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$$\rho^2 - \rho - \mu - 2\xi - 2\omega = 3(v + \theta),$$

then

$$\lambda = 2v + 2\theta - 2.$$

So the curve  $C$  meets the cone  $K$  outside  $P$  still  $2v - 2$  times, and  $P$  counts for two points of intersection. So the curve  $C$  also meets the conic  $c$ , lying on  $K$  only two times and consequently the curve  $d$ , having with  $c$ , five points in common at  $P$ , meets it also only two times.

**Chemistry.** — “*A contribution to the knowledge of the course of the decrease of the vapour tension for aqueous solutions.*”  
By Dr. A. SMITS. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM.)

1. In 1788 BLAGDEN<sup>1)</sup> discovered the relation between the lowering of the freezing point and the quantity of the solved substance. Among the substances which he examined, were however also some, which showed deviations, either in this sense that the lowering of the freezing point increased more rapidly or in that sense that it increased more slowly than the concentration.

RÜDORFF<sup>2)</sup>, who quite ignorant of BLAGDEN's work, made the same discovery in 1861, and COPPET<sup>3)</sup>, who ten years later (1871), continued RÜDORFF's investigations, came both to the result, that deviations from the rule first discovered by BLAGDEN, occurred both in one sense and in the other. A disproportionately rapid increase of the lowering of the freezing point with the concentration was found among others for NaBr, NaJ, CaCl<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> and also for NaCl, whereas for the nitrates of Na, NH<sub>4</sub>, Ba, Ca, Sr, Pb, Ag and for Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, NH<sub>4</sub>CNS the reverse was observed.

As an illustration of the course, as for NaBr etc. RÜDORFF had already adopted the formation of hydrates. COPPET assumed for the deviations for the nitrates, which are mostly anhydrous, that they are modified by the action of water or by the fall of the temperature in a certain, not further defined way.

Results analogous to those of BLAGDEN, RÜDORFF and COPPET were obtained by TAMMANN<sup>4)</sup> in 1887 when determining the decrease of the vapour tension. TAMMANN found namely, that for most of the salt

<sup>1)</sup> Wied. Ann. **39**, 1. (1890).

<sup>2)</sup> Pogg. **114**, 63. (1861); ib. **116**, 55 (1862); ib. **145**, 599 (1871).

<sup>3)</sup> Ann. Chim. Phys. (4) **23**, 366. (1871); ib. **25**, 502. (1872); ib. **26**, 98 (1872).

<sup>4)</sup> Wied. Ann. **24**, 523. (1885).

solutions the diminution of the vapour tension with increase of concentration increased more than the concentration, whereas for the nitrates of K, Na and for  $\text{KClO}_3$  the reverse was observed. The later investigations of BREMER<sup>1)</sup>, HELMHOLTZ<sup>2)</sup>, WALKER<sup>3)</sup> and DIETERICI<sup>4)</sup> gave the same result as those of their predecessors viz. this that in general the diminution of the vapour tension increases more rapidly than the concentration, and that the salts which form an exception to this rule are chiefly the anhydrous nitrates.

Up to 1903 the determinations of the freezing point of salt solutions of smaller concentrations than those which had been earlier investigated, yielded the result, that the molecular lowering of the freezing point *decreases* with increase of the concentration. As these measurements were continued to the concentration of  $\pm 1$  gr. mol. per 1000 gr.  $\text{H}_2\text{O}$ , it followed necessarily, that where the reverse course had been ascertained by the earlier observers, a minimum value had to occur in the molecular decrease of the freezing point, but for a concentration which lay above that where the investigators of later time had stopped.

In 1896, however, I had come to the conclusion in the determinations of the vapour tension by means of the micromanometer<sup>5)</sup>, that for dilute solutions, i.e. for solutions below the concentration of 1 gr. mol. per 1000 gr.  $\text{H}_2\text{O}$ , the molecular diminution of the vapour tension *increased* with the concentration. This was found inter alia for solutions of  $\text{NaCl}$ ,  $\text{KOH}$ ,  $\text{H}_2\text{SO}_4$  and  $\text{CuSO}_4$ , whereas for  $\text{KNO}_3$ -solutions the reversed course was found. This result was therefore in perfect accordance with what had been found by my predecessors for more concentrated solutions, but was directly opposed (except  $\text{KNO}_3$ ) to the results of the determinations of the freezing point.

The question was now: "Which results are the correct ones?"

In the determination of the boiling point I hoped to find a means to answer this question. After having applied some improvements to the method and after having rendered myself independent of the fluctuations of the atmospheric pressure by using a *manostat*, I began the investigations and the result was published in April 1900<sup>6)</sup>.

