Absorption of NO_2/N_2O_4 into Water and Dilute Nitric Acid in a Double Stirrer Absorber

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Abstract

This study was concerned with the estimation of the absorption rate of NO_2/N_2O_4 into water and dilute nitric acid in a double stirred cell absorber. The calculation that currently carried out is based on two concepts (criteria); only N_2O_4 species is considered as a transporting species across the interface, and the depletion of nitrous acid in the aqueous phase resulting nitrogen monoxide and producing nitric acid in the liquid phase. In additions, the calculation was based on a system of chemical reactions and their equilibria.

In general, the study had estimated the absorption rate of the equilibrium mixtures of the two species NO_2/N_2O_4 into water and dilutes nitric acid concentration that ranged between 10-wt % - 40 wt %. Although, the characteristic performance for the double stirrer cell absorber had examined, which elucidates the most suitable contact pattern between the gas phase and the liquid phase in comparison to absorption rate of other workers in different absorber types.

The estimation of the absorption rates in different isothermal absorption temperatures (10, 15, and 20 °C) was determined. Emphasis is put on different levels of nitrogen dioxide concentration 58, 87, and 116 $*10^{-6}$ gmol/cm^3. The absorption rates were determined by simultaneous measuring the nitric acid concentration in the liquid phase by implementing different measuring techniques (electrical conductivity meter, ultra violet spectrophotometer and acid-base titration method).

The absorption of N_2O_4, which was considered as the only transporting species in water and dilute nitric acid solutions, was conducted in a chemisorption process regime, which is mainly controlled by the hydrolysis reaction of N_2O_4 with water. This conclusion was ascertained through studying the effect of absorption temperature on the mass transfer rates.

It was postulated that the mass transfer rates had shown low values as temperature decreases which strictly attributed to its influences on the rate of hydrolysis of N_2O_4 in spite of its counter effect on the solubility of N_2O_4 as well as the gas equilibrium. Meanwhile, values of Hatta number, $H_{N_2O_4}(kD_{N_2O_4})^{1/2}$, were measured in according to the acid strength and absorption temperature. The Hatta number values had shown increased values with increased absorption temperature, in spite of the lower effect of absorption temperature on Henry constants which accompanied with a lesser degree of solubility of N_2O_4 in the liquid phase. As well as, the acid strength had shown similar effect on the rate of mass transfer, which simply attributed to low values of Henry coefficients and low rate of hydrolysis of N_2O_4 as a result of lesser existence of free molecules of water.

Introduction

The presence of nitrogen dioxide in the atmosphere represents a serious hazard, such as, fading the textile dye and additives, deterioration of cotton and nylon, and concentration of 100 ppm or more for a few minutes can be lethal to humans. Therefore, control of the emissions appears to be increasingly important need. Meanwhile, because of the worldwide demands for environmental protection, the NO_x concentration in the waste gas has to be reduced. Therefore, more sophisticated calculation methods for studying and designing the absorption step of nitric acid process are being developed (Werner *et al*, 1990).

The interaction of chemical reaction and mass transport is a subject of continuing interest to chemical engineering. The process has been extensively studied but the rate expressions and the stoichiometric relationships reported in these studies are conflicting (Komiyama and Inoue, 1978). Absorption mechanism has been reported that only N_2O_4 of the equilibrium mixture of NO_2 and N_2O_4 reacts with water (Sherwood, 1975). A model based on this hypothesis that N_2O_4 is the only transporting species results in a second order NO_2 concentration dependency of the absorption rate (Dekker *et al*, 1959; Kramers *et al*, 1951; Wendel and Pigford, 1958; Kameoka and Pigford, 1977). However, deviations had noticed by Andrew and Hanson (1961), and Sada *et al* (1979), especially at low concentration of NO_2. Furthermore, in the aqueous solution of nitrous acid, nitrogen oxides are evolved into gas phase and nitric acid is produced in the liquid phase, resulting in the depletion of nitrous acid, hence, it is a reverse process of absorption of nitrogen oxides into water (Komiyama and Inoue, 1978).

