502. *Cryoscopic Measurements in Sulphuric Acid. Part VI. The Solutes Nitronium Perchlorate and Ammonium Perchlorate. The Basicity of the Perchlorate Ion and the Acidity of Perchloric Acid. Notes on the Strengths of Some Oxy-acids.*

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Nitronium perchlorate and ammonium perchlorate in solvent sulphuric acid produce freezing-point depressions which show that the anion of these salts is largely solvolysed to free perchloric acid. Perchloric acid is thus a very weak acid in sulphuric acid. Its acidity constant is deduced, as well as the solvolysis constant of the perchlorate ion.

Disulphuric acid was shown to be an acid of medium strength in sulphuric acid (Part IV). Thus disulphuric acid, perchloric acid, and sulphuric acid form a widely spaced acidity series, similar to acetic acid, phenol, and water, though on a displaced scale. It might have been expected, on the basis of known rules concerning the strengths of inorganic oxy-acids, that disulphuric acid would prove to be a much stronger acid than perchloric acid. It is suggested that the stabilisation of oxy-anions, relatively to the acids, by mesomeric charge-distribution among oxygen atoms having partial double bonds, is a prime factor determining the strengths of oxy-acids.

(1) *The v-Factors of Nitronium and Ammonium Perchlorate.*—In an accompanying paper (*J.*, 1950, paper no. 505) Goddard, Hughes, and Ingold describe the preparation of a number of

crystalline nitronium salts. The first of these to be isolated in a pure state was nitronium perchlorate; and, when it was originally obtained, it was felt to be important to confirm that it had the expected ionic constitution. As regards the solid compound, the required evidence was provided by Dr. D. J. Millen by the method of Raman spectroscopy (*Nature*, 1946, **158**, 480; cf. *J.*, 1950, paper no. 509); and since then a complete X-ray analysis has been carried through by Professor E. G. Cox, Dr. G. A. Jeffery, and Mrs. M. R. Truter (*Nature*, 1948, **162**, 159). The author undertook to study the compound in solution in sulphuric acid, and in particular to ascertain whether, in such solutions, the solute is dissociated into its ions. The results were somewhat unexpected, and it therefore proved necessary to examine nitronium perchlorate and a well-known ionic perchlorate in parallel.

The first cryoscopic measurements on solutions of nitronium perchlorate in sulphuric acid revealed that this solute was producing approximately a three-fold, rather than a two-fold depression of the freezing point of the solvent. This suggested that, contrary to one's preconceptions, perchloric acid is so *weak* an acid that its salt was being nearly completely solvolysed.

In order to be certain that the observed effect was not a special property of the nitronium compound, but was really due to solvolysis of the perchlorate ion, some similar cryoscopic measurements were made with ammonium perchlorate as the solute. This salt also gave an approximately three-fold depression of the freezing point, in confirmation of the previous indication.

The incidental observation was made that dilute (say 0·05 molal) solutions of either nitronium perchlorate or ammonium perchlorate in sulphuric acid fume in ordinary air. This happens even when the solvent sulphuric acid has been pre-treated with a small amount (say 0·05 molal) of water, and so it cannot be due to an escape of sulphur trioxide from the solution. It is assumed to be due to the escape of perchloric acid, and thus to indicate the presence of the free acid in solution.

The freezing points of solutions of perchloric acid in sulphuric acid have been measured, though somewhat approximately, by Robles and Moles (*Anal. Fís. Quím.*, 1934, **32**, 474). They observed depressions corresponding to a normal molecular weight, and this is consistent with the conclusion that perchloric acid is ionised only to a very small extent in sulphuric acid.