<sup>1)</sup> Rec. tr. Chim. 6, 122. (1887).

<sup>2)</sup> Wied. Ann. 27, 568. (1886).

<sup>3)</sup> Zeitschr. f. phys. Chem. 2, 602. (1888).

<sup>4)</sup> Wied. Ann. 42, 513. (1893); ib. 62. 616. (1897). Ann. phys. Chem. 27, 4. (1898).

<sup>5)</sup> Archiv. Néerl. (2) 1 (1897).

<sup>6)</sup> These Proceedings II April 21 1900 p. 635, April 20 1901, III p. 717. In the same year (1900) JONES, CHAMBERS and FRAZER cyoscopically found minima for  $\text{MgCl}_2$  and  $\text{BaCl}_2$  lying at 0.1—0.2 gr. mol.

I arrived at the following result :

The molecular rise of the boiling point increased for solutions of NaCl and KCl from the concentration  $\pm 0.3$  gr. mol. per 1000 gr. H<sub>2</sub>O, both towards higher and towards lower concentrations, or in other words, the molecular rise of the boiling point proved to have a *minimum value* lying at  $\pm 0.3$  gr. mol. For the anhydrous nitrates of K, Na, Ba, Ag and Pb, however, the molecular rise of the boiling point proved, quite in concordance with the determinations of the vapour tension, to continually decrease with increase of the concentration.

The method which was the least accurate in appearance, proved to be able to point out a mistake both in the method of the freezing point and in that of the vapour tension. The first work was then to force the micromanometer to greater accuracy by applying some improvements, and then to repeat the experiments. In 1901<sup>1)</sup> a new series of experiments yielded really a result which qualitatively harmonized perfectly with that obtained by means of the boiling point method. For NaCl as well as for H<sub>2</sub>SO<sub>4</sub> a minimum occurred in the molecular decrease of the vapour tension, lying at  $\pm 0.5$  gr. mol. As before KNO<sub>3</sub>-solutions gave a strong decrease of *i* with increase of the concentration.

In the same year KAHLLENBERG<sup>2)</sup> found for solutions of NaCl, KCl, KBr, KJ and MgCl<sub>2</sub>, that the molecular rise of the boiling point increased continually with the concentration for the first and the last salt from the concentration  $\pm 0.2$  gr. mol. to  $\pm 5$  gr. mol., whereas for KCl, KBr and KJ a more or less clearly marked minimum was found.

BILTZ<sup>3)</sup> was the first to confirm my results with certainty in 1902. He found a minimum in the molecular rise of the boiling point, not only for KCl and NaCl, but also for RbCl and LiCl. His determinations of the freezing point of alkali chlorides showed only for LiCl a continual increase of the molecular lowering of the freezing point with the concentration; a minimum was not found, however, for the chlorides of the alkali metals by this method. For LiNO<sub>3</sub> and LiBr BILTZ found a faint minimum, whereas for the chlorides of the bivalent metals by the cryoscopic way very strongly pronounced minima were found, mostly lying between 0.1 and 0.2 gr.

<sup>1)</sup> These Proc. IV September 28 1901 p. 163.

<sup>2)</sup> Journ. Phys. Chem. 5, 339 (1901).

<sup>3)</sup> Zeitsch. f. Phys. chem. 40 s. 185 (1902).

mol., which is in accordance with the observations of JONES, CHAMBERS and FRAZER <sup>1)</sup>.

The first who by the cryoscopic way discovered minima in the molecular lowering of the freezing point for chlorides of the alkali metals below the concentration 1 gr. mol., were JONES and GETMAN <sup>2)</sup>, who published their results in the newly published *Jubelband für Ostwald*. It is remarkable that working with the common apparatus of BECKMANN these observers obtained more accurate results than RAOULT with his apparently ideal apparatus. For RAOULT found for NaCl-solutions up to the concentration 1 gr. mol. a regular decrease of the molecular lowering of the freezing point with increase of the concentration.

2. After having thus shortly pointed out what the boiling point method, the vapour tension method and the freezing point method have brought to light for the study of the non-diluted solutions, I proceed to give the results of the determinations of the diminution of the vapour tension of NaCl and NaNO<sub>3</sub>-solutions, made by means of the *micromanometer*, in which the aniline-water-manometer was replaced by the manometer of Lord RAYLEIGH <sup>3)</sup>. It seemed namely very desirable for the greater certainty of the results, to repeat some measurements with another apparatus, the accuracy of which did not differ too much from that of my manometer. Lord RAYLEIGH's invention was therefore very welcome to me, because his manometer was stated to reach an accuracy of  $\pm 0.00045$  m.m. Hg, and mine had an accuracy of 0.00025 m.m. Hg.