The estimation of the absorption rate that currently used is based on two criteria: (1) only N_2O_4 species is considered as a transporting species, (2) the depletion of nitrous acid in the aqueous phase resulting nitrogen dioxide and producing nitric acid in the liquid phase. The estimation of the absorption rates is planned to commence at different isothermal temperatures (10, 15, and 20 °C) and at different concentration levels of nitrogen dioxide (58, 87, and $116 * 10^{-6}$ $gmol/cm^3$). The absorption rates might be determined by simultaneous measuring the liquid phase concentration via three different techniques. Moreover, the speed of the stirrer in the gas phase of the double stirrer cell and the flow rate of the inlet gas stream must adjusted at some value to minimize the resistance in transporting of the two species NO_2/N_2O_4 in the gas phase. In addition high flow rate would recommend, to prevent achieving equilibrium between the $NO/NO_2/HNO_3/H_2O$.

The mechanism of absorption of nitrogen oxide into water and dilute nitric acid is known to be highly complex, involving reactions in both gas and liquid phase (Sherwood, 1975). The route involves N_2O_4 as the liquid phase reactant, it's formation in the gas phase. Although, the kinetics of absorption has been subjected to investigation principally by many works (Chambers and Sherwood, 1937; Denbigh and Prince, 1947; Caudle and Denbigh, 1953; Wendel and Pigford, 1958), however, interpretations of their experimental results had failed to come into agreement in many respects. While, Chambers and Sherwood (1937) supported the gas film diffusion step as the rate controlling, Denbigh and Prince (1947) believed that chemical reaction in the liquid phase controls the overall absorption. At the same time, Caudle and Denbigh (1953) in their investigation appears to reconcile the issue in that they had shown that the gas rate did affect the absorption insofar as local eddying and mixing in the reactant liquid phase. In addition, the disagreement had extended to pertain the existence of a gas-phase reaction between water vapor and nitrogen dioxide. Furthermore, there are compelling arguments for and against the gas phase production of nitric acid. Chambers and Sherwood (1937), Peter *et al* (1955) submit evidence in favor of a gas-phase reaction occurring simultaneously with the liquid phase reaction.

Incidentally, Miller (1987) had stated that the mass transfer and reaction of nitrogen dioxide occurs in the following sequence:

1. $2\,NO_2 \leftrightarrow N_2O_4$
2. $N_2O_{4\,(g)} \leftrightarrow N_2O_{4\,(l)}$
3. $N_2O_{4\,(l)} + H_2O_{(l)} \leftrightarrow HNO_{3\,(l)} + HNO_{2\,(l)}$

Step (1) gas phase dimerization of NO_2 equilibrates is so rapidly established that it may be assumed that NO_2 and N_2O_4 are continuously in equilibrium with each other (Hisatsune, 1961). JANAF (1971) reported the equilibrium constant for the dimerization reaction,

$$\log k_p = 0.698 * 10^{-9} \exp(6866/T) \cdots (1)$$

Furthermore, Moll (1966) reported the rate of hydrolysis (step 3):

$$\ln k = 6.38 - 3163/T \cdots (2)$$

Most experimental results reported by other investigators (Galderbank and Moo-Young, 1961; Komiyama and Inoue, 1980) agree well with this mechanism, however, deviations are reported by Andrew and Hanson (1961) especially at low concentrations of NO_2, as well as, at high concentration of nitric acid (Lefers and Van der Berg, 1982). Werner *et al.*, (1990) had stated that the chemical reaction between dinitrogen tetroxide and water yields nitric acid and nitrous acid (step 3). Furthermore, the nitrous acid would disproportionate into nitric acid, HNO_3, and water according to the following equation:

$$3\,HNO_2 \leftrightarrow HNO_3 + 2\,NO + H_2O$$

Decomposition of nitrous acid dose not take place rapidly if its concentration is low (Chambers and Sherwood, 1937). Both NO_2 and N_2O_4 are transferred from the gas bulk to the gas/liquid interface. Werner *et al.* (1990) had stated that the diffusion of mixed NO_2/N_2O_4 can be regarded as the diffusion of the hypothetical components NO^*_2, defined as:

$$C\,(NO^*_2) \longrightarrow C\,(NO_2) + 2\,C\,(N_2O_4)$$

Due to lower solubility of NO_2 in water, it is assumed that only N_2O_4 penetrates the gas liquid interface and reacts (Hoftyzer and Kwanter, 1972).

The reactive nature of N_2O_4 relative to its monomer NO_2 is indicated in systems other than those involving water. In a study of the kinetics of reactions of nitrogen dioxide with various alcohols, Carberry (1959) found that third-order kinetic characterized the initial reaction rate. When, however, their rate equation was written in terms of N_2O_4, second-order kinetics and a normal temperature dependency resulted. They simply concluded that N_2O_4; not NO_2 is the reactant species with alcohol. With this imposing body of evidence favoring N_2O_4 as the chief reactant candidate in various systems, it appears that equilibrium data for the nitrogen oxides-water system would be more logically expressed in terms of N_2O_4 rather than NO_2.

