

28. *Relative Oxidation Potentials of Nitric Acid Solutions.*

By R. G. MONK and H. J. T. ELLINGHAM.

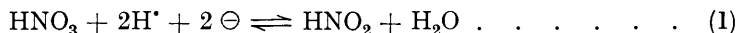
MEASUREMENTS of the *E.M.F.* of cells of the type Pt|HNO₃ solution|standard reference electrode, for nitric acid concentrations up to about 15*M* were made by Ihle (*Z. physikal. Chem.*, 1896, **19**, 577), and single potentials of the electrode system, Pt|HNO₃ solution, derived from his results (neglecting liquid-junction potential) have been quoted as representing the relative oxidising tendencies of nitric acid solutions of different concentrations. As Ihle showed qualitatively, however, these potentials are notably affected by additions of nitrite, and since no attempt was made to control or estimate the con-

centration of nitrous acid or other reducing substances in the various nitric acid solutions used, the observed "oxidation potentials" must have been affected to unknown and probably varied extents by traces of such substances which happened to be present in these solutions.

In later work on this type of electrode system, the concentration of reducing substances has been controlled by supplying nitric oxide to the electrode so as to establish the equilibrium $\text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O} \rightleftharpoons 3\text{HNO}_2$ (Abegg and Pick, *Z. anorg. Chem.*, 1906, **51**, 1; Moore, *J. Amer. Chem. Soc.*, 1913, **35**, 333; Klemenc and Hayek, *Z. anorg. Chem.*, 1930, **186**, 181; Bode, *ibid.*, 1931, **195**, 201). Such potential measurements have been confined, however, to concentrations up to about *M*-nitric acid; so also have investigations of this equilibrium by other methods (Lewis and Edgar, *J. Amer. Chem. Soc.*, 1911, **33**, 292; Abel and Schmid, *Z. physikal. Chem.*, 1928, **136**, 430). At higher concentrations, complications arise through the increasing importance of other equilibria, such as $\text{NO} + 2\text{HNO}_3 \rightleftharpoons 3\text{NO}_2 + \text{H}_2\text{O}$, which has been studied recently by Abel, Schmid, and Stein (*Z. Elektrochem.*, 1930, **36**, 692).

On the other hand, it is at higher concentrations that the oxidising properties of nitric acid become particularly strongly developed, and, owing to the importance of such solutions as oxidising systems, it seems very desirable to attempt to obtain at least some relative measure of their oxidising tendency. The present investigation has been undertaken with this object.

From the work of Ihle (*loc. cit.*) and from observations on the cathodic reduction of nitric acid solutions (Ellingham, J., 1932, 1565), there is good reason to believe that the electrode equilibrium



is readily established at an indifferent electrode in moderately concentrated nitric acid solutions containing nitrous acid, and that it may be the principal equilibrium controlling the electrode potential over wide ranges of concentration. If this is true, the single potential of such an electrode system with a specified nitric acid concentration at 25° will be given by :

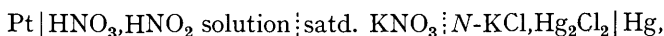
$$e = e_0' - 0.0296 \log [\text{HNO}_2] \quad . \quad . \quad . \quad (2)$$

where $[\text{HNO}_2]$ is the activity of nitrous acid in the solution, and e_0' a constant for the given nitric acid concentration, provided that the concentration of nitrous acid be kept sufficiently small compared with that of nitric acid, so that the activities of nitric acid and the hydrogen ion can be regarded as constant. For the general case where the nitric acid concentration is also varied,

$$e = e_0 + 0.0296 \log [\text{HNO}_3][\text{H}^+]^2/[\text{HNO}_2][\text{H}_2\text{O}] \quad . \quad . \quad . \quad (3)$$

where symbols in square brackets represent the activities of the corresponding substances in solution, and e_0 is a general constant—the standard electrode potential corresponding to the equilibrium (1). Owing to lack of information as to activities, especially of that of the hydrogen ion, in more concentrated nitric acid solutions, it is not possible to determine e_0 from values of e for solutions of known nitric acid and nitrous acid concentration by (3). If it be assumed, however, that the molar concentration of nitrous acid is a satisfactory measure of $[\text{HNO}_2]$ in nitric acid solutions containing very small proportions of nitrous acid, measurements of e for such solutions enable values of e_0' for various nitric acid concentrations to be calculated by (2). Values of e_0' obtained in this way should afford a relative measure of the oxidising tendency of nitric acid solutions of various concentrations.

