Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

Citation:

A. Smits, Investigations with the Micro-manometer, in: KNAW, Proceedings, 4, 1901-1902, Amsterdam, 1902, pp. 163-169

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always the same position, this fact can be demonstrated very clearly, as can also the whole process of the negative-inotropic action.

By accumulating the irritation the process may be much increased and lengthened. Fatigue comes readily in consequence. To obtain an equally great effect each time, it is necessary to insert comparatively long intervals between the periods of irritation. The conduction of the negative-inotropic action within the ventricle-wall takes place in a way different from the motory irritation. By compressing the muscular wall by means of a clasp the inotropic conducting power is raised sooner and under lower pressure than the motory one.

Experiments must still be made with regard to the swiftness of the inotropic conduction.

The speaker illustrated his lecture by the aid of a number of cardiograms.

Chemistry. — Dr. A. SMITS: "Investigations with the Micromanometer". (Communicated by Prof. V. A. JULIUS).

1. After the investigations, published under this title in Sept. 1899¹), I have been enabled by the great kindness of Prof. BAKHUIS ROOZEBOOM to continue my measurements.

Having made some improvements in the apparatus, which might possibly modify the results, it seemed very desirable to me to proceed with the measurements; moreover I considered the question, whether the decrease of the molecular vapour-tension continues to increase with the concentration also when the solution is still more diluted, as so important, that in my opinion nothing should be neglected, which might contribute to the solution of the question.

The improvements made were the following:

First the manometer was made from chosen tubes, which might be considered as perfectly cylindrical as appeared from the calibration.

Secondly all the taps were done away with, so that there was absolutely no occasion for leaks.

Thirdly the icebath was treated with more care, by excluding it from the surroundings by a thick layer of wool.

The measurements furnished the following result:

¹) Proc. Royal Acad. at Amsterdam, Vol. II. p. 88.

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Concentration in gr. mol. per 1000 gr. H ₂ O.	Pm in m.m Hg of 0°.	i
0.0591	0.149	1.79
0.1077 0.1426	0.143 0.142	1.70 1 72 ⁻ 1.71
0.1428 0.4527 0 4976	0.141	1.71
1.0808 1.2521	0.1432 0 1439	1.723
	$\rm H_2SO_4$	
0 0951	0.169	2.03
0 1208	0.156	1 87
0 4215	0 1603	1.93
0 9762	0.1716	2.063
	KNO3	
0.0400	0.153	1.8
0 1450	0.131	1.58
0.5997	0.1156	1 39
0 9288	0.1084	1.304

From this table follows that p_m (decrease of molecular vapourtension) and *i* attain a minimum in solutions of NaCl and of H₂ SO₄. For Na Cl this minimum lies near 0,45 gr. mol., for H₂ SO₄ it appears near \pm 0,1 gr. mol. The observations render the existence of these minima very probable, for they appear in a region of concentration, where the accuracy is still great enough to be sure of the course. As to the absolute value of p_m and *i*, we must keep in mind (165)

that e. g. for NaCl at the concentration 1 gr. mol. the deviation in the manometer was \pm 60 m.m., and the uncertainty of the reading was 0.1 m.m. The error in p_m and therefore also in *i* amounts therefore to \pm 0.17 pCt. at the concentration 1 gr. mol. It increases however with the dilution, so that it amounts to \pm 1.7 pCt. at 0.1 gr. mol. and to \pm 3 pCt. at 0.05 gr. mol. It is obvious that at the small concentrations the absolute value of p_m is comparatively untrustworthy. At the same time it is clear, that a very small difference of temperature between solutions and water or an exceedingly small leakage may conceal the minima from us.

With regard to the measurements with $K NO_3$ -solutions it is noteworthy that, as was previously found by me, p_m increases with the dilution in opposition to the solutions with NaCl and H₂SO₄. Very remarkable is also the quick decrease of p_m and *i* at increase of concentration, so that *i* has reached the abnormally small value 1.3 already at 0,9288 gr. mol.

The results found by means of the boiling-method ¹), are in qualitative concordance with the above mentioned. Owing to the great difference in the temperatures at which the observations are made (100°), a quantitative concordance could not be expected.

At 100° I found namely that the molecular increase of the boilingpoint and so also *i* for the salts NaCl, KCL and Sr $(No_3)_2$ reaches a minimum between the concentrations 0.1 and 0.5 gr. mol., whereas for the salts KNO₃, NaNo₃, Ba $(NO_3)_2$, AgNO₃ and Pb $(No'_3)_2$ a regular quick decrease of *i* was observed in case of increase of the concentration ²).

