Our value, 2.68, is 25% smaller, and this difference is much greater than our experimental error which is about 2%. However, it should be remembered that carbonic acid is a peculiar acid in that the proton (or deuteron) must come exclusively from the water. Thus the hydration equilibrium plays an important role and it probably will not be the same in H_2O and D_2O. This factor may account for the difference mentioned above.

We are indebted to the Class of 1900 Fund for a grant which enabled us to purchase the deuterium oxide used in this work.

Summary

The ratio of the first thermodynamic ionization constants of proto- and deuterio-carbonic acid has been determined potentiometrically using a cell without transference in which the electrodes were quinhydrone and silver–silver chloride. Using 99.1% D_2O the ratio, K_H/K_D, has been found to be 2.68 at 25°.

WILLIAMSTOWN, MASS. RECEIVED JUNE 10, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Conductivities of Concentrated Mixtures of the Nitrates of Some Uni-, Di-, and Trivalent Cations in Aqueous Solution

BY PIERRE VAN RYSSELBERGHE AND GOON LEE

As a further step in our investigation of the conductivity of concentrated mixtures of strong electrolytes[1] we have studied a number of nitrates of uni-, di-, and trivalent cations at different total concentrations ranging from 1 to 5 *N*. All possible types of binary mixtures have been included: two univalent cations, one uni- and one divalent cation, two divalent cations, one uni- and one trivalent cation, one di- and one trivalent cation, two trivalent cations. The method was essentially the same as in our previous work. The conductivities of the pure salts were found to be in close agreement with the existing standard data (I. C. T.; L. B. R.), except in three cases [$LiNO_3$, $Mg(NO_3)_2$, $Cr(NO_3)_3$] for which the standard data seem to be somewhat in error. Moreover, some conductivities of pure salts are reported here for the first time. Others have been obtained for the first time at 25°. The results are recorded in Table I in which we give the conductivities of twenty types of mixtures arranged in series corresponding to the same total equivalent concentration. We represent by x and $1-x$ the fractions of the total equivalent concentration corresponding to salts 1 and 2, salt 1 being the first in the title of the series. For each solution we give the specific and the equivalent conductivity and the difference $\Delta\Lambda$ between the measured conductivity and that calculated from the simple, uncorrected mixture rule:

$$\Lambda = x\Lambda_1 + (1 - x)\Lambda_2$$

Two series of mixtures (19 and 20) contain nitric acid as one of the components, the maximum amount of nitric acid present being in both cases half the total normality.

TABLE I

CONDUCTIVITIES OF CONCENTRATED MIXTURES AT 25°

Composition x	$1-x$	Specific conductivity	Equivalent conductivity Measured	Calculated	$-\Delta\Lambda$
	1.1	1 *N* mixtures of $KNO_3 + NaNO_3$			
1	0	0.09254	92.54		
3/4	1/4	.08798	87.98	88.37	0.39
1/2	1/2	.08324	83.24	84.19	.85
1/4	3/4	.07973	79.73	80.02	.29
0	1	.07585	75.85		
	1.2	2 *N* mixtures of $KNO_3 + NaNO_3$			
1	0	0.15848	79.24		
3/4	1/4	.14993	74.97	75.20	0.23
1/2	1/2	.14104	70.52	71.17	.65
1/4	3/4	.13383	66.92	67.12	.20
0	1	.12617	63.09		
	1.3	3 *N* mixtures of $KNO_3 + NaNO_3$			
1	0	0.21042	70.16		
3/4	1/4	.19996	65.99	66.00	0.01
1/2	1/2	.18413	61.38	61.85	.48
1/4	3/4	.17222	57.41	57.72	.31
0	1	.16075	53.58		
	2	5 *N* mixtures of $NaNO_3 + LiNO_3$			
1	0	0.19815	39.65		
3/4	1/4	.18944	37.89	38.28	0.39
1/2	1/2	.18167	36.42	36.72	.30
1/4	3/4	.17511	35.02	35.27	.25
0	1	.16910	33.82		

---

[1] Van Rysselberghe and Nutting, THIS JOURNAL, **56**, 1435 (1934); **59**, 333 (1937); Van Rysselberghe, Grinnell and Carlson, *ibid.*, **59**, 336 (1937).