Lord RAYLEIGH's manometer and the arrangement of this apparatus has been represented in fig. 1 and 2. *A* is a barometer tube, which branches into two parts at the top; the two branches are blown out to two bulbs of  $\pm 25$  mm. diameter at *BB*. In these bulbs extend two finely drawn out glass points, which are ground off to a sharp point at the lower end. On the tubes *LL*, of which the one more to the left is split up into two branches, as is seen in the horizontal projection, and which thus furnish three points of support, a glass plate *N* is laid which bears a mirror *M*, whose front is silvered. The glass plate *N* is fastened to the three points of support and the mirror *M* to the glass plate by means of water glass.

Lord RAYLEIGH had connected the tubes *CC* with his apparatus by means of straight glass tubes 3 meters long, but here some glass spirals  $\pm 35$  c.m. long have been added between them in order to prevent any wrenching.

<sup>1)</sup> Amer. chem. Journ. **23**, 89 (1900); ib. **23**, 512 (1900).

<sup>2)</sup> Zeitschr. f. Physik chem. **46**, 244 (1903).

<sup>3)</sup> Zeitschr. f. Physik chem. **37**, 713 (1901).

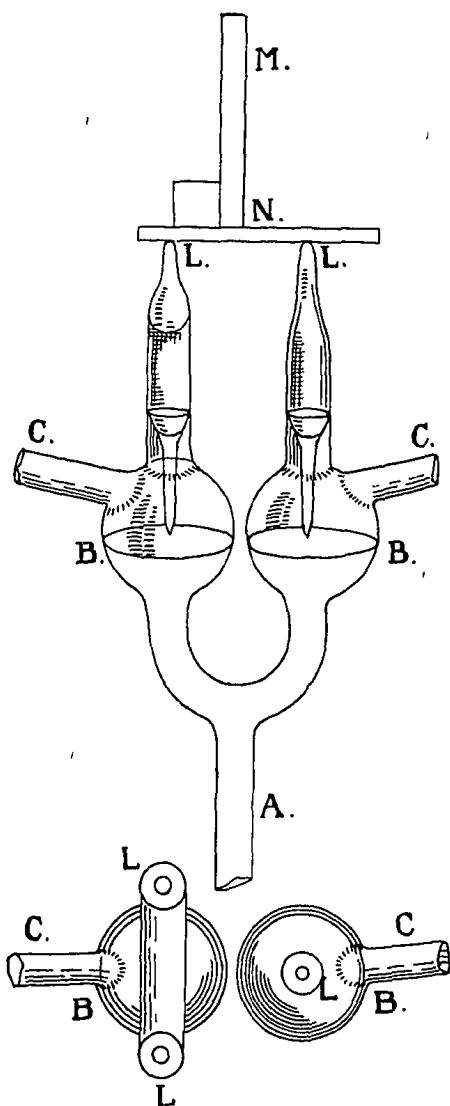


Fig. 1.

the clamp  $H^1$ ) and the screw  $R$ . This point can be very accurately determined, as we can observe the reflected images at the same time with the points and so it is as if we saw twice two points approach each other. If the light of an incandescent lamp  $g$ , concentrated by a lens, was thrown on the manometer through a mirror  $m$ , a great accuracy of adjustment could be reached after some practice, when

<sup>1</sup>) The clamp  $G$  serves for the rough adjustment.

<sup>2</sup>) As it proved necessary to prevent heating of the manometer as much as possible, a thick plate of asbestos  $u$  was adjusted between the incandescent lamp and the manometer; in this plate a glass vessel  $w$  was fastened with a solution of alum for the absorption of the rays of heat.

The manometer  $B$  with barometer tube  $A$  is (see fig. 2) fastened in a groove of a solid board  $P$  by means of Cailletet cement. This board is part of an adjusting table  $S$ , which can rotate round an horizontal axis by means of the screw  $R$ . This axis passes through the points of support of two sets of screws  $Z$ , only one of which is to be seen in the figure 2. The mirror of the manometer has been placed in such a way, that the axis mentioned is parallel to its front and coincides with its middle. The air trap  $V$ , in which the barometer tube ends, is by means of an India rubber tube provided with two clamps  $G$  and  $H$  and connected with a mercury reservoir  $K$ .

The principle, on which this manometer rests, is as follows:

If the barometer tube is filled with Hg as far as in the bulbs  $BB$  and if the pressure is the same in the two legs of the manometer, we can cause the two glass points to just touch the mercury mirrors, which are now in one horizontal plane, by using simultaneously the

the points were simultaneously observed through two magnifying glasses.

