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ON THE APPLICABILITY OF THE GAS LAWS TO STRONG ELECTROLYTES. II.

BY

J. N. BRØNSTED

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HOVEDKOMMISSIONÆR: ANDR. FRED. HØST & SØN, KGL. HOF-BOGHANDEL
BIANCO LUNOS BOGTRYKKERI
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1. Introduction.

In some previous papers[1] it was shown that the laws governing the behaviour of strong electrolytes in solutions are highly simplified if in stead of water a strong solution of another electrolyte is employed as solvent. Determinations of solubilities of allotropic salts and measurements of electromotive forces have made it likely, that the simple gas laws hold good for ions or salts when dissolved in other salt solutions the concentration of which is large when compared with the concentration of the dissolved ion or the dissolved salt.

These results are also expressible by means of the conception of the activity coefficient by stating that the quantity defined as the stoichiometric activity coefficient[2] of the dissolved salt or ion keeps a constant value with changing concentration. Whether based upon the ordinary view of equilibrium occurring between ions and undissociated molecules or on the modern theory of complete electrolytic dissociation[3], an explanation of the phenomenon must involve the assumption of constancy of the true activity coefficient of the ion which changes in concentration.

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[1] D. kgl. danske Vidensk. Selsk. Skrifter [7] **12**, 241 (1914) Meddel. från k. Vet. Akad.'s Nobelinstitut **5**, Nr. 25 (1919).

[2] D. kgl. danske Vidensk. Selsk. Mathem. fys. Meddel. **2**, Nr. 10 (1919). Journ. Amer. Chem. Soc. **42**, 761 (1920).

[3] S. R. Milner, Phil. Mag. [6] **23**, 553 (1912), **25**, 742 (1913).
N. Bjerrum, Zeitschr. f. Elektrochemie **24**, 321 (1918).
I. C. Ghosh, Journ. Chem. Soc. **113**, 449, 627, 707, 790 (1918).

On the question of complete or incomplete dissociation of strong electrolytes our results therefore will throw no light in dealing with solvents and solutes of similar ionic type. As will be shown in the following, however, valuable evidence regarding this point may be furnished by using solvents and solutes of different type.

The present investigation was made partly for the purpose of extending the results in the foregoing papers, and partly by employment of salts of different type as solvent and solute to procure information of the question of complete or incomplete dissociation.

2. Experimental method. The streaming electrode.

The electrometric method used in the previous measurements proved very suitable in the new experiments especially when a modification in the practical construction of the galvanic cell was introduced.

The principal feature of this modification consists in making the electrolytic solution flow through the solid electrode, this being present in the electrode vessel in the shape of a fine powder.

A silver-silver chloride electrode constructed according to this principle is shown in Fig. 1. The solution was allowed to run from the reservoir shown at the top of the figure through a capillary tube, then passing in succession through a plug of cotton wool (a), a layer of pure silver chloride (b), a mixture of silver chloride and powdered metallic silver (c) and a second plug of cotten (d). Thence it flowed through a rubber tube connecting the electrode tube with a T-tube, and finally was led away.

The mixture of silver chloride and silver powder (c) was pressed around a platinum wire sealed in the wall of the glass tube and forming one pole of the cell. The silver powder forming the metallic electrode was produced by reduction of a silver nitrate solution by ferrous sulphate, which yields the metal as the fine crystalline and homogeneous precipitate.

Combining this electrode through the T-Tube with another electrode of exactly the same construction we get a galvanic cell which has marked advantages. Of these the chief are as follows: The solid electrode, consisting in this case of silver and silver chloride mixture is deprived of all soluble impurities in the vessel itself by the washing action of the solution streaming slowly through the porous electrode. The washing must be continued until quite constant values of the potential are obtained. Further the method affords the great advantage, that we are able to change very easily from one solution to another without any alteration of the solid electrode. All the measurements mentioned in the following are thus carried out using the same two cells for all of the solutions. The values furnished in this way are very thoroughly controlled by starting with the same solution in both electrodes, the electromotive force in this case proving to be zero. The solution in one of the electrodes is then changed and the potential measured. Finally the two solutions in the electrodes are interchanged and the same electromotive forces in the opposite direction must be obtained if the cell functions satisfactorily.