TABLE I (*Continued*)

Composition x	$1 - x$	Specific conductivity	Equivalent conductivity Measured	Equivalent conductivity Calculated	$-\Delta\Lambda$
3.1 1 N mixtures of $KNO_3 + Cd(NO_3)_2$					
1	0	0.09236	92.36		
3/4	1/4	.08392	83.92	84.84	0.92
1/2	1/2	.07522	75.22	77.33	2.11
1/4	3/4	.06894	68.94	69.81	0.87
0	1	.06230	62.30		
3.2 2 N mixtures of $KNO_3 + Cd(NO_3)_2$					
1	0	0.15912	79.56		
3/4	1/4	.13947	69.78	71.53	1.75
1/2	1/2	.12313	61.56	63.50	1.94
1/4	3/4	.10778	53.89	55.47	1.58
0	1	.09487	47.44		
3.3 3 N mixtures of $KNO_3 + Cd(NO_3)_2$					
1	0	0.21009	70.03		
3/4	1/4	.18015	60.05	61.58	1.53
1/2	1/2	.15243	50.81	53.13	2.32
1/4	3/4	.12895	42.98	44.68	1.70
0	1	.10868	36.23		
4 3 N mixtures of $KNO_3 + Zn(NO_3)_2$					
1	0	0.21019	70.06		
3/4	1/4	.18973	63.24	63.75	0.51
1/2	1/2	.17035	56.78	57.44	.66
1/4	3/4	.14966	49.89	51.13	.24
0	1	.13446	44.82		
5.1 2 N mixtures of $KNO_3 + Cu(NO_3)_2$					
1	0	0.15928	79.64		
3/4	1/4	.14380	71.90	73.06	1.16
1/2	1/2	.13002	65.01	66.48	1.47
1/4	3/4	.11746	58.73	59.90	1.17
0	1	.10664	53.32		
5.2 3 N mixtures of $KNO_3 + Cu(NO_3)_2$					
1	0	0.21000	70.00		
3/4	1/4	.18482	61.61	62.98	1.37
1/2	1/2	.16200	54.00	55.92	1.95
1/4	3/4	.14368	47.89	48.93	1.04
0	1	.12570	41.90		
6.1 3 N mixtures of $LiNO_3 + Cd(NO_3)_2$					
1	0	0.14494	48.31		
3/4	1/4	.13504	45.01	45.29	0.28
1/2	1/2	.12613	42.04	42.29	.25
1/4	3/4	.11741	39.13	39.28	.15
0	1	.10881	36.27		
6.2 5 N mixtures of $LiNO_3 + Cd(NO_3)_2$					
1	0	0.16910	33.82		
3/4	1/4	.14894	29.78	30.57	0.79
1/2	1/2	.13345	26.69	27.34	.65
1/4	3/4	.11797	23.59	24.10	.51
0	1	.10432	20.86		
7 4 N mixtures of $LiNO_3 + Zn(NO_3)_2$					
1	0	0.16168	40.42		
3/4	1/4	.15711	39.27	39.33	0.06
1/2	1/2	.15277	38.19	38.26	.07
1/4	3/4	.14842	37.10	37.18	.08
0	1	.14440	36.10		
8 3 N mixtures of $LiNO_3 + Mg(NO_3)_2$					
1	0	0.14409	48.03		
3/4	1/4	.14032	46.77	46.87	0.10
1/2	1/2	.13679	45.59	45.72	.13
1/4	3/4	.13323	44.41	44.56	.15
0	1	.13120	43.40		
9.1 2 N mixtures of $Cu(NO_3)_2 + Cd(NO_3)_2$					
1	0	0.10664	53.32		
3/4	1/4	.10369	51.85	51.91	0.06
1/2	1/2	.10083	50.42	50.50	.08
1/4	3/4	.09805	49.03	49.08	.05
0	1	.09534	47.67		
9.2 3 N mixtures of $Cu(NO_3)_2 + Cd(NO_3)_2$					
1	0	0.12570	41.90		
3/4	1/4	.12146	40.49	40.51	0.02
1/2	1/2	.11728	39.09	39.11	.02
1/4	3/4	.11303	37.68	37.72	.04
0	1	.10896	36.32		
10.1 3 N mixtures of $Mg(NO_3)_2 + Cd(NO_3)_2$					
1	0	0.13120	43.40		
3/4	1/4	.12420	41.40	41.62	0.22
1/2	1/2	.11875	39.58	39.84	.26
1/4	3/4	.11373	37.91	38.05	.14
0	1	.10882	36.27		
10.2 5 N mixtures of $Mg(NO_3)_2 + Cd(NO_3)_2$					
1	0	0.14555	29.11		
3/4	1/4	.13102	26.20	27.05	0.75
1/2	1/2	.12119	24.24	24.99	.75
1/4	3/4	.11000	22.00	22.92	.92
0	1	.10432	20.86		
11 4 N mixtures of $Zn(NO_3)_2 + Cd(NO_3)_2$					
1	0	0.14440	36.10		
3/4	1/4	.13549	33.87	33.99	0.12
1/2	1/2	.12683	31.71	31.88	.17
1/4	3/4	.11808	29.52	29.77	.25
0	1	.11068	27.67		
12 3 N mixtures of $KNO_3 + Al(NO_3)_3$					
1	0	0.21019	70.06		
3/4	1/4	.19026	60.09	61.75	1.66
1/2	1/2	.15467	51.56	53.44	1.88
1/4	3/4	.12971	43.24	45.13	1.89
0	1	.11045	36.82		
13 4 N mixtures of $LiNO_3 + Al(NO_3)_3$					
1	0	0.16168	40.42		
3/4	1/4	.14832	37.08	37.36	0.28
1/2	1/2	.13567	33.92	34.30	.38
1/4	3/4	.12339	30.85	31.25	.40
0	1	.11276	28.19		
14 2 N mixtures of $KNO_3 + Cr(NO_3)_3$					
1	0	0.15857	79.29		
3/4	1/4	.13537	67.69	68.46	0.77
1/2	1/2	.11395	56.98	57.64	.66
1/4	3/4	.08986	44.93	46.81	1.88
0	1	.07198	35.99		
15 3 N mixtures of $Zn(NO_3)_2 + Al(NO_3)_3$					
1	0	0.13446	44.82		
3/4	1/4	.12701	42.34	42.82	0.48

