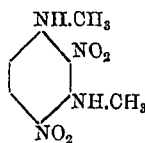


Citation:

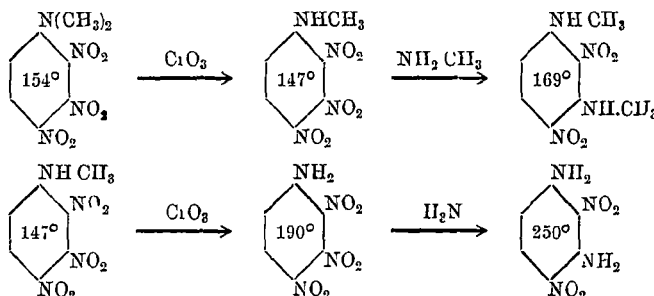
Sluiter, C.H., The influence of the hydration and of the deviations from the ideal gas-laws in aqueous solutions of salts on the solidifying and the boiling points, in:

KNAW, Proceedings, 17 III, 1914-1915, Amsterdam, 1915, pp. 1036-1046



This could further be proved by carefully oxydising the trinitro-compound (m.p. 154°) with chromic acid in acetic acid solution, which yields the monomethyl compound melting at 147° . This gives with alcoholic methylamine-solution the *m*-phenylene-derivative melting at 169° .

A continued oxidation with chromic acid yields from the trinitro-compound m.p. 154° , a 2,3,4-trinitroaniline (m.p. 190°), which on treatment with ammonia gives the above cited 2,4.-dinitrophenylene-diamine.



Utrecht.

Org. Chem. Lab. Univ.

Chemistry. — “*The influence of the hydration and of the deviations from the ideal gas-laws in aqueous solutions of salts on the solidifying and the boiling points.*” By Dr. C. H. SLUITER. (Communicated by Prof. A. F. HOLLEMAN.)

(Communicated in the meeting of December 30, 1914).

When, according to VAN 'T HOFF, we determine the irrationality coefficient (factor i) of good electrolytes in the well-known manner with the telephone bridge of KOHLRAUSCH, for different solutions from the formula $i = 1 + (n-1)\alpha$, in which n represents the number of ions that can be yielded by one molecule, and α the dissociation degree $= \frac{A_v}{A_{\infty}}$ (A = equivalent conductivity power), this appears to fairly increase with the growing dilution until almost the theoretical limit has been attained.

If by other means, namely by measuring the depression of the solidifying point, or the rise in the boiling point of the solutions, we try to determine, approximately the value of i according to the formula

$$i = \frac{\text{Observed depression S.p. or rise in B.p.}}{\text{Molecular depression S.p. or rise in B.p.} \times c'}$$

in which c' represents the number of gram-mols per 1000 grams of water, the values thus found, particularly in the case of concentrated solutions appear to agree very badly with the first named ones.

Two different causes can be adduced for these divergencies. First, the hydrations of the salt molecules and of their ions, owing to which a part of the water has been rendered inactive as a solvent. Hence, in the last formula a smaller value will be found for c' than it would have been if the salt had been really calculated on 1000 grams of solvent. The calculated value of i will thus be greater than it would have been without hydration. At high concentrations the amount of solvent withdrawn as water of hydration will be larger than at low concentrations, so that the influence on i will be most pronounced in the first case. Also, strongly hydrated salts such as MgCl_2 and CaCl_2 will exhibit greater differences of i than the but little hydrated ones such as NaCl and KCl .

The second cause of the divergencies lies in the relative applicability of the so-called "ideal gas-laws". When, according to VAN DER WAALS, the influence of the factors a and b on the gas pressure also applies to the osmotic pressure of the solutions, their solidifying and boiling points will also be affected thereby. We may compare solutions of salts to gases of high molecular weight because the mass of hydrated particles will be comparatively larger. With concentrations of about one gram-mol. per litre we may then expect that the factor b (volume of the particles) will exert a stronger influence than the factor a (proportional to the mutual attraction of the particles). The osmotic pressure, therefore also i will then be greater than one would expect it to be without those factors. At these large concentrations the hydration and the last named circumstance thus act on i in the same direction.

