153. *Kinetics of Nitrous Gas Absorption in Aqueous Nitric Acid.*

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Measurements have been made in a falling-film tower on the rate of reaction of nitrous gas with aqueous nitric acid of concentration 10—60%. Both gas and acid were circulated in closed systems, and the rate of absorption or evolution of nitrogen dioxide was determined by measurement of the rate of change of colour intensity of the circulating gas.

It was found that the absorption or evolution rate per unit area of interface could be expressed by the equation

$$V = k_a \{[N_2O_4] - C[N_2O_4]^{\frac{1}{4}}[NO]^{\frac{1}{2}}\}$$

Here $[N_2O_4]$ and [NO] refer to the concentrations in the gaseous phase and C is a constant which can be calculated from the known equilibrium constant of the reaction. The equation expresses fairly closely the measured velocity over a wide range of gas compositions and in both directions of the reaction, which is reversible.

The overall reaction in question is expressed by the equation $3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO$. The theoretical derivation of the above expression is based on the assumption that the actual rate-limiting step is the elementary reaction $N_2O_4 + H_2O \rightleftharpoons HNO_3 + HNO_2$. An alternative treatment, based on the assumption that the diffusional processes are rate-limiting, has given less satisfactory results.

Increase of acid concentration greatly increases the value of the constant C. It follows that the rate of absorption of nitrogen dioxide is much reduced at high acid concentrations (*e.g.*, over 40%), owing to the intrinsic reversibility of the reaction.

Increase in temperature causes a considerable decrease in the rate of absorption of dioxide. This is partly due to changes in the values of k_a and C, but is mainly a result of a shift in the equilibrium between NO_2 and N_2O_4. It appears that it is the latter which is the more reactive species in the total dioxide. The present results do not allow of any final conclusions with regard to a possible effect of gas-flow rate on the coefficient k_a. The application of the results to the design of nitric acid plants will be discussed elsewhere.

The reaction of nitrogen dioxide with water proceeds mainly according to the following stoicheiometric relation :

$$3NO_2 \text{ (or } 1\tfrac{1}{2}\ N_2O_4) + H_2O \rightleftharpoons 2HNO_3 + NO \quad . \ . \ . \ . \ . \ . \quad \text{(A)}$$

A certain amount of nitrous acid is also formed, but the quantity is generally quite small under conditions of efficient agitation of the liquid phase, as in a falling-film tower. The kinetics of the process may be expected to be somewhat complex, owing to the high degree of reversibility of the reaction (A) and also to the large number of molecular species which can take part in the various elementary reactions. These are NO_2, N_2O_4, NO, N_2O_3, H_2O, HNO_3, and HNO_2. Moreover, the observed absorption rate might be controlled either by chemical reaction or by diffusional processes. Under plant conditions, additional complications arise from the variations in conditions from one section of plant to another and also from the occurrence of the oxidation reaction

$$2NO + O_2 \longrightarrow 2NO_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (B)$$

The overall performance of a nitrous gas absorption plant is determined by the rate of both the reactions (A) and (B). Detailed kinetic information is available, however, only for the latter reaction, which has been studied extensively by Bodenstein and others. The only exact research on the rate of the absorption reaction is that of Chambers and Sherwood (*Ind. Eng. Chem.*, 1937, **29**, 1415). These workers investigated the effect of acid concentration and gas-flow rate at an almost constant gas composition. It was concluded that the rate of absorption was dependent on the speed of diffusion through a film of stagnant gas and mist at the interface.

The experimental work described below was carried out in 1937, before the publication of Chambers and Sherwood's work. The object was primarily to determine the effect on the absorption rate of (*a*) the composition of the gaseous phase, (*b*) the concentration of the acid, and (*c*) the temperature. These are the variables which are probably the most important in plant practice. The possible effects of gas and acid flow rates were given only a cursory examination and the values of these variables were generally kept at approximately the values which are realised in an absorption plant operating at atmospheric pressure.

The work has thus given values for the absorption rate under various conditions which are of technical interest and has been made a basis of the successful design of certain war-time nitric acid plants, as will be shown in a later paper. The results have also given some indications of the possible mechanism of the absorption process.

EXPERIMENTAL.

(a) *General Description of Method.*—The experimental method consisted in the circulation of a nitrous gas–nitrogen mixture round a closed system which contained a small falling-film tower. The concentration of nitrogen dioxide in the gaseous phase was determined by measurement of the colour intensity of the circulating gas by use of a photoelectric cell. Measurements of the colour intensity, and also of the total pressure of the circulating gas, were made at 30-second intervals during the course of the absorption and from these data, and the known equilibrium constants, the concentrations of each of the species NO_2, N_2O_4, NO, and N_2O_3 could be evaluated. The velocities were then obtained by taking tangents to the concentration curves.

The advantage of this method was that, since the gas composition changed during the course of each run, data were thus obtained on the effect on absorption rate of a much larger range of gas compositions than could otherwise have been examined. The acid was also circulated. Its concentration did not alter greatly during the course of each run.

The main items of the apparatus (Fig. 1) were as follows: absorption tower, *a*; electromagnetic pump, *b*, for acid circulation; blower, *c*, for gas circulation; gas reservoir, *d*; manometer, *e*; colour chamber, *f*; lamp, *g*; photocell, *h*; gas flow-meter, *j*; acid flow-meter, *k*; acid reservoir, *l*. The NO_2 and NO preparation apparatus, the vacuum system, and the potentiometer circuit, used in conjunction with the photocell, are not shown in the diagram. In the manometer (*e*), the mercury was protected from attack by a $\frac{1}{2}$ in. layer of α-bromonaphthalene.

(b) *Details of Gas and Acid Circulation.*—The falling-film tower was of $1\frac{1}{4}$ in. internal diameter and about 5 in. long. The absorption surface, computed from the dimensions, included the surface of the acid in the weir and in the foot of the tower.

The volume of the gas circulation system was 6·72 l., of which 0·51 l. was outside the thermostat. The gas-flow rate was generally of the order of 10—13 l./min. and was sufficient to give turbulent (or at least eddying) conditions in the absorption tower, as indicated in preliminary experiments with smoke.

The blower *c* (designed by Mr. R. A. Smith) was constructed of stainless steel and had a centrifrugal liquid seal surrounding the driving shaft, in order to prevent air leakage into the apparatus when the pressure was below atmospheric. This seal consisted of a disc *m* which was mounted on the shaft and rotated above a bath of liquid housed over the impellor casing. Round the periphery of the disc there was a wide flange which dipped into the liquid; the high speed of rotation (4000 r.p.m.) and the friction of the flange caused the liquid in the seal to be raised into a vertical ring; this sealed the periphery of the disc against the housing and very effectively prevented any leakage even at pressures as low as half an atmosphere.