TABLE I (*Concluded*)

Composition x	$1 - x$	Specific conductivity	Equivalent conductivity Measured	Equivalent conductivity Calculated	$-\Delta\Lambda$
1/2	1/2	.12116	40.39	40.82	.43
1/4	3/4	.11334	37.78	38.82	1.04
0	1	.11045	36.82		
16 4 N mixtures of $Cd(NO_3)_2 + Al(NO_3)_3$					
1	0	0.11068	27.67		
3/4	1/4	.11120	27.80	27.80	0.00
1/2	1/2	.11144	27.86	27.93	.07
1/4	3/4	.11186	27.97	28.06	.09
0	1	.11276	28.19		
17.1 2 N mixtures of $Cd(NO_3)_2 + Cr(NO_3)_3$					
1	0	0.09562	47.81		
3/4	1/4	.09034	45.17	44.76	−0.41
1/2	1/2	.08498	42.49	41.71	− .78
1/4	3/4	.07752	38.76	38.65	− .11
0	1	.07119	35.60		
17.2 4 N mixtures of $Cd(NO_3)_2 + Cr(NO_3)_3$					
1	0	0.11040	27.60		
3/4	1/4	.11170	27.92	27.25	−0.67
1/2	1/2	.11181	27.95	26.89	−1.06
1/4	3/4	.10963	27.43	26.54	−0.89
0	1	.10471	26.18		
18.1 1 N mixtures of $Al(NO_3)_3 + Cr(NO_3)_3$					
1	0	0.06264	62.64		
3/4	1/4	.05797	57.97	57.63	−0.34
1/2	1/2	.05349	53.49	52.62	− .77
1/4	3/4	.04828	48.28	47.61	− .67
0	1	.04260	42.60		
18.2 2 N mixtures of $Al(NO_3)_3 + Cr(NO_3)_3$					
1	0	0.09647	48.24		
3/4	1/4	.09207	46.04	45.08	−0.96
1/2	1/2	.08617	43.09	41.96	−1.13
1/4	3/4	.07997	39.99	38.82	−1.17
0	1	.07136	35.68		
18.3 4 N mixtures of $Al(NO_3)_3 + Cr(NO_3)_3$					
1	0	0.11232	28.08		
3/4	1/4	.11380	28.45	27.54	−0.91
1/2	1/2	.11413	28.53	26.99	−1.54
1/4	3/4	.11010	27.52	26.45	−1.07
0	1	.10361	25.90		
19 2 N mixtures of $HNO_3 + KNO_3$					
1	0		(289.80)		
1/2	1/2	0.36682	183.42	184.59	1.17
2/5	3/5	.31319	156.59	163.54	6.95
1/4	3/4	.25680	128.40	131.97	3.57
1/5	4/5	.23726	118.63	121.44	2.81
0	1	.15879	79.37		
20 2 N mixtures of $HNO_3 + Cd(NO_3)_2$					
1	0		(289.80)		
1/2	1/2	0.32599	163.00	168.83	5.83
2/5	3/5	.27131	135.66	144.63	8.97
1/4	3/4	.20242	101.21	108.30	7.09
1/5	4/5	.18164	90.82	96.24	5.42
0	1	.09572	47.86		

