

*Citation:*

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to which

	$s_1$	$s_2$	$s_3$	$s_4$	$s_5$	$s_6$	$s_7$	$s_8$	$s_9$	$s_{10}$	$s_{11}$	$s_{12}$	
$t_1$	$b_1$	$b_2$	$b_3$	$b_4$	$b_5$	$b_6$	$-a_1$	$-a_2$	$-a_3$	$-a_4$	$-a_5$	$-a_6$	. . . (7).

belongs as supplementary "assemblant".

If we omit one of the columns from the "assemblant" (6) the determinants in the remaining columns (see Chapter I of the above-named paper) are divisible by the supplementary determinant of the assemblant.

From this "assemblant" the coefficients of the resultant follow immediately.

Thus we find for the resultant between  $y$  and  $z$ :

$$p_{12,13,14,15} y^4 + p_{11,13,14,15} y^3 z + p_{11,12,14,15} y^2 z^2 + p_{11,12,13,15} y z^3 + p_{11,12,13,14} z^4 = 0 \quad \dots (8),$$

for the resultant between  $x$  and  $z$ :

$$p_{3,6,10,15} x^4 + p_{1,6,10,15} x^3 z + p_{1,3,10,15} x^2 z^2 + p_{1,3,6,15} x z^3 + p_{1,3,6,10} z^4 = 0 \quad \dots (9),$$

for the resultant between  $x$  and  $y$ :

$$p_{2,4,7,11} x^4 + p_{1,4,7,11} x^3 y + p_{1,2,7,11} x^2 y^2 + p_{1,2,4,11} x y^3 + p_{1,2,4,7} y^4 = 0 \quad (10),$$

where the coefficients represent determinants contained in "assemblant" (6) after one of the columns having been omitted and where the indices indicate which rows must be left out of the "assemblant" to obtain the determinant represented by the symbol. All the coefficients of the equations (8), (9) and (10) are now still divisible by the same linear factor, namely by  $b_6$  if we leave the sixth column out of the "assemblant", in general by the supplementary determinant of the "assemblant" (7).

**Chemistry.** — Prof. V. A. JULIUS presents on behalf of Dr. A. SMITS of Amsterdam a paper on „*Investigations with the Micromanometer.*”

After I had published in 1896 the first results obtained with the micromanometer<sup>1)</sup>, I continued my investigations to inquire whether the course observed for NaCl, KOH and cane-sugar would also appear in other compounds.

<sup>1)</sup> Dissertation „*Untersuchungen mit dem Mikromanometer*” 1896. Verslag Koninkl. Akad. v. Wetensch. te Amsterdam, Wis- en Natuurk. Afd. pag. 292, 1897. Archives Neerl. Série II, Tome I, p. 89, 1897.

Before, however, examining other compounds, I wished to make some further experiments with Na Cl, KOH and sugar solutions, because I had made a slight improvement in the apparatus; I had namely brought the legs of the manometer nearer together, so that they were only 2 m.m. distant, which diminished the error in the observation. Before communicating the results of those observations, I shall first shortly state my former results, to facilitate a comparison. The meaning of  $p_w, p_s, p_m, N$  and  $n$  is as follows.

$p_w$  = tension of the gas of pure water expressed at 0° in m.m. Hg.

$p_s$  = " " " " " solution " " " " " "

$p_m$  = mol. decrease of the tension of the gas " " " " " "

$N$  and  $n$  indicate the number of mol. of water and solved substance found in the solution :

## Na Cl.

Concentration in gr mol. per 1000 gr H <sub>2</sub> O.	$p_w - p_s$ in m.m. Hg.	$p_m$ in m.m. Hg.	$i = \frac{p_w - p_s}{p_w} \cdot \frac{N}{n}$
0.02842	0.00344	0.121	1.5
0.03546	0.00477	0.131	1.6
0.08813	0.01223	0.139	1.67
0.17680	0.02477	0.140	1.69
0.35527	0.05026	0.141	1.70
0.8854	0.12646	0.143	1.718
1.8228	0.26757	0.147	1.765

## KOH

Concentration in gr mol. per 1000 gr H <sub>2</sub> O.	$p_w - p_s$ in m.m. Hg.	$p_m$ in m.m. Hg.	$i = \frac{p_w - p_s}{p_w} \cdot \frac{N}{n}$
0.03035	0.00409	0.135	1.6
0.05564	0.00763	0.137	1.65
0.09992	0.01382	0.138	1.66
0.16626	0.02321	0.140	1.68
0.33464	0.04786	0.143	1.72
0.51342	0.07504	0.146	1.76
0.75044	0.11170	0.149	1.700
1.0356	0.15867	0.153	1.842
2.6422	0.47601	0.180	2.166

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## CANE SUGAR.