On this evidence it is presumed that the reactions which take place on the dissolution of nitronium and ammonium perchlorates in sulphuric acid can be approximately represented as follows :

$$NClO_6 + H_2SO_4 = NO_2^+ + HClO_4 + HSO_4^-$$
$$NH_4ClO_4 + H_2SO_4 = NH_4^+ + HClO_4 + HSO_4^-$$
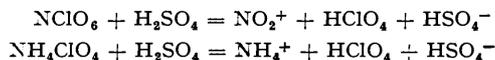
Accordingly, the ν-factors for each solute were calculated from the observed freezing-point depressions, using equation (5) of Part I, and substituting, in the first instance, $s_2 = 1$ and $\nu_2 = 3$ in the nearly-unit correction factor. This preliminary calculation made it obvious that the true ν-factors would prove to be a little less than 3.

The whole procedure was then refined by making allowance for the known disturbances. The first of these is ion solvation. It has been concluded already that nitronium and ammonium hydrogen sulphates have solvation numbers of approximately 2 and 1, respectively (cf. Parts I and III); and hence we should substitute $s_2 = 3$ in the case of nitronium perchlorate, and $s_2 = 2$ in that of ammonium perchlorate, instead of $s_2 = 1$, in the nearly-unit correction factor in equation (5) of Part I.

The second disturbance relates to the effect of the hydrogen sulphate ion, which is produced by the solvolysis of the perchlorates, first in repressing the ionisation of the pre-treatment water, and secondly in repressing the residual autoprotolysis of the solvent sulphuric acid. These effects make the apparent freezing-point depressions ($\Delta\theta$), given by the added perchlorate, too small. A correction for this was calculated by a method of cyclic approximation. Initially the solvolysis of the perchlorate ion was taken to be complete, and, using the autoprotolysis constant of sulphuric acid, and the data given in Part II for the degree of ionisation of water, an approximate correction to the observed freezing-point depression was calculated. From this, an approximate ν-factor was computed, which was then used in order to calculate a better approximation to the quantity of hydrogen sulphate ion which is formed by solvolysis of the perchlorate ion, and hence to calculate a better approximation to the correction to be applied to the observed freezing-point depressions. From the corrected depression ($\Delta\theta'$), an improved ν-factor was calculated using the appropriate form of equation (5) of Part I. The results of the measurements, and the final values of the ν-factors calculated from them, are in Table I.

TABLE I.

Freezing points of solutions of perchlorates in sulphuric acid.

Molality of salt (Δm_2).	F. p. (° c.).	Depressions.		v-Factor.	Molality of salt (Δm_2).	F. p. (° c.).	Depressions.		v-Factor.
		Obs. $\Delta\theta$.	Corr. $\Delta\theta$.				Obs. $\Delta\theta$.	Corr. $\Delta\theta$.	
Expt. No. 31.	Salt = NH_4ClO_4.		Molality of water (m_3) = 0·075.		Expt. No. 17.	Salt = NO_2ClO_4.		Molality of water (m_3) = 0·060.	
—	9·720	—	—	—	—	9·886	—	—	—
0·00696	9·598	0·122°	0·124°	2·96	0·00654	9·774	0·112°	0·115°	2·91
0·03055	9·189	0·531	0·544	2·95	0·01508	9·625	0·261	0·266	2·92
0·04526	8·939	0·781	0·800	2·93	0·02734	9·405	0·481	0·489	2·95
0·06405	8·611	1·109	1·133	2·93	0·03637	9·240	0·646	0·656	2·97
0·07907	8·349	1·371	1·397	2·93				Mean	2·94
0·08800	8·218	1·502	1·529	2·88					
			Mean	2·93					

(2) *The Solvolysis (or Basicity) Constant of the Perchlorate Ion.*—The result that the v-factors for nitronium and ammonium perchlorate are not exactly equal to 3 means that the chemical equations written above do not accurately represent the stoicheiometry of the processes which take place when the salts are dissolved in the solvent. It means, in short, that the solvolytic process

$$ClO_4^- + H_2SO_4 \rightleftharpoons HClO_4 + HSO_4^-$$
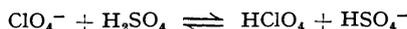
is appreciably incomplete.

