Kinetics of Nitrogen Tetroxide Absorption in Water

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The rate of absorption of nitrogen peroxide into water at 25° and 40°C. has been found to be a linear function of the concentration of nitrogen tetroxide in the gas phase and directly proportional to the interfacial partial pressure of the same species.

The rate of absorption is independent of gas velocity over a range of Re_G from 170 to 350. The results plotted as absorption rate divided by interfacial partial pressure of nitrogen tetroxide show no effect of liquid rate or contact time between gas and liquid over a tenfold range of contact time from 0.03 to 0.3 sec. This indicates that the rate-controlling step during nitrogen dioxide absorption into water is the rate of hydrolysis of nitrogen tetroxide.

The absorption rate decreases with increasing temperature from 25° to 40°C., owing to the shift of the equilibrium in the gas phase away from the reacting species nitrogen tetroxide toward nitrogen dioxide and owing to the decreased solubility of nitrogen tetroxide in water. The effect of these factors on absorption more than offsets the effect of the increase in reaction rate and higher diffusivity on absorption at 40°C.

The reaction rate constant for the hydrolysis of nitrogen tetroxide has been determined and the solubility of dissolved but unreacted nitrogen tetroxide in equilibrium with gaseous nitrogen tetroxide has been found.

Despite the large quantities of nitric acid made by the absorption of nitrogen oxides into water, the kinetics of the reactions involved are not yet fully explained. These reactions are commonly written as

$$2NO + O_2 \rightarrow 2NO_2 \qquad (1)$$

$$2NO_2 \rightleftharpoons N_2O_4 \qquad (2)$$

$$\left\{\begin{array}{c} 3NO_2 \\ \text{or} \\ \tfrac{3}{2}N_2O_4 \end{array}\right\} + H_2O \rightleftharpoons 2HNO_3 + NO \qquad (3)$$

The reaction shown in Equation (3) is the least-understood step of the three.

Future efforts to improve the already high efficiency of absorption towers where reaction (3) is carried out will be based on a better understanding of the kinetics of this reaction. To add to the knowledge of this reaction, a study has been made of the kinetics of the absorption and reaction of nitrogen peroxide* with water. Others (*4*, *6*, *20*) who have studied this same problem have shown that nitrogen tetroxide is the reacting species in Equation (3) and that the rate-controlling step during absorption is the reaction between nitrogen tetroxide and water, although there is some disagreement as to whether this reaction occurs in the vapor or liquid phase or both. The two-film theory of absorption has been used in some cases (*3*, *5*, *7*) to analyze absorption results, while in others (*4*, *6*, *20*) the data have been interpreted in terms of chemical reaction kinetics alone. A different approach was taken in the present work. The results reported here were obtained with the aid of the penetration or unsteady state absorption plus reaction theory (*12*), which mathematically combines the effects on absorption of simultaneous diffusion and chemical reaction in the liquid phase.

LITERATURE REVIEW

Studies of the absorption of nitrogen peroxide into aqueous solutions have been made in both short and long wetted-wall columns (*3* to *7* and *21*) and on bubble-cap plates (*20*). The results obtained in long wetted-wall columns (about 3 ft. long) by Bolshakoff (*3*) and Chambers and Sherwood (*5*) indicated that gas-film resistance controlled the absorption of nitrogen dioxide into aqueous solutions of nitric acid and sodium hydroxide. Eagleton, Langer, and Pigford (*7*) reported that the slow rate of reaction between dissolved nitrogen dioxide and liquid water limited the rate of nitrogen dioxide absorption into strong caustic solutions in long wetted-wall columns. Peters and Holman (*21*) studied the effects of temperature and water-vapor concentration on the absorption of nitrogen peroxide into aqueous solutions of sodium hydroxide and sodium chloride in long wetted-wall columns. They concluded that both gas- and liquid-phase reactions between nitrogen tetroxide and water occurred and that the rate of absorption was controlled by these reactions.

Denbigh and coworkers (*4*, *6*), working with short wetted-wall columns (less than 7 in.), reported, before Peters and Holman (*21*), that the absorption rate of nitrogen peroxide into aqueous solutions of nitric acid, sodium hydroxide, and calcium chloride was proportional to nitrogen tetroxide concentration in the gas phase. They too had concluded that the speed of absorption was determined by the reaction of nitrogen tetroxide and water and not by diffusion.

Peters, Ross, and Klein (*20*) absorbed nitrogen peroxide into aqueous nitric acid in a bubble-cap-plate column and concluded that the rate-controlling step was the chemical reaction between nitrogen tetroxide and water in the gas phase.

The existence of a homogeneous vapor-phase reaction between nitrogen peroxide and water is an unsettled question of major importance in studies on the mechanism of nitrogen oxide absorption into water. If such a reaction does occur to an appreciable extent, the interpretation of absorption results must take it into consideration. The evidence in support of such a reaction is summarized:

1. Chambers and Sherwood (*5*) ob-

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*Nitrogen peroxide refers to the equilibrium mixture of nitrogen dioxide and nitrogen tetroxide.

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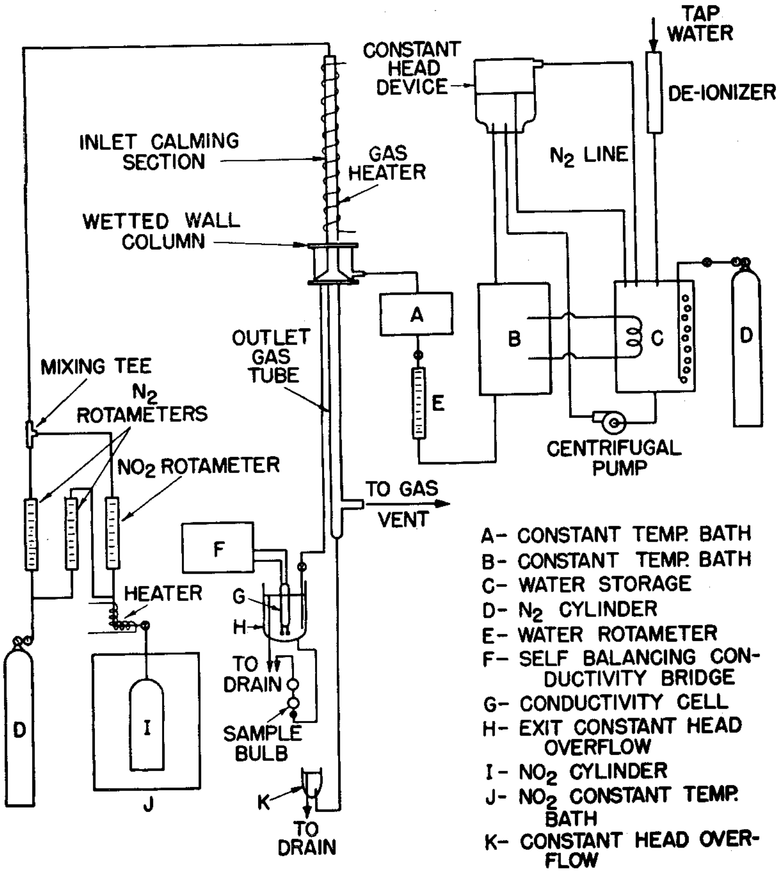