Discussion

In all the mixtures, except those of chromium nitrate with cadmium nitrate and of chromium nitrate with aluminum nitrate, the conductivity calculated according to the mixture rule is larger than the measured conductivity. As previously observed with other types of mixtures, the maximum difference between measured and calculated conductivities in a series of given total equivalent concentration follows the same trend as the difference between the conductivities of the pure salts. This is shown in Table II where the various groups of mixtures are classified according to the value of the difference λ between the conductivities of the pure salts, $\Delta\Lambda$ being the largest departure from the mixture rule in the series. If one excludes the mixtures of chromium nitrate with cadmium and aluminum nitrates and those containing nitric acid, Table II could be combined with the corresponding tables of our previous papers. We note, however, that $\Delta\Lambda$ for 1 N mixtures of $KNO_3 + NaNO_3$ is larger than for the 1 molal mixtures previously studied.

TABLE II

N	Mixtures	λ	$-\Delta\Lambda$
2	$HNO_3 + Cd(NO_3)_2$	241.94	8.97
2	$HNO_3 + KNO_3$	210.43	6.95
2	$KNO_3 + Cr(NO_3)_3$	43.30	1.88
3	$KNO_3 + Cd(NO_3)_2$	33.80	2.32
3	$KNO_3 + Al(NO_3)_3$	33.24	1.89
2	$KNO_3 + Cd(NO_3)_2$	32.12	1.94
1	$KNO_3 + Cd(NO_3)_2$	30.06	2.11
3	$KNO_3 + Cu(NO_3)_2$	28.10	1.95
2	$KNO_3 + Cu(NO_3)_2$	26.32	1.47
3	$KNO_3 + Zn(NO_3)_2$	25.24	0.66
1	$Al(NO_3)_3 + Cr(NO_3)_3$	20.04	− .77
1	$KNO_3 + NaNO_3$	16.69	.85
3	$KNO_3 + NaNO_3$	16.58	.48
2	$KNO_3 + NaNO_3$	16.15	.65
5	$LiNO_3 + Cd(NO_3)_2$	12.96	.79
2	$Al(NO_3)_3 + Cr(NO_3)_3$	12.56	−1.17
4	$LiNO_3 + Al(NO_3)_3$	12.23	0.40
2	$Cd(NO_3)_2 + Cr(NO_3)_3$	12.21	− .78
3	$LiNO_3 + Cd(NO_3)_2$	12.04	.28
4	$Zn(NO_3)_2 + Cd(NO_3)_2$	8.43	.25
5	$Mg(NO_3)_2 + Cd(NO_3)_2$	8.25	.92
3	$Zn(NO_3)_2 + Al(NO_3)_3$	8.00	1.04
3	$Mg(NO_3)_2 + Cd(NO_3)_2$	7.13	0.26
5	$NaNO_3 + LiNO_3$	5.83	.39
2	$Cu(NO_3)_2 + Cd(NO_3)_2$	5.65	.08
3	$Cu(NO_3)_2 + Cd(NO_3)_2$	5.58	.04
3	$LiNO_3 + Mg(NO_3)_2$	4.63	.15
4	$LiNO_3 + Zn(NO_3)_2$	4.32	.08
4	$Al(NO_3)_3 + Cr(NO_3)_3$	2.18	−1.54
4	$Cd(NO_3)_2 + Cr(NO_3)_3$	1.42	−1.06
4	$Cd(NO_3)_2 + Al(NO_3)_3$	0.52	0.09