We can employ the determined v-factors in order to compute the equilibrium constant for this solvolytic reaction—in other words, the constant which represents the basic strength of the perchlorate ion. The derived values are highly sensitive to experimental error, because they depend essentially on the small differences between v and 3; but the calcuation has been made, using the data for ammonium perchlorate, which are slightly better than those obtained for the nitronium salt. The results are given in Table II.

The solvolysis constant being defined by the equation

$$K_b(ClO_4^-) = [HClO_4][HSO_4^-]/[ClO_4^-]$$

with the concentration expressed in molalities, K_b has been computed from the cryoscopic results by means of the equation

$$K_b = \{(v-2)^2\Delta m_2 + (v-2)m_4\}/(3-v)$$

where Δm_2 is the molality of the salt, and m_4 is that of the hydrogen sulphate ion produced from the water with which the solvent was pre-treated. The concentration m_4 was computed from the data given in Part II for the degree of ionisation of water in sulphuric acid, due allowance being made for the effect of the presence of extraneous hydrogen sulphate ions, which in this case was that produced by solvolysis of the perchlorate ion; and the concentration of this hydrogen sulphate ion was calculated, with sufficient accuracy to provide a starting point for the calculation of m_4, simply from the concentration of added perchlorate and the observed v-factor.

TABLE II.

Solvolysis of ammonium perchlorate in sulphuric acid (Expt. 31).

Δm_2.	m_4.	v.	$K_b(ClO_4^-)$.	Δm_2.	m_4.	v.	$K_b(ClO_4^-)$.
0·00696	0·0720	2·96	1·88	0·06405	0·0689	2·93	1·70
0·03055	0·0703	2·95	2·08	0·07907	0·0687	2·93	1·87
0·04526	0·0697	2·93	1·62	0·08800	0·0682	2·88	1·04
						Mean	1·70

Adopting the value $K_b(ClO_4^-) = 1·7$ g.-mol. kg.$^{-1}$, and reversing the process of calculation, theoretical curves have been constructed for the depression of the freezing point of sulphuric acid by ammonium perchlorate. Such a curve, drawn for the case in which the solvent has been pre-treated with water in 0·075 molal concentration, is shown in Fig. 1, in association with the experimental points for nitronium and ammonium perchlorates.

(3) *The Acidity Constant of Perchloric Acid.*—From the value $K_b(ClO_4^-) = 1·7$ g.-mol. kg.$^{-1}$ for the solvolysis constant of the perchlorate ion, and the figure deduced in Part IV (*J.*, 1950, 2516) for the autoprotolysis constant of sulphuric acid, $K_{ap} = [H_3SO_4^+][HSO_4^-] =$

$1\cdot7 \times 10^{-4}$ g.-mol.^{2} kg.$^{-2}$, one can calculate the acid dissociation constant of perchloric acid in sulphuric acid. We have

$$K_a(\text{HClO}_4) = \frac{[\text{H}_3\text{SO}_4{}^+][\text{ClO}_4{}^-]}{[\text{HClO}_4]} = \frac{K_{ap}(\text{H}_2\text{SO}_4)}{K_b(\text{ClO}_4{}^-)} = 1\cdot0 \times 10^{-4} \text{ g.-mol. kg.}^{-1}$$

(4) *Note on the Acidities of Oxy-acids.*—In Parts II and IV (*J.*, 1950, 2493, 2516) the first dissociation constant of disulphuric acid was found to be $K_a(\text{H}_2\text{S}_2\text{O}_7) = 0\cdot020$ g.-mol. kg.$^{-1}$. The value now obtained for the dissociation constant of perchloric acid is $K_a(\text{HClO}_4) = 0\cdot00010$ g.-mol. kg.$^{-1}$. Thus, in sulphuric acid as solvent, disulphuric acid is a much stronger acid than is perchloric acid.

FIG. 1.