Much difficulty was experienced in finding a suitable liquid for this seal, on account of the tendency of the nitrous gas to be transmitted through the liquid to the external atmosphere, by solution. Mercury was finally chosen, although it suffered from the disadvantage of reacting with the nitrous gas in the blower until the surface of the mercury had become covered with corrosion product.

(c) *Measurement of the Nitrogen Dioxide Concentration.*—Of the gases present in the apparatus only the dioxide had appreciable absorption for light of wave-lengths within the range of sensitivity of the photocell. The determination of the colour intensity thus gave an instantaneous measure of the concentration of this oxide.

The current from the photocell, which was of the rectifier type, was passed through an external resistance, and the potential difference across this resistance was measured by use of a potentiometer. The illumination was by means of a 24-watt motor-car lamp operating on two 12-volt accumulators in parallel. The discharge of the accumulators caused a slow and steady fall in the zero reading of the photocell and it was necessary to allow for this in each absorption run.

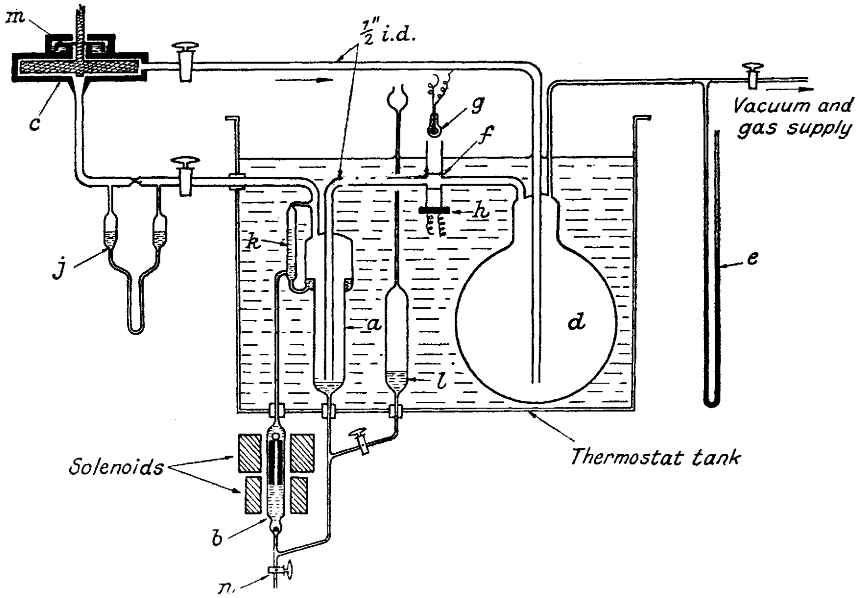
The photoelectric equipment was calibrated against measured pressures of nitrogen dioxide in the apparatus before each run, and the function log E/E_0 was plotted against p_{NO_2}. Here E_0 is the P.D. at zero dioxide pressure and E is the potential difference at partial pressure p_{NO_2}. This calibration was found to vary very little from day to day and was also found to be unaffected by the vibration of the blower.

(d) *Details of Experimental Procedure.*—Nitrogen dioxide, prepared by heating lead nitrate, was dried, liquefied, and fractionated to constant vapour pressure.

In carrying out an absorption experiment the blower, whilst running, was first blown through with nitrogen. The rest of the apparatus was evacuated, and dioxide was then admitted in small batches, and at each batch the photocell reading was calibrated against the measured pressure. Finally, a measured quantity of nitrogen was admitted as a diluent, and the gas was put into circulation by means of the blower. Then, when conditions were steady, the acid was introduced from the reservoir, *l*, and the electro-magnetic pump was set into operation. Complete wetting of the tower was attained within 5—10 seconds. An electrical device was caused to sound a bell at 30-second intervals throughout the run, and at these moments simultaneous readings were taken on the manometer and potentiometer. The readings were continued for 10—20 minutes, by which time they had become constant, the acid and gas having come to equilibrium. Finally, the acid was released from the apparatus through tap *n* (and was subsequently analysed for HNO_3 and HNO_2) and the nitrous gas was purged out of the apparatus with air, in order to obtain a check on the zero of the photoelectric equipment.

FIG. 1.

Diagram of Apparatus.



In a few experiments the reaction was carried out in the reverse direction, by using an initial gas consisting of nitric oxide in nitrogen. In these runs it was the rate of *evolution* of nitrogen peroxide which was measured.

(e) *Treatment of Experimental Results.*—The photocell readings were used to calculate directly the instantaneous values of the NO_2 concentration in the circulating gas. Since the NO_2–N_2O_4 equilibrium is set up extremely rapidly (Selle, *Z. physikal. Chem.*, 1923, **104**, 1) the corresponding N_2O_4 concentrations could be calculated by use of the Bodenstein equilibrium constant (*ibid.*, 1922, **100**, 75). The total concentration, $[NO_2] + 2[N_2O_4]$, was thus known throughout the run. (A small correction for the presence of very low concentrations of N_2O_3 was applied.) Then, knowing the volume of the apparatus and the area of absorbing acid surface, it was possible to obtain the rate of absorption (or evolution) of total dioxide per unit surface, by taking chords between the successive measured points on the concentration curve. The method was thus only dependent on the accuracy of the photocell readings ($\pm$ 0·001 ats. partial pressure of NO_2) and on the calculation of the equilibrium concentration of N_2O_4.

The other molecular species present in the gaseous phase at any moment were N_2, N_2O_3, NO, and HNO_3, and H_2O vapour. (The vapour pressure of HNO_2 was neglected as it is very small; Abel, *Monatsh.*, 1929, **54**, 855; *Z. physikal. Chem.*, 1928, **136**, 430.) Approximate values for the H_2O and HNO_3 partial pressures were estimated at each moment of the run from the data of subsidiary experiments in which the rate of vaporisation of acid of various concentrations was measured in the falling-film tower. The value of the nitrogen partial pressure was known, being equal to that which was introduced into the apparatus at the beginning of the experiment. The sum, S, of the NO and N_2O_3 concentrations was then obtained by difference, and the individual values of these concentrations were then calculated by solving the two equations, $[NO] + [N_2O_3] = S$ and $[N_2O_3] = K'[NO][NO_2]$, where K' is Abel and Proisl's equilibrium constant (*Z. Electrochem.*, 1929, **35**, 712).