Fig. 1. Diagram of apparatus.

served a mist while absorbing nitrogen peroxide into aqueous solutions of sodium hydroxide and nitric acid. They postulated that this mist was caused by the condensation of the nitric acid produced by the vapor-phase reaction.

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \qquad (4)$$

They also observed nitric oxide in the exit gas from the absorbers, during all runs, including those where sodium hydroxide solutions were used as the absorbents, and concluded that this nitric oxide could result only from the gas-phase reaction of Equation (4), since they believed that the dioxide, once absorbed, reacted with sodium hydroxide according to

$$2NO_2 + 2NaOH \rightarrow NaNO_2 + NaNO_3 + H_2O \qquad (5)$$

from which no nitric oxide could be produced.

2. Eagleton, Langer, and Pigford (*7*) also detected nitric oxide in the gaseous effluent when absorbing nitrogen peroxide into sodium hydroxide solutions in a long wetted-wall column, and a mist was observed in the gas phase during one experiment.

3. Peters, Ross, and Klein (*20*) observed a mist during runs where nitrogen dioxide was absorbed into water on a bubble-cap plate.

4. Peters and Holman (*21*) found nitric oxide in the exit gas stream from their long wetted-wall–column absorber when absorbing nitrogen peroxide into aqueous solutions. Thus the hypothesis of a gas-phase reaction has always been based on the presence of a mist and nitric oxide in the exit gas from absorbers.

On the other hand, there is evidence that there is no homogeneous reaction between water and nitrogen peroxide in the vapor phase:

1. Kuzminikh and Udintseva (*14*) attempted to measure the pressure change which should occur in a constant-volume system if a homogeneous vapor-phase reaction took place between nitrogen peroxide and water. They found no change and concluded that no reaction had occurred in the vapor phase.

2. Harris (*11*) performed similar experiments and also observed no reaction. No mist was observed when nitrogen dioxide and water vapors were contacted.

3. Simon (*25*) studied the gaseous reaction over various catalysts, such as activated carbon and silica gel, and did observe a reaction. However in the absence of these catalysts he found no reaction between nitrogen dioxide and water. His experimental method included a qualitative analysis for nitric oxide in the exit gas stream from the reaction chamber. He also observed no mist in the reaction chamber in the absence of liquid water.

4. In direct contradiction to part of the evidence cited in support of a vapor-phase reaction, Denbigh and Prince (*6*) observed no mist during any of their runs while absorbing nitrogen peroxide into nitric acid solutions in a short column.

5. No mist was observed during any of Caudle and Denbigh's (*4*) experiments, and no nitric oxide was found in the exit gas stream during the absorption runs where sodium hydroxide solutions were used. This evidence excluded the possibility of a gas-phase reaction according to

$$N_2O_4 + H_2O \rightleftharpoons HNO_3 + HNO_2 \qquad (6)$$

since the nitrous acid would have decomposed to yield nitric oxide by

$$2HNO_2 \rightleftharpoons H_2O + NO_2 + NO \qquad (7)$$

6. During a few of his experiments on the oxidation of nitric oxide to nitrogen dioxide with oxygen, Bodenstein (*2*), adding water vapor to the NO–O_2 mixture, found no change in the course of the reaction from the case where water vapor was absent. If water vapor reacts with nitrogen dioxide, it should have affected his results.

Since the evidence on this question appears as strong for as against, it is difficult to conclude from past work whether or not a homogeneous gas-phase reaction does occur. In this research a fog appeared during a few absorption runs in which the concentration of nitrogen dioxide in the gas phase was large, but its presence had no effect on absorption rate since results obtained with and without fog present were in complete agreement. Therefore the data of this investigation were interpreted with the assumption that no gas-phase reaction occurred, and most of the experiments were carried out under conditions such that no fog could be seen.

THEORY

The penetration theory can be used to predict absorption rates or to interpret absorption experiments when absorption occurs under conditions which meet the restrictions of the theory: (1) the liquid phase is in laminar motion with no mixing taking place during absorption; (2) no concentration gradients exist in the liquid before exposure to the gas; (3) molecules of absorbed gas diffuse into the liquid only a very short distance compared with the total liquid depth; and (4) gas and liquid are in physical equilibrium at the interface. The differential equations which describe absorption under these conditions constitute the mathematical model of the penetration theory. These equations have been integrated for the cases of physical absorption of a gas and for absorption plus simultaneous reaction in the liquid phase where the reaction is first or second order (*19*, *24*).

In the past the majority of the investigations where the penetration theory was involved have been concerned with establishing the validity of the theory by comparing measured absorption rates with those predicted from the theory. Since good agreement has been obtained (*8, 13, 16, 17, 18, 23, 29*), the validity of the theory was assumed in this study, and it was used, together with measured absorption rates of nitrogen peroxide into water, to calculate the reaction-rate constant for the hydrolysis of nitrogen tetroxide and the equilibrium solubility of this species in the unreacted form in water. Neither of these quantities can be obtained conveniently by other means.

APPARATUS

The apparatus, shown schematically in Figure 1, consisted of a short wetted-wall column and auxiliary apparatus for producing and measuring gas and liquid streams flowing to the column. Constant-temperature controllers were used to bring these streams to the desired operating temperatures.