Measurements have been made, therefore, of the *E.M.F.* of the cell



using nitric acid solutions of several different concentrations to which various small amounts of sodium nitrite had been added, the actual concentration of nitrous acid at equilibrium being determined analytically. The *E.M.F.* of this cell is taken as a measure of the single potential, e , of the electrode system, Pt | $\text{HNO}_3, \text{HNO}_2$ solution, with reference to the normal calomel electrode, and all values of e quoted below have this significance. Strictly, the

values of the *E.M.F.* should be corrected for liquid-junction potential in order to obtain e , since the use of saturated potassium nitrate solution as intermediate liquid is not likely to eliminate this factor completely, especially at higher nitric acid concentrations. There is, however, no means of determining the magnitude of the residual liquid-junction potential for these solutions, and uncorrected *E.M.F.* data have therefore been used throughout.

EXPERIMENTAL.

Solutions of accurately known nitric acid concentration (ranging from M to about $12M$) and of various approximately known nitrous acid concentrations (up to about $0.3M$) were prepared by running ice-cold sodium nitrite solution under a cooled nitric acid solution. The amount of nitric acid used (in the form of a standard solution) was that calculated to give the desired concentration of this acid when the solution was made up to a standard volume at 25° , due allowance having been made for that converted into sodium nitrate by reaction with the nitrite. After complete mixing had occurred, the solution was transferred to a thermostat and made up to the standard volume (50 c.c.) when its temperature had risen to 25° .

The sodium nitrite had been recrystallised from aqueous solution and dried over sulphuric acid in a vacuum. The nitric acid had been twice redistilled (once over potassium and silver nitrates).

Solutions prepared in this way were introduced into the electrode vessel, which consisted of a glass tube fitted with a ground-glass stopper through which was sealed a thin platinum wire. Welded to the end of this wire, so as to hang freely in the solution, was the electrode of stout platinum wire, the lower part of which was coiled into the form of a flat spiral. After each measurement, the electrode was washed, left for a short time in distilled water, and then heated to whiteness in the blowpipe flame. A bent capillary tube sealed to the bottom of the electrode vessel led to an intermediate vessel containing saturated potassium nitrate solution. The siphon tube of a normal calomel electrode dipped into a second intermediate vessel containing saturated potassium nitrate which communicated with the first by way of an **H**-tube, one limb of which was plugged with filter-paper.

The cell was set up in a thermostat at 25° , and its *E.M.F.* measured at intervals until constancy was attained. The time required for this decreases with increasing concentrations of both nitric and nitrous acids. In the more dilute nitric acid solutions, the effect of nitrous acid in catalysing the establishment of equilibrium (Ihle, *loc. cit.*) is very marked, and, if the nitrous acid concentration is also low, several hours may be required for the *E.M.F.* to become constant. In such cases, values of e were plotted against time in order to be able to follow the approach to equilibrium conditions. In the most dilute nitric acid solution employed ($1.045M$) the results became unreliable owing to uncertainty as to the establishment of true equilibrium. In the more concentrated solutions values of e were reproducible to about 1 millivolt.