The main sources of inaccuracies in the results were as follows. (1) The gas flow-rate was rather variable and tended to decrease during the course of a run. (2) There was an uncertainty in the temperature amounting to ± 2°, owing to the blower's being outside the thermostat tank. (However, the absorption rate was not found to be very dependent on temperature.) (3) The area of absorbing surface in the falling-film tower was indefinite to the extent of 2—3%. (4) There was an uncertainty of ± 1 second in the taking of the potentiometer and pressure readings at the desired moment. (5) The mercury in the blower seal reacted with nitrogen dioxide and at an appreciable rate, at least until the mercury had become covered with corrosion product. (The course of the reaction was tested by experiment, as there is some controversy in the literature, and it was found to be $2NO_2 + Hg = HgNO_3 + NO$.) In each run the acid was not admitted to the absorption tower until the reaction with the mercury had become relatively slow.

It is evident that there were appreciable inaccuracies, probably not exceeding 10%, due to the difficulties of the technique. A summary of the results obtained in the most satisfactory runs is given in Tables I, II, and III. In these tables col. 2 gives the time in minutes from the moment the acid

TABLE I.

Rate of dioxide absorption at 25°, (kg.-moles NO_2/m^2. sec.) × 10^6.

(I.A. and F.A. are initial and final acids, respectively, in %HNO_3 and %HNO_2; G.R. = gas rate, l./min.; A.R. = acid rate, c.c./min.)

Details.	Time, mins.	Concns., g.-moles/l. × 10^3. NO_2.	NO.	Abs. rate.	Acid concn., %.	$k_g \times 10^3$, Eq. (3).	$k_a \times 10^2$, Eq. (4).	$k_a \times 10^2$, Eq. (7).
	0·0	4·2	3·7	—	9·5	—	—	—
I.A. 9·5%, 0·0%	0·5	3·6	3·5	36	10·1	3·6	1·7	1·7
F.A. 11·8%, 0·85%	1·0	3·0	3·4	28	10·6	3·8	1·9	1·9
G.R. 12	1·5	2·6	3·3	22	10·9	3·8	1·9	1·9
A.R. 310	3·0	1·6	3·2	10	11·4	3·4	2·3	2·3
	4·0	1·2	3·3	5	11·6	2·5	2·0	2·0
	0·0	7·6	4·9	—	9·5	—	—	—
I.A. 9·5%, 0·0%	0·5	6·0	5·2	100	12·0	4·3	1·7	1·7
F.A. 16·5%, 1·3%	1·0	5·1	5·4	65	13·0	3·7	1·6	1·6
G.R. 10	2·0	3·9	5·8	32	14·4	2·9	1·3	1·3
A.R. 310	3·0	3·1	6·3	20	15·1	2·6	1·3	1·3
	4·0	2·5	6·9	13	15·5	2·4	1·3	1·3
	6·0	1·6	7·8	6	16·0	2·1	1·4	1·4
	0·0	6·9	4·0	—	9·3	—	—	—
I.A. 9·3%, 0·0%	1·0	4·5	5·0	70	12·2	4·9	2·1	2·1
F.A. 15·3%, 1·3%	1·5	3·7	5·3	47	13·1	4·6	2·1	2·1
G.R. 0—2·8 mins., 10; from 2·8 mins. on, 8	2·0	3·05	5·7	33	13·7	4·4	2·1	2·1
	2·5	2·5	6·1	22	14·1	4·1	2·1	2·1
A.R. 680	3·0	2·1	6·3	15	14·5	3·7	2·0	2·0
	4·0	1·55	6·8	8	14·9	2·9	2·0	2·0
	0·0	6·7	2·5	—	14·7	—	—	—
I.A. 14·7%, 1·2%	0·5	5·4	4·0	90	16·4	4·7	1·8	1·8
F.A. 20·4%, 1·1%	1·0	4·6	4·6	58	17·4	3·9	1·7	1·7
G.R. 10	1·5	3·8	5·3	42	18·2	3·9	1·7	1·7
A.R. 0—3 mins., 650; from 3 mins. on, 790	2·0	3·4	5·8	31	18·6	3·4	1·6	1·6
	3·0	2·5	6·7	19	19·3	3·5	1·8	1·8
	4·0	1·8	7·5	11	19·7	3·2	2·0	2·1
	0·0	5·5	1·4	—	44·3	—	—	—
I.A. 44·3%, 0·0%	1·5	3·9	2·9	27	44·7	—	—	1·3
F.A. 45·1%, *ca.* 0·6%	2·0	3·4	3·2	22	44·8	—	—	1·4
G.R. 5	3·0	2·8	3·7	13	44·9	—	—	1·4
A.R. 310	5·0	2·05	4·4	5	45·0	—	—	1·5
	12·0	1·4	5·0	0	45·1	—	—	—
	18·0	1·4	5·0	0	45·1	—	—	—
	0·0	7·9	7·1	—	44·3	—	—	—
I.A. 44·3%, 0·0%	2·0	4·9	10·2	47	45·6	—	—	1·5
F.A. 46·4%, *ca.* 1·2%	3·0	4·0	11·2	26	45·9	—	—	1·4
G.R. 9	4·0	3·4	11·7	16	46·1	—	—	1·4
A.R. 310	16·0	2·2	13·1	0	46·4	—	—	—

Table II.

Dioxide absorption at 40°. (Units, etc., as in Table I.)