Theoretical curve ($\text{K}_b = 1\cdot7$) *for the depression of the freezing point of sulphuric acid by ionising perchlorates.*
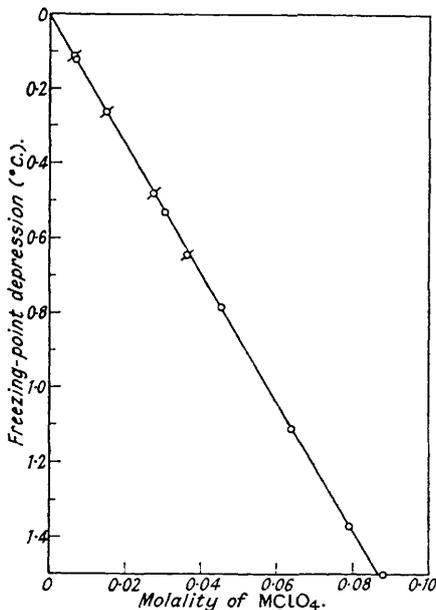
Experimental points for nitronium perchlorate -◯-.
         ,,   ,, *ammonium perchlorate* ◯.

Now although perchloric acid has long been regarded as the strongest known acid, it could have been deduced, from certain proposed relationships between the aqueous ionisation constants of inorganic oxy-acids, that disulphuric acid would be stronger. Kossiakoff and Harker (*J. Amer. Chem. Soc.*, 1938, **60**, 2047) calculated the aqueous ionisation constants of a number of inorganic oxy-acids on the basis of the assumption that all the acids possess single-bonded octet structures, and that differences of acidity can be attributed to differences of the electrostatic energy of removal of the proton from the acid to the surrounding water. This method has been criticised by Ricci (*ibid.*, 1948, **70**, 109), who has shown that the aqueous pK values of oxy-acids H_aXO_b, of any total charge, are given to the same order of accuracy, *viz.*, to about one pK unit, by the purely empirical equation, p$K = 8 - 9m + 4n$, where m is the formal positive charge on the central atom, X, and $n = b - a$ is the number of formal negative charges carried by the oxygen atoms, and the word " formal " means computed for the equal sharing of electron-duplets in single-bonded octet structures. He has applied this formula with similar success to complex acids, such as diphosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$, by treating the central group, POP in this case, as a " compound atom " X in the formula H_aXO_b. Pauling (" General Chemistry," Freeman, San Francisco, 1947, p. 394) has also given rules for the evaluation of approximate aqueous ionisation constants of inorganic oxy-acids $\text{XO}_n(\text{OH})_a$: the first rule states that successive ionisation constants, K_1, K_2, K_3 . . . stand in the ratio $1 : 10^{-5} : 10^{-10}$ . . . , and the second rule is that first ionisation constants are given approximately by the formula p$K_1 \sim 7 - 5n$.

Assuming that these rules and methods have a certain validity for very strong acids (for

which they cannot directly be tested), we may compute theoretical aqueous pK values for acids such as sulphuric and perchloric acids; and we may even include disulphuric acid in the treatment by adopting Ricci's device of regarding the central group, here SOS, as the compound atom X. The results of these calculations are in Table III.

TABLE III.

Calculated aqueous pK values of some strong acids.

Method.	H_2SO_4: pK_1.	$HClO_4$: pK.	$H_2S_2O_7$: pK_1.	pK_2.
Kossiakoff and Harker	−3·0	−7·3	—	—
Ricci	−2	−7	−12	−8
Pauling	−3	−8	−13	−8

Thus it appears that, so far as first ionisations are concerned, disulphuric acid, perchloric acid, and sulphuric acid form a widely-spaced series in order of decreasing acidity, comparable, though on a displaced scale, to the series acetic acid (pK 5), phenol, (pK 10), and water (pK 16). Perhaps, therefore, one should have expected that disulphuric acid would be a somewhat weak acid, and perchloric acid a very weak acid, in solvent sulphuric acid, just as acetic acid is a somewhat weak acid, and phenol a very weak acid, in solvent water. It does not seem to have been established (or even, as far as is known, suggested) before that disulphuric acid is in principle a much stronger acid than perchloric acid.

