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Chemistrie. — Professor H. W. BAKHUIS ROOZEBOOM presents a communication from Dr. A. SMITS entitled: "*Determination of the decrease of vapour-tension of a solution of Na Cl at higher temperatures.*"

(Read January 26, 1901).

Introduction.

Continuing some earlier researches,[1]) I have performed some measurements between 50° and 80° with regard to the decrease of vapour tension of Na Cl solutions. The apparatus, which I used for that purpose was a small BREMER oil-tensimeter[2]). The source of heat was an oil-bath, the temperature of which could be kept constant within 0 15° by means of a stirring apparatus and an electrical regulator. The accuracy of the method applied did not appear to be greater than 1 m.m. of oil. This is the reason, why I could not continue the measurements below the concentration 0,1 gram molecule per 1000 grams of H_2O. The results were as follows:

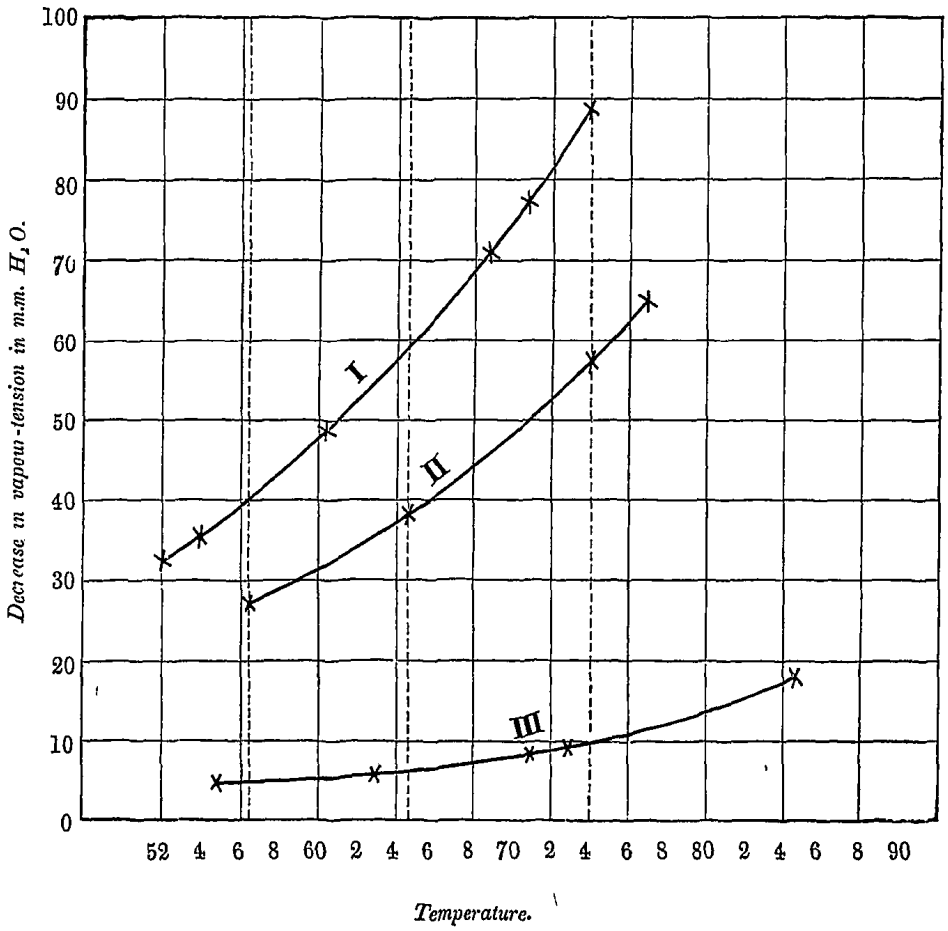
Concentration in gram mols of Na Cl per 1000 grams of H_2O	Temperature	Observed difference in m.m. of oil at the observation temperature	Difference in m m. of H_2O at 4°.
0 7414	52°.15	36.5	32 5
	54°.0	40.0	35.6
	60°.38	55.0	48.7
	68°.75	80.0	70.5
	70° 9	88 0	77.4
0.4958	56°.4	30.0	26.6
	64°.6	43.5	38 4
	74°.0	65.0	57 0
	77°.0	75.0	65.6
0.0996	54°.4	5 5	4 9
	63°.0	7.0	6.2
	71°.0	10.0	8.8
	73° 0	11.0	9.7
	84° 8	21.0	18.2

[1]) Report Kon. Akad. v. Wet. 30 Sept. (1899) p. 160; 27 Jan. (1900) p. 471; 21 April (1900) p. 714.