Concentration in gr. mol per 1000 gr. H <sub>2</sub> O.	$p_w - p_s$ in m.m. Hg.	$p_m$ in m.m. Hg.	$i = \frac{p_w - p_s}{p_w} \cdot \frac{N}{n}$
0.02138	0.00178	0.083	1.0
0.04630	0.00388	0.084	1.0
0.08488	0.00705	0.083	1.0
0.17287	0.01440	0.083	1.00
0.28340	0.02366	0.084	1.00
0.77912	0.06485	0.083	1.001
1.8821	0.17453	0.093	1.115

For NaCl and KOH-solutions I found that the molecular depression of the vapour tension, and so  $i$ , became greater, when the concentration increased. For cane sugar solutions the molecular depression of the vapour tension and so  $i$ , was found constant between the concentration 0.02138 and 0.77912 gr. mol. per 1000 gr. H<sub>2</sub>O. Only for the last concentration 1.8821 gr. mol. per 1000 gr. H<sub>2</sub>O a higher value was found for the mol. depression of the vapour tension and for  $i$  than for the other concentration.

The results of the observations with the improved manometer follow. As the determination of the course was my principal object, I chose some solutions with a great difference of concentration.

## Na Cl

Concentration in gr. mol per 1000 gr. H <sub>2</sub> O.	$p_w - p_s$ in m.m. Hg.	$p_m$ in m.m. Hg.	$i = \frac{p_w - p_s}{p_w} \cdot \frac{N}{n}$
0.033028	0.00435	0.132	1.6
0.34057	0.04793	0.141	1.69
1.7533	0.25724	0.147	1.764
2.1927	0.33406	0.153	1.832
4.6362	0.78345	0.169	2.032

## KOH

Concentration in gr. mol. per 1000 gr. H <sub>2</sub> O.	$p_w - p_s$ in m.m. Hg.	$p_m$ in m.m. Hg.	$i = \frac{p_w - p_s}{p_w} \cdot \frac{N}{n}$
0.03476	0.00470	0.135	1.6
0.42374	0.06454	0.152	1.83
1.1912	0.19505	0.164	1.969
2.5995	0.48440	0.186	2.241

## CANE SUGAR.

Concentration in gr. mol. per 1000 gr. H <sub>2</sub> O.	$p_w - p_s$ in m.m. Hg.	$p_m$ in m.m. Hg.	$i = \frac{p_w - p_s}{p_w} \cdot \frac{N}{n}$
0.02602	0.00219	0.084	1.0
0.17225	0.01479	0.086	1.03
0.45413	0.03972	0.087	1.05
1.0811	0.09074	0.090	1.08

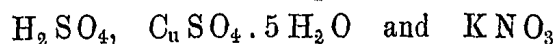
These few determinations were sufficient to prove that for Na Cl, KOH and cane sugar the molecular depression of the vapour tension, and so  $i$ , increases with the concentration.

The second series of KOH solutions is more reliable than the first, because great care has been taken to keep the second series of solutions free from carbonic acid. Probably this is the reason, that the values for  $i$  in the second table of solutions of KOH are a little higher than in the first.

The second table of solutions of cane sugar is also more accurate than the former, because the temperature of the waterbath in which the manometer is placed, was about 10° lower in the second series than in the first. At a lower temperature the accuracy is greater, because the manometer then reaches its position of equilibrium sooner than at a higher temperature.

It is evident that it is not much use to calculate the value for  $i$  for concentrations above 1 gr. mol. per 1000 gr. water. Nevertheless this calculation has been made here to facilitate a comparison with my former observations.

