XCIX.—*Some Physical and Chemical Properties of Strong Nitric Acid.*

By Victor Herbert Veley and John Job Manley.

In a recently published communication (this vol., p. 658), by W. N. Hartley, on the "Absorption spectra of nitric acid in various states of concentration," this author deals with certain physical and chemical properties of the concentrated acid, and partly confirms our earlier investigations bearing on this subject.

Moreover, since our more recent publications on the physical properties of nitric acid (*Proc. Roy. Soc.*, 1901, **69**, 86, and *Phil Mag.*, 1902 [vi], **3**, 118), an important investigation by R. Knietzsch (*Ber.*, 1901, **34**, 4069) has appeared on the production of sulphur trioxide from flue gases, in which attention is drawn to the very remarkable alteration in physical and chemical properties of sulphuric acid containing 97—98 per cent. H_2SO_4. In the present communication, it is our desire to place on record, with reference to Hartley's communication, certain observations on nitric acid having a concentration of from 78 to 100 per cent. HNO_3, and to call attention to the close parallelism between nitric and sulphuric acids between the limits of 94 to 100 per cent. Hartley assumes the existence of orthonitric acid, H_3NO_4, from the observations of W. H. Perkin, senr., Pickering, ourselves, and others, and regards the anhydrous acid as having probably a bimolecular structure, $H_2N_2O_6$; acids of concentration between 78 and 100 per cent. are considered to be mixtures of these two compounds, the former of which is an active agent, whilst the latter is inert.

So far as we are aware, the molecular weight of the anhydrous acid has not been determined or inferred either from the cryoscopic method or from investigations on the capillarity or dielectric constants, although the tendency of hydroxyl compounds to exist in some polymeric state supports Hartley's view.

Knietzsch apparently regards sulphuric acid containing 96 per cent. H_2SO_4 as forming a kind of eutectic solution, but in the case of nitric acid of similar concentration we have considered the possibility of an initial formation of the compound $2HNO_3,N_2O_5$; unfortunately, the properties of nitric acid containing nitric anhydride in solution have not been investigated, doubtless owing to experimental difficulties.

As the methods which we adopted for the measurement of the several physical constants have been fully described in our previous publications, we only bring forward our unrecorded results.

Densities.

In the following table, the values are given for the densities (reduced to a vacuum) of nitric acid from 78 to 100 per cent. concentration at 4°/4°, 14·2°/4°, and 24·2°/4° respectively. Confirmatory determinations made at different times, and with different instruments, are omitted:

TABLE I.

Percentages.	Specific gravities.		
	4°/4°.	14·2°/4°.	24·2°/4°.
78·22	1·47129	1·45504	1·43964
79·14	—	1·46011	1·44372
79·59	1·47496	—	—
81·97	1·48391	1·46680	1·45092
84·90	1·49495	—	—
85·21	1·49581	—	—
85·80	—	1·47826	1·46224
87·55	1·50211	—	—
87·90	—	1·48491	1·46891
89·73	1·50898	1·49125	—
92·34	1·51804	1·49968	1·48264
94·04	1·51949	1·50149	1·48516
95·62	1·52192	1·50358	1·48677
96·64	1·52510	1·50632	1·48887
97·33	—	1·50911	1·49137
98·07	1·53212	1·51298	1·49543
99·97	1·54212	1·52236	1·50394

If the densities are plotted as ordinates and the percentages as abscissæ, the values from 78 to 92 per cent. are on a straight line (within the limits due to analytical errors), and the value for 100 per cent. is situated on the same straight line produced, but the values from 92 to 100 per cent. lie on a curve below the straight line, the point of greatest concavity being at 96 per cent. approximately.

This phenomenon, although not strictly comparable, is analogous to that observed for sulphuric acid by Pickering, Knietzsch, and others, in that in the former case the densities increase continuously but slightly, whilst in the latter these increase up to 96—97 per cent. and then decrease.

