

Citation:

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Chemistry. — “*Determinations of the diminution of vapourpressure and of the elevation of the boiling point of dilute solutions*”, by Dr. A. SMITS (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

Introduction.

In a former article ¹⁾ the apparatus has been described, which has enabled me to ascertain the decrease of the vapourpressure and the elevation of the boiling point of dilute solutions.

The method of experimenting when determining the diminution of vapourpressure is already described there, so that it is only necessary to say here that in determining the elevation of the boiling point, the manostat is always set at the same pressure; the thermometer, which remains continuously in the boiling water, controls the action of the manostat, since a small change of pressure in the apparatus is immediately betrayed by a change of temperature.

Regarding the accuracy of the two methods, the preference must be given to the determination of the increase in the boiling point. If, in the method for determining the diminution of vapourpressure, the decrease in the vapourpressure of the solution is to be calculated from the observed fall in the boiling point of pure water, it is necessary to use the table constructed by REGNAULT ²⁾ for the maximum pressure of watervapour, which gives the differences for each 0.1°. It is plain that errors are committed here; in the first place because the table is not quite correct and secondly because interpolation must be resorted to. The value of i obtained from the value of the decrease in the vapourpressure thus calculated can, therefore, not be very accurate. In the determination of i from the elevation of the boiling point, it is only necessary to divide by a constant factor; in this method the values of i can only be affected by a constant error.

I have, therefore, applied the two methods to the same solutions of Na Cl, but in the case of the other salts, the elevation of the boiling points only has been determined. The results, which I have obtained with solutions of Na Cl, K Cl and K NO₃ are included in the following tables. Between each of the different series of observations of the Na Cl-solutions, the manostat was set at a different pressure.

¹⁾ Proceeding Royal Acad. Jan. 27, 1900, p. 471.

²⁾ Mémoires de l'Acad. T. XXI, p. 632.

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R e s u l t s :

N a C l .

Concentration in gr. mols. per 1000 grs. of H ₂ O.	Observed decrease of the boiling point of the pure water.	Calculated dimi- nution of the vapour pressure at 99.424° in m m. of Hg.	<i>i</i>
0.0500	0.048	1.27	1.89
0.0750	0.073	1.94	1.93
0.1001	0.093	2.47	1.84
0.5001	0.468	12.41	1.85
1.0000	0.965	25.37	1.89

N a C l .

Boiling point of the pure water = 99.424° *t* = 5.18¹⁾.

Concentration in gr. mols. per 1000 grs. of H ₂ O.	Elevation of the boiling point of the solution.	Molecular elevation of the boiling point.	<i>i</i>
0.0500	0.050	10.00	1.93
0.0750	0.075	9.99	1.93
0.1001	0.096	9.60	1.85
0.5001	0.471	9.42	1.82
1.0000	0.968	9.68	1.869
2.0798	2.120	10.20	1.969

N a C l .

Boiling point of the pure water = 99.793° *t* = 5.19.

Concentration in gr. mols. per 1000 cc. of H ₂ O.	Elevation in the boiling point of the solution.	Molecular-elevation of the boiling point.	<i>i</i>
0.0500	0.049	9.81	1.89
0.1000	0.095	9.50	1.83
0.5000	0.472	9.44	1.82
0.7497	0.717	9.56	1.84
1.0000	0.970	9.70	1.869

¹⁾ *t* = molecular elevation of the boiling point calculated from VAN 'T HOFF's formulae $t = \frac{0.02 T^2}{w}$. N.B. Although very few of the solutions are weak enough to warrant the calculation of *i*; this has been done for all concentrations to facilitate the comparison with previous results.

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NaCl.

Boiling point of the pure water = 99.61° $t = 5.19^{\circ}$.

Concentration in gr. mols. per 1000 grs. of H ₂ O.	Elevation of the boiling point of the solution.	Molecular elevation of the boiling point.	<i>i</i>
0.0560	0.049	9.68	1.87
0.10115	0.096	9.48	1.83
0.50566	0.479	9.47	1.82
1.0112	0.979	9.68	1.865

KCl.

Boiling point of the pure water = 99.695° $t = 5.19$.

Concentration in gr. mols. per 1000 grs. of H ₂ O.	Elevation of the boiling point of the solution.	Molecular elevation of the boiling point.	<i>i</i>
0.0504	0.050	9.93	1.91
0.1008	0.091	9.03	1.74
0.5037	0.455	9.03	1.74
1.0074	0.926	9.19	1.771

KNO₃.

Boiling point of the pure water = 99.691° $t = 5.19$.

Concentration in gr. mols. per 1000 grs. of H ₂ O.	Elevation of the boiling point of the solution.	Molecular elevation of the boiling point.	<i>i</i>
0.0499	0.051	10.21	1.97
0.0998	0.095	9.52	1.83
0.4991	0.450	9.02	1.74
0.7486	0.648	8.65	1.67
0.9981	0.858	8.57	1.651

From these tables it is apparent, that in the case of NaCl *i* reaches a minimum value at about 0.1 gr. mol. per 1000 grs. of water when the diminution of the vapourpressure is determined, and at about 0.5 gr. mol., when the elevation of the boiling point is deter-

mined. In the case of KCl, i also reaches a minimum between the concentrations 0.1 and 0.5 gr. mol. From 0.5 gr. mol. upwards a rise of i is observed as the concentration increases. Above 0.5 gr. mol. the results are therefore, qualitatively, the same as with the micromanometer. Below this concentration i seems to increase again with the dilution. In the case of KNO_3 i increases proportionally with the dilution just as I have observed with the micromanometer. Both at 100° and at 0° a solution of KNO_3 seems to behave differently to solutions of KCl and NaCl.