One of the important features of a short wetted-wall column is that it produces a falling film of water which is contacted by a gas stream for a known period of time over a known area. Figure 2 shows a column assembled to do this. During operation water enters at the liquid inlet, fills the inlet liquid reservoir, passes through the inlet slot, and flows down the wetted-wall section in a smooth film. Near the exit slot some ripples always appear on the liquid surface. The water follows the flared portion of the glass and leaves the absorption section through the exit slot formed by the exit-gas tube and the glass, passes through the liquid outlet, and flows to the sampling bulb. The length of the interfacial area was measured with a millimeter scale beginning at the bottom edge of the inlet-gas tube and extending to the top edge of the exit-gas section. The inlet and exit slots were maintained completely full during all absorption experiments. The critical dimensions of the wetted-wall columns used are given in Table 1.

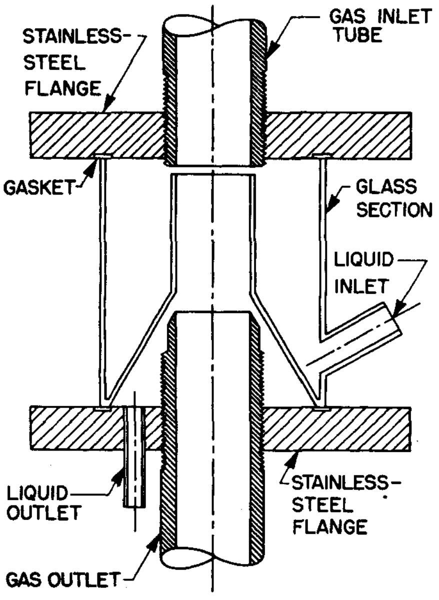

Fig. 2. Short wetted-wall column.

TABLE 1. DIMENSIONS OF WETTED-WALL COLUMNS

Column length,* cm.	Column I.D., cm.	Interfacial area, sq. cm.
1.61	2.54	12.9
4.15	2.41	31.4
8.72	2.54	69.4

*Length includes slots formed by inlet and exit gas tubes and column.

The auxiliary equipment for the gas-feed system was designed to give mixtures of nitrogen and nitrogen peroxide in known concentrations at the wetted-wall column. Gas and liquid flowed concurrently through the column to avoid contact before the wetted-wall section.

Nitrogen peroxide of purity reported greater than 99% was used without further purification, and nitrogen with less than 0.004% impurities was used for the carrier gas. Deionized water, purged of all gases except nitrogen, was used as the solvent in all experiments.

The solutions from the wetted-wall column absorber were analyzed for the total oxides of nitrogen absorbed. A sample of the solution was pipetted under the surface of a known volume of standard carbon dioxide–free sodium hydroxide solution containing 10 ml. of 1.5% hydrogen peroxide solution. This basic solution was then back-titrated with carbon dioxide–free standard hydrochloric acid to obtain the amount of base equivalent to all absorbed nitrogen oxides in whatever form, expressed as nitrogen dioxide. The results of the analysis in this form were sufficient for the purposes of this investigation.

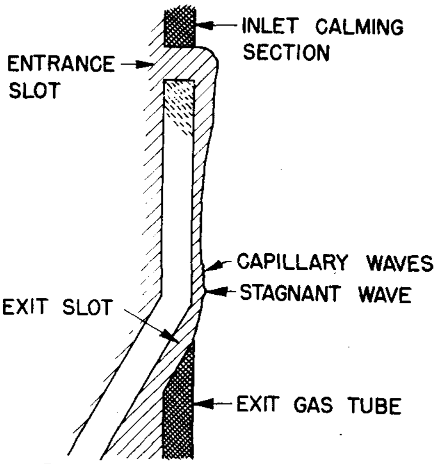

Fig. 3. Cross section of wetted-wall column.

SURFACE OF WATER LAYER

It was stated earlier that ripples appeared on the surface of the water in the wetted-wall column near the exit liquid slot. A qualitative study was made during this research of the liquid flow conditions in the 4.15-cm. column to determine what caused these ripples and what effect they had on the absorption rate of a gas.

Figure 3 is a cross section of one side of a column showing the shape of the liquid layer. The layer is thickest at the entrance slot and thins out as it proceeds down the column. Just above the exit slot a series of waves appears on the liquid surface. Their size and position depend on the liquid rate. These waves were always present despite changes in the exit slot width, variations in water rate, or the presence of a moving gas stream, as long as no liquid was allowed to spill over into the exit gas tube section. The waves are the result of the deceleration of the liquid surface to zero velocity by the top of the exit gas line. A similar phenomenon can be observed in front of a fish line submerged in a moving stream. A wave pattern is evident upstream of the line no matter what the liquid velocity. Lamb (*15*) discusses this situation at length and shows that the velocity of propagation depends on the interfacial tension.

Two types of waves were visible on the liquid surface. The first kind, labeled *capillary* waves in Figure 3, had a relatively small wave length, and the second, called *stagnant* waves, was of distinctly larger wave length and amplitude. Another difference between the waves was the speed with which they formed just after a spillover, that is, after a liquid overflow at the exit slot into the exit gas line ceased. The capillary waves appeared immediately thereafter, but the stagnant waves formed more slowly and progressed upstream from the exit slot at a low rate to a steady position which depended on the liquid velocity. This position varied from about 1 to 12 mm. from the top of the exit-gas tube section, the height being inversely related to the liquid rate. A small band of capillary waves riding on top of the stagnant wave extended another 2 or 3 mm. upstream.

Qualitative studies were made of liquid-surface conditions by introducing a very narrow dye streak onto the surface of the liquid and observing its behavior as it flowed down the column. The streak was undisturbed as it moved on the water surface through the capillary waves, but immediately on contacting the stagnant wave the dye streak broadened, indicating that the condition of the surface below the stagnant wave was different from that above it. When 320-mesh alundum powder was blown onto the surface of the moving liquid in the wetted-wall column, the particles were swept rapidly through the area above the stagnant wave but were decelerated on the surface below the stagnant wave and sometimes moved in a direction opposite to the total water flow. The stagnation of this lower portion of the surface was probably due to the accumulation of a monomolecular layer of surface-active organic compounds which could be present in the water in trace amounts. A surface covered with a layer of this type would be expected to be only partially effective for gas absorption. Experimental observations of a decreased effectiveness of this type have been made by Lynn, Straatemeier, and Kramers (*16*) in a wetted-wall absorber and by Kennedy (*13*) in a rotating drum absorber. The carbon dioxide absorption studies of this investigation have confirmed their results. Therefore it was decided to remove the stagnant surface once every 30 sec. by causing a momentary spillover of liquid into the exit-gas tube section by pinching a rubber portion of the exit-liquid line for ½ sec. The stagnant area thus never had time to develop completely; yet only a negligible fraction of the solution containing absorbed gas was lost. A dye-streak test showed that intermittent spilling over maintained the stagnant wave at a position much lower than with no spillover. During the carbon dioxide–absorption experiments of this research, results obtained with and without spillover showed that operation with spillover resulted in less scatter and more proximity to the predictions of the penetration theory.

