first increase, then remain constant and finally decrease when the amount of water reaches about 40 percent. When using alcohol-water mixtures as solvent, it appeared that the decrease in concentration causes a rise and the addition of a substance with a common ion a lowering of the constant.

Dr. LULOFS research [1]), which may be usefully extended in various directions, points, like the results quoted, to the desirability of a study of the conductivity of the alcoholates when dissolved in the pure alcohols (partly carried out by CARRARA) or in mixtures of alcohol and water. It will then be possible to ascertain whether there exists a parallellism between the change of the reaction-constants and that of the conductivity.

Chemistry. — Professor BAKHUIS ROOZEBOOM presents a communication from Dr. A. SMITS: „*On the progressive change of the factor i as function of the concentration.*"

(Read March 30, 1901).

Of the salts, which I have already investigated, $K N O_3$ [2]) is the only one for which the factor i decreases with increasing concentration. It, therefore, seemed to me very interesting to ascertain whether other nitrates behave similarly.

$K N O_3$ being an anhydrous salt, I purposely chose nitrates of which no hydrates are known.

In this investigation I have availed myself of my improved Landsberger apparatus [3]), which is sufficiently accurate for my purpose.

Before proceeding to mention the results, I will first draw attention to some points to which attention should be paid in the determination of boiling points by this method.

In determining the boiling point of pure water, it is noticed that the boiling point continuously rises during the progress of the experiment. In my apparatus this rise amounted 0.01^0 in 25 minutes. The explanation of this phenomenon is found in the continual increase in height of the column of water in consequence of the condensation of the aqueous vapour, which takes place. When the column of water increases in height, the pressure and consequently

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[1]) Further particulars in his dissertation, Amsterdam, 1901.

[2]) Proc. 21 April 1900 714.

[3]) Proc. 26 May 1900 31.

the boiling point is raised. As I wished to make up solutions of different concentrations by adding to the water (of which I had determined the boiling point) some salt thereby causing an increase in the height of the column, it was necessary to know the increase of temperature, which corresponded to a certain increase in the height of the column of liquid.

I, therefore, conducted a series of boiling point determinations of pure water in which the height of the liquid was varied. In this way I found, that an increase of 10 m.m. in the height of the column corresponded with a rise of 0.01° in the temperature.

Theory requires for 10 m.m. water at 100° an increase of the boiling point about thrice as large. The explanation of this difference must be looked for in the vigorous mixing, which occurs in the boiling liquid owing to which, as will be readily understood, the theoretical increase cannot be obtained. As the degree of mixing is moreover dependent on the relation between the amount of steam transmitted in unit time and the volume of the boiling liquid, the observed rise in temperature will depend on the dimensions of the apparatus and the method of working. That a fairly complete mixing took place in my apparatus was proved by an investigation of the temperature of the different liquid layers. This investigation originated in the following phenomenon. I happened to find that, when the thermometer inside the liquid was raised or lowered to the extent of 1 c.m., a change of 0.005° was noticed in the temperature. Was this to be considered as a proof that the temperature of the different liquid layers was unequal, or must the explanation be found in the change of the height of the column of liquid caused by the altered position of the thermometer?

This question was decided by first ascertaining the influence of a certain increase in the height of the column of water while leaving the position of the thermometer unchanged and then repeating the experiment taking care, that the thermometer before and after the addition of water reached to the same depth. Both determinations gave exactly the same result from which follows, that the temperature of the different layers of water of the strongly moving boiling column of liquid is the same and that, therefore, the small increase of temperature of 0.005° was caused by the change in the height of the column of liquid already mentioned. From the foregoing it appears that an increase in the height of the column of boiling liquid exercises an influence which cannot be neglected, so that it is necessary to find out by measurement of the increase of height, whether or not on addition of salt a correction ought to be applied.

RESULTS.

$NaNO_3$.

Concentration in gr. mol. per 1000 gr. H_2O.	Increase of the boiling point of the solution.	Mol. increase of the boiling point.	i
0.0462	0.044°	9.516	1.83
0.0852	0.080°	9.389	1.81
0.4448	0.398°	8.948	1.72
0.8630	0.771°	8.876	1.71

$Ba(NO_3)_2$.

0.0461	0.070°	15.190	2.92
0.0868	0.104°	12.103	2.33
0.4233	0.466°	11.009	2.12
0.8890	0.911°	10.248	1.97

$Sr(NO_3)_2$.

0.0429	0.050°	11.664	2.24
0.0848	0.098°	11.561	2.22
0.4142	0.493°	11.903	2.29
0.9005	1.094°	12.148	2.34

$AgNO_3$.