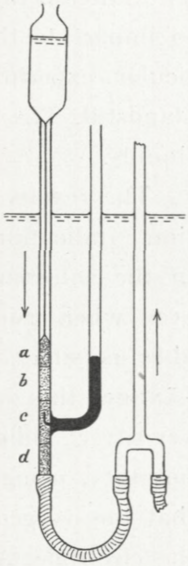

Fig. 1.
The streaming electrode.

The speed of the streaming solution depends upon the tightness of the cotten plug and the compressed powders and upon the difference between the position of the level in the reservoir and the surface of the outflowing solution. The latter being changeable by simple means, we are able to impart to the liquid a velocity convenient for the particular experiment or, if required, bring the flow to a standstill. The readings were always made with stationary liquids.

The results obtained with these cells fulfilled expectation. Indications, however, were found that air contained in the solutions may appreciably influence the potential even when using as electrode a metal as difficultly oxidizable as silver. It was known from experiments of Bodländer[1] that oxygen exerts a very strong effect on the silver-silver iodide electrode, and experiments in this laboratory, using small concentrations of the iodide showed that the oxygen is nearly entirely used up in contact with the electrode. Also with less oxidizable electrodes the possibility of a similar effect ought to be allowed for, and further investigation in this direction has been initiated.

As an important advantage caused by the nature of the problem before us we may finally include the smallness of the liquid-liquid potential. This in most cases has been negligible but when necessary it has been calculated by means of the Henderson formula[2] and a corresponding small correction introduced in the figures observed.

3. The solvents and the solubility of silver chloride therein.

The solutions serving as solvents in the cells were potassium nitrate, sodium nitrate and magnesium sulphate

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[1] Zeitschr. f. anorg. Chemie **39**, 197 (1904).

[2] Zeitschr. f. physikal. Chemie **59**, 118 (1907), **63**, 325 (1908).

all of the concentration 2 mol. and magnesium sulphate, 1 mol. These solvents were mixed with chlorides or silver salts of equal concentration. Since we have to determine the interdependance between potential and concentration of Cl^- or Ag^+ in these solutions the chlorine content, if any, had to be carefully determined. The solutions of KNO_3 and $MgSO_4$ were made with recrystallized salts and showed no reaction on addition of silver nitrate. For the $NaNO_3$ solution was employed a more impure preparation and in this case a considerable amount of chlorine was present. In all cases the chlorine concentration of the solvent was determined electrometrically by measuring cells of the type

$$\mathrm{Ag.Ag\,Cl} \left| \mathrm{Solvent\ (n)} \right| \begin{matrix}\mathrm{solvent\,(n-c)} \\ \mathrm{chloride\ (c)}\end{matrix} \left| \mathrm{Ag\,Cl.Ag} \right. \qquad (1)$$

n representing the total equivalent concentration of the solution and c the concentration of the chlorine added. For the calculation of the chlorine concentration x of the solvent the simple gas laws were applied:

$$\pi = 0.0581 \log \frac{c}{x} \qquad (1)$$

due regard being payed to the content of chlorine caused by the solubility of AgCl.

As this largely depends on the concentration and nature of the solvent employed it was necessary to determine it beforehand by means of cells of the type:

$$\mathrm{Ag} \left| \begin{matrix}\mathrm{solvent\ (n-c_1)} \\ \mathrm{silver\ salt\ (c_1)}\end{matrix} \right| \begin{matrix}\mathrm{solvent\,(n-c_2)} \\ \mathrm{chloride\ (c_2)}\end{matrix} \left| \mathrm{Ag\,Cl.Ag} \right. \qquad (2)$$

furnishing the electromotive force

$$\pi = 0{,}0581 \log \frac{c_1 c_2}{s^2} \qquad (2)$$

where s stands for the solubility of silver chloride in the pure solvent concerned.