Details.	Time, mins.	Concns., NO_2.	NO.	Abs. rate.	Acid concn., %.	$k_g \times 10^3$, Eq. (3).	$k_a \times 10^2$, Eq. (4).	$k_e \times 10^2$, Eq. (7).
	0·0	4·5	1·8	—	9·6	—	—	—
I.A. 9·6%, 0·0%	0·5	3·9	1·6	17	9·8	2·7	2·0	2·0
F.A. 11·1%, 0·3%	1·0	3·5	1·6	13	10·0	2·4	1·9	1·9
G.R. —	1·5	3·1	1·6	10	10·2	2·1	1·9	1·9
A.R. 310	2·0	2·7	1·6	9	10·4	2·4	2·1	2·1
	0·0	6·5	7·0	—	9·5	—	—	—
I.A. 9·5%, 0·0%	0·5	5·45	6·8	35	9·9	3·4	2·1	2·1
F.A. 11·5%, 0·8%	1·0	4·65	6·5	27	10·2	3·3	2·2	2·2
G.R. 11	2·0	3·35	6·6	14	10·6	2·7	2·2	2·2
A.R. 0—1·75 mins., 310;	2·5	2·95	6·8	11	10·8	2·6	2·2	2·2
from 1·75 mins. on, 220	3·0	2·65	6·9	9	10·9	2·4	2·2	2·2
	4·0	2·1	7·1	5	11·1	1·8	2·0	2·0
	0·0	8·7	8·2	—	9·5	—	—	—
I.A. 9·5%, 0·0%	0·5	7·3	8·0	57	10·2	3·6	1·9	1·9
F.A. 13·2%, 0·9%	1·0	6·1	8·0	44	10·9	3·6	2·1	2·1
G.R. 11	1·5	5·1	8·3	33	11·4	3·5	2·3	2·3
A.R. 310	2·0	4·2	8·6	25	11·7	3·6	2·5	2·5
	3·0	2·9	9·4	14	12·3	3·3	2·9	2·9
	4·0	2·15	10·1	8	12·5	2·9	3·1	3·2
	0·0	6·6	5·3	—	30·1	—	—	—
I.A. 30·1%, 0·0%	0·5	5·5	5·0	42	30·4	4·0	2·5	2·6
F.A. 31·9%, 0·5%	1·0	4·6	5·3	30	30·7	3·8	2·5	2·8
G.R. 12	1·5	3·9	5·6	23	31·0	3·6	2·7	3·0
A.R. 310	2·0	3·3	5·8	18	31·2	3·5	2·9	3·4
	3·0	2·4	6·2	10	31·4	3·1	3·1	4·0
	0·0	9·9	7·0	—	30·1	—	—	—
I.A. 30·1%, 0·0%	0·5	8·2	7·6	75	30·8	4·0	2·0	2·1
F.A. 33·6%, 0·7%	1·0	6·9	8·1	52	31·3	3·6	2·0	2·1
G.R. 11	1·5	5·9	8·5	42	31·7	3·6	2·1	2·3
A.R. 310	2·0	5·2	8·9	33	32·0	3·4	2·2	2·4
	3·0	3·9	9·5	20	32·5	3·1	2·3	2·9
	4·0	3·0	10·0	12	32·9	2·7	2·4	3·4
	0·0	9·6	6·7	—	37·1	—	—	—
I.A. 37·1%, 0·0%	0·5	7·6	7·7	75	37·5	—	—	2·6
F.A. 39·0%, 0·7%	1·0	6·3	8·2	48	37·9	—	—	2·6
G.R. 13	1·5	5·4	8·6	34	38·1	—	—	2·6
A.R. 0—2¼ mins., 310;	2·0	4·6	8·9	25	38·3	—	—	2·8
from 2¼ min. on, 270	2·5	4·1	9·3	18	38·4	—	—	2·7
	3·0	3·7	9·5	13	38·5	—	—	2·7
	0·0	10·5	5·1	—	44·3	—	—	—
I.A. 44·3%, 0·0%	1·0	7·5	6·8	41	45·5	—	—	1·9
F.A. 46·6%, 0·7%	1·5	6·6	7·1	29	45·8	—	—	1·9
G.R. 10	2·0	6·0	7·4	20	46·1	—	—	1·8
A.R. 0—1½ mins., 330; from 1½ mins. on, 240	3·0	5·3	7·8	10	46·3	—	—	1·4
	0·0	6·4	4·5	—	43·9	—	—	—
I.A. 43·9%, 0·0%	0·5	5·7	4·4	25	44·0	—	—	2·0
F.A. 44·3%, *ca.* 0·5%	1·0	5·0	4·6	19	44·1	—	—	2·1
G.R. 8	1·5	4·55	4·7	15	44·2	—	—	2·2
A.R. 310	2·0	4·15	4·8	11	44·2	—	—	2·2
	0·0	7·8	4·9	—	44·3	—	—	—
I.A. 44·3%, 0·0%	0·5	6·9	5·0	25	44·6	—	—	1·3
F.A. 45·7%, 0·6%	1·0	6·4	5·1	20	44·8	—	—	1·2
G.R. 3	1·5	5·9	5·2	16	45·0	—	—	1·2
A.R. 310	2·0	5·5	5·3	13	45·1	—	—	1·2
	3·0	4·9	5·6	8	45·3	—	—	1·1
	0·0	8·6	7·5	—	44·4	—	—	—
I.A. 44·4%, 0·0%	0·5	7·6	7·7	34	44·6	—	—	1·4
F.A. 45·5%, 0·8%	2·0	6·3	8·3	18	45·1	—	—	1·4
G.R. 4	3·0	5·6	8·5	12	45·2	—	—	1·3
A.R. 220	4·0	5·2	8·7	8	45·3	—	—	1·2
	0·0	12·4	5·0	—	59·2	—	—	—
I.A. 59·2%, 0·0%	0·5	11·5	5·3	45	59·2	—	—	2·1
F.A. 59·0%, 1·1%	1·0	10·9	5·4	25	59·1	—	—	1·7
G.R. 10	1·5	10·5	5·5	15	59·0	—	—	1·5
A.R. 310	2·0	10·3	5·5	10	59·0	—	—	1·2

TABLE III.

Dioxide evolution at 25° and 40°. (Units, etc., as in Table I.)

Details.	Time, mins.	Concns., NO_2.	NO.	Evoln. rate.	Acid concn., %.	$k_e \times 10^2$, Eq. (7).
40°.	0·0	0·4	10·8	(8)	43·9	—
I.A. 43·9%, 0·0%	1·0	1·1	9·5	6	43·4	2
F.A. 42·1%, *ca.* 0·6%	2·0	1·6	8·8	4	42·8	2
G.R. 9	12·0	2·6	7·6	0	42·1	—
A.R. 310	18·0	2·6	7·8	0	42·1	—
40°.	0·0	0·0	19·7	(45)	52·1	—
I.A. 52·1%, 0·0%	1·0	3·7	16·7	35	50·6	3·0
F.A. 49·2%, 0·9%	2·0	5·1	15·1	20	49·9	3·9
G.R. 14	7·5	6·1	14·0	0	49·2	—
A.R. 310	10·5	6·1	14·0	0	49·2	—
40°.	0·0	0·0	21·9	(70)	59·2	—
I.A. 59·2%, 0·0%	0·5	3·4	17·4	62	57·5	1·7
F.A. 53·6%, 0·6%	1·0	5·0	15·7	51	56·3	1·8
G.R. 16	1·5	6·3	14·4	39	55·3	2·0
A.R. 310	2·0	7·0	13·7	27	54·6	2·3
	12·0	8·0	13·9	0	53·6	—
40°.	0·0	0·3	15·6	(45)	59·2	—
I.A. 59·2%, 0·0%	0·5	2·2	13·7	42	58·2	1·3
F.A. 54·6%, 1·1%	1·0	3·6	12·4	40	57·3	1·4
G.R. 11	1·5	4·7	11·4	35	56·5	1·4
A.R. 310	2·0	5·7	10·6	22	55·8	1·3
25°.	0·0	0·0	10·9	—	44·3	—
I.A. 44·3%, 0·0%	0·5	0·1	10·7	1·5	44·1	—
F.A. 42·5%, *ca.* 0·8%	1·0	0·2	10·2	2	44·0	—
G.R. 10	2·0	0·4	9·6	3	43·8	—
A.R. 310	4·0	0·8	8·8	2	43·3	—
	12·0	1·25	8·1	0	42·5	—
25°.	0·0	0·0	20·4	(85)	59·0	—
I.A. 59·0%, 0·0%	0·5	2·2	17·5	46	57·4	1·7
F.A. 55·3%, 1·6%	1·0	3·0	15·9	32	56·4	1·7
G.R. *ca.* 12	1·5	3·4	15·1	20	56·0	1·4
A.R. 310	2·0	3·7	14·5	13	55·7	1·3
	8·5	3·9	13·6	0	55·3	—