EXPERIMENTAL PLAN

Since a fog occurred during absorption when the total nitrogen peroxide concentration was greater than about 25 mole % and occasionally even as low as 5 mole %, the nitrogen peroxide concentration was always maintained below 25 mole % in the experiments reported here, and no fog was apparent during most of the runs. In those few cases where it did occur it was only barely visible and had no detectable effect on the absorption rate.

The gas-film resistance introduced by the inert carrier, N_2 was investigated by using ammonia as the solute to develop a correlation with which the gas-film resistance could be estimated when NO_2 was substituted for NH_3. Absorption studies of carbon dioxide into water were also made to check the operation of the column. The detailed results of the carbon dioxide experiments are reported elsewhere (*29*). It is sufficient to say here that the results showed excellent agreement with published data (*13*, *17*), an indication that the columns were being operated properly. Following this the effects of gas rate, gas composition, water rate, or contact time between gas and liquid, and temperature on the absorption of nitrogen peroxide into water were studied. The nitrogen peroxide fraction of the gas stream, expressed as moles of $NO_2 + 2N_2O_4$ divided by total moles, was varied between 0.06 and 0.20. The range of gas rates covered Re_G from 170 to 350. Water rates were adjusted to give contact times between gas and liquid from 0.03 to 0.3 sec., and experiments were carried out at 25° and 40°C. The original data can be found in a thesis by one of the authors (*29*).

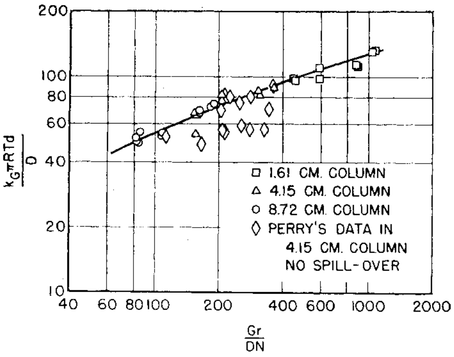

Fig. 4. Gas-film coefficient correlation based on ammonia absorption experiments.

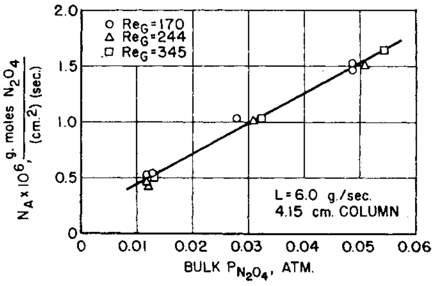

Fig. 5. Effect of gas rate and gas composition on N_2O_4 absorption.

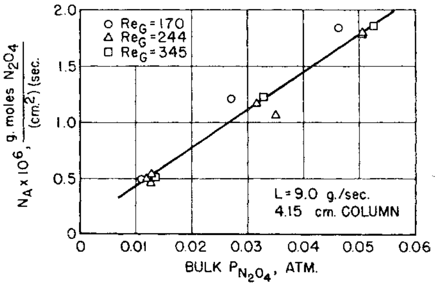

Fig. 6. Effect of gas rate and gas composition on N_2O_4 absorption.

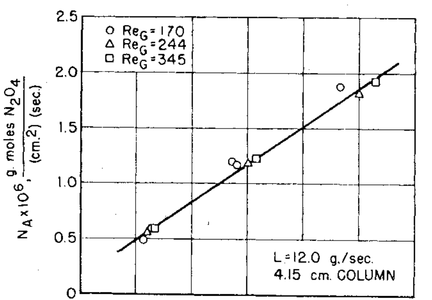

Fig. 7. Effect of gas rate and gas composition on N_2O_4 absorption.

AMMONIA ABSORPTION

A gas-film resistance correlation for short wetted-wall columns was obtained from a series of ammonia absorption experiments. The data, shown in Figure 4, were correlated on the basis of a material-balance equation which assumes no back pressure of ammonia at the liquid surface.

$$\frac{k_G \pi RTd}{D} = \left(\frac{2G_r p_{BM}}{DNP}\right)\left(\frac{p_{G_1} - p_{G_2}}{p_{G_1} + p_{G_2}}\right) \quad (8)$$

Perry's data (*18*) on a short wetted-wall column, included for comparison in Figure 4, fall below the best line through the data of this research and show greater scatter because Perry had no spillover at the exit slot of his column.

NITROGEN DIOXIDE–NITROGEN TETROXIDE ABSORPTION STUDIES

Effect of Gas Rate

Three levels of gas rate were examined: 0.11, 0.15, and 0.22 total g.-moles of gas/min., corresponding to Re_G of 170, 244, and 345. These rates were selected so that inordinate amounts of NO_2 and N_2 would not be consumed and the concentration of nitrogen oxides in the gas stream might still be varied over a moderate range. The gas-rate investigations were carried out in the 4.15-cm. column at 25°C. with liquid rates of 6.0, 9.0, and 12.0 g./sec. The absorption rates at the three gas velocities are plotted as a function of the average composition of the bulk gas phase in Figures 5, 6, and 7. It can be seen that the gas rate had no apparent effect on the quantity absorbed.

Effect of Gas Composition

The absorption rate was measured as a function of nitrogen peroxide composition in all three columns, with the result that the rate was proportional to nitrogen tetroxide partial pressure in the bulk gas stream at all gas rates and contact times, and at both temperatures of operation. The lower curves in Figures 8, 9, and 10 are plots of a portion of the data taken in the 8.72-cm. column at 25°C. This is representative of the remainder of the data from the 1.61- and 4.15-cm. columns in that the points for bulk composition also fell on straight lines whose intercepts were not zero.