The behavior of the $Cr(NO_3)_3$ + $Cd(NO_3)_2$ and $Cr(NO_3)_3$ + $Al(NO_3)_3$ mixtures seems abnormal, particularly in 4 *N* solutions where some mixtures exhibit larger conductivities than those of the two pure salts. We have noticed that the slope of the conductivity curve of $Cr(NO_3)_3$ is, at least in the range of concentrations here studied, appreciably smaller than the slopes for the other nitrates, these being all nearly equal. When the conductivities of $Cr(NO_3)_3$ and of the other salt in the mixture are nearly equal, there is a positive $\Delta\Lambda$ due to this difference in the slopes. When the conductivities are quite different, as in the 2 *N* mixtures with KNO_3, $\Delta\Lambda$ is negative because the effect of this difference is larger than that of the difference in the slopes.

On account of the very large difference between the conductivity of pure nitric acid and that of KNO_3 or $Cd(NO_3)_2$ we would expect $-\Delta\Lambda$ to be much larger than is observed. We found in our previous work that, with salts, a difference of 100 in Λ corresponds to a $\Delta\Lambda$ of 14 to 16. The abnormal behavior of mixtures containing acids was pointed out in one of our papers and is evidently connected with the peculiar mechanism of proton conductivity. A common ion effect on the degree of ionization of nitric acid would tend to increase the lowering of the conductivity with respect to the mixture rule. Such an effect is to be expected, whether we accept Rao's[2] claim that nitric acid, alone among all nitrates, is incompletely dissociated, or whether we make the less drastic and more reasonable assumption that, at these high concentrations, nitric acid is less completely dissociated than the salts. The corresponding effect on the conductivity of mixtures containing nitric acid apparently is overshadowed to a certain extent by an effect in the opposite direction due to the adjustment of mobilities.

Strong evidence for the incomplete dissociation of nitrates is provided by Davies'[3a] recent analysis of Van Rysselberghe and Nutting's data[3b] on the conductivity of mixtures of KNO_3 with NaCl and of $NaNO_3$ with KCl. Davies gives a striking explanation for the fact that the calculated Λ's are smaller than the experimental values in the former group of mixtures, and larger in the latter. On the basis of dissociation constants previously obtained for KNO_3 and $NaNO_3$ he is able to calculate $\Delta\Lambda$ values in excellent agreement with the experimental ones.

Summary

1. Conductivities of twenty groups of binary mixtures of nitrates of uni-, di-, and trivalent cations have been measured at total equivalent concentrations ranging from 1 to 5 *N*.

2. All mixtures studied, except those of chromium nitrate with cadmium and aluminum nitrates, exhibit conductivities lower than the values calculated from the simple mixture rule. The departure from the mixture rule is the larger the larger the difference of the conductivities of the pure salts.

3. The behavior of mixtures containing chromium nitrate and of those containing nitric acid is briefly discussed.

STANFORD UNIVERSITY, CALIF.

RECEIVED SEPTEMBER 26, 1938

---

[2] Rao, *Proc. Roy. Soc.* (London), **A127**, 279 (1930).

[3] (a) Davies, *J. Chem. Soc.*, 448 (1938); (b) Van Rysselberghe and Nutting, THIS JOURNAL, **59**, 333 (1937).