started to flow down the absorption tower, and cols. 3 and 4 give the corresponding concentrations of NO_2 and NO. The concentrations of N_2O_4 and N_2O_3 are not shown in the tables, but are readily calculable by use of the equilibrium constants. The estimated partial pressures of H_2O and HNO_3 vapour are also not shown but were very small. The partial pressure of diluent nitrogen was that necessary to make the total pressure up to 1 atm. at the commencement of each run.

The gaseous concentrations are expressed as g.-moles/l., which is equivalent to kg.-moles/m.^{3}. The absorption or evolution rate is expressed as kg.-moles/m^2. sec., a unit convenient for application of the results in plant practice.

Details of the initial and final acid concentrations, etc., are given in col. 1, together with interpolated figures in col. 6. The figures quoted for HNO_2 include the dissolved nitrous gas expressed as HNO_2, as determined by titration with permanganate.

In order to economise space, the tables do not include the results obtained at all the time intervals in each run; in particular, the data obtained when the absorption rate had become too low to be accurately measurable have been omitted. However, in those runs in which the gas composition appeared to reach a definite constancy, the limiting values have been included for use in calculating the equilibrium constant.

Qualitative Results.—Certain qualitative results and observations were as follows.

(*a*) The rate of dioxide absorption was found to be greater the higher its concentration and the lower the nitric oxide concentration. Similarly, in those runs in which the reaction was carried out in the reverse direction, the rate of nitric oxide absorption was greater the higher its concentration and the lower the dioxide concentration.

(*b*) At the same concentration of total dioxide and of nitric oxide the rate of absorption of dioxide was greater at 25° than at 40°.

(*c*) Increase of acid concentration caused a decrease in the rate of absorption of dioxide. Conversely, an increase of acid concentration caused an increase in the rate of absorption of NO, in those runs in which the reaction rate was measured in the reverse direction. The rate of reaction of NO with dilute acids was very low.

(*d*) An initially colourless and nitrous-free acid was generally used in the experiments, but after circulation in the tower a green colour always developed. This coloration came to a maximum within 1—2 minutes after first introduction of the acid and then remained apparently constant. It was the more marked the more concentrated the acid. At the end of each run, a titration with permanganate usually gave 0·5—1·5% of nitrous acid and dissolved gas, both reckoned as HNO_2.

(*e*) The tangent to the curve of the NO concentration could be used to calculate an approximate figure for its rate of evolution. This was generally less than one-third of the rate of dioxide absorption, and this was no doubt due to the formation of nitrous acid and to nitric oxide remaining in solution after the occurrence of the reaction. It appeared that the liquid phase became saturated with nitrous acid and dissolved gas during the first 1 or 2 minutes of each run, and thereafter the nitric oxide was evolved. In some of the runs colourless gas could be seen to be bubbling out of solution in the acid in the pump.

(*f*) No formation of visible mist was observed, in contrast to Chambers and Sherwood's observations. There was some condensation of acid in the gas blower, but none in the reservoir, *d*.

DISCUSSION.

Treatment of Equilibrium Data.—The equilibrium constant of reaction (A) is given by

$$K = \frac{p_{NO} \cdot p^2_{HNO_3}}{p^3_{NO_2} \cdot p_{H_2O}} = K_1K_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $K_1 = p_{NO}/p^3_{NO_2}$ and $K_2 = p^2_{HNO_3}/p_{H_2O}$ (pressures in atms.); K_1 and K_2 are not true constants but are convenient factors into which to split K. In particular, K_1 will vary with change of acid concentration.

The equilibrium partial pressures of NO_2 and NO, as measured in those runs in which the gas composition became constant, are shown in Table IV, together with the corresponding calculated values of K_1. The data include results from runs carried out on both the forward and the reverse direction of the reaction as indicated by the letters F and R.

TABLE IV.

Equilibrium data.

Run.	Temp.	Equilibrium conditions.			$\log_{10} K_1$.
		HNO_3, %.	p_{NO_2}, atm.	p_{NO}, atm.	
R	25°	42·5	0·030	0·197	3·86
F	25	45·1	0·034	0·122	3·49
F	25	46·4	0·054	0·320	3·31
R	25	55·3	0·095	0·332	2·59
R	40	42·1	0·067	0·200	2·82
R	40	49·2	0·156	0·360	1·98
R	40	53·6	0·205	0·357	1·62

Values of K_1 have been determined experimentally by Abel, Schmid, and Stein (*Z. Electrochem.*, 1930, **36**, 692), Chambers and Sherwood (*J. Amer. Chem. Soc.*, 1937, **59**, 316), and Epshtein (*J. Gen. Chem. U.S.S.R.*, 1939, **9**, 792), using a variety of experimental methods. The values of $\log_{10} K_1$ obtained by these workers are shown in Fig. 2, together with the values from Table IV. It is evident that the values obtained in the present work are in very good agreement with those in the literature, and this gives support to the method of calculating the concentrations of nitrogen mon- and di-oxide in the gas-circulating system, as described previously. [Values of K_1 were also obtained by Burdick and Freed (*J. Amer. Chem. Soc.*, 1921, **43**, 518). Their values are different from the results of all the later workers and have not been included in Fig. 2. It has been suggested by Chambers and Sherwood that true equilibrium was not obtained in Burdick and Freed's experiments.]

The calculation of the equilibrium constant, K, of the reaction is dependent on a knowledge of the vapour pressure of nitric acid. The matter has been discussed by Forsythe and Giauque (*J. Amer. Chem. Soc.*, 1942, **64**, 48). For the present purpose a knowledge of K_1 is sufficient.