The linear relation between the absorption rate and nitrogen tetroxide bulk composition suggests very strongly that the rate-limiting step in the process is the reaction between 1 molecule of nitrogen tetroxide or 2 of nitrogen dioxide and water. The nitrogen dioxide concentration is related to the nitrogen tetroxide in the gas by the equilibrium constant

$$K_p = \frac{p_{N_2O_4}}{(p_{NO_2})^2} \qquad (9)$$

Hence the linear relation found between absorption rate and $p_{N_2O_4}$ means that a similar relation exists between the rate and the square of p_{NO_2}. The two reactions which could occur in solution are

$$N_2O_4 + H_2O \rightleftharpoons HNO_2 + HNO_3 \qquad (10)$$

or

$$2NO_2 + H_2O \rightleftharpoons HNO_2 + HNO_3 \qquad (11)$$

If liquid-phase diffusion of the oxide after absorption had any effect whatsoever on the absorption rate and if nitrogen dioxide were actually the reacting species according to Equation (11), the over-all rate would be proportional to some power of nitrogen dioxide concentration between 1 and 2. (The diffusion rate would be proportional to the first power of nitrogen dioxide concentration and the reaction rate probably to the square of the nitrogen dioxide concentration, giving an over-all effect of nitrogen dioxide concentration to somewhat smaller than the second power.) A similar line of reasoning for nitrogen tetroxide indicates that the absorption rate would be proportional to the first power of nitrogen tetroxide concentration, as found experimentally in this work. Therefore it was concluded that, at least under the conditions studied, nitrogen tetroxide is the compound which dissolves and reacts with water more rapidly. A less convincing argument also in favor of this conclusion is the greater likelihood of a bimolecular reaction occurring, according to Equation (10), rather than a termolecular one, as expressed by Equation (11).

To apply the concepts of the penetration theory to the results of this work, it was necessary to know the partial pressure of the material being absorbed at the point in the gas phase adjacent to the gas-liquid interface. The average value of this quantity through the column was used. To calculate it Herron's equation, as quoted by Eagleton *et al.* (*7*), for the simultaneous diffusion of nitrogen dioxide and nitrogen tetroxide through a stagnant gas film was used. [See Equation (12).] The equation was derived by assuming that the two substances are locally at chemical equilibrium everywhere in the gas film.

$$N_A = 2K_p(k_G)_{N_2O_4}[(p_{NO_2})^2 - p_{iNO_2})^2] + (k_G)_{NO_2}[(p_{NO_2} - p_{iNO_2})] \qquad (12)$$

The interfacial partial pressure of nitrogen tetroxide is related to that of nitrogen dioxide by Equation (9). With Equation (12) and the gas-film coefficient correlation developed during this work, the interfacial partial pressure of nitrogen tetroxide could be obtained. The upper curves in Figures 8, 9, and 10 are plots of absorption rate as a function of interfacial partial pressure of nitrogen tetroxide for the results obtained with the 8.72-cm. column. The interfacial concentration of nitrogen textroxide is appreciably less than the bulk nitrogen tetroxide. A straight line through these results passes through the origin, showing a direct proportionality between N_A and $(p_i)_{N_2O_4}$. Therefore nitrogen tetroxide is the species which dissolves and reacts more rapidly.

Effect of Liquid Rate

The change in absorption rate with contact time between gas and liquid was studied by varying the water rate through the columns. All three of the columns were employed to give as wide a variation of contact time as possible. Figure 11 shows the results plotted as absorption rate divided by interfacial partial pressure of nitrogen tetroxide vs. contact time. Each point on this graph represents the average of all the runs made at that particular contact time. The points were weighted, according to the number of runs making up the average, to locate the best line through the data. There is no trend of the data with time over the tenfold range covered. This independence of the rate and the contact time also means that end effects, such as partial stagnation of the liquid at the exit slot, which might change the contact time, probably had very little effect on the absorption rate of nitrogen tetroxide into water.

A series of runs was made at 40°C. to determine the effect of temperature on absorption rate. It was found, as seen in Figure 11, that a slight decrease of $N_A/(p_i)_{N_2O_4}$ with increased temperature occurred, even when runs were made at the same interfacial partial pressure. The decrease, which may not be significant because of the scatter in the data, is probably due to the lower solubility of nitrogen tetroxide in water at the higher temperature, which more than offsets the increase of diffusivity of nitrogen tetroxide in water once the molecule has been absorbed. If the data had been plotted as absorption rate vs. total nitrogen peroxide in the gas, the rate would have been found to be lower at the higher temperature.

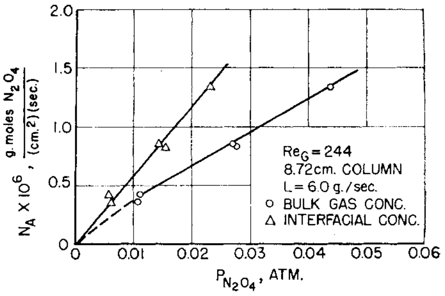

Fig. 8. Absorption results, L = 6.0 g./sec.

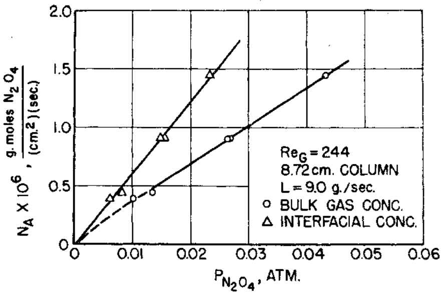

Fig. 9. Absorption results, L = 9.0 g./sec.

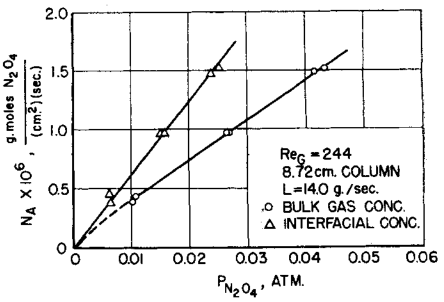

Fig. 10. Absorption results, L = 14.0 g./sec.