It occurred to me that possibly also for these latter salts a minimum might appear, but not before the concentrations are much greater; by consulting tables about determinations of the boiling point of concentrated solutions³) however, I observed that even for very great concentrations the mol. increase of the boiling-point preserves the same quick decrease.

When considering the here-mentioned results, we should be inclined to generalize and say: all salts which behave abnormally at higher concentrations, as NaCl, KCl, $H_2 SO_4$, $Sr (NO_3)_2$ and probably a great many substances more, will behave normally in very diluted state and show a minimum.

^{&#}x27;) Proc. Royal Acad. at Amsterdam. Vol. II p. 469.

²) Proc. Royal Acad. at Amsterdam. Vol. III p. 717.

³) LEGBAND, Ann. de Chim. et de Phys T. LIII. Poggend. Ann. Bd. XXXVII.

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In my opinion the minimum would indicate the point, where the influence of the deviation from the diluted state in this special case becomes so great, that the direction in which i varies is thereby reversed.

A difficulty remains in the difference between what has been observed by means of the method of decrease of the vapour-tension and that of the lowering of the freezing-point. Not only is there e.g. for Na Cl solutions a difference in absolute value of i at every concentration, but above the concentration 0,5 gr. mol. there had up to now not been found an increase of i with the concentration by means of the freezing-point method, whereas this singular course has been so clearly observed by means of the method of vapourtension at 0° and that of the boiling-point at 100°.

Though it was formerly found that below the concentration 1 gr. mol. the molecular lowering of the freezing-point and with it *i* pretty quickly decreased with increase of the concentration, this is no longer so. RAOULT¹) found a very slow decrease with increase of the concentration; afterwards CHROUSTCHOFF²) found constant values and a few months ago KAHLENBERG³) published the following results, which confirm my suspicion, that possibly also at the determination of the freezing-point soon a minimum may be found.

Concentration in gr mol. per 1000 gr. H ₂ O	Lowering of the freezing-point.	Molecular lowering of the freezing-point	z
0 2043	0.693	3.393	1 82
0 4359	1.512	3 469	1.86
0 5077	1.750	3.447	1 85
0.6713	2,300	3.426	1.84
0 8400	2.866	3 412	1 83
0.9814	3.395	3.459	1 86

¹) Zeitschr. f. Phys. chem. 27. S. 617 (1898).

²) Comt. Rend. 131. p. 883 (1900).

³) Journal of Phys. chem 5, 339 (1901).

It seems probable to me that, if the experimental methods are continually improved, the results will finally be found to agree, as the theory requires.

3. In a treatise, called: "The theory of electrolytic dissociation as viewed in the light of facts recently ascertained", KAHLENBERG¹) states results obtained in determining the conductivity, the lowering of the freezing-point and the raising of the boiling-point of not diluted solutions. Here he arrives at the expected result, that in most cases the degree of dissociation indicated by the conductivity, deviates strongly from that, found when following the two other methods. He found i. a. that several salts, which in aqueous solution at a certain concentration are not only not dissociated, but even somewhat polymerized according to the lowering of the freezingpoint and the raising of the boiling-point, yet conduct the electric current.

This occurs i.a. with sulphates of Mg, Zn, Cd, Ni, Co, Fe and Cu.

KAHLENBERG, as well as myself found, that the molecular raising of the boiling-point increases with the concentration for Na Cl, K Cl and also for K Br, Kg, Mg Cl₂ and Ba Cl₂, for the molecular lowering of the freezing-point of Na Cl-solutions he found the course already mentioned, while JONES, CHAMBER and FRAZER²) discovered minima for Mg Cl₂ and Ba Cl₂ in the region of concentration 0, 1-0, 6.

The molecular conductivity, on the other hand, increased regularly with the dilution.

I must point out here that KAHLENBERG in his experiments on the raising of the boiling-point of Na Cl- and K Cl-solution did not find a minimum, though he began with the concentration ± 0.2 ; possibly, however, his method, adapted for more concentrated solutions, was not sensible enough.

Finally the remarkable fact must be mentioned, that it would follow from the raising of the boiling-point of the just mentioned sulphates of Mg, Zn, Cd, Ni, Co, Fe and Cu, that the polymerization is greater at 100° than at 0° and that minima occur both at 100° and at 0°.

As KAHLENBERG has already stated, the investigations on nonaqueous solutions have brought to light, that though a salt in solution shows a normal molecular weight, yet the solution can conduct the electric current. This has been proved for solutions of $Ag NO_3$ in

¹⁾ Journ. of Phys. Chem. 5. p. 339 (1901).