As regards the accuracy of the results, I may say that the greatest error of each thermometer was $0,002^\circ$. If these errors of the two thermometers have opposite signs, the error of observation amounts to $0,004^\circ$. As, however, each determination lasted 15 minutes, a reading being taken every 5 minutes, the average error must have been really less than $0,004^\circ$ which is confirmed by the thorough agreement of the results obtained in the three series of observations on the NaCl solutions.

Earlier observations.

W. LANDSBERGER¹⁾ has already found in 1898 that more concentrated solutions of NaCl show a rise in the molecular increase of the boiling point when the concentration increases. From his molecular weight determinations, I have calculated the following values for the molecular increase of the boiling point and for i .

NaCl.

$t = 5.12.$

Concentration in gr. mols per 1000 grs. of H_2O .	Elevation of the boiling point.	Molecular weight found.	Mol. elevation of the boiling point.	i
0.7145	0.676	32.2	9.46	1.82
1.0581	1.026	31.4	9.70	1.87
1.0872	1.080	30.7	9.93	1.91
1.1077	1.067	31.6	9.63	1.85
1.2427	1.235	30.6	9.94	1.91
2.0735	2.177	29.0	10.50	2.02
2.0855	2.186	29.0	10.50	2.20

¹⁾ Zeitschr. f. Anorg. Chem. XVII 452. (1898).

Excepting the value of i for the concentration 1.1077 gr. mol., which is very probably too small on account of an experimental error, we also notice here a perceptible increase of i with increasing concentration.

LANDSBERGER says regarding the results:

„Die angeführten Zahlen für Natriumchlorid lehren, das die Dissoziation in wässriger Lösung mit steigender Konzentration fortschreitet.“

Although this conclusion seems to me to be erroneous I have quoted it in order to show that LANDSBERGER regards the observed changes as essential.

For concentrated solutions of Na Cl and K Cl, LEGRAND¹⁾ has already noticed the same phenomenon as I have now done for the more diluted ones.

From the following table this progressive change is plainly visible.

Number of grams of Na Cl per 100 grs. of H ₂ O.	Number of grams of K Cl per 100 grs. of H ₂ O.	Number of grams of KNO ₃ per 100 grs. of H ₂ O.	Increase in the boiling point.
7.7	9.0	12.2	1°
13.4	17.1	26.4	2°
18.3	24.5	42.2	3°
23.1	31.4	59.6	4°
27.1	37.8	78.3	5°

We see from this table that with Na Cl and K Cl the elevation of the boiling point increases more rapidly than the concentration, whilst with KNO₃ the reverse is the case. At greater concentrations the molecular elevation of the boiling point of solutions of Na Cl and K Cl seems to increase with the concentration, whilst for solution of KNO₃ it steadily declines.

Summary of the results.

The result is, therefore, that the progressive change observed with concentrated solutions of KNO₃ also occurs with dilute solutions, whilst with concentrated solutions of Na Cl and K Cl it ends at a concentration of 0.5 gr. mol. where it takes another direction.

In my determinations of vapourpressure with the micromano-

¹⁾ Ann. de Chim. et de Phys. T. LIII. Poggend. Ann. Bd. XXXVII.

meter, I did not notice a minimum of the molecular diminution of vapourpressure; it is possible that the cause of this is as follows:

At about 100°, I observed a minimum at the concentration of 0.5 gr. mol.; should the position of this minimum alter with the temperature which is quite possible, it may occur that at lower temperatures it is displaced in the direction of still more dilute solutions and that at 0° it may fall below the concentrations with which I was able to make sufficiently accurate observations.

To decide whether there really is a minimum which changes its position with the temperature, I propose to make further measurements of the diminution of vapourpressure of solutions at temperatures between 0° and 100°.

Amsterdam, University Chem. Laboratory.
April 1900.

Physiology. — “*Some reflexes on the respiration in connection with LABORDE's method to restore, by rhythmical traction of the tongue, the respiration suppressed in narcosis*”. By M. A. VAN MELLE (Communicated by Prof. C. WINKLER).

In the *Weekblad van het Nederlandsch Tijdschrift voor Geneeskunde*, March 31, 1900. Dr. WENCKEBACH inserts a note on LABORDE's communications in the Académie de Médecine, which are published in the *Bulletins de l'Académie de Médecine*, N°. 45 1899 en N°. 2, 4, 5, 6. 1900 and with slight modifications in the *Comptes Rendus de la Société de Biologie*: 1899. N°. 39 and N°. 2, 4, 5. 1900.

In this communication LABORDE gives fuller details about a method in which rhythmical traction of the tongue is used to restore the paralyzed respiration. An explanation is to be found for this phenomenon, as it cannot be considered as anything but a reflectory action, originating from the sensible nerves of the first air-passages on the so-called centres of respiration. LABORDE thinks, that according to his experiments the reflectory action depends on the Nn. laryngei superiores, the electrical and mechanical excitation of which brings about an “arrest” during the active respiration, whereas it restores the respiration when the latter was suppressed.

In the laboratory of Prof. WINKLER, under whose guidance important investigations on the mechanism of the respiration have been