RESULTS IN TERMS OF THE PENETRATION THEORY

The controlling chemical step in the absorption process is the bimolecular reaction between dissolved nitrogen tetroxide and liquid water:

$$N_2O_{4(aq)} + H_2O_{(l)} \xrightarrow{k_c} HNO_{2(aq)} + HNO_{3(aq)} \qquad (13)$$

The water concentration always greatly exceeds the tetroxide, and so the reaction can be considered a pseudo-first-order one. For a first-order chemical reaction accompanying absorption, Sherwood and Pigford (*24*) give the following equation derived on the basis of the penetration theory.

$$N_A = \sqrt{k_c D}[1 + \tfrac{1}{2}(k_c t) + \cdots]c_i \qquad (14)$$

The fact that the absorption rate at constant interfacial concentration of nitrogen tetroxide is not affected by the time of contact between gas and liquid t indicates that the reaction rate constant k_c is large. Equation (14) can be simplified to

$$N_A = \sqrt{k_c D}(c_i)_{N_2O_4} \qquad (15)$$

where $(c_i)_{N_2O_4}$ is the concentration at the interface of the dissolved but unreacted nitrogen tetroxide in water. This equation can be rewritten in the form

$$\frac{N_A}{(p_i)_{N_2O_4}} = \sqrt{k_c D}\,\frac{(c_i)_{N_2O_4}}{(p_i)_{N_2O_4}} \qquad (16)$$

For the physical solution of nitrogen tetroxide in water,

$$N_2O_{4(g)} \rightleftharpoons N_2O_{4(aq)} \qquad (17)$$

the equilibrium constant

$$K_1 = \frac{(c_i)_{N_2O_4}}{(p_i)_{N_2O_4}} \qquad (18)$$

is a measure of the solubility of unreacted nitrogen tetroxide in water. $N_A/(p_i)_{N_2O_4}$ has been measured in this research and found to depend only on the temperature. Although it cannot be measured directly, the diffusivity D of nitrogen tetroxide in water can be estimated from the Wilke correlation (*30*). Thus, on the basis of the experiments, there is a relation between the equilibrium constant for the physical solution of nitrogen tetroxide in water K_1 and the rate constant for hydrolysis of nitrogen tetroxide, k_c:

$$k_c = \left[\frac{N_A}{(p_i)_{N_2O_4}}\right]^2 \frac{1}{D}\left(\frac{1}{K_1}\right)^2 \qquad (19)$$

Inserting the known quantities from Figure 11 in Equation (19) one obtains

$$k_c = 2.68 \times 10^{-4}\left(\frac{1}{K_1}\right)^2 \text{ at } 25°\text{C.} \qquad (20)$$

$$k_c = 1.66 \times 10^{-4}\left(\frac{1}{K_1}\right)^2 \text{ at } 40°\text{C.} \qquad (21)$$

To carry the analysis of the data further, one must resort to an independent source of physico-chemical data. Abel and Schmid (*1*), who have made an extensive study of the kinetics of nitrous acid formation and decomposition, showed that the decomposition of nitrous acid takes place by a sequence of steps stoichiometrically equivalent to the reaction

$$3HNO_2 \xrightarrow{k_1} H^+ + NO_3^- + 2NO + H_2O \qquad (22)$$

and during the initial stages

$$-\frac{d(HNO_2)}{dt} = k_1 \frac{(HNO_2)^4}{(p_{NO})^2} \qquad (23)$$

Values of k_1 determined by Abel are quoted in Table 2.

TABLE 2. RATE CONSTANTS OF ABEL AND SCHMID FOR NITROUS ACID DECOMPOSITION

T, °C.	k_1, (liters)^4/(g. moles)^4(min.)(atm.)^2
0	0.602
12	3.63
25	46
40	525

To explain the rate, Equation (23), Abel and Schmid proposed the mechanism

$$4HNO_{2(aq)} \rightleftharpoons N_2O_{4(aq)} + 2NO_{(g)} + 2H_2O_{(l)} \qquad (24)$$

a relatively rapid equilibrium

$$N_2O_{4(aq)} + H_2O_{(l)} \xrightarrow{k_c} HNO_{2(aq)} + H^+ + NO_3^- \qquad (25)$$

a slower, rate-determining step

For the equilibrium step, Equation (24), one writes

$$K_2 = \frac{(N_2O_4)(p_{NO})^2}{(HNO_2)^4} \qquad (26)$$

or

$$\frac{(HNO_2)^4}{(p_{NO})^2} = \frac{(N_2O_4)}{K_2} \qquad (27)$$

Thus from Equations (23) and (27)

$$-\frac{d(HNO_2)}{dt} = \frac{k_1(N_2O_4)}{K_2} \qquad (28)$$

Since a net total of three molecules of nitrous acid decompose when one molecule of nitrogen tetroxide disappears and from Equation (25)

$$-\frac{d(N_2O_4)}{dt} = \frac{1}{3}\frac{k_1(N_2O_4)}{K_2} = k_c(N_2O_4) \qquad (29)$$

$$k_c = \frac{1}{3}\left(\frac{k_1}{K_2}\right) \qquad (30)$$

The concentration of dissolved but unreacted nitrogen tetroxide can be related to the partial pressure in the gas by the equilibrium constant K_1 as given in Equation (18). If K_1 is substituted into Equation (26), one obtains

$$K_2 = \frac{K_1(p_{N_2O_4})(p_{NO})^2}{(HNO_2)^4} \qquad (31)$$

With

$$\frac{K_2}{K_1} = \frac{(p_{N_2O_4})(p_{NO})^2}{(HNO_2)^4} = K_3 \qquad (32)$$

$$k_c = \frac{1}{3}\frac{k_1}{K_1 K_3} \qquad (33)$$

Abel, to find K_3, made use of the data of Pick (*22*), who measured standard electrode potentials at 25°C. for the reactions

$$2HNO_{2(aq)} + 2H^+ = 2NO_{(g)} + 2H_2O_{(l)} - 2e;\ E° = 0.98 \text{ volt} \qquad (34)$$

$$N_2O_{4(g)} + 2H^+ = 2HNO_{2(aq)} - 2e;\ E° = 1.07 \text{ volts} \qquad (35)$$

Subtracting (35) from (34) one obtains

$$4HNO_{2(aq)} = N_2O_{4(g)} + 2NO_{(g)} + 2H_2O_{(l)};\ E° = -0.09 \text{ volt} \qquad (36)$$

from which $\Delta F° = 4{,}150$ cal./mole can be calculated. The equilibrium constant for reaction (36) is K_3; it can be obtained from the expression relating the free energy change and equilibrium constant.

$$\Delta F° = -RT \ln K_3 \qquad (37)$$

$$K_3 = 9.1 \times 10^{-4} \frac{(\text{atm.})^3(\text{liter})^4}{(\text{g.-mole})^4} \text{ at } 25°\text{C.} \qquad (38)$$