When at smaller concentrations, a becomes predominant, the osmotic pressure, hence also i , will become smaller than would be the case according to the ideal gas-laws. Now, as a rule, the question is whether a can overcome not only the influence of b but also that of the hydration of some kind of salt, so that i really becomes smaller than would be the case without one of these perturbing factors.

In the determination of Δ we are only concerned with the number of ions present in a certain volume of the solution so that the said perturbing factors exert no influence on the calculation of i . The relation $\frac{\Delta_V}{\Delta_\infty}$ therefore indicates the actual value of i when V represents the reciprocal value of the number of gram-mols per 1000 cc. of solution.

I have endeavoured to ascertain, by the measurement of Δ the depression of the solidifying point and the rise in the boiling point at equal concentrations and temperatures, in how far these considerations are in agreement with the result of i in the case of NaCl, KCl, MgCl₂, and CaCl₂. The arrangement of the experiments did not admit of making direct experiments at equal concentrations. I have, therefore approximated the values of i as accurately as possible by graphic interpolation. Properly speaking I ought to have determined Δ at the solidifying and boiling points of the solution instead of at 0° and 100°. As, however, the change of i with the temperature is very slow, this correction would not counterbalance the inaccuracies which would then be introduced owing to the great experimental difficulties.

I have also occupied myself with the calculation of i from saturated vapour determinations of saline solutions, were we can expect the same divergencies as in the dynamic determinations. Notwithstanding detailed and laborious experiments I have not succeeded in obtaining, in this manner, results sufficiently accurate for controlling the above mentioned values of i . I will only mention that i , when accurately determined within one decimal, gave the same results with the statical and the dynamical method.

In the "*Chemisch Weekblad*" (1915) will appear a more elaborate description of the apparatus employed by me and the corrections applied for the calculation of i , whilst the agreement and the differences of my results with those of other observers will also be discussed.

The following points of a more general importance, I wish to mention here.

The manner in which the conductivity power of the water, used in the Δ determinations, is computed is generally carried out by multiplying the specific conductivity power of the water with the dilution of the solution expressed in cc.

This empirical method, however, keeps no account with the position of the sliding contact on the measuring bridge. The following deduction may demonstrate, however, that this position exerts a strong influence on the correction to be applied. Suppose:

W_O = resistance of the *solution*.

W_B = comparison resistance on the *bridge*.

W_W = resistance of the "conductivity *water*".

W = corrected resistance of the solution in case the water possessed an infinitely great resistance.

If we assume that the conductivity power of the water is independent of the nature of the solution (as will be certainly the case with neutral salts) we have:

$$\frac{1}{W_W} + \frac{1}{W} = \frac{1}{W_O} \quad \text{or} \quad \frac{1}{W} = \frac{1}{W_O} - \frac{1}{W} \quad \dots \quad (1)$$

If we call the parts of the bridge wire, when the solution is shunted in a and b and those when the water only is shunted in c and d we have:

$$\frac{W_O}{W_B} = \frac{b}{a} \quad \text{or} \quad \frac{1}{W_O} = \frac{a}{b} \times \frac{1}{W} \quad \dots \quad (2)$$

and

$$\frac{W_W}{W_B} = \frac{d}{c} \quad \text{or} \quad \frac{1}{W_W} = \frac{c}{d} \times \frac{1}{W_B} \quad \dots \quad (3)$$

Substitution of (2) and (3) in (1) gives:

$$\frac{1}{W} = \frac{1}{W_B} \left(\frac{a}{b} - \frac{c}{d} \right) \quad \dots \quad (4)$$

If we put x the correction to the left, hence the diminution of a , which must be applied in the case when the water had an infinitely great resistance, we find in a similar manner:

$$\frac{1}{W} = \frac{a-x}{b+x} \times \frac{1}{W_B} \quad \dots \quad (5)$$

Substitution of (4) in (5) gives:

$$\frac{a-x}{b+x} = \frac{a}{b} - \frac{c}{d} \quad \text{or} \quad \frac{a-x}{b+x} = \frac{ad-bc}{bd}, \quad \text{hence } x = \frac{b^2c}{d(a+b)-bc}.$$