The position which the mirror  $M$  occupies in this adjustment, so the zero position, could be accurately determined by means of a scale and a reading telescope with a cross wire. If now a difference in pressure was brought about e.g. such that the mercury mirror in the left leg fell somewhat and that in the right leg rose somewhat, the adjustment of the two points on the mercury mirrors could be again reached by turning the adjusting table, to which the manometer is fastened, over a small angle to the left by means of the screw  $R$ , for which at the same time the screw  $H$  was to be used, as the bulbs  $BB$  are no perfect spheres, and have not perfectly the same diameter either.

When the glass points are again placed in the required way and the reading glass is again read, it is clear, that we can calculate the difference in level of the mercury mirrors in a simple way from the angle of rotation, when we know, the distance between the glass points. If this distance is  $l$ , the angle of rotation  $\alpha$ , the difference in height between the two mercury mirrors is:

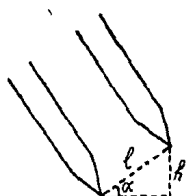


Fig. 3.

$$h = l \sin \alpha.$$

If we represent the deviation observed with the telescope expressed in m.m.  $a$  and the distance from the scale to the mirror  $b$ , then  $\text{tg } 2\alpha = \frac{a}{b}$ , for which we may write  $\text{tg } \alpha = \frac{a}{2b}$  provided  $\alpha$  be very small.

As further for small angles  $\sin \alpha = \text{tg } \alpha$ , we may write in this case:

$$h = l \text{tg } \alpha = \frac{la}{2b} \dots \dots \dots (1)$$

If the angles are too large for this assumption, we get the following form for  $h$ :

$$h = \frac{la}{2b} \left( 1 - \frac{3}{2} \frac{a^2}{4b^2} \right) \dots \dots \dots (2)$$

The distance between the glass points was determined by means of a comparator and amounted to 24.66 m.m. =  $l$ . The distance from the scale to the mirror amounted to 2735 m.m. =  $b$ .

It now proved that when the deviation  $a$  was smaller than 100 m.m., formula (1) could be applied, whereas for larger deviations formula (2) appeared to be required.

The accuracy of adjustment, obtained in this arrangement with

Lord RAYLEIGH's manometer, appeared to amount to 0.1 scale division or to 0.00045 m.m. Hg, whereas with my manometer it amounted to 0.00025 m.m. Hg, as has been said before.

Fig. 4 represents the whole arrangement. *A* is the micromanometer, *B* the automatic mercury air-pump, *C* the manometer of Lord RAYLEIGH and *D* the reading glass with scale and mirror, *a* is a strip of mirror, cut from a sphere. In the focus an incandescent lamp *b* is placed, over which a glass cup has been placed enveloped with filtering paper. A parallel pencil of rays falls through the glass scale *c* and is reflected by the mirror *M* from the manometer into the reading glass *d*.

From this figure the connection of *C* with *A* through the long glass tubes *e* and *f* is also clearly visible. The results obtained by this arrangement are summarized in the following tables.

T A B L E I.

Na Cl.

Concentration in gr. mol. p 1000 gr. H <sub>2</sub> O	$p_u - p_s$ in m m. Hg of 0°.	$p_m$ <sup>1)</sup> in m m. Hg of 0°.	$i = \frac{p_w - p_s}{p_w} \frac{N}{n} = \frac{p_m}{0.08316}$ <sup>2)</sup>
0 0441	0 00720	0.163	1.96
0.1073	0 01619	0.151	1.81
0 3823	0 05533	0.1447	1 740
0 6299	0 09125	0 1449	1 742
0 9887	0.14564	0 1473	1.771
2 0476	0 31017	0 1515	1 822
3 3524	0.53442	0.1594	1 917

With the aniline-water manometer the following results had been before obtained.

We see from this that the tables I and II harmonize very well qualitatively; both give a minimum value of *i* for the concentration  $\pm 0.5$  gr. mol.

That there are differences in many cases in the absolute values of *i* is probably due to the uncertainty which exists in applying the temperature correction when working with my manometer. In future

<sup>1)</sup>  $p_m$  = molecular diminution of vapour tension.

<sup>2)</sup> 0.08316 = theoretical mol. diminution of vap. tens. at 0°.



T A B L E II.

Na Cl.