Diffusion Theory of Absorption Rate.—The experimental results for the absorption rate, as given in Tables I—III, have been expressed as the quantity of total dioxide absorbed per unit time *per unit area*. It has therefore been assumed that the rate is proportional to the area of the acid surface. Strong confirmation of this assumption is available from the results of Chambers and Sherwood. These workers used both a falling-film tower and a batch absorption vessel. The absorption rate, expressed per unit area of interface, was found to be about the same in the two types of apparatus, despite a large difference in the ratio of this area to the volumes of the bulk phases. The rate of reaction is thus determined by the area of the acid–gas interface. It seems likely that the reaction takes place either at the surface itself or in a region very close to it. This view is not inconsistent with the possibility of some reaction in the gaseous phase, resulting in mist formation, provided it takes place in the interfacial region, whose volume is proportional to the area of the absorbing surface.

Whilst this view of the process serves to reconcile various observations, it does not indicate the nature of the rate-limiting process. This might be the evaporation of water, the diffusion of NO_2 and N_2O_4 into the interfacial region, the diffusion of NO out of the region, or finally the actual collisional process of the chemical reaction. In considering these different possibilities, it is necessary to bear in mind the reversibility of the reaction and the fact that any expression for the absorption rate must reduce to zero when the composition of the gaseous phase is that which is at equilibrium with the acid.

Chambers and Sherwood found that the rate of absorption was increased by raising the flow of gas. It was suggested therefore that the rate-limiting process was the diffusion of NO_2 and N_2O_4 up to the interface through a stagnant film of mist and inert gas. Their theoretical expression for the absorption rate, V, is then of the form

$$V = \frac{PD_{NO_2}}{RTp_Bx}\left\{\frac{2D_{N_2O_4}}{D_{NO_2}}\cdot p_{N_2O_4} + p_{NO_2}\right\} \quad (2)$$

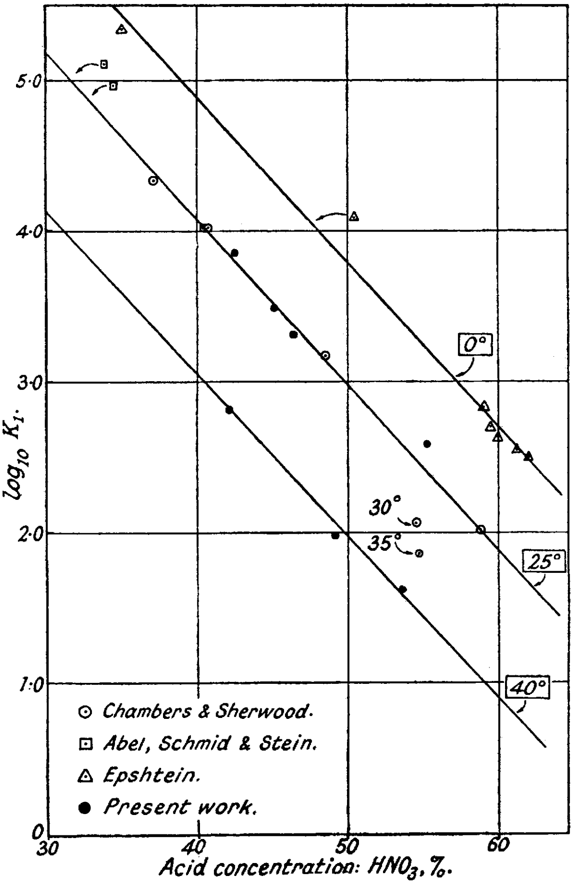
In this equation P is the total pressure, p_B the mean partial pressure of inert gas in the film, x the effective film thickness, and the D's and p's refer to the diffusion coefficients and partial pressures, respectively, of N_2O_4 and NO_2.

From the present point of view there are three objections to this expression. (1) The velocity, V, does not become zero when the concentrations of NO_2 and N_2O_4 are such that they are at equilibrium with the acid and with the NO. (2) No allowance is made for the very considerable effect of NO concentration on absorption rate. (3) Even with dilute acid, where the reverse reaction is negligible, the equation does not correctly express the effect of NO_2 and N_2O_4 concentration on the absorption rate.

With regard to the third point, the work of Chambers and Sherwood was carried out at an almost constant gas composition and they were therefore unable to show whether their theoretical expression was in agreement with experiment. Now the ratio $2D_{N_2O_4}/D_{NO_2}$ can be calculated from kinetic theory as 2·86, and the quantity outside the bracket in equation (2) can be taken as approximately constant in any one of the runs of the present work. The equation can therefore be rearranged as follows :

$$\frac{V}{2{\cdot}86\,[N_2O_4] + [NO_2]} = k_g \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

FIG. 2.



$\log_{10} K_1$ *plotted against* HNO_3 *concn.* (%).

Values of k_g calculated from the present results are shown in col. 7 of Tables I and II. There is seen to be a pronounced fall in the value of k_g during the course of each experiment as the gas composition changes : k_g is thus not a true constant.

It seems, therefore, that the diffusion theory does not account very satisfactorily for the facts, especially the reversibility of the reaction and the effect of gas composition. These are dominating factors in plant practice and it is important to make adequate allowance for them. The alternative theory which is put forward below is based on the assumption that it is the *chemical reaction* in the interfacial region which controls the measured rate of absorption.

Chemical Kinetics Theory of Absorption Rate.—Considering for the moment absorption in acids more dilute than 30%, the present results can be represented with very fair accuracy by the simple relation

$$V = k_a[N_2O_4] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The calculated values of k_a are shown in col. 8 of Tables I and II and may be compared with the values of k_g. The coefficient of variation is rather smaller for k_a than for k_g (16% as compared to 21%) and also, which is more significant, the values of k_a do not show any systematic drift during the course of a run. (The results of the third, fourth, and fifth runs in Table II are, however, unsatisfactory in this respect.)

This linear relation between the absorption rate and the N_2O_4 concentration, or equally the square of the NO_2 concentration, indicates that the rate-limiting process may be a reaction involving one molecule of N_2O_4 or two molecules of NO_2, *e.g.*,

$$N_2O_4 + H_2O \longrightarrow HNO_3 + HNO_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (C)$$

$$\text{or } 2NO_2 + H_2O \longrightarrow HNO_3 + HNO_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (D)$$

If both reactions take place simultaneously, it would be expected that the absorption rate would be expressible by the relation

$$V = a[N_2O_4] + b[NO_2]^2$$

However, since $[N_2O_4] = K[NO_2]^2$, this equation can be reduced to either of the equivalent forms

$$V = k_a[N_2O_4] \text{ or } V = k_a'[NO_2]^2$$

The mean values of k_a and k_a' from the experimental data for the dilute acids are as follows:

$$\text{at } 25°,\ k_a = 1{\cdot}8 \times 10^{-2},\ k_a' = 3{\cdot}0$$

$$\text{at } 40°,\ k_a = 2{\cdot}3 \times 10^{-2},\ k_a' = 1{\cdot}3$$

The formulation of the reaction according to equation (C) thus gives a positive temperature coefficient, whilst formulation by equation (D) gives a negative coefficient. It seems likely, however, that reaction (C) takes place to the greater extent as it only involves a bimolecular collision. Expressed alternatively, the increase in the absorption rate at reduced temperatures (at the same concentration of total dioxide) is probably due to the increase in the proportion of the more reactive N_2O_4 rather than to any actual increase in the velocity coefficient. However, this is not an essential point in the present treatment.