After this repetition of my former observations, experiments were made with solutions of the following substances:



The results are given in the following tables.

H<sub>2</sub>SO<sub>4</sub>

Concentration in gr. mol. per 1000 gr. H <sub>2</sub> O	$p_w - p_s$ in m.m. Hg.	$p_m$ in m.m. Hg.	$i = \frac{p_w - p_s}{p_w} \cdot \frac{N}{n}$
0.02090	0.00336	0.161	1.9
0.04968	0.00819	0.165	2.0
0.24960	0.04204	0.168	2.03
0.50418	0.08713	0.173	2.08
1.11431	0.21057	0.181	2.215
2.1795	0.44246	0.203	2.441

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CuSO<sub>4</sub>

Concentration in gr. mol per 1000 gr H <sub>2</sub> O	$p_w - p_s$ in m m Hg.	$p_m$ in m m. Hg.	$i = \frac{p_w - p_s}{p_w} \frac{N}{n}$
0.02348	0.00086	0.037	0.6
0.09860	0.00525	0.053	0.7
0.24519	0.01585	0.065	0.78
0.49378	0.03276	0.066	0.80
0.99612	0.06790	0.068	0.820
1.2162	0.09656	0.079	0.955

By concentration the number of gr. mol. CuSO<sub>4</sub> per 1000 gr. H<sub>2</sub>O is represented.

KNO<sub>3</sub>

Concentration in gr. mol. per 1000 gr. H <sub>2</sub> O.	$p_w - p_s$ in m m. Hg.	$p_m$ in m.m. Hg.	$i = \frac{p_w - p_s}{p_w} \frac{N}{n}$
0.02051	0.00287	0.140	1.7
0.25342	0.03241	0.130	1.54
0.51074	0.05569	0.109	1.31
1.0465	0.08671	0.083	0.996

It appears from what precedes that of the examined compounds KNO<sub>3</sub> is the only exception with regard to its course.

If the concentration of H<sub>2</sub>SO<sub>4</sub> and CuSO<sub>4</sub> increases, the molecular depression of the vapour tension, and also  $i$ , becomes greater, whereas for KNO<sub>3</sub> the reverse takes place.

It is remarkable, that the values for  $i$  of CuSO<sub>4</sub> always remain below unity, if we assume that there are in the solution CuSO<sub>4</sub> molecules, whereas the values for  $i$  calculated from the conductivity have been always found to be larger than unity.<sup>1)</sup>

The most interesting result, however, is that of KNO<sub>3</sub>, for it shows that the course of NaCl etc. is probably not general.

When I was occupied with these observations, Mr. DIETERICI<sup>2)</sup>

<sup>1)</sup> PICKERING, Berl. Ber. 25 pg. 1315, 1892.

<sup>2)</sup> Wied. Ann. 62, pg. 616, 1897.

published a treatise „Ueber die Dampfdrucke verdünnter wässriger Lösungen bei 0° C.“

He describes there in what way he has succeeded in making his aneroid more sensible, so that he could also examine diluted solutions with it. The results obtained for solutions which I have also examined, follow. To facilitate comparison some of my results are also mentioned.

## Na Cl

DIETERICI		SMITS	
Concentration in gr. mol. per 1000 gr. H <sub>2</sub> O	$p_m$ in m.m. Hg.	Concentration in gr. mol. per 1000 gr. H <sub>2</sub> O.	$p_m$ in m.m. Hg.
0.0732	0.121	0.02842	0.121
0.154	0.131	0.03516	0.134
0.294	0.146	0.08813	0.139
0.454	0.144	0.17680	0.140
0.964	0.147	0.35587	0.141
		0.8854	0.143
		1.8228	0.147

H<sub>2</sub> SO<sub>4</sub>

DIETERICI		SMITS	
Concentration in gr. mol. per 1000 gr. H <sub>2</sub> O	$p_m$ in m.m. Hg.	Concentration in gr. mol. per 1000 gr. H <sub>2</sub> O.	$p_m$ in m.m. Hg.
0.0542	0.144	0.01090	0.161
0.0871	0.127	0.04963	0.165
0.1088	0.145	0.21960	0.163
0.1771	0.143	0.50418	0.173
0.221	0.156	1.41131	0.184
0.263	0.159	2.1795	0.203
0.350	0.159		
0.436	0.167		
0.892	0.177		