Determination of Nitrous Acid by Means of Lead Peroxide.—The determination of small amounts of nitrous acid in relatively concentrated nitric acid solutions presents some difficulty, since standard analytical methods become inaccurate or inapplicable under these conditions. A method suitable for the present purpose was devised, however, by utilising the reaction $PbO_2 + HNO_2 + HNO_3 = Pb(NO_3)_2 + H_2O$. Lead peroxide was purified by boiling with 10% sodium hydroxide solution and then with dilute nitric acid. After being washed free from nitrate by distilled water, it was preserved under dilute nitric acid. Before use, the peroxide was filtered off and again washed in order to ensure removal of any traces of nitrate.

For the determination, excess of the wet peroxide was introduced into a conical flask and shaken into a suspension with a little water. The nitrous acid solution, diluted if necessary so that its nitric acid concentration was less than $6M$, was run in and kept for 10 minutes with occasional shaking. The residual peroxide was then filtered off on a sintered-glass filter and washed thoroughly with distilled water. The lead in the filtrate and washings was determined gravimetrically as sulphate.

In order to test the reproducibility of the method, samples of approximately $6M$ -nitric acid to which various small amounts of nitrite had been added were kept for 2 hours with occasional shaking, and 25 c.c. portions of each sample were then allowed to react with the peroxide under the above conditions. For one such sample the weights of lead sulphate obtained from the several portions were respectively 0.0634, 0.0631, 0.0638, and 0.0631 g.; giving a nitrous acid concentration of $0.0083_5 M$ with a probable error of about 0.5%. Over the range of nitrous acid concentration used, the probable error of the determination estimated in this way is of the order of 1%. Blank determinations on nitric acid solutions (up to $6M$)

which had been freed as far as possible from nitrous acid gave up to 0.8 mg. of lead sulphate per 25 c.c., which corresponds to 0.0001M-nitrous acid. Since, according to relation (2) above, an error as great as 8% in the nitrous acid concentration represents an error of only 1 millivolt in the electrode potential, the accuracy of the analytical method is adequate for the present purpose.

Results.—The observed values of e are shown plotted against $\log c_{\text{HNO}_2}$ in the accompanying figure, where c_{HNO_2} denotes concentration of nitrous acid in g.-mol. per litre. Each line on this diagram refers to the concentration of nitric acid specified below it. In each case the line is drawn with the theoretical slope of 0.0296, and in the position which best represents the points corresponding with the lower concentrations of nitrous acid.

It will be seen that, for values of $\log c_{\text{HNO}_2}$ between 3.5 and about 1.0, the values of e for each concentration of nitric acid vary closely in accordance with the relation

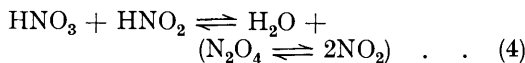
$$e = e_0' - 0.0296 \log c_{\text{HNO}_2} \quad (2a)$$

Values of e_0' obtained by extrapolation of the lines are as follows :

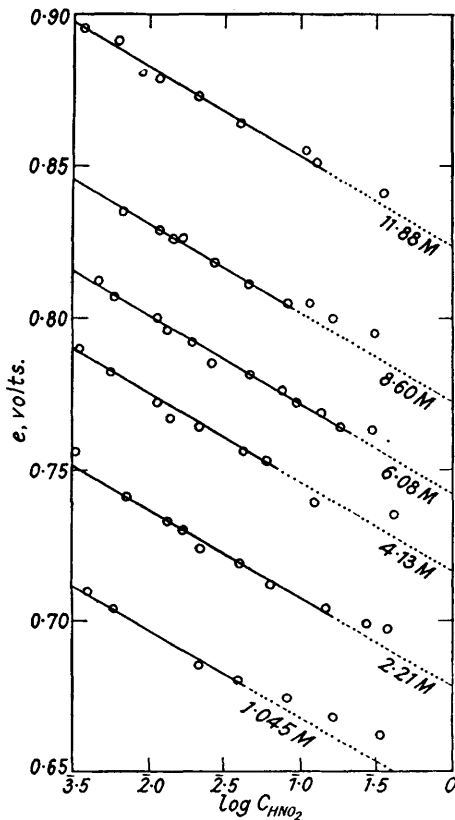
HNO ₃ , g.-mols. per l.....	11.88	8.60	6.08	4.13	2.21	1.045
e_0' , volt	0.824	0.772	0.742	0.716	0.678	0.638

DISCUSSION.