Two further conclusions which may be drawn from the results on weak acids are: (*a*) k_a does not appear to depend on acid concentration; (*b*) there is no apparent effect of nitrous acid concentration, as shown in the fourth run of Table I. The absorption rate in dilute acids is thus determined almost entirely by the concentration of dinitrogen tetroxide in the gaseous phase, according to equation (4). However, with acids in the range 30—60% this simple relation no longer holds, and the measured absorption rate is found to become markedly dependent on the concentration of nitric oxide, and to a greater extent the stronger the acid. It is reasonable to attribute this effect to the increasing degree of reversibility of the reaction as the acid concentration is raised.

In the more concentrated acids we assume that the forward reaction continues to be proportional to the tetroxide concentration. A term for the reverse reaction is also introduced into the velocity equation and this term we take to be a power function of the NO and N_2O_4 concentrations:

$$V = k_a[N_2O_4] - \text{const. } [N_2O_4]^p[NO]^q$$

or

$$V = k_a\{[N_2O_4] - C[N_2O_4]^p[NO]^q\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

At equilibrium this equation must obviously reduce to the form $[NO]/[N_2O_4]^{3/2}$ = const., in accordance with the stoicheiometry of the overall process (A). This condition imposes a limitation on the choice of possible exponents in equation (5). The condition is clearly $(1 - p)/q = \frac{3}{2}$; for example, $p = 0$, $q = \frac{2}{3}$, or $p = \frac{1}{4}$, $q = \frac{1}{2}$, etc. Good correlation of the experimental data has been obtained by use of the latter pair of exponents, and this choice is also supported by the work of Abel (*Z. physikal. Chem.*, 1928, *A*, **132**, 55, 64; 1928, *A*, **134**, 279; 1928, *A*, **136**, 135, 419, 430; 1930, *A*, **148**, 337).

Abel and his collaborators carried out an exhaustive study on the rate of formation and decomposition of nitrous acid in the gas and the liquid phase system containing the species HNO_3, HNO_2, H_2O, NO, NO_2, N_2O_4, and N_2O_3. It was concluded that there are two elementary reactions in this system:

$$N_2O_4 + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} HNO_2 + HNO_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (C)$$

$$2HNO_2 \rightleftharpoons NO + NO_2 + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (E)$$

It was found that (C) is slow and controls the overall rate, whilst (E) is relatively very rapid and can be regarded as being at equilibrium. In the experimental work the agitation of the bulk phases was vigorous and it appears that the diffusion of reactants across the gas–liquid interface did not affect the measured reaction rates. Abel was therefore able to treat the process as a normal example of chemical kinetics.

In the system studied by the present authors the same molecular species were present, and it is reasonable to suppose, therefore, that the *elementary reactions which took place were also the same*, i.e., Abel's reactions (C) and (E). The two systems differed only in the relative proportions of the different species, with the result that the overall process in Abel's system was the formation or decomposition of nitrous acid, and in our own system was the formation or decomposition of nitric acid. The compounding of the elementary reactions in the two cases is as follows :

$$\begin{array}{ll}
4HNO_2 \rightleftharpoons 2NO + 2NO_2 + 2H_2O & \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (E) \\
\underline{N_2O_4 + H_2O \rightleftharpoons HNO_3 + HNO_2} & \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (C) \\
\underline{3HNO_2 \rightleftharpoons 2NO + HNO_3 + H_2O} & \quad \text{overall process} \\
2N_2O_4 + 2H_2O \rightleftharpoons 2HNO_3 + 2HNO_2 & \quad . \; . \; . \; . \; . \; . \; . \; . \quad (C) \\
\underline{2HNO_2 \rightleftharpoons NO + NO_2 + H_2O} & \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (E) \\
\underline{\underline{3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO}} & \quad \text{overall process} \; . \; . \; . \; . \quad (A)
\end{array}$$

As described above, Abel's evidence is that reaction (C) is rate-controlling and reaction (E) is relatively so rapid that it can be regarded as being at equilibrium. These conclusions agree well with our own observations; in dilute acids the absorption rate was proportional to the N_2O_4 concentration, as would be expected if reaction (C) controls the rate, and secondly, there was a rapid development of a steady state of coloration of the absorbing acid, corresponding to the setting up of the equilibrium (E).

We consider now the kinetics of the overall process (A) taking place in a *homogeneous* system. With reaction (C) as the rate-controlling step, and allowing for its reversibility, we obtain for the overall rate of the process the equation

$$\frac{-\,\mathrm{d}(NO_2)}{\mathrm{d}t} = \frac{3}{2}\{k_1[N_2O_4][H_2O] - k_2[HNO_3][HNO_2]\}$$

where k_1 and k_2 are the velocity constants of the forward and the reverse reaction. The symbol (NO_2) signifies the total concentration of NO_2 and N_2O_4 reckoned as NO_2. The factor $\frac{3}{2}$ allows for the reappearance of NO_2 by reaction (E).

The assumption of equilibrium of reaction (E) gives the relation

$$\begin{aligned}
[HNO_2] &= \text{const.} \times [NO_2]^{\frac{1}{2}}[NO]^{\frac{1}{2}}[H_2O]^{\frac{1}{2}} \\
&= \text{const.} \times [N_2O_4]^{\frac{1}{4}}[NO]^{\frac{1}{2}}[H_2O]^{\frac{1}{2}}
\end{aligned}$$

Combining the two equations we have

$$\begin{aligned}
\frac{-\,\mathrm{d}(NO_2)}{\mathrm{d}t} &= \frac{3}{2}\{k_1[N_2O_4][H_2O] - \text{const.}\ [HNO_3][N_2O_4]^{\frac{1}{4}}[NO]^{\frac{1}{2}}[H_2O]^{\frac{1}{2}}\} \\
&= \frac{3}{2}k_1[H_2O]\left\{[N_2O_4] - \frac{\text{const.}\ [HNO_3]}{k_1[H_2O]^{\frac{1}{2}}}\,.\,[N_2O_4]^{\frac{1}{4}}[NO]^{\frac{1}{2}}\right\} \\
&= k\{[N_2O_4] - C[N_2O_4]^{\frac{1}{4}}[NO]^{\frac{1}{2}}\} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)
\end{aligned}$$

where $k = \frac{3}{2}\,k_1[H_2O]$, and C depends on the concentration of the acid.

