \frac{p_0}{p} = \Delta \tau \frac{S}{R\tau_0^2} \cdot \frac{\tau_0}{\tau}$$

or

$$\frac{\Delta p}{p_0} + \frac{1}{2} \left( \frac{\Delta p}{p_0} \right)^2 = \Delta \tau \frac{S}{R\tau_0^2} \cdot \frac{\tau_0}{\tau}$$

From this we see that for solutions, which are not very much diluted both sides of the equation (9) are too small. If the error were the same in both sides it would naturally be eliminated from the difference of the equations (7) and (8), so that a comparison of the results of solutions, which are not very much diluted, might be arrived at by applying the equations (7) and (8).

If the equations (7) and (8) were of universal application, then we ought to find for all concentrations

$$i_d = i_v$$

and because

$$i_d + \frac{1}{2} \left( \frac{\Delta p}{p_0} \right)^2 \frac{N}{n} = i_v \frac{\tau_0}{\tau}$$

we should find

$$\frac{1}{2} \left( \frac{\Delta p}{p_0} \right)^2 \frac{N}{n} = i_v \left( \frac{\tau_0}{\tau} - 1 \right) \dots \dots \dots (10)$$

This equation is no longer true for solutions which are not very much diluted, for in that case we find

$$\frac{1}{2} \left( \frac{\Delta p}{p_0} \right)^2 \frac{N}{n} > i_v \left( \frac{\tau_0}{\tau} - 1 \right) \dots \dots \dots (11)$$

For most of the solutions which have been examined this difference is, however, so small, that it may be neglected, but when the greatest concentration 1 gram mol. per 1000 grams of water is reached it becomes distinctly perceptible. This is easily shown by the following table in which  $i$  has been calculated from the molecular lowering of the freezing point, and from the molecular decrease of the vapour tension by dividing these by 1.863, and 0.08316 respectively.

*Cane-sugar.*

T A B L E V.

Concentration.	mol. lowering of the freezing point.	mol. decrease of the vapour tension.	$i$		Difference in %
			RAOULT	SMITS	
1.0107	2.0676	0.08994	1.110	1.082	-2.5
0.5056	1.9565	0.08761	1.050	1.057	+0.7
0.2500	1.9224	0.08668	1.033	1.042	+0.9
0.1250	1.8976	0.08576	1.020	1.031	+1
0.0652	1.8860	0.08543	1.013	1.027	+1.4
0.0284	1.8667	0.08421	1.004	1.013	+0.9

*Sodium chloride.*

T A B L E VI.

Concentration.	mol. lowering of the freezing point.	mol. decrease of the vapour tension.	<i>i</i>		Difference in %
			RAOULT	SMITS	
1.0000	3.4237	0.1437	1.838	1.728	— 6.1
0.4887	3.4283	0.1419	1.840	1.707	— 7
0.2393	3.4313	0.1407	1.842	1.692	— 8
0.1179	3.4581	0.1396	1.856	1.679	— 9.5
0.05829	3.5564	0.1372	1.909	1.650	—13.6

If we now compare the differences in the last column of these tables with those of the fifth column of tables II and IV, we see that on the whole they agree with each other; only at the greatest concentration the differences are 0.4 and 0.5 percent greater. For this concentration the disparity, as represented by equation (11), is very perceptible.

If, for instance, we calculate for the concentration 1.0107 gram mols. (Table V)

$$\frac{1}{2} \left( \frac{\Delta p}{p_0} \right)^2 \frac{N}{n} \text{ and } i_v \left( \frac{\tau_0}{\tau} - 1 \right)$$

we find for the first quantity the value 0,013 and for the second 0,008. If we now add to RAOULT's *i* 0,008 and to my own 0,012, we naturally obtain again, just as in table II, a difference of 2,1 percent for this concentration. In the same manner the difference of 0,5 percent disappears at the greatest concentration of Na Cl.

The foregoing teaches us up to what concentration we can in this case make a comparison by means of *i*. We are therefore, obliged to stop at the concentration 1 gram molecule. Up to the concentration 1 gram mol. the values of *i* must agree within 0,1—0,2 percent by whatever method they have been obtained. In this we must, however, not forget that the factor *i* is not to be considered as a dissociation factor, but as a quantity of which we do not as yet know the true significance.

I consider it an indisputable fact that *i* generally increases with the concentration in solutions which are *not very dilute*.



The determinations of the vapour tensions, at 0° and between 50° and 70°<sup>1)</sup> and also the determinations of the boiling point (from the concentration  $\pm 0,3$  gram mol. up to higher concentrations) lead to this conclusion.

The fact that RAOULT, who continued his experiments up to the concentration 1 gram. mol., observed a fall of  $i$  with an increase of the concentration points to an error. RAOULT ought also to have observed a rise of  $i$  with the concentration of his *stronger solutions*.

The possibility of an error in RAOULT's determinations is also corroborated by the latest communication from CHROUSTCHOFF<sup>2)</sup> entitled „Recherches Cryoscopiques” where the thermometer has been replaced by a thermo-element accurate to 0.0005°. In the case of Na Cl, he found between the concentrations  $\frac{1}{4}$  and  $\frac{1}{64}$  gram mol. a constant molecular lowering of the freezing point. In the case of K Br, he found between the concentrations  $\frac{1}{4}$  and  $\frac{1}{128}$  gram mol. *an increase of the molecular lowering of the freezing point with increasing concentration*. In the case of K<sub>2</sub> SO<sub>4</sub>, however, he noticed the reverse change between the concentrations  $\frac{1}{4}$  and  $\frac{1}{64}$  gram molecule. The fact that a small alteration in the method influences the results and even alters the course proves that the freezing point method is attended by unknown sources of error, in the case of electrolytes at any rate. I consider that CHROUSTCHOFF has made a great improvement by determining the concentration of the solution after the separation of ice.

Finally there are also determinations of the freezing point where a minimum of  $i$  has been found; I obtained this also by means of the method of boiling in the case of solutions of Na Cl or K Cl. JONES, CHAMBERS and FRAZER<sup>3)</sup> found minima for the solutions of the chlorides and bromides of Mg, Ca, Ba and further for Cu SO<sub>4</sub>, H<sub>3</sub> PO<sub>4</sub>, H Cl, CH<sub>3</sub> CO O Na, Cd I<sub>2</sub>, Sr I<sub>2</sub> and Zn Cl<sub>2</sub>; as a rule these minima lie below the concentration 0.5 mol.

Finally I wish to express my hearty thanks to Mr. VAN LAAR for the assistance he has rendered.

*Amsterdam*, Chem. Lab. Univers. Jan. 1901.

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1) See preceding article.

2) Comptes Rendus CXXXI p. 883 (1900)

3) Amer. Chem. Journal Vol. 23, p. 89 and 512 (1900,,