Equation (33) becomes

$$k_c = 361\frac{k_1}{K_1} \qquad (39)$$

From Table 2 a value of 46 at 25°C. is available for k_1, where the units are in moles per liter and minutes. If this is converted to moles per cubic centimeter and seconds and substituted in Equation (39), one obtains

$$k_c = \frac{0.281}{K_1} \qquad (40)$$

Equations (40) and (20) involve the rate constant for hydrolysis of nitrogen tetroxide k_c and the equilibrium constant K_1. With these simultaneous equations one finds at 25°C.

$$k_c = 290 \text{ sec.}^{-1}$$

$$K_1 = 9.55 \times 10^{-4} \text{ g.-moles/(cc.)(atm.)}$$

The solubility, expressed as a Henry's Law constant, is $H = 58$ atm./(g.-moles N_2O_4)/(g.-mole solution). For comparison, H for carbon dioxide is 1,640 at 25°C.; therefore nitrogen tetroxide is about thirty times more soluble than carbon dioxide. From the absorption runs made at 40°C. one can procure

$k_c = 1{,}340 \text{ sec.}^{-1}$

$K_1 = 3.52 \times 10^{-4}$ g.-moles/(cc.)(atm.) or

$H = 158$ atm./(g.-mole N_2O_4)/(g.-mole solution)

The energy of activation for the hydrolysis of nitrogen tetroxide and the heat of solution of nitrogen tetroxide in water can be estimated from the knowledge of k_c and K_1 at two temperatures.

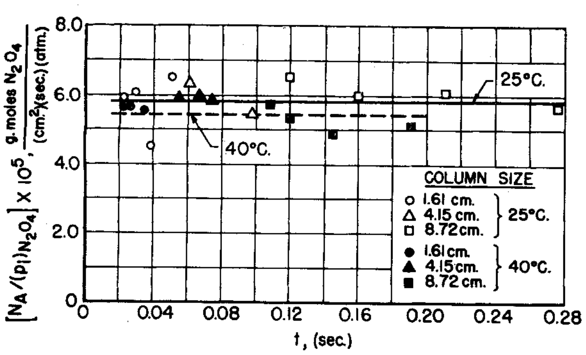

Fig. 11. Effect of absorption time on absorption rate.

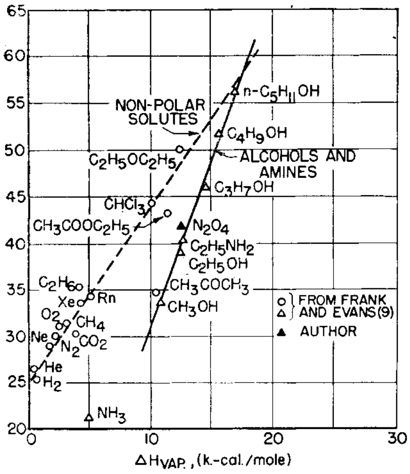

Fig. 12. Thermodynamic properties of nonionic solutes in water.

$$\Delta H_{act} = 18.8 \text{ k.-cal./g.-mole}$$

$$\Delta H_{soln} = -12.3 \text{ k.-cal./g.-mole}$$

This value of activation energy is a reasonable one for reactions in solution, and the heat of solution is of the same order of magnitude as an estimate of −14.1 k.-cal./g.-mole at 18°C. given for nitrogen tetroxide into water by Thomsen (*26*).

COMPARISON OF RESULTS WITH LITERATURE INFORMATION

The phenomenon of a white fog or mist during nitrogen dioxide absorption is not new. A mist is often visible in the absorption towers used to manufacture nitric acid. Previous authors specifically called attention to its occurrence in long wetted-wall columns (*5*, *7*). However Denbigh and co-workers (*4*, *6*) observed no mist, and Peters and Holman (*21*) state that they eliminated mist during NO_2 absorption by carefully filtering the inert carrier gas before using it. In most of the experiments made in this research, although the nitrogen was not filtered, no fog was visible even after nitrogen dioxide had contacted liquid water in the column. When hydrogen chloride was mixed with nitrogen and passed through the column, mist occurred similar in appearance to what was observed occasionally during nitrogen dioxide absorption. In addition the author (*28*) observed a mist when pure phosgene was absorbed into water and aqueous solutions of sodium hydroxide. This suggests a possible explanation for the mist phenomenon.

When a highly soluble gas is absorbed which has a large heat of solution and reaction with water, the temperature of the water surface rises, causing vaporization of some water. As this water vapor diffuses outward into the cooler gas stream condensation occurs in the form of minute droplets: a fog. Absorption of gas can take place into these droplets generating, in the case of nitrogen peroxide, nitric acid within them.

Further evidence in support of this hypothesis was found when a temperature gradient was deliberately imposed on the NO_2–H_2O system in the present research. The water in the wetted-wall column was held at 40°C. inlet temperature, and an NO_2–N_2O_4–N_2 gas stream 15° cooler was passed through the absorber. A very dense mist ensued, but as the gas temperature was increased the amount of mist decreased until only a trace was visible when both gas and liquid were at 40°C. According to the hypothesis the amount of water vapor condensing to form fog decreased as the gas temperature was increased.

For a nitrogen peroxide system absorption into water droplets would yield nitric oxide which would then escape into the gas stream because of its low solubility in nitric acid solutions. This could account for the occurrence of nitric oxide in the exit gas from Chambers' (*5*) column. The heat of reaction between nitrogen peroxide and water or sodium hydroxide solution could have caused some water to be vaporized which, condensed as described, absorbed nitrogen dioxide and desorbed nitric oxide. The heat of reaction between nitrogen dioxide and the water droplets would generate heat in the gas phase which would raise the temperature and account for a temperature rise in the gas stream, also reported by Chambers. Fog droplets escaping from the column with the exit gas would give an acid reaction, even though the liquid phase is alkaline, in agreement with observations. Thus neither the occurrence of a mist nor the presence of nitric oxide in the exit gas stream from an absorber should be used as conclusive evidence of a vapor-phase reaction between nitrogen dioxide and water.

The absence of a gas-rate effect on absorption rates is in complete agreement with Bolshakoff (*3*), as recalculated by Eagleton, *et al.* (*18*), who found no effect in the range of Re_G from 125 to 1,100 when the partial pressure of $NO_2 + 2N_2O_4$ was 0.04 atm. or greater. Bolshakoff used a long wetted-wall column and absorbed into aqueous solutions of sodium hydroxide. Denbigh and Prince (*17*), who were the only other investigators to use gas rates as low as those of this research, found only a small effect of gas velocity.