[2]) Rec. des Trav. Chim. des Pays-Bas 6, 126.

To express the observed difference of level of the oil at different temperatures in m.m. of H_2O at 4°, the specific gravity of the olive oil was determined at various temperatures.

By means of the figures occurring in the fourth column, the decrease in the vapour tension of the three different solutions is shown at different temperatures in the following graphical representation.



The molecular decreases of the vapour tensions of the three solutions have been calculated for three temperatures: 56,4°, 64,6° and 74,0°.

The pressures of II were known for these temperatures; for I and III they have been obtained by graphical interpolations. The value of I at 74° has been got by a small extrapolation which, on account of the regular course of the line, is sufficiently accurate.

Concentration	Temperature	Decrease in vapour tension in m.m. H_2O at 4°.	Molecular decrease in vapour tension Hg. at 0°.	i
0.7414	74°	89.0	8.83	1.77
0.4958	»	57.0	8.49	1.7
0.0996	»	10.5	7.8	1.6
0.7414	64 6°	59.0	5.85	1.77
0.4958	»	38.4	5.66	1.7
0.0996	»	6.5	4.8	1.5
0.7414	56.4°	39 8	3.95	1.75
0.4958	»	26 6	3.92	1.7
0.0996	»	5	3.4	1.5

The value of i has been obtained by dividing the experimentally found decrease in vapour tension by the calculated decrease, when no electrolytic dissociation had taken place. This theoretical value was obtained by means of VAN 'T HOFF's equation

$$\Delta p = \frac{n}{N} p .$$

If we now take a solution, which contains 1 gram mol. per 1000 grams of water and then ask what will be the decrease of the vapour tension of this solution at 74°, then the data are $n = 1$, $N = 55{,}6$ and $p = 276{,}6$ (REGNAULT) and consequently

$$\Delta p_{74^\circ} = \frac{1}{55{,}6} \times 276{,}6 \quad = 4{,}98.$$

For 64,6° we find

$$\Delta p^{64{,}6} = \frac{1}{55{,}6} \times 183{,}7 \quad = 3{,}30$$

and for 56,4°

$$\Delta p_{56{,}4} = \frac{1}{55{,}6} \times 125{,}65 = 2{,}26.$$

Review of the Results.

Although better results are obtainable by using my micromanometer and boiling apparatus, the above method is still accurate enough to demonstrate the course of the molecular decrease of vapour tension as a function of the concentration. It appears from the experiments, that the molecular decrease of vapour tension does not show a minimum between 56° and 74°, but continually increases with the concentration.

To pronounce on the strength of these results, that the minimum, which has been found at 100° by means of the boiling point method between the concentrations 0,5 and 0,1 gram mol. per 1000 grams of H_2O, has already disappeared at 74° appears to me to be too sweeping. A repetition of these measurements by means of a more accurate method might enable us to answer this interesting question, but provisionally there is not much chance for this. The great difficulty is caused by the temperature. In order to proceed further, it would be required to keep the bath constant at each temperature within 0,05°; this has been unattainable as yet. It is perhaps possible to obtain a bath of a very constant temperature by allowing some liquid or other to boil under a pressure, which is kept constant to 1 m.m. of H_2O by the manostat [1]) but in how far this method will be a practical one for my purpose remains to be seen.

The state of affairs at the moment is as follows:

1. It has been found by means of the micromanometer that at 0°, between the concentrations 0.05 and 2 gram mol. per 1000 grams of H_2O, the molecular decrease of vapour tension increases with the concentration in the case of either electrolytes or non-electrolytes except with KNO_3.

2. An increase of the molecular decrease of vapour tension, when the concentration is increased has also been observed with the oil-tensimeter from 56°—74° between the concentration 0.1 and 1 gram per 1000 grams of H_2O in the case of Na Cl solutions.

3. The same progressive change of the molecular increase of the boiling point has been observed with my boiling apparatus at 100° for solutions of Na Cl and K Cl between the concentrations ± 0.3 and 1.0 gram mol. that is to say an increase of the molecular increase of the boiling point with a rise of the concentration.

Between the concentrations 0.1 and 0.5 gram mol. at about 0.3

[1]) Report Nov. 27 1897.

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 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 [1]) 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:

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

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:

$$\Delta\tau = \tau - \tau^0 = \frac{R\,\tau\,\tau_0}{W}(f - \log c) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

[1]) Zeitschr. Physik. Chemie 15, S. 457 (1894).