Equation (6) thus gives the rate of disappearance of dioxide in a homogeneous system containing the molecular species in question. This equation may also be expected to apply when there are two phases, gas and liquid, provided it is the chemical reaction which continues to determine the overall rate. This is the basic assumption of the present treatment.

The theory thus leads to an expression for the absorption rate identical with (6), except in so far as it is necessary to change the dimensions of constants, etc., to represent a rate per unit area instead of a rate per unit volume :

$$V = k_a\{[N_2O_4] - C[N_2O_4]^{\frac{1}{4}}[NO]^{\frac{1}{2}}\} \quad . \; . \; . \; . \; . \; . \; . \quad (7)$$

This equation is identical in form with equation (5) which was deduced on empirical grounds. At equilibrium the equation reduces to

$$[\mathrm{NO}]_{\mathrm{eq.}}/[\mathrm{N_2O_4}]^{3/2}{}_{\mathrm{eq.}} = 1/C^2$$

$$\therefore \quad [\mathrm{NO}]_{\mathrm{eq.}}/[\mathrm{NO_2}]^3{}_{\mathrm{eq.}} = K^{3/2}/C^2, \text{ where } K = [\mathrm{N_2O_4}]/[\mathrm{NO_2}]^2.$$

But $(p_{\mathrm{NO}}/p^3{}_{\mathrm{NO_2}})_{\mathrm{eq.}} = K_1$, of which values are given in Fig. 2. Hence at temperature $t°$,

$$C = \frac{K^{\frac{3}{4}}}{K_1{}^{\frac{1}{2}}} \cdot \frac{273}{22{\cdot}4\ (273 + t)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The constant C can thus be calculated from equilibrium data and values are given in Table V. The numerical factor in equation (8) arises from the conversion of K_1 into units of concentration.

TABLE V.

Calculated Values of C, *the Constant in Equation* (7).

Acid concn., wt.-%.	Temp. 40°.			Temp. 25°.		
	K.	$\log_{10} K_1$.	$\log_{10} C$.	K.	$\log_{10} K_1$.	$\log_{10} C$.
40	56	3·05	−1·63	170	4·07	−1·75
50	56	1·96	−1·08	170	2·97	−1·20
60	56	0·89	−0·55	170	1·88	−0·66

The adequacy of equation (7) has been tested by evaluating k_a for each of the experimental measurements and the results are given in col. 9 of Tables I and II and col. 7 of Table III. It is seen that the values of k_a are generally fairly constant within any one experimental run, with the exception of three runs of Table II, where there was a systematic drift. With these exceptions, therefore, equation (7) gives a fairly good representation of the complex effect of gas composition on the absorption process. It also allows fully for the reversibility and it is particularly satisfactory that the equation, with the same value of k_a, can be applied whether NO_2 is being absorbed or evolved.*

Conclusions.—As shown in the previous section, the use of equation (7) gives a fairly good representation of the effect of the change in gas composition in any one experimental run, as shown by the approximate constancy of the calculated values of k_a. Between one run and another, however, there is appreciable variation of k_a, as shown by inspection of Tables I—III.

It is to be emphasised that the experimental method in use was not of the highest accuracy, but was primarily adapted to the exploration of the effect of wide ranges of gas composition. With this proviso in mind, Tables I—III show no evidence of a systematic effect on k_a either of acid flow rate or of acid concentration. On the other hand, there are indications of a small effect of gas velocity.

Chambers and Sherwood found evidence of a considerable dependence of absorption rate on the flow of gas and obtained the best treatment of their own data by taking the absorption rate as proportional to the 0·8 power of the Reynolds number (Re).† Taken on their own, the present

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* It may be noted, however, that equation (7) is not satisfactory when the gaseous phase contains NO but no dioxide. This was the case at the commencement of the runs of Table III, for which the values of the evolution rate of NO_2, extrapolated to zero time, are shown in parentheses. Equation (7), and the mechanism of reactions (C) and (E), cannot account for the attack of pure NO on nitric acid, for which the probable reaction is

$$\mathrm{NO} + \mathrm{HNO_3} \rightleftharpoons \mathrm{NO_2} + \mathrm{HNO_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (F)$$

If it is assumed that reactions (C), (E), and (F) are operative simultaneously, equation (7) must be modified as follows :

$$V = k_a\{[\mathrm{N_2O_4}] - C[\mathrm{N_2O_4}]^{\frac{1}{4}}[\mathrm{NO}]^{\frac{1}{2}}\} + k_f\left\{\frac{[\mathrm{N_2O_4}]^{\frac{3}{4}}[\mathrm{NO}]^{\frac{1}{2}}}{C} - [\mathrm{NO}]\right\} \quad . \quad . \quad . \quad . \quad (9)$$

Rough values of k_f can be worked out from the zero-time data of Table III. These values are found to be about one-tenth of the value of k_a in 60% acid but are very much smaller in weaker acids. The result is that the second term in the above equation is generally much smaller than the first, except when NO is in great excess. Under normal conditions, equation (9) does not differ appreciably from equation (7), in its numerical value, and the simpler equation can therefore be used. This is equivalent to the neglect of the reaction (F).

† The Reynolds number is defined by

$$\mathrm{Re} = vd\rho/\eta$$

where v, ρ, and η are the linear velocity, the density, and the viscosity respectively of the circulating gas, and d is the diameter of the absorption tower.

results do not provide very definite evidence, but the best correlation of both sets of results can probably be obtained by taking k_a as proportional to $\mathrm{Re}^{0.5}$.* Alternatively, the variations in the present results may be due only to experimental error and not to any real effect of gas velocity.

It is to be noted also that the present experiments were conducted at low values of the linear rate of gas flow, such as obtain in nitrous gas absorption plants. In Chambers and Sherwood's work the Reynolds number was much higher (upwards of 1550, as compared to a maximum of 530 in the present experiments). The two sets of results are therefore not very comparable.

In conclusion, the object of the present work has been to investigate the effect on absorption rate of gas composition, acid concentration, and temperature, which are the most significant variables in plant practice. The main result has been to show that equation (7), which is derived from a chemical kinetic treatment of the absorption process, gives a satisfactory basis of interpretation. The equation accounts for the behaviour of wide ranges of gas composition on either side of the equilibrium point. The main effect of acid concentration is on the constant C of the equation, and the effect of temperature is on the constants C and k_a and on the relative proportions of NO_2 and N_2O_4. To this extent the present work may form a basis to which refinements may be added. There is undoubtedly scope for much further experimental work, particularly on the rate of absorption in acids more concentrated than 50% and on the effect of wide ranges of gas velocity.

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