Concentration in gr. mol. p. 1000 gr. H <sub>2</sub> O	$p_w - p_s$ in m m. Hg of 0°	$p_m$ in m.m. Hg of 0°.	$i = \frac{p_w - p_s}{p_w} \frac{N}{n} = \frac{p_m}{0,08316}$
0 0591	0 00879	0.149	1 79
0 0643	0 00139	0.146	1.76
0 1077	0.01541	0 143	1.72
0 4527	0 06400	0.144	1 70
0 4976	0 06987	0 141	1 70
1 0808	0 15484	0 143	1 723
1 2521	0 18014	0 144	1 730
1 8228	0.26757	0 147	1 765
2.1927	0.33406	0.153	1 832
4 6362	0 78345	0.169	2 032

it will therefore be advisable to place the manometer in a thermostat. Up to this time the manometer was placed in a glass vessel, through which the water of the aqueduct flowed. If a correction is rendered unnecessary by keeping the manometer at constant temperature, the greater sensitiveness of the aniline-water-manometer will be still more apparent <sup>1)</sup>).

For the comparison of the results of the determinations of the vapour pressure with those obtained in a cryoscopic way, the results of RAOULT <sup>2)</sup>, JONES and GETTMAN and mine for NaCl-solutions are placed side by side in the following table.

So RAOULT did not find a minimum in the factor  $i$  in spite of his

<sup>1)</sup> After having read my publication in the Archives Néerlandaises, BATELLI made some measurements with a manometer which differed from mine only in so far, that it was erected in reversed position, in order to make the closure with mercury instead of with oil possible. This change was sufficient, as Prof. CASSUTO, under whose superintendence BATELLI seems to have worked, wrote to me, to omit my name altogether in the publication in the Ann. de Chim. et de Phys. T. XXV 1902, though they used the most essential part of my work viz. a dilute solution of Na OH, Na<sub>2</sub> CO<sub>3</sub> or glass, which causes the aniline to run in a tube of the aqueous solution, and to which the great accuracy is actually due.

<sup>2)</sup> Zeitschr. f. Physik. Chem. 27, 638 (1898).

## T A B L E III.

Na Cl.

Concentration	$i_G$ —RAOULT.	$i_G$ —JONES and GETMAN.	$i_D$ —SMITS.
0.05	1.91	1.89	1.96
0.1	1.86	1.86	1.81
0.5	1.84	1.891	1.74
1.0	1.838	1.906	1.77
2.0		2.007	1.82
3.0		2.190	1.92

$i_G = i$  calculated from the lowering of the freezing point

$i_D = \text{» } \text{» } \text{» } \text{»}$  diminution of the vapour tension.

method which seemed so very accurate, though he continued the experiments up to the concentration 1 gr. mol.; JONES and GETMAN, however, found a strongly pronounced minimum lying at the concentration  $\pm 0.1$  gr. mol., whereas the determinations of the vapour tension give a minimum at  $\pm 0.5$  gr. mol.

I have already pointed out in a previous paper<sup>1)</sup>, that only for the case that we have to deal with *exceedingly diluted* solutions the value of  $i$  calculated from the lowering of the freezing point must be in harmony with that calculated from the diminution of the vapour tension.

For the calculation of  $i$  from the lowering of the freezing point the following equation is used:

$$i_G = \Delta T \frac{S}{RT_0^2} \frac{N}{n} \dots \dots \dots (1)$$

and for the calculation of  $i$  from the diminution of the vapour tension, we applied the equation

$$i_D = \frac{\Delta p}{p_0} \cdot \frac{N}{n} \dots \dots \dots (2)$$

For exceedingly diluted solutions  $i_G = i_D$  or

$$\frac{\Delta p}{p_0} \frac{N}{n} = \Delta T \frac{S}{RT_0^2} \cdot \frac{N}{n} \dots \dots \dots (3)$$

or

$$\frac{\Delta p}{p_0} = \Delta T \cdot \frac{S}{RT_0^2} \dots \dots \dots (4)$$

<sup>1)</sup> These Proc. III, Febr. 23 1901, p. 507.

For not very dilute solutions this is however no longer the case and as VAN LAAR<sup>1)</sup> found, for them the following relation holds:

$$\log \frac{p_0}{p} = \Delta \cdot T \frac{S}{RT_0^2} \cdot \frac{T_0}{T} \dots \dots \dots (5)$$

or

$$\frac{\Delta p}{p_0} + \frac{1}{2} \left( \frac{\Delta p}{p_0} \right)^2 = \Delta T \frac{S}{RT_0^2} \cdot \frac{T_0}{T} \dots \dots \dots (6)$$

If therefore we wish to compare the results of non-diluted solutions, we can e.g. calculate instead of  $i_G = i_D$  according to (1) and (2) the following values:

$$I_G = \Delta T \frac{S}{RT_0^2} \cdot \frac{T_0}{T} \cdot \frac{N}{n}$$

or

$$I_D = \left[ \frac{\Delta p}{p_0} + \frac{1}{2} \left( \frac{\Delta p}{p_0} \right)^2 \right] \frac{N}{n}$$

which theoretically must have exactly the same value.