## CANE SUGAR.

DIETERICI.		SMITS	
Concentration in gr. mol. per 1000 gr. H <sub>2</sub> O.	$p_m$ in m.m. Hg.	Concentration in gr. mol. per 1000 gr. H <sub>2</sub> O.	$p_m$ in m.m. Hg.
0.116	0.067	0.02602	0.084
0.255	0.078	0.17225	0.086
0.506	0.080	0.45413	0.087
0.991	0.088	1.0811	0.090

It appears from these tables that Mr. DIETERICI's results for Na Cl and cane sugar agree very well with mine.

The same might be said of H<sub>2</sub> SO<sub>4</sub>, but that Mr. DIETERICI found a lower value for  $p_m$  for the concentration 0,0871 than for the concentration 0,0542. He makes the following remark about this :

„Die Lösungen der Schwefelsäure zeigen eine deutliche Abnahme der molecularen Dampfspannungsverminderung mit der Verdünnung in dem Concentrationsintervall 1 bis 0.1 gr. mol.; unterhalb dieser Verdünnung scheint wieder eine Zunahme einzutreten; indessen lässt sie sich aus den Dampfspannungsbeobachtungen allein nicht sicher constatiren und ich würde die Zahlen überhaupt nicht mitgetheilt haben, wenn nicht die Gefrierpunktsbeobachtungen von LOOMIS<sup>1)</sup> und PONSOT<sup>2)</sup> auch eine Zunahme der molecularen Gefrierpunktsverminderungen bei grösserer Verdünnung als 0.1 gr. mol. ergeben.“

By repetition of his experiments, which will be discussed presently, Mr. DIETERICI found no decided increase of  $p_m$  for concentrations below 0.1 gr. mol., but oscillating values, so that we may say, that also for H<sub>2</sub> SO<sub>4</sub> qualitative agreement exists, as the oscillations just mentioned are due to the influence of errors of observation.

Mr. ABEGG<sup>3)</sup> has tested Mr. DIETERICI's observations by comparing the latter's results quantitatively with those obtained by the determination of the lowering of the melting point.

In doing this Mr. ABEGG came to the conclusion, that there must be a fault in Mr. DIETERICI's method of observation, which induced

<sup>1)</sup> LOOMIS, Wied. Ann. 51, pag. 500—524, 1894; 57, pag. 465—529, 1896; 60, pag. 523—547, 1897.

<sup>2)</sup> PONSOT, Recherches sur les congélations, GAUTHIER et VILLARS, Paris, 1896.

<sup>3)</sup> R. ABEGG, Wied. Ann. 64, pag. 500—505, 1898.



Mr. DIETERICI<sup>1)</sup> to repeat his experiments once more, now making use of an aneroid which could give a deviation not to one side only as before, but to both sides. As changes of temperature exercise a great influence on the zero position of the aneroid, it was placed in a waterbath. After having determined the constant of this aneroid, he repeated his observation and obtained the following results.

To facilitate comparison I shall again add some of my results.

## Na Cl

DIETERICI.		SMITS.	
Concentration in gr. mol. per 100 <sup>a</sup> gr. H <sub>2</sub> O.	$\rho_m$ in m.m. Hg	Concentration in gr. mol. per 1000 gr. H <sub>2</sub> O.	$\rho_m$ in m.m. Hg.
0.0690	0.152	0.02842	0.121
0.0976	0.156	0.03546	0.134
0.1500	0.150	0.08813	0.139
0.2176	0.148	0.17680	0.140
0.2996	0.1505	0.35587	0.141
0.4900	0.1515	0.88510	0.143
0.9788	0.1515	1.8228	0.147

H<sub>2</sub>SO<sub>4</sub>

DIETERICI.		SMITS.	
Concentration in gr. mol. per 1000 gr. H <sub>2</sub> O.	$\rho_m$ in m.m. Hg.	Concentration in gr. mol. per 1000 gr. H <sub>2</sub> O.	$\rho_m$ in m.m. Hg.
0.0624	0.168	0.02090	0.161
0.1106	0.180	0.04968	0.165
0.1472	0.167	0.24960	0.168
0.2323	0.168	0.50418	0.173
0.4483	0.171	1.11431	0.184
0.9505	0.177		

<sup>1)</sup> DIETERICI, Ann. der Phys. und Chemie, 27, 4, 1898.

