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X. *The Ionic and Thermal Coefficients of Nitric Acid.* By V. H. VEILEY, D.Sc., F.R.S., and J. J. MANLEY, Daubeny Curator, Magdalen College, Oxford*.

IN a former investigation† we have published determinations of the electric conductivity of nitric acid of different concentrations at the three temperatures 0°, 15°, and 30° C. obtained by the method of Kohlrausch with certain modifications. It has for some time been noted that the strong mineral acids do not follow Ostwald's dilution law

$$\frac{\mu^2}{(\mu_\infty - \mu)V\mu_\infty} = K; \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and though the results obtained are more in accordance with the Rudolphi-van't Hoff‡ equation

$$\frac{\alpha^3}{(1-\alpha)^2V} = K, \quad \alpha = \frac{\mu}{\mu_\infty}, \quad . \quad . \quad . \quad . \quad (2)$$

yet the relation can only be regarded as empirical.

It seemed, therefore, of interest to calculate from our conductivity determinations the amount of ionization $\frac{\mu}{\mu_\infty}$ at the different percentage concentrations; for though results for dilute samples have been given by Kohlrausch§ and others, yet no data have been published for more concentrated samples. The value for the molecular conductivity at infinite dilution or $\mu_\infty = K10^7$, according to the data of Kohlrausch is $K_{18} = 342$, or $K_{15} = 325.4$ when reduced by the formula

$$\mu_{15} = \mu_{18} 342(1 + .0162[15-18]). \quad . \quad . \quad . \quad (3)$$

In the following Table values are given: in column I. the percentage concentration, in II. the corresponding molecular dilution, in III. the values for $\mu \times 10^7$, and in IV. the values for $\frac{\mu}{\mu_\infty}$, the quotient of ionization.

It will be observed that there is an irregularity in the results for the samples from 98 per cent. to 100 per cent., which is consequent upon a reversal in the conductivity values; and in our work mentioned above attention was drawn not only to this point, but also that whereas nitric acid behaves

* Communicated by the Authors.

† Phil. Trans. 1898, A. p. 365.

‡ Zeits. f. physikal. Chem. xvii. p. 385 (1895), and xviii. p. 301 (1895).

§ Wied. Ann. xxvi. p. 196 (1885).

as other electrolytes in possessing a positive temperature-coefficient for concentrations up to 96 per cent., yet beyond this point it behaves as a metallic conductor in possessing a negative temperature-coefficient.

TABLE I.

Percentage Proportion.	Molecular Dilution.	μ_{15} in mercury units $\times 10^7$.	$\frac{\mu_{15}}{\mu_{15\infty}}$
1.30	4.568	288.0	0.885
3.12	1.956	281.5	0.865
5.99	1.164	258.9	0.796
10.13	0.559	228.0	0.701
15.32	0.349	190.1	0.571
20.11	0.251	159.3	0.487
25.96	0.180	123.5	0.379
30.42	0.144	100.1	0.308
33.81	0.123	85.8	0.263
35.90	0.112	73.6	0.226
39.48	0.096	63.8	0.196
45.01	0.077	47.9	0.117
51.78	0.059	32.6	0.102
53.03	0.056	30.4	0.093
58.20	0.045	22.2	0.086
61.20	0.040	18.6	0.057
65.77	0.032	13.3	0.041
69.53	0.028	10.3	0.032
73.82	0.022	6.43	0.020
76.59	0.019	5.03	0.015
78.90	0.017	3.27	0.010
84.08	0.012	1.09	0.004
86.18	0.010	0.94	0.003
87.72	0.007	0.62	0.002
89.92	0.007	0.36	0.001
91.87	0.006	0.17	0.0005
94.32	0.004	0.07	0.0002
96.12	0.002	0.035	0.0001
98.50	0.001	0.016	0.00005
98.85	0.001	0.013	0.00004
99.27	0.001	0.017	0.00005
99.97	0	0.007	0.00002

It is evident that this phenomenon cannot be explained by the aid of the ionic dissociation theory, as the number of free ions would not exceed four per 1000. As we have observed a similar abnormality in other physical properties, and especially in the contractions as calculated from the density determinations, we consider it probable that the result is due to an incipient formation of the compound $2\text{HNO}_3 \cdot \text{N}_2\text{O}_5$, which is prepared by dissolving nitrogen pentoxide in anhydrous nitric acid.

The values for μ for the acids of lower percentage concentration (1 per cent. to 42 per cent.) are generally somewhat lower than those given by Kohlrausch ; but those for $\frac{\mu}{\mu_{\infty}}$ are more in accordance with those calculated by Jones* from the freezing-point determinations.

Kohlrausch and Hallwachs† have pointed out that there is an undoubted relation between the contraction, produced even in very dilute solutions of electrolytes, and ionic dissociation, since non-electrolytes do not show this phenomenon. In the present instance, though the points of alteration of direction of curvature are the same both for the contractions and the quotient of ionic dissociation, if expressed in terms of percentages, yet correlation of the two phenomena does not appear to be of a simple character.

Coefficients of Expansion.

Very few data of the coefficients of expansion of nitric acid have as yet been recorded. Kobl‡, many years ago as a result of his density determinations, observes as follows :—
“ Le coefficient de la dilatation de l'acide azotique est assez élevé. Ainsi pour l'acide azotique monohydrate, le coefficient moyen de dilatation entre 0 degré et 15 degrés est $a = .001263$, c'est à dire environs trois fois plus fort que celui de l'eau.”