In obtaining the values of e_0' recorded above, it is assumed that the electrode potential is determined by the equilibrium (1). Other electromotively active reducing substances besides nitrous acid are probably present at appreciable concentrations in the solutions, but in so far as they are in true equilibrium with nitric and nitrous acids their presence will not affect the validity of relations (2) and (3). On the other hand, if such substances affect the accuracy of the analytical determination of nitrous acid, the interpretation of the experimental results in terms of these relations becomes more difficult. Actually, the only substances likely to produce an appreciable effect of this kind are nitrogen trioxide and peroxide, the latter existing in the solutions in accordance with the equilibria



It can be shown, however, that for solutions of specified nitric acid concentration, the error in the determination of nitrous acid due to the reaction $2\text{NO}_2 + \text{PbO}_2 = \text{Pb}(\text{NO}_3)_2$ will cause a deviation of $0.0296/\sqrt{1 + kc_{\text{HNO}_3}}$ from the theoretical slope of the e - $\log c_{\text{HNO}_2}$ line, where c_{HNO_3} is the apparent nitrous acid concentration corresponding to the weight of lead sulphate obtained, and k is a constant which involves the equilibrium constants of (4) and the ratio $[\text{HNO}_3]/[\text{H}_2\text{O}]$ for the given nitric acid solution. This deviation evidently decreases with increase in c_{HNO_3} . Actually, however, the experimental points agree closely with the theoretical slope



of the e - $\log c_{\text{HNO}_2}$ lines over a considerable range extending to the lowest values of c_{HNO_2} investigated. It would seem, therefore, that any deviation due to this cause must occur in the region of still lower values of c_{HNO_2} . On the other hand, the presence of nitrogen trioxide in equilibrium with nitrous acid will cause a deviation which

increases with c_{HNO_2} , and is probably partly responsible for the deviations actually observed at higher values of c_{HNO_2} . Nevertheless, although the presence of nitrogen peroxide and trioxide may not cause any deviation from the theoretical slope of the lines in the lower part of the concentration range investigated, it may, of course, affect the positions of these lines and hence the values of e_0' . Hence, values of e_0' may not be true oxidation-reduction potentials for the simple system nitric-nitrous acid. They should, however, afford a relative measure of the oxidising tendencies of nitric acid solutions of various concentrations with respect to reactions in which nitric acid is reduced to nitrous acid and such concentrations of nitrogen peroxide and trioxide as may exist in equilibrium with it. Values of e_0' are therefore referred to as *relative oxidation potentials* of the nitric acid solutions.

The actual deviations of the $e-\log c_{\text{HNO}_2}$ lines from the rectilinear form at high values of c_{HNO_2} are attributed partly to the presence of nitrogen trioxide and partly to divergencies between the molar concentration and activity of nitrous acid, which must be expected to become notable in this range, especially since such solutions also contain considerable amounts of sodium nitrate (derived from the nitrite added) which may affect the activities of both nitric and nitrous acids.