The results found in this way for 2 mol. solutions of KNO_3 and $MgSO_4$ are given in the following tables where by c are denoted equivalent concentrations:

Table I. Solubility of AgCl in KNO_3 solution, 2 mol. at 20°.

c_{KCl}	c_{AgNO_3}	π	s
0,025	0,05	0,3705	$2{,}29 \cdot 10^{-5}$
0,05	0,025	0,3702	2,30 —
0,02	0,02	0,3413	2,31 —
		Mean. . .	$2{,}30 \cdot 10^{-5}$

Table II. Solubility of AgCl in $MgSO_4$ solution, 2 mol. at 20°.

c_{MgCl_2}	$c_{Ag_2SO_4}$	π	s
0,016	0,016	0,3336	$2{,}153 \cdot 10^{-5}$
0,016	0,040	0,3567	$2{,}156 \cdot 10^{-5}$
		Mean. . .	$2{,}15 \cdot 10^{-5}$

These values for s are much greater than those given in the literature[1] for the solubility in pure water. According to the determinations of Kohlrausch and Böttger the value $s = 1.1 \cdot 10^{-5}$ may be adopted, only half of the value found when using the solvents above. There is, however, nothing unfamiliar in this phenomenon since as a rule solubilities in water are strongly increased when other heteroionic salts are added to the solvent. We should rather expect the previous electrometric measurements of Goodwin and Thiel to yield data more deviating from

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[1] S. f. inst. the article Silber in Abegg und Auerbachs Handbuch der anorganischen Chemie.

those found by the conductance method than is really the case.

The measurements according to the scheme (1) for testing the solvent gave the following result at 20°.

Table III.

System	n	c	π	x	s_0	x_0
$KNO_3 + KCl$	2	0,01	0,155	0,000021	0,000023	0
$NaNO_3 + NaCl$[1]	2	0,01	0,1135	0,000113	0,000018	0,000110
$MgSO_4 + MgCl_2$[2]	2	0,02	0,149	0,000054	0,000017	0,000049
$MgSO_4 + MgCl_2$	4	0,01	0,155	0,000021	0,0000215	0

x is the Cl^--concentration calculated by formula (1) and consequently including the clorine from the dissolution of AgCl. In the last column are given the corrected values x_0. These show that the two solvents KNO_3,2n and $MgSO_4$,4n are practically free from chlorine while especially in the $NaNO_3$-solution a considerable amount of chlorine is present.

4. The results.

As appearing from the foregoing the type of cells used for the activity measurements was:

$$\mathrm{Ag}\cdot\mathrm{AgCl}\left|\begin{matrix}\text{solvent}\,(n-c_1)\\ \text{chloride}\ (c_1)\end{matrix}\right|\begin{matrix}\text{solvent}\,(n-c_2)\\ \text{chloride}\ (c_2)\end{matrix}\left|\mathrm{AgCl}\cdot\mathrm{Ag}\right. \tag{3}$$

and:

$$\mathrm{Ag}\left|\begin{matrix}\text{solvent}\,(n-c_1)\\ \text{silver salt}\,(c_1)\end{matrix}\right|\begin{matrix}\text{solvent}\,(n-c_2)\\ \text{silver salt}\,(c_2)\end{matrix}\left|\mathrm{Ag}\right. \tag{4}$$

for determination with chlorine ions and silver ions respec-

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[1] The value of s_0 is computed from the corresponding figure for the K-system and the solubility ratio s_{KNO_3} / s_{NaNO_3} known from unpublished measurements.

[2] The value of s_0 is computed from the corresponding figure for $MgSO_4$ 4n and the general shape of the solubility curve for uni-univalent salts.

tively, while the theoretical calculation of the electromotive, force was undertaken according to the equation:

$$\pi = 0{,}0581 \log \frac{c_1}{c_2} \qquad (3)$$

valid for t = 20°, the temperature of all the experiments.

a) **Potassium nitrate as solvent**, n = 2. The first measurements were made with mixtures of KNO_3 and KCl. The results are given in table IV where π_l indicates the liquid-liquid potential calculated according to Henderson's formula:

Table IV. $KNO_3 + KCl$, n = 2.

c_1	c_2	π_{obs}	π_l	π_{cor}	π_{cal}
0,20	0,10	0,01744	+0,00004	0,0175	0,0175
0,10	0,05	1757	2	176	175
0,05	0,025	1746	1	175	175

The nearly complete agreement between π_{cor} and π_{cal} shows the gas laws to hold in this system up to solutions as strong as 0,2 n.