If $L = a + b = c + d =$ length of the bridge wire and if we neglect bc in regard to dL we have: $x = c \times \frac{b^2}{Ld} = c \times \frac{b^2}{L(L-c)}.$

If, herein we again neglect Lc in regard to L^2 we get:

$$x = c \times \left(\frac{b}{L} \right)^2.$$

Consequently the further the sliding contact is situated towards the right, the smaller will be the corrections to be applied. In my measurements W_B was always chosen in such a manner that b was as small as possible without the telephone minima becoming less sharp. Not a single other observer appears to have applied this

correction in this manner, which, with great dilutions, can cause a difference in the value of Λ of several percentages. When now we represent their results of Λ , graphically as a function of the logarithm of the dilution, the curved lines in the vicinity of $V = 2000$ and higher often exhibit very peculiar bends so that sometimes the graphical approximation of Λ_{∞} becomes impossible. The curved lines deduced from my results all appear to run asymptotically with a line parallel to the dilution axis, as required by theory.

The approximation of Λ_{∞} , particularly at 100° , is rather uncertain, because with very great dilutions the above described correction method for the conductivity water also fails. In order to get comparable results, I have applied the empirical method of BREDIG¹⁾ and of NOYES²⁾ taking $\Lambda_{\infty} = \Lambda_{1000} + 2,5 N$ at 25° ($N =$ product of the valencies of anion and cation). I have chosen the coefficient of N at 0° so much smaller and at 100° so many times larger as the proportional decrease and increase of Λ_{1000} amounts to at those temperatures.

In the measurements at 100° which were carried out in a steam-bath, the solution being kept under a pressure of 3 atm. to prevent evolution of vapour at the electrodes, a correction had to be applied for the influence of the barometer indication on the steam-temperature. For this purpose the temperature coefficient of Λ of the different salts as determined by JONES³⁾ between 0° and 65° , was used with a proportional reduction to 100° .

Here follow the thus corrected results of i at different dilutions (V) at 0° and 100° . For each measurement the concentration at 15° was determined separately and in this way eventual errors caused by pipetting off and delivering into the measuring vessel were avoided.

The depression of the solidifying points was determined according to the method of ROBERTSON and WALKER⁴⁾ in which corrections for the influence of the radiation and for the slowness with which the temperature exchange takes place, are done away with. The liquid siphoned off from the ice-saltsolvent mixture was rapidly brought to the temperature of the room and titrated. The thermometer in the DEWAR vessel remained constant for a considerable time when this vessel was properly surrounded by ice.

The concentrations all relate to a temperature of 15° .

¹⁾ Zs. phys. Chem. **13**, 191. (1894).

²⁾ Technol. Quart. **17**, 293 (1904).

³⁾ Carnegie Inst. of Washington, publ. **170** (1912).

⁴⁾ Proc. Royal Soc. **24**, 363 (1902).

V	$\Delta 0^\circ$	$i 0^\circ$	$\Delta 100^\circ$	$i 100^\circ$
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Sodium chloride

1	48.41	1.7191	219.3	1.6094
2	51.53	1.7656	242.4	1.6736
4	54.28	1.8063	260.7	1.7244
10	57.72	1.8576	283.1	1.7868
20	60.04	1.8921	298.8	1.8305
40	61.81	1.9183	315.2	1.8760
100	63.47	1.9430	331.5	1.9210
400	65.32	1.9703	346.3	1.9625
1000	65.82	1.9777	351.8	1.9777
2000	66.04	1.9811	355.0	1.9865
∞	67.32	2	359.8	2

Magnesium chloride.

1	68.02	2.0552	306.2	1.8860
2	77.03	2.1950	373.8	2.0816
4	85.71	2.3296	430.3	2.2452
10	96.50	2.4970	491.9	2.4234
20	104.4	2.6196	534.4	2.5462
40	110.6	2.7156	567.2	2.6416
100	117.0	2.8152	611.8	2.7702
400	123.3	2.9126	657.1	2.9016
1000	125.9	2.9532	675.0	2.9532
2000	127.1	2.9716	680.5	2.9690
∞	128.9	3	691.1	3

$\Delta 0^\circ$	$i 0^\circ$	$\Delta 100^\circ$	$i 100^\circ$
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Potassium chloride.