The structural basis of the methods of calculation mentioned above has previously received a certain amount of discussion. The electrostatic calculations of Kossiakoff and Harker were based on single-bonded octet structures. The parameters in Ricci's equation were related to the formal charges of octet structures, though it would be possible to give other structural meanings to the same quantities. Pauling stated that his second rule can be understood on the basis that the charge on the anion of the acid becomes more divided, and therefore less potent in attracting the hydrogen ion, the larger the value of n. However, this idea seems hardly consistent with his view (*op. cit.*, p. 163) that the most important of the structures of the oxy-acids are the octet structures, in which every single-bonded, non-hydroxyl, oxygen atom carries a formal negative charge.

Hunter, Phillips, and Sutton (*J.*, 1945, 146) have presented a strong case in favour of the view that, in compounds such as oxy-acids, the oxygen atoms, which in octet formulæ would be singly-bonded and have formal negative charges, are more correctly represented as doubly-bonded and without formal charges, as in classical chemical formulæ. It is possible with the aid of such doubly-bonded structures to understand how the oxy-acids fall into distinct groups with respect to their dissociation constants, as is illustrated in Table IV; for the larger the number of double bonds, the more the total charge can become distributed in the mesomeric anion, thus increasing its relative stability. In the Table, the recorded pK values are taken

TABLE IV.

Classification of aqueous ionisation constants of inorganic oxy-acids.

Group 1. X(OH)ₐ (very weak acids).	pK_1 (1).	pK_2 (1).	Group 2. XO(OH)ₐ (weak acids).	pK_1 (1/2).	pK_2 (2/3).
B(OH)₃	9·2	—	PO(OH)₃	2·1	7·2
Si(OH)₄	10·0	—	HPO(OH)₂	1·8	6·2
Ge(OH)₄	8·6	12·7	H₂PO(OH)	2·0	
As(OH)₃	9·2	—	AsO(OH)₃	2·3	7·0
Sb(OH)₃	11·0	—	NO(OH)	3·3	
Te(OH)₆	6·2, 8·8	10·4	SO(HO)₂	1·9	7·0
Cl(OH)	7·2		SeO(OH)₂	2·6	8·3
Br(OH)	8·7		TeO(OH)₂	2·7	8·0
I(OH)	11·0		ClO(OH)	2·0	
			IO(OH)₅	1·6	6·0

Group 3. XO₂(OH)ₐ (strong acids).	pK_1 (1/3).	pK_2 (1/2).	Group 4. XO₃(OH)ₐ (very strong acids).	pK_1 (1/4).
SO₂(OH)₂	—	1·9	ClO₃(OH)	—
SeO₂(OH)₂	—	2·0	MnO₃(OH)	—
IO₂(OH)	0·8			

from lists given by Ricci and Pauling, and, as an indication of the degree of distribution of the anionic charge, a figure is given, against each heading " pK," which is the value in electronic units of the charge carried by one oxygen atom.

Obviously factors other than charge distribution among atoms enter into the determination of pK values. The effect of the electronegativity of the central atom is clearly seen in a series such as $Cl(OH)$, $Br(OH)$, $I(OH)$, or $SO(OH)_2$, $SeO(OH)_2$, $TeO(OH)_2$. It is to induced electronegativity, *i.e.*, to the inductive effect of an acyl group introduced in place of hydrogen, that one attributes the greater strengths of poly-acids than of their parents, as is illustrated by the comparison of diphosphoric acid, $pK_1 = 0.9$, with phosphoric acid, $pK_1 = 2.1$, or of disulphuric acid with sulphuric acid as discussed above.

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