In a second series of measurements mixtures of KNO_3 and $AgNO_3$ were employed. The results were the following:

Table V. $KNO_3 + AgNO_3$, n = 2.

c_1	c_2	π_{obs}	π_l	π_{cor}	π_{cal}
0,20	0,10	0,01781	−0,00010	0,0177	0,0175
0,10	0,05	1762	5	176	175
0,05	0,025	1783	2	178	175
0,025	0,0125	1749	1	175	175

Even if these figures do not exhibit as satisfactory a course as in the foregoing case they must be considered as corroborative of our assumption.

b) Sodium nitrate as solvent, n = 2. The content of Cl^- in the »pure« solvent was 0,000110 as calculated above, a figure that must be added to the synthetical concentration. The results obtained with these solutions and given in table VI:

Table VI. $NaNO_3 + NaCl$, n = 2.

c_1	c_2	π obs	π_1	π cor	π cal
0,1001	0,01011	0,05779	+0,00005	0,0578	0,0579
0,01011	0,001110	5591	0	559	557

prove again in satisfactory agreement with the calculations.

c) Magnesium sulphate as solvent, n = 2 (equiv. normal).

The Cl^- content of the »pure« solvent was 0,000049 as indicated in table III. The concentrations have been correspondingly corrected. The system examined was $MgSO_4 + MgCl_2$. No correction has been introduced for π_1 since this is negligible in this system. The data are given in Table VII.

Table VII, $MgSO_4 + MgCl_2$, n = 2.

c_1	c_2	π obs	π cal
0,20005	0,02005	0,0562	0,0580
0,02005	0,002049	573	575
0,002049	0,000250	524	530

The difference of 0,6 millivolt between the last values of π_{obs} and π_{cal} is undoubtedly due to the uncertainty inherent in the use of such highly diluted a solution as 0,00025 n. On the other hand the deviation of 1,8 millivolt in the case of the strongest solutions must certainly be looked upon as of real significance indicating that the activity coefficient of the chlorine ion decreases slightly when its concentration increases. The significance of this phenomenon will be discussed further on.

d) Magnesium sulphate as solvent, n = 4. In the first series of experiments with this solvent mixtures of $MgSO_4$ and Ag_2SO_4 were employed. Also in this case the liquid-liquid potential was negligible. The results are tabulated below:

Table VIII. $MgSO_4 + Ag_2SO_4$, n = 4.

c_1	c_2	π_{obs}	π_{cal}
0,040	0,016	0,0229	0,0231
0,016	0,002	528	525

exhibiting a satisfactory agreement between observed and calculated π values.

In the second series as in the case of n = 2 mixtures of $MgSO_4$ and $MgCl_2$ were employed. While in all the foregoing series only those solutions were examined for which the laws of the simple gases were expected to hold good on account of relatively moderate concentrations of the solutions employed, the concentration of magnesium chloride in the present case was allowed to vary within very wide limits the most concentrated solution containing even pure $MgCl_2$. We can therefore no longer expect the requirements of the gas laws to be fulfilled over the whole range of concentrations. The very course of the deviations, however, enables certain deductions to be made about the important question of the dissociation of salts.

When dealing with a uni-univalent salt as KCl dissolved in a strong solution of another uni-univalent salt as KNO_3 the measurement of the chlorine-ion potential with changing concentration will give no possibility of ascertaining whether or not a complete dissociation of the chloride takes place. It is true that the scheme of dissociation:

$$KCl \leftrightarrows K^+ + Cl^-$$

usually implies increasing dissociation when the concentration falls. On account of the almost constant K^+ ion concentration due to the presence of the strong KNO_3 solution serving as solvent the mass action law, however, will here give:

$$\frac{c_{Cl^-}}{c_{KCl}} = \text{constant}$$

showing a change in the concentration of the Cl^- ion directly proportional to the total chlorine concentration. Determination of the stoichiometric activity coefficient, therefore, will yield constant values in both cases, leaving no possibility of discriminating between the cases of complete and incomplete dissociation.

It is obvious that the employment of heteroionic salts as $NaCl + KNO_3$ will give no better information. Using, however, salts of different types as $MgCl_2$ and $MgSO_4$ and assuming an equilibrium according to the scheme:

$$MgCl_2 \rightleftarrows Mg^{++} + 2\ Cl^-$$

to take place we shall find by application of the mass action law:

$$\frac{C^2_{Cl^-}}{C_{MgCl_2}} = \text{constant} = k$$

an equation that evidently demands deviations from the requirements of the simple gas laws to occur and to be perceptible if the equilibrium constant k has a sufficiently small value.