63.83	1.7773	267.1	1.6704
66.41	1.8089	286.9	1.7201
68.69	1.8366	306.4	1.7686
71.50	1.8709	329.2	1.8262
73.52	1.8954	343.8	1.8628
75.44	1.9187	361.3	1.9067
77.46	1.9432	374.1	1.9389
79.63	1.9699	385.9	1.9685
80.61	1.9817	391.0	1.9813
81.00	1.9865	392.7	1.9856
82.11	2	398.5	2

Calcium chloride.

76.33	2.1128	326.2	1.9356
85.02	2.2392	394.3	2.1308
93.10	2.3570	445.7	2.2786
103.2	2.5042	506.1	2.4518
110.5	2.6108	546.2	2.5668
116.8	2.7030	587.8	2.6838
123.8	2.8048	621.9	2.7838
131.3	2.9144	664.5	2.9060
134.2	2.9562	682.1	2.9566
135.0	2.9680	686.2	2.9680
137.2	3	697.4	3

For the calculation of the number of gram-mols per 1000 grams of water the formula $c' = \frac{1000 c}{1000d - cM}$ was used, in which c represents the directly-titrated concentration, d the sp. gr. of the solution and M the molecular weight of the salt.

For the calculation of i the theoretical value $1,855^\circ$ was chosen for the molecular depression in 1000 cc of water.

We then have $i = \frac{t}{1,855 \cdot c'}$, when t is the depression of the solidifying point.

The graphic representation, in which t is represented as function

c'	Depres- sion of S.p. t	$i = \frac{t}{1,855 c'}$
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Sodium chloride.

0.9539	3.180°	1.797
0.6224	2.095	1.814
0.4011	1.361	1.829
0.3772	1.283	1.833
0.1702	0.586	1.857
0.1501	0.518	1.861
0.04014	0.142	1.91
0.03042	0.109	1.93
0.01161	0.042	1.95

Magnesium chloride.

0.9583	6.063°	3.410
0.9795	4.726	3.185
0.7078	4.033	3.072
0.5322	2.847	2.883
0.4889	2.577	2.841
0.3852	1.972	2.759
0.2280	1.146	2.710 ¹⁾
0.1917	0.964	2.711
0.08023	0.408	2.741
0.03135	0.163	2.80
0.01352	0.074	2.95

c'	Depres- sion of S.p. t	$i = \frac{t}{1,855 c'}$
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Potassium chloride.

0.9486	3.201°	1.819
0.7964	2.696	1.821
0.6120	2.078	1.830
0.5016	1.710	1.838
0.3047	1.051	1.859
0.1571	0.549	1.884
0.07565	0.269	1.918
0.02283	0.082	1.94
0.01301	0.047	1.95

Calcium chloride.

1.0092	5.966°	3.188
0.8156	4.494	2.970
0.6285	3.243	2.782
0.4840	2.401	2.674
0.3422	1.645	2.590
0.2992	1.424	2.565
0.1968	0.933	2.556 ¹⁾
0.1384	0.664	2.586
0.07150	0.354	2.669
0.03555	0.181	2.74
0.01297	0.070	2.91
0.00611	0.034	3.0

¹⁾ Minimum value of i .

of the concentration, yields for NaCl and KCl almost straight lines whereas those for MgCl_2 and CaCl_2 exhibit a slight bending upwards at the greater concentrations.

The values of i exhibit with MgCl_2 and CaCl_2 a minimum for $c = \pm 0,2$, whilst also here, contrary to the calculation from Δ , those of MgCl_2 are larger than those of CaCl_2 . Also the difference between NaCl and KCl is here smaller than followed from the Δ determinations.

The most trustworthy observations of other investigators mostly agree well with those of mine for KCl and NaCl, whereas those for MgCl_2 and CaCl_2 exhibit at both sides deviations of at most 2 % of the value of t according to the graphic representation.