There is considerable support in the literature for the linear relationship found in this work between absorption rate and bulk gas-phase nitrogen tetroxide concentration. Denbigh and coworkers (*4*, *6*) and Peters, Ross, and Klein (*20*) concur and account for it by assuming that the reaction between nitrogen tetroxide and water is the rate-controlling chemical step in the process. The latter authors believed the reaction to occur in *both* gas and liquid phases, but Denbigh (*4*) stated only that it must occur near the gas-liquid interface. Denbigh and Prince (*6*) expressed the relation between rate of absorption of nitrogen peroxide and bulk nitrogen tetroxide concentration in the gas by the equation

$$N_A = k_a(p_{N_2O_4}) \qquad (41)$$

when absorbing into dilute nitric acid solutions in the absence of nitric oxide. This equation indicates that their plots of N_A vs. $p_{N_2O_4}$ passed through the origin, although a small intercept was found in every case in this research when plotting bulk $p_{N_2O_4}$. The use of interfacial $p_{N_2O_4}$ has been shown to eliminate this intercept in the present paper. The average values of k_a found by Denbigh and Prince at 25° and 40°C. are compared with the average slope of lines from plots of N_A vs. bulk N_2O_4 partial pressure for this investigation (for example, Figures 5, 6, and 7) in Table 3. The agreement is fair considering that the average for this research included results for all liquid rates. The influence of temperature on k_a, also shown in Table 3, is nearly the same in the two investigations.

In these experiments no effect of liquid rate (or time of contact between gas and liquid) on $N_A(p_i)_{N_2O_4}$ was found. This is in accord with the results of Denbigh and Prince (*6*) who found no effect of liquid rate on $N_A/(p_{N_2O_4})$ bulk and Caudle and Denbigh (*4*) who reported only a slight effect on a similar quantity.

TABLE 3. COMPARISON OF D. AND P. RESULTS WITH THIS WORK

Temp., °C.	k_a (D & P.), cm./sec.	$\frac{(k_a)\ 40°}{(k_a)\ 25°}$	k_a (this work), cm./sec.	$\frac{(k_a)\ 40°}{(k_a)\ 25°}$
25	1.8		0.71	
40	2.3		0.94	
		1.28		1.32

The small decrease in $N_A(p_i)_{N_2O_4}$ with a temperature rise from 25° to 40°C. means that at a constant value of total nitrogen peroxide in the gas the absorption rate for nitrogen peroxide decreased with an increase in temperature. This occurs because more nitrogen peroxide must be present at 40°C. to give the same nitrogen tetroxide concentration at the interface, owing to the shift in the NO_2-N_2O_4 equilibrium. Webb (*27*) and Denbigh and Prince (*7*) also found this decrease in absorption at higher temperatures.

Although the proposed mechanism of the absorption process is supported by all of the experimental evidence available, it may be reasonably asked whether another mechanism, possible involving other chemical species, may not also be able to account for the experimental facts. That many different compounds involving nitrogen and oxygen are possible and that many are chemically reactive toward water is obvious. Therefore is the proposed mechanism the true one? Are the chemical properties of dissolved nitrogen tetroxide molecules, inferred from the experimental data, those of a real or imaginary chemical substance? Although an unequivocal answer to such questions may not be possible, in view of the limitations of the data owing to experimental errors of observation, it can be stated that with a high degree of probability the suggested mechanism *is* the true one, since it can be shown that the derived thermodynamic properties of the tetroxide are reasonable values. Several independent pieces of experimental evidence, each independent of the other, have been employed, and each has assumed the existence of the tetroxide molecules. The numerical values of heat and entropy of solution derived from all the data through the chain of assumptions could hardly represent acceptable thermodynamic properties unless all the assumptions were essentially correct. If one of the mutually dependent results can be shown to be correct, all must be essentially true.

Frank and Evans (*10*) have plotted the entropy of vaporization of various nonionic solutes in water vs. the heat of vaporization of the gases from aqueous solution as shown in Figure 12. The points on this plot may be divided into two groups: (*a*) nonpolar solutes, and (*b*) alcohols and amines. An entropy of vaporization for dissolved but unreacted nitrogen tetroxide of −42.2 cal./°K. can be calculated from the values of K_1 and ΔH_{soln} at 25°C. to give the point for nitrogen tetroxide plotted on Figure 12. It is seen that this point falls close to the line for alcohols and amines, as might be expected on the basis of hydrogen bonding since alcohols, amines, and nitrogen tetroxide (which has four oxygen atoms available) have the opportunity to hydrogen bond in water solution. The fact that the observed values of ΔS and ΔH lie at a reasonable position in Figure 12 lends support to the validity of both thermodynamic properties and the rate data obtained for nitrogen tetroxide.

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NOTATION

c_i = interfacial concentration of solute, g.-moles/cc.
d = wetted-wall column I.D., cm.
D = diffusivity, sq. cm./sec.
$\Delta F°$ = standard free energy change, cal./g.-mole
G_r = relative gas rate, cc./sec.
H = Henry's law constant, atm./(g.-mole N_2O_4)/(g.-mole solution)
ΔH_{act} = energy of activation, k.-cal./g.-mole
ΔH_{soln} = heat of solution, k.-cal./g.-mole
k = reaction rate constant, subscript denotes reaction
k_a = slope of curve of N_A vs. $p_{N_2O_4}$, g.-moles/(sq. cm.)(sec.)(atm.)
k_c = pseudo-first-order rate constant, sec.$^{-1}$
k_G = gas-film coefficient, g.-mole/(sq. cm.)(sec.)(atm.)
K = equilibrium constant, subscript denotes reaction
L = liquid flow rate, g./sec.
N = wetted-wall column length, cm.
N_A = average absorption rate, g.-moles N_2O_4/(sq. cm.)(sec.)
p = partial pressure of gas, atm.
P_{G_1} = partial pressure of solute at inlet to column, atm.
P_{G_2} = partial pressure of solute at exit from column, atm.
P = total pressure, atm.
p_{BM} = log mean partial pressure of inert gas, atm.
Re_G = gas Reynolds number
t = time of contact between phases, sec.
T = temperature, °K.

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