I have already shown before<sup>2)</sup>, that the error committed by putting  $i_G = i_D$  instead of  $I_G = I_D$  for not very dilute solutions, is not sensible before we reach the concentration  $\pm 1$  gr.

If we now compare the results obtained by RAOULT, JONES, GETMAN and myself by means of the factor  $I$ , we get the following table:

T A B L E IV.  
Na Cl.

Concentration	$I_G$ —RAOULT.	$I_G$ —JONES and GETMAN.	$I_D$ —SMITS.
0.05	1 91	1.89	1.96
0.10	1 86	1 87	1.81
0.50	1 85	1.904	1 75
1.00	1 86	1.931	1 80
2.00		2 064	1.88
3.00		2.293	2.03

It is obvious that the second column is now qualitatively in concordance with the two following; also the factor  $I$  derived from the observations of RAOULT, gives a minimum, but it is very faint, so faint, that it did not appear in the calculation of  $i_G$  (table III)<sup>3)</sup>.

<sup>1)</sup> Zeitschr. f. physik. Chem. 15, 457 (1894).

<sup>2)</sup> These Proceedings III, Febr. 23 1901 p. 512.

<sup>3)</sup> This has already been shown by VAN LAAR in a somewhat different way. (Archives Teijler 8 (1903)).

We see further that the differences between the third and the fourth column in this table are about as great as in table IV, so that it is sufficient to calculate  $i_G$  and  $i_D$  for a first investigation of the concordance of the results obtained by different methods.

The investigation of  $\text{NaNO}_3$ -solutions yielded the following result.

T A B L E V.

 $\text{NaNO}_3$ .

Concentration in gr mol. p 1000 gr. $\text{H}_2\text{O}$	$p_w - p_s$ in m m. Hg of $0^\circ$ .	$p_m$ in m m Hg of $0^\circ$ .	$i = \frac{p_w - p_s}{p_w} \frac{N}{n} = \frac{p_m}{0,08316}$
0 0515	0 00718	0 143	1 72
0 0901	0 01257	0 139	1 68
0 3385	0 04578	0 1352	1.626
0 8328	0 11042	0 1326	1 594
2 8168	0 33126	0 1176	1.414
4 0544	0 46119	0 11375	1 268
7 3151	0 79056	0 10807	1 300

It follows from this table, that the factor  $i$  decreases continually with  $\text{NaNO}_3$ -solutions.

Also JONES and GETMAN have observed the same course in their determinations of the freezing point, which follows from the following table.

T A B L E VI.

 $\text{NaNO}_3$ .

Concentration.	Molecular freezing point depression	$i$
0 05	3 440	1 85
0 10	3 428	1 843
0.20	3 345	1 798
1 00	3.198	1.719
2.00	3.074	1 653
3.00	2 967	1.596

3. The minimum in  $i$  may be brought about by the formation of hydrates in solution. I showed already before<sup>1)</sup>, how great the influence can be, which the formation of hydrates in solution can exert on the course of the factor  $i$ , specially with regard to not very dilute solutions.

For very small concentrations, however, the number of water molecules is so predominant, that the number of molecules withdrawn from the solution, practically does not bring about any change in the molecular concentration. Towards higher concentrations the increase of the molecular concentration in consequence of the formation of hydrates augments continually, and so it may be assumed, that for a certain concentration it has increased so much, that it has become equal to the diminution of the molecular concentration in consequence of the retrogression of the electrolytic dissociation. If this is the case,  $i$  has reached its smallest value, and will increase towards higher concentration, because the influence of the formation of hydrates prevails more and more over the retrogression of the electrolytic dissociation.

Besides the above mentioned formation of hydrates, we may generally assume auto-complex-formation and hydrolysis, so that probably many electrolytes form a system so intricate, that some time will probably elapse before the desired insight into it will be acquired. Referring here to salts of strong bases and acids I could leave hydrolysis out of account. The auto-complex-formation has not been discussed, because it brings about a diminution of the molecular concentration, and was therefore of no use for the explanation of the phenomenon.

4. Finally I will call attention to the very remarkable fact, that solutions of  $\text{NaNO}_3$ , which qualitatively behave in a very normal way, do not follow the dilution law of OSTWALD, whereas solutions of  $\text{KNO}_3$  follow this law according to my measurements, and as the deviations for  $\text{NaNO}_3$  solutions lie in this direction that  $K$  increases with the concentration as is seen in the following table, this points to an influence as e. g. occurs for  $\text{NaCl}$  solutions, but in a much smaller degree<sup>2)</sup>.