The determinations of the boiling points were carried out in metal vessels internally silver plated and surrounded by a steam jacket. In order to avoid corrections for the barometric pressure, a second vessel with pure water was always boiled under exactly the same conditions as the one containing the saline solution. An exchange of the thermometers in the two vessels could always take place without any danger of escape of vapour by placing these thermometers in a thin-walled tube containing mercury. These tubes were placed in the two vessels at an equal depth so that no correction for the hydrostatic pressure was required. By lengthening the refrigerating tube until it penetrates lower into the boiling vessel it was avoided that the colder reflux water had an influence on the thermometer bulb.

A retardation of boiling was counteracted by placing in each vessel 200 grams of clear glass beads and 10 silver tetrahedrons. A correction of the concentration for the water withdrawn from the solution by evaporation was applied. By experimenting this was determined as 0.2 % of the concentration when the vessel contained 250 cc. of liquid. The concentration was determined before as well as after the boiling and then yielded no measurable differences. The necessary scale corrections were introduced on the thermometer. The calculation of c' from c was executed as directed above. Here also, these quantities relate to a temperature of 15° .

The graphic representation in which t was again plotted as function of c shows that the faintly bent curved lines for NaCl and KCl almost coincide, NaCl now being situated a little higher than KCl. Just as with the solidifying points, MgCl_2 is again higher than CaCl_2 .

In the calculation of i the theoretical value $0,52^\circ$ was again chosen for the molecular increase of the boiling point in 1000 cc. of water. The values of i now exhibit with all salts a minimum, with NaCl and KCl for $c' = \pm 0,3$ and with MgCl_2 and CaCl_2 for $c' = \pm 0,2$.

The results of other investigators exhibit in a graphic representation, also mutually, much stronger differences than with the depressions of the solidifying point. As a rule the values found by me are situated lower, probably in consequence of a retardation of boiling during measurements in glass apparatus according to BECKMANN. My observations show a good relative agreement with those of SMITS ¹⁾, although this observer, notwithstanding metal vessels, always found somewhat higher values. In part, these small differences are probably due to the correction of c' for the water evaporated, which SMITS does not seem to have applied. Here follow my results.

For the purpose of comparison of the results here obtained I have

c'	B.p. increase t	$i = \frac{t}{0.52 c'}$
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Sodium chloride.

1.0342	0.950°	1.767
0.7729	0.694	1.726
0.5147	0.454	1.697
0.3532	0.310	1.688
0.2601	0.228	1.686 ¹⁾
0.1721	0.153	1.710
0.0962	0.089	1.78
0.05128	0.049	1.84

Magnesium chloride.

1.0151	1.633°	3.094
0.7698	1.116	2.785
0.5146	0.672	2.510
0.3551	0.435	2.356
0.2558	0.304	2.282 ¹⁾
0.1671	0.199	2.286
0.0946	0.115	2.34
0.04832	0.060	2.39

c'	B.p. increase t	$i = \frac{t}{0.52 c'}$
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Potassium chloride.

1.0263	0.932°	1.748
0.7751	0.686	1.703
0.5106	0.445	1.675
0.3482	0.301	1.663 ²⁾
0.2622	0.227	1.664
0.1703	0.148	1.670
0.1053	0.094	1.72
0.05619	0.052	1.78

Calcium chloride.

1.0052	1.562°	2.988
0.7499	1.054	2.704
0.5101	0.657	2.477
0.3482	0.421	2.326
0.2528	0.298	2.264
0.1712	0.202	2.270
0.0972	0.117	2.32
0.05183	0.064	2.37

¹⁾ Zs. phys. Chem. **39**, 385 (1901).

²⁾ Minimum value of i .