## CANE SUGAR.

DIETERICI.		SMITS.	
Concentration in gr mol. per 1000 gr H <sub>2</sub> O	$\rho_m$ in m.m. Hg.	Concentration in gr. mol. per 1000 gr. H <sub>2</sub> O.	$\rho_m$ in m.m. Hg.
0.1506	0.084	0.02602	0.086
0.2653	0.084	0.17225	0.086
0.4993	0.087	0.45413	0.087
1.0122	0.0905	1.0811	0.090

It is remarkable that the agreement of Mr. DIETERICI's results with mine for Na Cl-solutions, which was closest before, is now least perfect, while the agreement for cane sugar may be said to be absolute.

If we leave the oscillation for the two smallest concentrations out of account, the agreement of the H<sub>2</sub>SO<sub>4</sub> solution is also very close. It is very difficult to find an explanation for this fact, as an error in the constants of our apparatus cannot cause this difference.

Mr. DIETERICI puts the solutions and the water in small platinum tubes, 3 cm. high and with a diameter of 1,2 c.m., which are connected with the apparatus in such a way (cemented), as to exclude shaking, whereas I put the solutions and the water in glass bulbs connected with the apparatus by means of mercury valves, in order to be able to shake them thoroughly. I consider this of the highest importance, both when freeing the solution and the water from air and during the experiment.

I consider shaking as necessary for preventing differences of temperature, Mr. DIETERICI, on the other hand, fears to bring them about by shaking. If, however, I read the manometer ten minutes after having shaken the bulbs carefully, I get always the same results by repetition of the experiment.

Moreover in Mr. DIETERICI's experiments the platinum tubes which lead to the bottle and are cemented to glass tubes, are not quite immersed in the icebath, which may cause slight differences of temperature, specially because these small platinum tubes have a small thermal capacity.

Mr. DIETERICI, who himself, makes the preceding remark, thinks it possible that a difference of temperature of 0,0025° may occur, in spite of this careful protection of the icebath against absorption of heat. As a difference of temperature of 0,0025° agrees with a

difference of tension of 0.001 mm. Hg., Mr. DIETERICI takes as limit of his accuracy 0,001 mm. Hg. Therefore he states clearly, that he draws only qualitative conclusions. I am, however, convinced, that the difference in temperature in my bulbs, which have a volume of 100 ccm., is less than  $0,0025^{\circ}$ , which also appears from the fact that when I read the manometer, when comparing water with water, the manometer indicated accurately to 0,1 mm. the same difference of position, as when there was communication between the two sides of the manometer, and the bulbs were closed.

As a deviation of the manometer of 0,1 mm. agrees with  $\pm 0,00025$  mm. Hg, the difference of temperature of the two bulbs must be exceedingly small.

Some time ago prof. JAHN at Berlin wrote to me to ask, whether I was sure, that my solution had been perfectly free from air and if I would repeat some of my experiments once more, after having first reduced the solutions in vacuum to half of its original volume by means of evaporation.

First I tried to comply with Prof. JAHN's wish in the following way.

The bulbs with water and solution were successively shut off from the apparatus by turning a tap and the air was exhausted by means of a velocity pump, while they were heated softly. During this the tube, connecting the bulb with the apparatus, was moistened with condensed vapour of water. Through the rise of the temperature the grease with which the tap (by means of which the communication of the bulb with the apparatus was broken off or restored), was greased, spread over the inside wall of the tube, and this is the reason why I could not make use of this way of boiling. It seems namely, that the vapour tension of a layer of water on the greased part of the tube is so small, that the water was not distilled into the bulb, though the bulb was cooled to  $0^{\circ}$  and the temperature of the room was  $\pm 20^{\circ}$ . I was therefore obliged to apply another method, by which rise of temperature was excluded. The most practical method appeared to be the following.