²) Amer. Chem. Journ. 23, p, 89, 512 (1900).

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pyridine and benzolnitriel¹) and also for solutions of $\operatorname{Cd} J_2$, Li Cl, Na J, Hg Cl and NH₄ C NS in acetone²). It has further appeared, that KJ, NaJ, KbJ, NH₄J and KCNS solved in liquid SO₂³), conduct the electric current, notwithstanding their molecular weights are found to be abnormally great.

4. Chiefly on account of what has been mentioned here, KAHLENBERG considers the dissociation theory of AERHENIUS as untenable. Not sharing this opinion, I have mentioned his principal objections to the dissociation theory.

KAHLENBERG has made experiments on non-diluted solutions, and this is a great impediment for the refutation of the correctness of the dissociation.

For according to theory the degree of dissociation found from the conductivity, can agree with that calculated from the lowering of the freezing-point, the decrease of vapour-tension and the raising of the boiling-point, only in case of exceedingly diluted solutions.

In what way a deviation from the diluted state will be felt in general, is not known, but what I have observed for NaCl, KCl and $H_2 SO_4$ -solutions, where minima of the molecular decrease of vapour-tension and raising of the boiling-point are found at ± 0.5 gr. mol. and below it, gives the conviction, that already at these small concentrations the deviation from the diluted state brings about an influence, which is so great as to even reverse the direction of the course of the molecular decrease of vapour-tension and the raising of the boiling-point.

That this influence is in very close connection with the nature of the salt, follows from the fact that for $NaNo_3$, KNO_3 etc. no minimum appears even at very great concentrations, which as I have already mentioned, may be due to the rapid decrease of the electric dissociation with increase of the concentration ⁴).

It has been shortly mentioned that also non-aqueous solutions make us acquainted with facts, which seem at first sight in opposition to the theory of ARRHENIUS, but to state with certainty that they are really so, seems premature to me.

If for aqueous solutions we should like to have a greater quan-

¹) WERNER, Zeit. Anorg. Chem. 15, 1 (1897).

²) DUTOIT, FRIDERICH, Bull. Soc. Chim. Paris. (3), 19, 334 (1898).

³) WALDEN, Ber. Chem. Ges. Berlin 32, 2862. (1899).

⁴) Proc. Royal Acad at Amsterdam, Vol. 111. p. 717. (1901).

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tity of observations at our disposal, this is of course the case in a much higher degree for non-aqueous solutions.

It is certain that in general the results obtained by the determination of the conductivity, do not agree with those found by a non-electric method, but the question is, what conclusions we have to draw from this.

Have we to conclude from what precedes, that the conductivity does not always indicate the degree of dissociation, or must we say that determinations of the molecular weight in solutions, which are not exceedingly diluted, do not always give information about the degree of dissociation?

It seems to me that there is more to be said in favour of the latter conclusion and that the results obtained indicate that in not very much diluted solutions ions may occur at the same time with products of polymerization or association and so may be in equilibrium with them.

Before the incorrectness of this supposition has been conclusively proved, we should not reject the dissociation theory of ARRHENIUS, which has rendered so many and such important services to chemical science.

Mathematics. — "On the Theory of the Biquadratic Rest". By Prof. LEOPOLD GEGENBAUER (extract of a communication to Prof. JAN DE VRIES).

The way followed in the various textbooks of the theory of numbers and even in most lectures on this subject for the generalisation of the quadratic $\left(\frac{m}{n}\right)$, cubic $\left[\frac{m}{n}\right]$ and biquadratic $\left(\left(\frac{m}{n}\right)\right)$ restcharacters, explained at first only for prime denominators, seems to make the introduction of the generalised symbol appear rather arbitrary; hence it does not satisfy the thinking student. The symbol referred to is namely defined either as was already done by JACOBI by the equation

$$\binom{m}{\mu\nu} = \binom{m}{\mu} \binom{m}{\nu} \operatorname{resp.} \left[\frac{m}{\mu\nu} \right] = \left[\frac{m}{\mu} \right] \left[\frac{m}{\nu} \right] \operatorname{resp.} \left(\binom{m}{\mu\nu} \right) = \left(\binom{m}{\mu} \right) \left(\binom{m}{\nu} \right)$$

that is, by assuming the existence of the theorem of multiplication for the denominator (e.g. DIRICHLET, "Vorlesungen über Zahlen-

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