<i>C</i> Gram mol. p. L. solution	<i>i</i> from Δ at 0°	<i>i'</i> at solidifying point	<i>i' - i</i> at 0°	<i>i</i> from Δ at 100°	<i>i'</i> from boiling point	<i>i' - i</i> at 100°
<i>Sodium chloride</i>						
1.000	1.719	1.795	0.076 ↑	1.609	1.764	0.155 ↑
0.750	1.742	1.807	0.065 ↑	1.642	1.725	0.083 ↑
0.500	1.766	1.821	0.055 ↑	1.674	1.697	0.023 ↑
0.250	1.806	1.846	0.040 ↑	1.724	1.687	-0.037 ↓
0.100	1.858	1.884	0.026 ↑	1.787	1.776	-0.011 ↓
0.050	1.892	1.905	0.013 ↑	1.831	1.840	0.009 ↓
<i>Potassium chloride</i>						
1.000	1.777	1.816	0.039 ↑	1.670	1.748	0.078 ↑
0.750	1.793	1.823	0.030 ↑	1.695	1.702	0.007 ↑
0.500	1.809	1.837	0.028 ↑	1.720	1.674	-0.046 ↓
0.250	1.837	1.869	0.032 ↑	1.769	1.665	-0.104 ↓
0.100	1.871	1.906	0.035 ↑	1.826	1.723	-0.103 ↓
0.050	1.895	1.928	0.033 ↑	1.863	1.784	-0.079 ↓
<i>Magnesium chloride</i>						
1.000	2.055	3.485	1.430 ↑	1.886	3.094	1.208 ↑
0.750	2.125	3.140	1.015 ↑	1.984	2.773	0.789 ↑
0.500	2.195	2.858	0.663 ↑	2.082	2.498	0.416 ↑
0.250	2.330	2.718	0.388 ↑	2.245	2.282	0.037 ↑
0.100	2.497	2.736	0.239 ↑	2.423	2.338	-0.085 ↓
0.050	2.620	2.780	0.160 ↑	2.546	2.390	-0.156 ↓
<i>Calcium chloride</i>						
1.000	2.113	3.195	1.082 ↑	1.936	3.006	1.070 ↑
0.750	2.176	2.913	0.737 ↑	2.033	2.719	0.686 ↑
0.500	2.239	2.684	0.445 ↑	2.131	2.470	0.339 ↑
0.250	2.359	2.562	0.205 ↑	2.279	2.264	-0.015 ↓
0.100	2.504	2.632	0.128 ↑	2.452	2.318	-0.134 ↓
0.050	2.611	2.710	0.099 ↑	2.567	2.373	-0.194 ↓

represented i graphically from the solidifying and the boiling points as a function of c .

From this I have interpolated the values of i at the same concentrations as used in the determination of A . The third decimal of i' is, however, very vague on account of the powerful bends in the vicinity of the minima, which the thus obtained lines exhibit. From the differences of the dynamically obtained values of i' and those of i from A at corresponding temperatures we can control the previously mentioned views with a sufficient accuracy. From this appears the following.

At 0° i' is always greater than i and the difference increases regularly with the concentration (with KCl we found small oscillations in the third decimal, so within experimental errors). With the most hydrated salt, namely MgCl_2 , the increase of $i' - i$ is the strongest, then follows CaCl_2 , then NaCl , whilst the feeblest hydrated salt KCl shows the least increase of $i' - i$. With MgCl_2 and CaCl_2 the factor b seems to predominate in the large concentrations for there the decrease of $i' - i$ with the dilution is much stronger than it is in the case of NaCl . Not in the case of a single salt does the factor a become so predominant that the influence of the hydration becomes also subdued. At 100° , on the other hand, $i' - i$, in the case of all salts, occasionally becomes negative, so that the influence of a is there stronger than that of b and the hydration together. With NaCl and KCl $i' - i$ even exhibits a minimum, so that with these salts in the smallest concentrations the hydration seems to gain the best of a .

With MgCl_2 and CaCl_2 the differences at 100° are smaller than at 0° owing to the lesser hydration of these salts at a higher temperature. At the smallest concentrations the predominance of a steadily increases so that finally $i' - i$ becomes fairly strongly negative.

As in the calculation of i the choice of A_∞ had to be rather arbitrary, whereas the molecular depression of the solidifying points and the rise of the boiling points could not be determined in a direct manner in consequence of the same perturbing influences that occurred in the solutions investigated, I cannot credit the results of $i' - i$ with possessing absolute values. The direction in which $i' - i$ changes with the concentration will, however, remain the same when another choice is made from the said constants. This direction and the velocity with which the change takes place can, however, just give us some insight into the strength of the influence of the perturbing causes, each separately. For a more detailed discussion on this point, I must again refer to the more elaborate article in the *Chemisch Weekblad* (1915).

Dec. 1914. *Chem. Laboratory of the H.B.S. Bois le Duc.*