0.0473	0.044°	9.294	1.79
0.0908	0.087°	9.246	1.78
0.4409	0.382°	8.665	1.67
0.9146	0.741°	8.102	1.56

$Pb(NO_3)_2$

0.0474	0.070°	14.760	2.84
0.0869	0.090°	10.351	1.99
0.4174	0.418°	10.014	1.93
0.8793	0.824°	9.371	1.80

These tables show that while the factor i for $NaNO_3$, $Ba(NO_3)_2$, $AgNO_3$ and $Pb(NO_3)_2$ diminishes perceptibly with the increase of the concentration, it takes in the case of $Sr(NO_3)_2$ a course, which quite agrees with that observed with KCl and $NaCl$.

Although five out of the six anhydrous nitrates investigated gave the same result, the exception, noticed in the case of $Sr(NO_3)_2$, shows that the fact, that a salt is anhydrous or not anhydrous, has no definite influence on the progressive change of i.

Let us now consider what is to be learned from the determinations of the electrolytic conductivity of solutions of the salts KCl, KNO_3, $NaCl$ and $NaNO_3$.

KRANNHALS [1] found at $99°.4$ the following:

$K Cl$ ($\mu_\infty = 348$) [2].

Concentration	Mol. conductive power μ.	% increase of $\frac{\mu}{\mu_\infty}$ in the concentration interval $1-^1/_{16}$ gr. mol.	i	% increase of i in the concentration interval $1-^1/_{16}$ gr mol.
1	240 0	} 29	1.69	} 11.9
$^1/_{16}$	309 9	}	1.89	}

$K NO_3$ ($\mu_\infty = 340$).

1	205.8	} 38.5	1 605	} 14.6
$^1/_{16}$	285.1	}	1.84	}

$Na Cl$ ($\mu_\infty = 316$).

1	204.4	} 31.1	1.65	} 12.1
$^1/_{16}$	268.1	}	1.85	}

$Na NO_3$ ($\mu_\infty = 309$).

1	173.7	} 45.4	1.56	} 16.6
$^1/_{16}$	252.5	}	1.82	}

[1] Zeitschr. f. Physik. Chem. 5, S. 250 (1890).
[2] Instead of μ_∞ here is taken μ_{1000}, but it is easy to demonstrate, that for our purpose this manner of acting is permitted.

In these tables it is assumed, that for the concentration given the quotient $\dfrac{\mu}{\mu_\infty}$ represents the degree of dissociation.

It appears, however, from JAHN's investigation that this is not the case even for very small concentrations.

The mobility of the K and Na ions appears to increase very perceptibly with the concentration, so that for liquids, which are not excessively dilute, $\dfrac{\mu}{\mu_\infty}$ is greater than the degree of dissociation, while the difference is continually increasing with the concentration.

All the values of i occurring in this table ought, therefore to be diminished by a certain amount which should reach a maximum for the greatest concentration.

If we now started from the supposition that the corrections, which ought to be applied in the case of the above mentioned salts in order to get the true degree of dissociation, exercise about the same influence on the progressive change of i, it would follow from this table that in the case of $K NO_3$ and $Na NO_3$ the degree of dissociation and consequently the theoretical value of i (from the conductivity) diminishes much more rapidly with the increase of the concentration than in the case of $K Cl$ and $Na Cl$ [2]).

Should this be confirmed by more accurate determinations of the degree of dissociation of more concentrated solutions it might provide an explanation of the fact, that the experimental i (from the decrease of vapour tension and increase of boiling point) increases with the concentration in the case of not very diluted solutions of $K Cl$ and $Na Cl$ whereas the reverse happens with $K NO_3$ and $Na NO_3$.

The change of the experimental i is due not only to the change of the dissociation, but also to the influence of the deviation from the diluted condition. Researches on non-electrolytes render it probable that this last influence will cause the experimental i to increase with the concentration and will, therefore, possess a sign opposite to that of the influence of the dissociation change.

As one of the influences increases the experimental values of i and the other one tends to reduce them, the final result will depend on the relative magnitudes of the two influences.

If then the dissociation in the case of one salt diminishes much

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[1]) Zeitschr. f. Physik. Chem. 33, 545 (1900).

[2]) The corrections cannot as yet be deduced from JAHN's research, as these have been determined for greater dilutions only.

less rapidly with an increase of the concentration than in the case of another salt, it is possible that, while in the one case a very slow increase of the experimental i is observed (K Cl, Na Cl), the reverse may be the case with the other (K NO$_3$, Na NO$_3$).

In conclusion it may be remarked that the results of the freezing point determinations of not very dilute solutions have not been discussed in this paper because some doubt has been thrown on them by their disagreeing with those obtained by the determination of the vapour tensions and boiling points.

Amsterdam, Chem. Lab. University, March 1901.

(May 18, 1901).