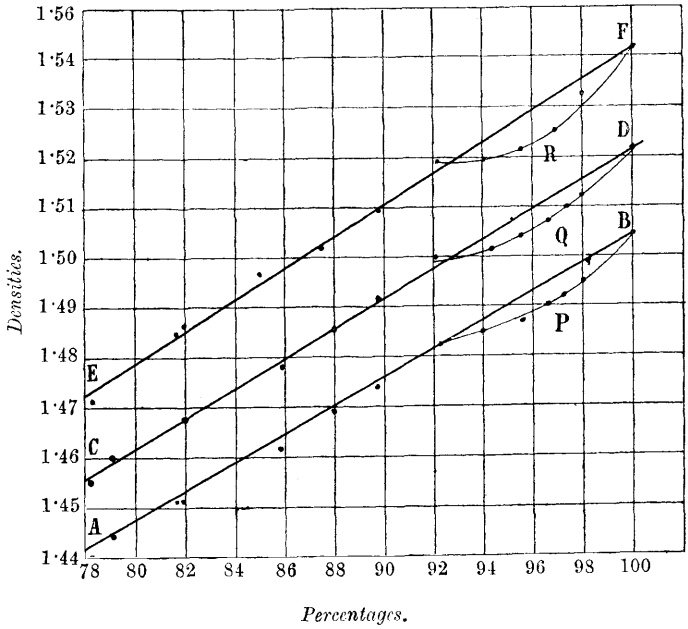
In Curve I (p. 1017), the values for 24·2°/4° are given along *APB*, for 14·2°/4° along *CQD* and 4°/4° along *ERF* respectively.

Contractions.

If the contractions are deduced from the densities and calculated from an equation

$$C_1 = C - a(\Delta p) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

wherein C_1 is the contraction to be calculated, C the contraction at the selected origin of coordinates, in these cases at 77·7 or 78·0 per cent. ($H_3NO_4 = 78{\cdot}02$ per cent. HNO_3), a, a constant, and Δp, difference of percentage, then, as shown in the three succeeding tables, the



CURVE I.

values for $C \times 10^{-5}$ from 78 to 92 per cent. are in accordance with those deduced from such an equation, within the limits of analytical errors. But from 92 to 100 per cent. the divergence is considerable and the maximum difference occurs at or about 96 per cent.

TABLE II.

Contractions at 4°.

C at 77·7 per cent. $= 4660$, $a = -205$.

Percentages.	Values found.	Values calculated.	Difference.
78·22	4528	4554	−26
79·59	4216	4272	−56
81·93	3803	3799	+4
85·21	3063	3120	−53
87·55	2642	2641	+1
89·73	2179	2193	−14
92·34	1658	1658	nil
94·04	1122	1310	−88
95·62	672	986	−314
96·64	438	777	−339
98·07	252	482	−232
99 97	8	8	nil

TABLE III.

Contractions at 14·2°.

C at 78 per cent. $= 4590$, $a = -208$.

Percentages.	Values found.	Values calculated.	Difference.
78·22	4553	4545	+8
79·14	4351	4353	−2
81·97	3709	3764	+55
85·86	2917	2969	−42
87·90	2500	2531	−31
89·73	2154	2150	+4
92·34	1626	1607	+19
94·04	1130	1255	−125
95·62	672	925	−253
96·67	448	713	−265
97·33	333	571	−238
98·07	247	415	−168
99·97	8	8	nil

TABLE IV.

Contractions at 24·2°.

C at 77·7 per cent. $= 4623$, $a = -195$.

Percentages.	Values found.	Values calculated.	Difference.
78·22	4503	4522	−19
79·14	4391	4339	+52
81·93	3797	3795	+2
85·80	3024	3040	−16
87·90	2633	2631	+2
92·34	1770	1766	+4
94·04	1314	1433	−119
95·62	849	1126	−277
96·64	596	927	−331
97·33	486	793	−307
98·07	419	648	−229
99·97	6	6	nil

Owing to the great differences in the values for the contractions, it is not convenient to illustrate the foregoing results by curves drawn on a sufficiently small scale.

Electrical Conductivity.