The results found in these systems are given in the next table:

Table IX. $MgSO_4 + MgCl_2$, n = 4.

c_1	c_2	π_{obs}	π_1	π_{cor}	π_{cal}
4,00	2,00	0,01249	— 0,00032	0,01217	0,01750
2,00	0,40	3504	25	3479	4063
0,40	0,08	3948	5	3943	4063
0,08	0,016	4037	1	4036	4063
0,016	0,0032	4060	0	4060	4063

To afford a better survey of these results the electromotive forces between the most dilute solution and any of the others are calculated from these figures and tabulated below.

Table X. $MgSO_4 + MgCl_2$, n = 4.

c_1	c_2	π_{cor}	π_{cal}	$\Delta\pi$
4,00	0,0032	0,16735	0,17993	— 0,01258
2,00	32	15518	16044	726
0,40	32	12035	12183	144
0,08	32	08083	08122	26
0,016	32	04060	04063	3

The measurements are again seen to agree very exactly with the requirements of the gas laws in the more dilute solutions. As the concentration increases the deviation under $\Delta\pi$ becomes greater, changing very nearly proportionally with the concentration according to the expression:

$$\Delta\pi = 0{,}0037\ c.$$

In Fig. 2 the value of $\Delta\pi$ is plotted against the concentration, exhibiting an almost rectilinear course.

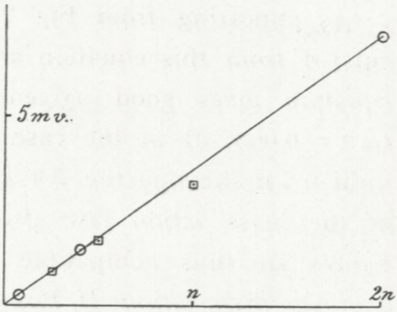

Fig. 2.

The squares indicate calculated values, the circles observed values of $\Delta\pi$.

We shall now test if these results are compatible with the requirements of equation (4):

$$\frac{C^2_{Cl^-}}{C_{MgCl_2}} = k \tag{4}$$

Introducing in this the total chlorine concentration c we obtain

$$\frac{C - C_{Cl^-}}{2} = \frac{C^2_{Cl^-}}{k}$$

or since

$$\Delta\pi = 0{,}0581\ \log \frac{c}{C_{Cl^-}}$$

the following expression:

$$\Delta\pi = 0{,}0581\ \log \frac{4\ c}{-\ k + \sqrt{k^2 + 8\ kc}}.$$

By insertion of $c = 0{,}1$ and $\Delta\pi = 0.00037$ we find the value of k:

$$k = 13{,}3$$

and hence

$$\Delta\pi = 0{,}0581 \log \frac{4\ c}{-\ 13{,}3 + \sqrt{176{,}9 + 106{,}4\ c}}$$

As appearing from Fig. 2 where the $\Delta\pi$-values, calculated from this equation are indicated by squares, this equation gives good agreement with the measurements ($\Delta\pi = 0{,}0037\ c$) in the case of the more dilute solution until 0,5 n showing the $\Delta\pi$-curve as calculated by means of the mass action law also to be a straight line. The figures are thus compatible with the assumption of incomplete dissociation. If, however, the eoncentration of the undissociated $MgCl_2$ be calculated, which is possible on the assumption of the validity of the gas laws by means of:

$$\frac{C^2_{Cl^-}}{C_{Mg\,Cl_2}} = 13{,}3$$

we find for $c = 0{,}1$ $C_{MgCl_2} = 0{,}0007$ only, showing that in spite of the solution being very concentrated with regard to Mg^{++}, the amount of undissociated $MgCl_2$ is only 0,7 $^0/_0$ of the total chlorine concentration $c = 0{,}1$. In pure $MgCl_2$ of the same concentration, therefore, it must be much smaller and quite unable to account for the very considerable deviations of a such solution from ideal conditions.