<sup>1)</sup> Archiv. Néerl. (2) 1 (1897).

<sup>2)</sup> That  $\text{KNO}_3$ -solutions harmonize better with the theory than  $\text{NaNO}_3$ -solutions is in accordance with the results of experiments made by ABEGG and BODLANDER (Zeitschr. f. anorg. Chem. 20, 453 (1899)), from which could be derived, that the tendency to complex-formation depends on the degree of the tendency to ionisation, which latter tendency is indicated by the tendency of dissociation. The greater the tendency to ionisation the smaller the tendency to complex-formation. According to WILSMORE (Zeitschr. f. physik. Chem. 35, 318 (1900)) the tension of dissociation is for  $K=3.20$  and for  $\text{Na}=2.82$ , from which would follow, that kalium salts have a slighter tendency to complex-formation than natrium salts.

T A B L E VII.

NaNO<sub>3</sub>.

From the determinations of the vapour tension at 0° with Lord RAYLEIGH'S manometer.

Concentration.	Degree of Dissociation $\alpha$	$K = c \frac{\alpha^2}{1-\alpha}$
0.0515	0.72	0.09
0.0901	0.68	0.16
0.3585	0.63	0.35
0.8328	0.59	0.72

From the determinations of the boiling point at  $\pm 100^\circ$ .

0.0462	0.83	0.19
0.0852	0.81	0.28
0.4448	0.72	0.76
0.8630	0.71	1.50

T A B L E VIII.

KNO<sub>3</sub>.

From the determinations of the vapour tension at 0° with the aniline-water-manometer.

Concentration.	Degree of dissociation $\alpha$	$K = c \frac{\alpha^2}{1-\alpha}$
0.0400	0.81	0.14 <sup>1)</sup>
0.1450	0.58	0.12
0.5997	0.39	0.15
0.9288	0.304	0.12
		average 0.13

From the determinations of the boiling point at  $\pm 100^\circ$ .

0.1000	0.91	0.92 <sup>2)</sup>
0.4091	0.74	1.05
0.7486	0.67	1.02
0.9981	0.651	1.21
		average 1.05

<sup>1)</sup> We must not attach too much importance to the absolute value of  $K$ , as a slight error in the sensibility of the manometer appears in  $K$  greatly magnified.

<sup>2)</sup> By this method we cannot make use of more diluted solutions to test the dilution-law, as the error of the observation has too much influence then. For the concentration 0.1 gr. mol. per 1000 gr. H<sub>2</sub>O this influence is already fairly strong. If e.g. for this concentration we had found a rise of the boiling point of 0.1° instead of 0.099°, we should have had  $\alpha = 0.93$  and  $K = 1.23$ .

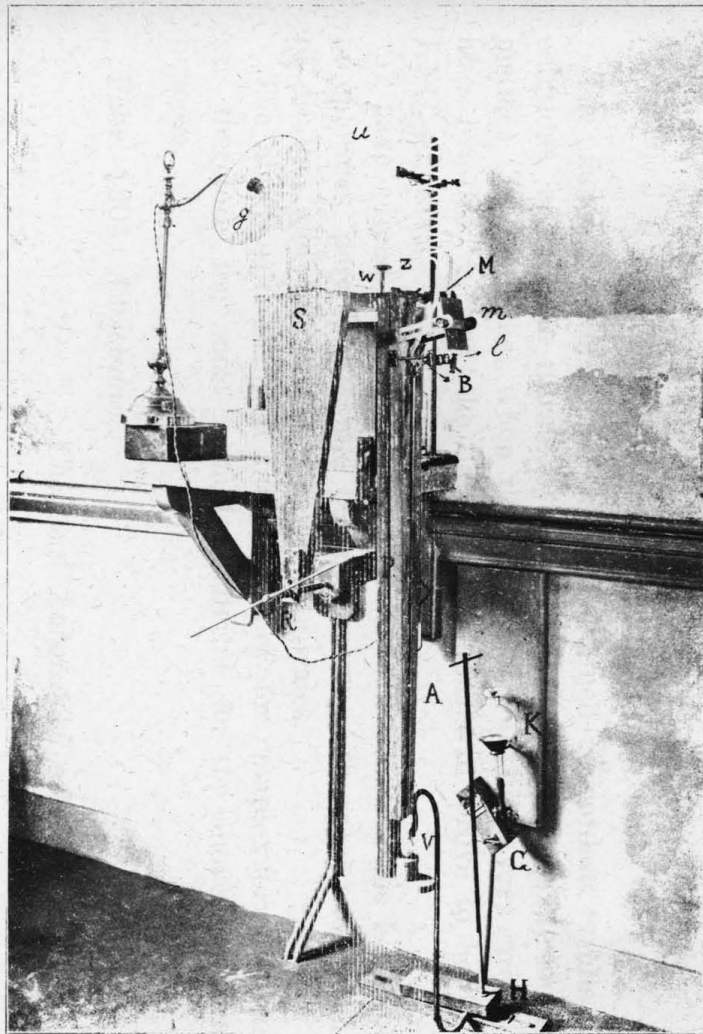


Fig. 2.