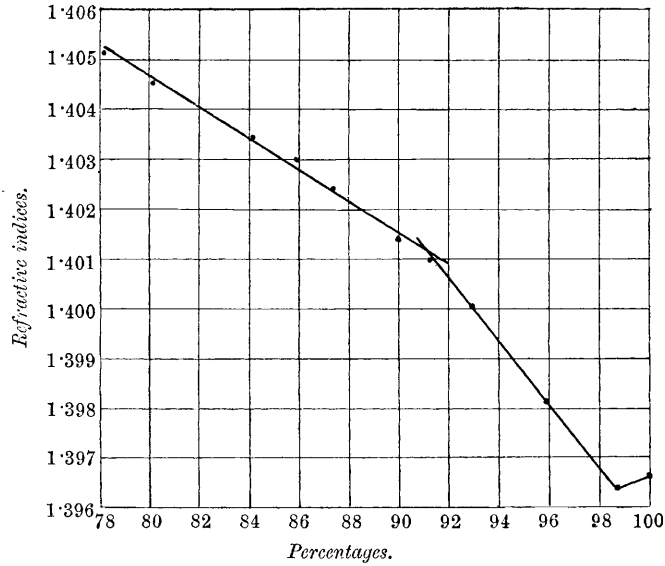
We have previously shown that nitric acid of about 96 per cent. concentration shows a minimum conductivity, and, moreover, at concentrations above 94 per cent. it behaves as a metallic, and not as an electrolytic, conductor in possessing negative temperature coefficients. As regards the former point, the observations of Knietzsch in the case of sulphuric acid are precisely analogous, but he does not appear to have studied the temperature coefficients of sulphuric acid either immediately below or above the limit of the anhydrous acid, H_2SO_4.

Refractive Indices.

If a curve is drawn having for coordinates the refractive indices (μ_{D14}) of nitric acid and the corresponding percentage compositions, the points which indicate concentrations of from 78 to 91 per cent. lie on a straight line, but the values from 91 to 98 per cent. are situated on another straight line, then from 98 to 100 per cent. there is a slight reversal, as in the case of the electrical conductivities (see Curve II, p. 1020). At present, the only observations on the refractive indices of concentrated sulphuric acid are those by van der Willigen (*Archives Musée Teyler*, 1868, **1**, 74), which are not carried beyond a con-

centration of 94·7 per cent. (approximately). We hope shortly to carry out an investigation on this subject.

It would thus appear from the above considerations that nitric acid containing about 96 per cent. anhydrous acid, like sulphuric acid of a similar concentration, forms a kind of eutectic solution (compare



CURVE II.

Knietzsch, *ibid.*), and adopting Hartley's hypothesis of an admixture or combination of orthonitric and nitric acids, such an acid would probably have the composition $3H_2N_2O_6,H_3NO_4$ (95·9 per cent. HNO_3). Determinations of the physical constants of nitric acid containing nitric anhydride in solution might throw further light on this point.

Chemical Properties.

It is a further point of interest to ascertain if there are certain substances on which nitric acid of the above-mentioned critical concentration is less reactive than more or less concentrated acids, just as the analogous sulphuric acid is less reactive on iron and steel. We understand that Hartley proposes to study the chemical properties of concentrated nitric acid more fully and precisely, with the view of ascertaining its constitution. To our previous observations on this subject, we now add the following: Nitric acid of approximately 100 per cent. concentration nitrated cotton directly without addition of sulphuric acid, and so far as qualitative experiments went, it appeared that cotton thus directly nitrated was as inflammable as ordinary gun-cotton. Difficulties were experienced in estimating the

proportion of nitrous acid (or nitrogen peroxide) by means of the *m*-phenylenediamine reaction, doubtless owing to some secondary reaction.

Summary.

Nitric acid of 96 per cent. and sulphuric acid of 98 per cent. concentration show definitely marked characteristics, analogous, although not in all cases strictly parallel, as regards certain properties, more especially density, contraction, and electrical conductivity; also in the case of the former, refractive indices, as investigated by ourselves, and in the case of the latter chemical reactivity, boiling point, vapour pressure, and, to a less degree, viscosity and capillarity, as investigated by Knietzsch.

The precise constitution of acids having these critical concentrations remains at present a matter for further inquiry.