These results however may be looked upon from another point of view also. If a salt solution gradually changes into another the total concentration remaining constant, the activity coefficient f of an extraneous ion present in small and constant concentration usually will be altered too, corresponding to a different dissolving power of the two solvents. Let x be the molecule ratio of the one of the solvents, $1 - x$ of the other and let us assume the alteration in x to produce proportional alterations in the dissolving power of the mixed solvent according to $\Delta f = kx$. The gas laws then evidently will hold good for the extraneous ion, if x or k be sufficiently small. If the change in the dissolving power manifests itself not only towards the extraneous ion but also towards the ions of the solvent itself the same conditions of sufficiently small values of x and k may be claimed for the correctness of the assumption to be tested in the present paper. That the gas laws have been proved to hold good even at 0,2 molal solutions of KCl in KNO_3 ($n = 2$) means that k in this case must be rather small. That deviations become appreciable in mixtures of $MgCl_2$ and $MgSO_4$ at concentrations as low as $c = 0{,}05$ on the other hand may be explained by assuming a greater value for k in this case. Solubility measurements carried out in this laboratory with uni-univalent salts, exhibiting in all cases greater values for $MgCl_2$ than for $MgSO_4$, confirm this view.

e) General results. Considered as a whole the results from this section lend strong support to the theory that the simple gas laws are valid for ions present in salt solutions, the concentration of which is large compared with the concentration of the ion concerned. The range of concentrations within which the law applies, however, depends upon the nature of the solvent and the dissolved salt. While valid for 0,2 molal or probably still higher concentrations in mixtures of uni-univalent salts the law begins to fail in the neighbourhood of 0,05 molal in mixtures of $MgCl_2$ and $MgSO_4$. This behaviour may be explained on the assumption of incomplete dissociation, but evidence is provided for the simple explanation according to which the change in dissolving power of the solvent is held responsible for the deviations observed.

According to this view we shall find the treatment of all equilibria including strong and weak electrolytes in solution highly simplified, when such equilibria are allowed to be established using a strong salt solution instead of water as solvent.

5. On the validity of the gas laws at small total concentration.

In addition to the above experiments with strong solutions some measurements were carried out covering solutions as dilute as 0,1 mol. The purpose of these measurements were to discover whether the change in the molal fraction x over the whole range of concentration from x = 0 to x = 1 in the case of dilute solutions may correspond to a constant activity coefficient or to activity coefficients changing in conformity with the dissolving power of the solvent.

The solutions employed were mixtures of KCl and KNO_3 of the constant total concentration 0,1, the concentration of KCl changing from 0,01 to 0,1 molal. The type of the cells consequently was:

$$\mathrm{Ag\cdot AgCl}\;\left|\;\begin{matrix}\mathrm{KCl}\ (c_1)\\ \mathrm{KNO_3}\ (0{,}1-c_1)\end{matrix}\;\right|\;\begin{matrix}\mathrm{KCl}\ (c_2)\\ \mathrm{KNO_3}\ (0{,}1-c_2)\end{matrix}\;\left|\;\mathrm{AgCl\cdot Ag}\right.$$

where c_2 changes from 0,01 to 0,1 and $c_1 = 0{,}1$.

The measurements were carried out at 20° with the aid of streaming electrodes exactly as the foregoing. The results are given in table XI.

Table XI. $KCl + KNO_3$, n = 0,1.

c_1	c_2	π_{obs}	π_1	π_{cor}
0,1	0,05	0,01718	+ 0,00039	0,01757
0,1	0,02	4026	60	4086
0,1	0,01	5769	70	5839

The electromotive forces between 0,01 mol solutions and the others calculated from these figures are given in the next table together with the theoretical values:

Table XII. $KCl + KNO_3$, n = 0,1.

c_1	c_2	π_{cor}	π_{cal}	$\Delta\pi$
0,01	0,02	0,01753	0,01750	0,00003
0,01	0,05	4082	4063	0,00019
0,01	0,10	5839	5813	0,00026

The agreement between π cor. and π cal. as shown by these figures is very remarkable. It is true that the values of $\Delta\pi$ possess no high percentage accuracy on account of the relatively considerable liquid-liquid potential. This, however, cannot obscure the fact that the gas laws hold exceedingly well, showing only a slight decrease in the activity coefficient of Cl^- when the concentration rises from 0 to 0,1. This agreement with the gas laws is particularly striking when compared with the deviations exhibited when the very same change in the KCl-concentration takes place in the absence af KNO_3. The two activity curves I and II respectively are shown in Fig. 3.