As regards the variation of the relative oxidation potential, e_0' , with the molar concentration of nitric acid, c_{HNO_3} , the graph of e_0' against $\log c_{\text{HNO}_3}$ gives a line which is definitely curved, e_0' increasing more rapidly with $\log c_{\text{HNO}_3}$ at higher values of the latter. A much less notable curvature is obtained if e_0' is plotted against $\log p_{\text{HNO}_3}$, where p_{HNO_3} is the partial pressure of nitric acid over solutions of the various nitric acid concentrations, a quantity which should be proportional to the activity of the acid in these solutions. The curvature disappears entirely if $e_0' + 0.0296 \log [\text{H}_2\text{O}]$ be plotted against $\log p_{\text{HNO}_3}$, where $[\text{H}_2\text{O}]$, the activity of water in the solutions, is measured by the ratio of the partial pressure of water, $p_{\text{H}_2\text{O}}$, over solutions of the various nitric acid concentrations to that over pure water at the same temperature. Using data for p_{HNO_3} and $p_{\text{H}_2\text{O}}$ obtained by Taylor at 25° (*Ind. Eng. Chem.*, 1925, 17, 633) and by Klemenc and Nagel at 12.5° and 30° (*Z. anorg. Chem.*, 1926, 155, 257), the latter being graphically interpolated to give values at 25°, the empirical relation

$$e_0' + 0.0296 \log [\text{H}_2\text{O}] = 0.817 + 0.064 \log p_{\text{HNO}_3}$$

is found to be obeyed within the limits of probable error over the whole concentration range of nitric acid solutions investigated. The accompanying table shows this for round concentrations of nitric acid at 25°, the values of e_0' being obtained by interpolation from the $e_0'-\log c_{\text{HNO}_3}$ curve.

HNO_3 , g.-mol./l.	e_0' (volt).		$\log p_{\text{HNO}_3}$.	$\log p_{\text{H}_2\text{O}}$.	$y = e_0' +$ $0.0296 \log [\text{H}_2\text{O}]$.	$y -$ $0.064 \log p_{\text{HNO}_3}$.
2	0.673	K	- 2.27	1.33	0.672	0.818
4	0.714	K	- 1.63	1.28	0.711	0.815
6	0.741	K	- 1.27	1.22	0.736	0.817
8	0.765	{ K	- 0.95	1.12	0.758	0.819
		{ T	- 0.91	1.17	0.759	0.820
10	0.789	{ K	- 0.56	1.01	0.778	0.814
		{ T	- 0.49	1.05	0.779	0.815
12	0.826	{ K	- 0.05	0.86	0.811	0.814
		{ T	- 0.14	0.93	0.813	0.822
						Mean 0.817

T = Taylor; K = Klemenc and Nagel.

The general form of this empirical relation is compatible with the theoretical expression

$$e_0' + 0.0296 \log [\text{H}_2\text{O}] = e_0 + 0.0296 \log [\text{HNO}_3][\text{H}']^2$$

obtained by eliminating $[\text{HNO}_2]$ from relations (2) and (3). Beyond this, it is not possible to go at present owing to lack of knowledge regarding liquid-junction potentials, the activity of the hydrogen ion in the more concentrated nitric acid solutions, and possible effects of nitrogen peroxide and trioxide on the relative oxidation potential. It may be noted, however, that the value $+ 0.649$ of e_0' for 1.29*M*-nitric acid, in which, according to the data of Lewis and Randall ("Thermodynamics," 1923, p. 567) and Abel, Redlich, and Lengyel

(*Z. physikal. Chem.*, 1928, **132**, 189), the stoichiometric activity of nitric acid should be practically unity, corresponds very closely with the value $+0.93_5$ on the hydrogen scale ($+0.65_2$ against the normal calomel electrode) calculated by Pick (*Z. Elektrochem.*, 1920, **26**, 182) for the standard potential of the equilibrium $\text{NO}_3' + 3\text{H}' + 2\ominus \rightleftharpoons \text{H}_2\text{O} + \text{HNO}_2$, which is identical with equilibrium (1) in respect of activity relations.

From the values of e_0' obtained above, it appears that the nitric acid solutions used by Ihle for his potential measurements (*loc. cit.*) contained 10^{-4} to 4×10^{-3} g.-mol. of nitrous acid or equivalent reducing substance per litre, whereas the specially treated solutions used by one of us (*loc. cit.*) for cathode-potential measurements contained only about 10^{-5} g.-mol. per litre.

IMPERIAL COLLEGE, LONDON, S.W. 7.

[Received, December 17th, 1934.]