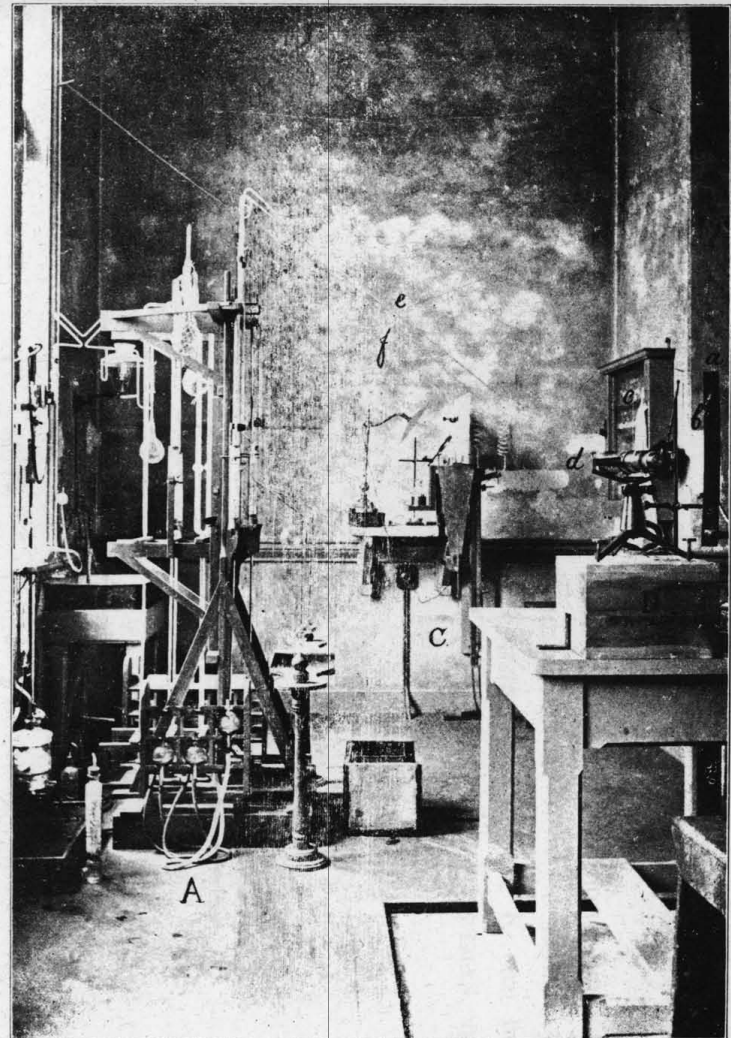


Fig. 4

It is remarkable that the law of dilution proves to apply here up to fairly high concentrations. It would therefore be interesting to carry on the series towards higher concentrations to see where the deviations begin to appear.

That the freezing point method is inferior to the vapour tension method and the boiling point method with a view to accuracy follows also from the fact, that no constant values for  $K$  can be calculated from the observations of LOOMIS, JONES and GETMAN, as appears from the following table.

T A B L E IX.

KNO<sub>3</sub>.

From the determinations of the freezing point.

Concentration.	Degree of dissociation $\alpha$	$K = c \frac{\alpha^2}{1-\alpha}$
0 05	0 83	0 21
0 10	0 78	0 28
0 20	0.71	0 35
0.40	0 69	0.78
0.50	0.65	0 61
1 00	0.47	0 41

} LOOMIS<sup>1)</sup>.

} JONES and GETMAN.

The fact, however, that BILTZ<sup>2)</sup> obtained concordant results for solutions of caesium nitrate by means of the freezing point method justifies the hope, that when the experiments are made very carefully, also by this method the law of dilution will prove to hold for KNO<sub>3</sub>-solutions.

I have agreed with Dr. BILTZ that he will examine the behaviour of chlorates, perchlorates and permanganates with regard to the law of dilution and I shall investigate the nitrates.

The above salts manifest little tendency for complex formation and are therefore the most suitable material for the above mentioned purpose.

Febr. 1904, *Amsterdam*.

*Chemical Laboratory of the University.*

<sup>1)</sup> Phys. Rev. **3**, 279 (1896).

<sup>2)</sup> loc. cit.