Marignac gave values for the constants a , b , and c in the equation

$$V_t = V_0(1 + at + bt^2 + ct^3) \dots \dots (4)$$

for a few samples ; and lastly Lunge and Rey§ published the corrections of densities at 15° for temperatures between 13° and 17°, in all seventeen values. From our density determinations at 4°, 14°·2, and 24°·2 corrected to a vacuum we have calculated the values for the mean cubic expansion or values of a from the equation

$$V_t = V_4(1 + at) \dots \dots (5)$$

These values expressed as $\alpha \times 10^{-6}$ are given in the following table.

* *Zeits. f. physikal. Chem.* xii. p. 623 (1893).

† *Göttingen Nachrichten*, 1893, pp. 350-357. Cf. Drude and Nernst, *Zeits. f. physikal. Chem.* xv. p. 79 (1894).

‡ *Ann. Chim. Phys.* [4] x. p. 140.

§ *Zeits. f. angew. Chemie*, 1891, p. 167, and 1892, p. 10.

Percentage.	$\alpha \times 10^{-6}$, 4°-14°·2.	$\alpha \times 10^{-6}$, 14°·2-24°·2.	Percentage.	$\alpha \times 10^{-6}$, 4°-14°·2.	$\alpha \times 10^{-6}$, 14°·2-24°·2.
0·625	100	158	56·29	980	950
2·732	150	241	58·32		950
4·595	205	246	60·42	1000	
7·585	283	265	60·60		990
10·75	341	370	62·84		1038
13·99	391	403	65·80	1058	1043
14·95	402	446	67·85		1060
16·88	428	455	71·60	1054	
18·44	476	525	75·64	1088	1076
19·32	484		76·55	1088	1076
23·89	540	542	78·22	1095	
25·50	550	585	81·93	1143	1093
28·97	629	608	85·21	1143	1096
30·17	647	637	87·90		1096
33·55	700	672	92·24	1200	1141
38·10	770		94·04	1200	1141
42·33	817	790	95·62	1200	1141
44·41	847	801	96·64	1222	1172
46·56	864	817	97·33		1190
51·24	942	907	98·07	1250	1210
54·60	980	950	100·00	1274	1240

The value obtained for the 100-per-cent. acid for the temperature-limit 4°-14°, namely ·001274, approximates very closely to that obtained by Kolb, namely ·001263 between the limits 0°-15°; but it appears that he made an arithmetical mistake in referring to the value as about three times as great as the mean coefficient of water between the same limits; this latter, according to Rosetti's tables, is ·000047, so that the value for nitric acid is nearly thirty times as great (actually 27·1).

The above results show that as regards the mean coefficient of expansion, nitric acid of different concentrations does not behave as if it were a mere mixture of the acid and water.

The following selected values illustrate this point:—

Percentage.	Sum of Coefficients calculated at 4°-14°·2.	Coefficient found at 4°-14°·2.
10·75	180×10^{-6}	341×10^{-6}
30·17	417×10^{-6}	647×10^{-6}
51·24	676×10^{-6}	942×10^{-6}
75·64	978×10^{-6}	1088×10^{-6}
94·04	1126×10^{-6}	1200×10^{-6}

In every case the found value exceeds that calculated, though the difference decreases as the percentage-concentration increases.

Though there seems to be no simple relation between the

ratios of the calculated and found coefficients of expansion, on the one hand, and the factor of ionic dissociation, on the other, yet such a general result as that given above would follow if the sums of the coefficients of expansion of the separated ions, namely, $\widehat{H}$ and $\widehat{NO_3}$, were greater than that of the undissociated molecule HNO_3 . The general result is, however, probably complicated by the affinity of the acid for water and the consequent formation of either hydrates or of complex molecular structures (say x), each of which would have its particular coefficient. The net result is expressible by a general equation :

$$K = \Sigma [k(H_1) + k'(NO_3) + k''(HNO_3) + k'''(x) \dots]. \quad (6)$$

A further point of interest is that the values for the lower temperature-limit are for the lower percentage concentrations less than the values for the higher temperature-limit, yet for the higher percentage concentration this relation is reversed ; the reversal takes place at about 40 per cent.

If a curve be drawn in which the mean coefficients for either limits of temperature are expressed in terms of percentages, the observational results are found to lie approximately upon four straight lines—namely, firstly, from 1 to 8 per cent.; secondly, from 11 to 54 per cent.; thirdly, from 54 to 70 per cent.; and, fourthly, from 70 to 93 per cent.; and the remainder upon an irregular curve.

With regard to these several points, it may be noticed that the 54 per cent. corresponds to that of maximum contraction as found by Kolb and ourselves, while the irregularity from 92 to 100 per cent. has already been alluded to. The behaviour of nitric acid as regards this physical property is so far different from sulphuric acid, which has been completely investigated by Pickering*, in that, firstly, the variations are much more marked; and, secondly, the maximum value occurs at 100 per cent., while that of sulphuric acid is at about 86 per cent., from which point the value of the coefficient decreases to 98 per cent., and from this concentration up to 100 per cent. slightly increases.

In conclusion, we trust that we may be allowed to raise a plea for the more complete investigation of the physical properties of solutions of liquids in liquids of a high degree of concentration as regards the solute. The results to be obtained will, we believe, be as full of interest as those already obtained with solutions of a high degree of dilution as regards the solvent water.

Oxford, October 1901.

* Journ. Chem. Soc. 1890, p. 114.