When at the ordinary temperature most of the air was exhausted from the bulbs with water and solution by means of the velocity-pump, all the remaining air was expelled by bringing about the communication of the bulbs with the apparatus, after first having closed the bulbs for drying. The communication between the bulbs and the apparatus was interrupted after some moments, and when the vapour of water had been absorbed by the drying bulbs, the

air of the apparatus was exhausted by means of an automatical mercury airpomp. This was repeated till the bulbs were free from air.

In order to comply with Prof. JAHN's wish, I brought about a communication between the bulbs with water and solution and one of the drying bulbs (filled with  $H_2SO_4$ ). When the air is greatly rarefied,  $H_2SO_4$  absorbs the vapour of water quickly and the water and the solution, having the temperature of the room  $\pm 20^\circ$  (the bulbs being continually shaken), evaporated quickly, in consequence of which the temperature of the water and the solution fell considerably. To prevent congelation the bulb was now and then warmed with the hand. The temperature of the bulb with  $H_2SO_4$  rose considerably during this absorption of water, and it was also frequently shaken. When the water and the solution had been reduced to the half of their former quantity by evaporation, the bulbs were shut off from the apparatus. Every solution was first treated in this way, after which the bulbs were placed in ice, and the experiment began.

The concentration of the solutions was determined by weighing  $\pm 50$  gr. solution in a flask with a long neck, and then the water was evaporated according to the method applied by Mr. ANDREAE<sup>1)</sup> While the flask was being heated in a waterbath, a weak current of air was drawn over the solution. After all the water had been evaporated, the flask was placed in an airbath of  $170^\circ$ , while all the time a stream of air was drawn over it. In this way it is also possible to expel the water from NaCl-solutions without any loss of weight of salt.

I may further add that I had altered the apparatus somewhat for these experiments. Instead of two bulbs, I used three; one filled with water and the two others with solution. One of these bulbs with solution remained untouched during the whole series and served as a test. These three bulbs were placed in a copper trough, which was surrounded by a larger wooden one in such a way that there remained a space of 6 cm. all round. This space was filled up with small pieces of ice, while the copper trough was filled with a paste of fine ice and water. Two pieces of paste board, which could move across each other and were provided with slits, served as a lid. In this way I was quite sure of a constant temperature and yet I could shake the bulbs thoroughly.

In order to make it possible to read the manometer more accurately,

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<sup>1)</sup> Journ. f. prakt. Chem. 22, p. 456, 1884.

a glass scale divided into m.m. was adjusted behind the legs of the manometer. The error of reading amounted to less than 0,1 mm, so to less than  $\frac{1}{4000}$  m.m. Hg.

The results of the research with NaCl solutions follow.

## Na Cl

Concentration in gr. mol per 1000 gr H <sub>2</sub> O	$p_u - p_s$ in m.m. Hg.	$p_m$ in m m Hg	$i = \frac{p_w - p_s}{p_w} \frac{N}{n}$
0.05185	0.00675	0.130	1.6
0.10733	0.01476	0.138	1.65
0.25770	0.03650	0.141	1.70
1.0307	0.14626	0.112	1.706
1.6078	0.23082	0.144	1.726

From this table follows that the changed method of experimenting has had no influence on the course of the molecular depression of the vapour tension. The differences of the absolute values are due to the use of a new manometer, the sensibility of which was to be determined anew.

As to the results obtained by another method, we have to mention, that LOOMIS and PONSOT have found that in general the molecular lowering of the freezing point of greater concentration to the concentration of 0,1 gr. mol. decreases in case of rarefaction as well for electrolytes as for non-electrolytes, whereas below these concentrations both investigators observed an increase of the molecular lowering of the freezing point, when the rarefaction increased. Mr. LOOMIS expresses his astonishment, that other investigators have not discovered this minimum, as this is so evident for binary chlorides, that it may be easily shown with an ordinary thermometer divided into  $\frac{1}{10}^\circ$  and with a beaker.

Mr. R. ABEGG, who points out some inaccuracies in his criticism on the researches of Mr. LOOMIS, doubts of the results of Mr. LOOMIS and also of those of PONSOT.

Mr. ABEGG finds for KCl between the concentrations 0.009 gr. mol. and 0.4007 gr. mol. per 1000 gr. water a mol. lowering of the freezing point, increasing with the rarefaction. He has not observed a minimum.