The question arises whether the result found in this case for the chlorine ion in mixed solutions of KCl and KNO_3 may be a general one. It is easily seen that this cannot be the case, because if the same law were applicable to all of the constituent ions, the same activity coefficient would also obtain for the unmixed solutions and, therefore, also the same osmotic pressure at the same concentrations. Conditions as simple as these, however, do not prevail. The freezing point lowering of KCl is about 4 per cent larger than of KNO_3 at $c = 0{,}1$. The activity of an extraneous ion is nearly 4 per cent higher in KCl than in KNO_3 at the same concentration, as appears from unpublished determinations of solubility. If we assume the chlorine ion to be acted upon by the changing solvent in the same way as an extraneous ion, the just mentioned influence of KCl and KNO_3 on the activity of uni-univalent ions should lead one to expect considerably greater deviations from the gas laws than those really found, namely $\Delta\pi = 1$ millivolt instead of 0,26 millivolt at $c = 0{,}1$. We must therefore conclude the ions of the varying solvent itself to be acted upon differently from extraneous ions of small constant concentration even if the same direction of the action may be admitted in the two cases.

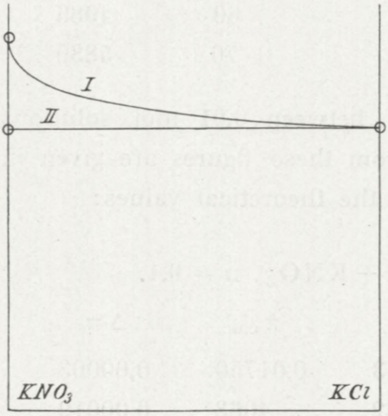

Fig. 3.

Ordinate indicates activity of Cl^-. Abscisse concentration of KCl from 0 to 0,1 n. Curve I valid for pure KCl solutions. Curve II for mixed solutions of KCl and KNO_3 of the total concentration 0,1 n.

The results of Loomis, Essex and Meachan[1] regarding the potential of HCl in mixtures of HCl and KCl at the total concentration 0,1 likewise point in the direction that

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[1] Journ. Amer. Chem. Soc. **39**, 1133 (1917).

slight changes in the activity coefficient take place with varying concentration of the mixture. The authors consider their results from the standpoint of the isohydric principle and hold alteration in the dissociation of the hydrochloric acid responsible for the deviations. Calculating the stoichiometric activity coefficient of HCl from the figures given we find this increasing with increasing proportion of the acid in conformity with the fact that this solution possesses a smaller dissolving power than potassium cloride.

In a recent paper Ming Chow[1] communicates measurements in the same system leading to practically constant values of the activity coefficient which is somewhat in opposition to the conclusion of the just cited article.

Further discussion of the work of these authors, however, raises questions which are closely connected with the results obtained by the solubility measurements referred to above, and which more suitably may be treated in connection with those.

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[1] Ibid. **42**, 497 (1920).

Physico-chemical Laboratory of the Royal Polytechnical Institute of Copenhagen.

Færdig fra Trykkeriet den 20. September 1920.

MATHEMATISK-FYSISKE MEDDELELSER

UDGIVNE AF

DET KGL. DANSKE VIDENSKABERNES SELSKAB

1. BIND (Kr. 8,80):

		Kr. Ø.
1.	Christiansen, C.: Experimentalundersøgelser over Gnidningselektricitetens Oprindelse. VI. 1917	0.25
2.	Knudsen, Martin: Fordampning fra Krystaloverflader. 1917.	0.25
3.	Brønsted, J. N., og Petersen, Agnes: Undersøgelser over Omdannelsen af reciproke Saltpar, samt over Benzidin-Benzidinsulfat-Ligevægten. Affinitetsstudier XI. 1917	0.60
4.	Andersen, A. F.: Sur la multiplication de séries absolument convergentes par des séries sommables par la méthode de Cesàro. 1918	0.90
5.	Brønsted, J. N.: En thermodynamisk Relation mellem Blandingsaffiniteterne i delvis mættede Opløsninger og dens Anvendelse til Affinitetsbestemmelse. Affinitetsstudier XII. 1918	0.90
6.	Nielsen, Niels: Recherches sur les polynomes d'Hermite. 1918	1.75
7.	Pedersen, P. O.: Om Townsends Teori for Stødionisation. 1918	0.30
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2. BIND:

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3. BIND:

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