Nor has Mr. RAOULT <sup>1)</sup> found a minimum, but he found nearly constant values down to 0,1 gr. mol. for the molecular lowering of the freezing point. They did not differ more than 0,1 pCt.

In my opinion, however, the question remains, whether at this moment the highest degree of accuracy has already been reached in the method of the lowering of the freezing point.

It is quite possible that the air which is solved in the water and the solutions, causes the results, obtained for the determination of the lowering of the freezing point, to be faulty.

If e.g. the quantity of air in a solution depends upon the quantity of salt solved in it, the error made is not constant, and it can even render the course of the mol. lowering of the freezing point, quite faulty.

Mr. RAOULT has tried to reduce the error caused by solution of air in water and solution to a minimum by saturating at the temperature of the room the water and the solution with air. Mr. RAOULT states further that diluted solutions absorb the same quantity of air as pure water. Prof. JAHN, however, communicated to me in a letter that the coefficient of absorption of air for diluted solutions depends on the concentration and increases by diluting.

It is therefore of the greatest importance for the determination of the freezing point to examine accurately the influence of the concentration on the coefficient of absorption for air. As long as this influence is not sufficiently known, Mr. RAOULT's determinations, however accurately made, are in my opinion not quite reliable.

In connection with what precedes, it seems to me, that Mr. ABEGG <sup>2)</sup>, who, led by the differences between the results obtained by means of the lowering of the freezing point and the decrease of vapour tension, came to the conclusion that there must be a fault in the method of the determination of the decrease of the vapour tension of Mr. DIETERICI, has attached too much importance to his determinations.

In the first place the influence of concentration on the absorption of air has not yet been fully ascertained, as I said before, and secondly, even though this influence were perfectly known, a quantitative comparison between the results of the determination of the decrease of vapour tension and the lowering of the freezing point is not yet raised above doubt, when the solutions and the water are not in exactly the same circumstances in both methods. There would, however, be no objection to a comparison, when the lowering

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<sup>1)</sup> Zeitschr. f. Phys. Chemie: 27. pg. 617. 1898.

<sup>2)</sup> Wied. Ann. 64, pag. 487, 1898.

of the freezing point was determined of solutions quite free from air.

I regret that Mr. DIETERICI, who was acquainted with my investigations, has not mentioned, that in 1896 I published results which agreed perfectly with those he found with his aneroid and which he published in 1897.

I intended to investigate other substances than NaCl in the way Prof. JAHN recommended, but my manometer got defect while I was engaged with experiments on KCl, so that I had to put off this investigation.

At the end of this treatise I feel obliged to express my thanks to Prof. H. C. DIBBITS for the great kindness with which he placed at my disposal the apparatus required for my researches.

**Physics.** — Prof. VAN DER WAALS presents on behalf of Mr. E. H. J. CUNÆUS a paper on: *“The determination of the refractivity as a method for the investigation of the composition of co-existing phases in mixtures of acetone and ether”*.

#### *Introduction.*

The aim of this investigation was to examine the relation between the compositions of the co-existing vapour- and gas phasis and to find out the relation between the composition of the vapour and the pressure.

When I began my experiments only the investigation of LINEBARGER<sup>1)</sup> had been published; since then those of LEHFELDT<sup>2)</sup> and HARTMAN<sup>3)</sup> have also appeared.

The great difficulty of the investigation of this relation lies in the determination of the composition of the vapour; I have tried to do so without first condensing the vapour, and without chemical analysis, by means of the determination of the refractivity. I was induced to use this method by the experiments of RAMSAY and TRAVERS on the refractivity of gases and some gaseous mixtures<sup>4)</sup>.

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<sup>1)</sup> Journ. of the American Chem. Soc. Vol. XVII N<sup>o</sup>. 8; Aug. 1895. Chem. News, Vol. 72, N<sup>o</sup>. 1871, v.v. Oct. 1895.

<sup>2)</sup> Phil. Mag. (5) Vol. 40, 46.

<sup>3)</sup> Dissertation for a doctor's degree, Leyden 1899.

<sup>4)</sup> Proc. Roy. Soc. Vol. LXII, p. 225, 1897.