During the last sixty years several investigators have studied the production of nitric acid in an absorption column. Chambers and Sherwood (1937) interpreted their results on the basis of the two-film theory and found the gas film to be the rate controlling. However, the absorption rate was lower than that was expected from similar absorption experiments with other gases. Accordingly, they explained this discrepancy to the formation of mist in the gas phase. Whereas, Denbigh and Prince (1947) reconciled from their experiments that the absorption rate was controlled by the chemical reaction between N_2O_4 and water in the liquid phase. In addition, they did not find an indication of gas phase reaction. While, Peter *et al.* (1955) stated that the reaction between N_2O_4 and H_2O in the gas phase close to the interface was rate controlling. So far, Wendel and Pigford (1958) stated the controlling mechanism in the absorption to be the homogeneous liquid phase reaction of dissolved N_2O_4 with water. However, their data indicates that the gas phase resistance also plays an important role in the absorption rate. The two film theory of absorption been frequently used by many investigators to analyze absorption results, while others had been interpreted in terms of the chemical reaction kinetics alone. However, some studies had considered the penetration and the film theories for simulating the rate of absorption and the simultaneous reaction of nitric oxide in aqueous nitric acid solutions. Carta and Pigford (1983) had found that the solution of the penetration theory had been found to be in qualitative agreement with the experimental observations. However, they found due to the autocatalytic nature of the reaction, the film theory significantly disagrees with the penetration theory outside some special cases.

Many studies had been considered the absorption of nitrogen tetroxide into aqueous solution in both short and long wetted columns and also in bubble cap plates, Table (2). The results obtained in long wetted-columns (3 ft long) conducted by Bolshakoff (1934) and Chambers and Sherwood (1937) indicated that the gas-film resistance controlled the absorption of nitrogen dioxide into aqueous solution of nitric acid and sodium hydroxide. Whereas, Eagleton and Pigford (1948) 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. Peter *et al*, (1955) studied the effects of temperature and water vapor concentration on the absorption of nitrogen tetroxide into aqueous solution of sodium hydroxide and sodium chloride in long wetted-column. They clarified that both gas-and liquid phase reactions between nitrogen tetroxide and water occurred and that the rate of absorption was controlled by these two reactions.

Denbigh and Prince (1947); Caudle and Denbigh (1953), conducted their experiments in a short wetted-wall column (less than 7 inch) and reported before Peters and Holman (1955) that the absorption rate of nitrogen tetroxide 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.

In a dramatic detour, Peters *et al*, (1955) had carried their experiments in bubble-cup-plate column to study the absorption of nitrogen tetroxide into aqueous nitric acid and concluded that the rate controlling step was the chemical reaction between nitrogen tetroxide and water in the gas phase.

The existence of a homogenous vapor phase reaction between nitrogen tetroxide 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 reaction is summarized: -

1. Chambers and Sherwood (1937) observed a mist while absorbing nitrogen tetroxide into aqueous solution of sodium hydroxide and nitric acid. They postulated that this mist was caused by the concentration of nitric acid produced by the vapor-phase reaction.

$$3\,NO_2 + H_2O \longrightarrow 2\,HNO_3 + NO$$

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, since they believed that the dioxide once absorbed, reacted with hydroxide according to:

$$2\,NO_2 + 2\,NaOH \longrightarrow NaNO_2 + NaNO_3 + H_2O$$

From which no nitric oxide could be produced.

2. Peters *et al*, (1955) found nitric oxide in the exit gas stream from a long wetted-column absorber when absorbing nitrogen tetroxide into aqueous solution. Thus the hypothesis of a gas-phase reaction has always 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 tetroxide in the vapor phase,

3. Kuzminykh and Udintseve (1954) attempted to measure the pressure change, which should occur in a constant-volume system if a homogeneous vapor-phase reaction took place between nitrogen tetroxide and water. As they found no change, they concluded that no reaction had occurred.
4. In direct contradiction to part of the evidence cited in support of vapor-phase reaction, Denbigh and prince (1947) observed no mist during any of their runs while absorbing nitrogen tetroxide into nitric acid solution in a short column.
5. No mist was observed during any of the Caudle and Denbigh's (1953) experiments, and no nitric oxide was found in the exit stream during the absorption runs where sodium hydroxide solutions were used. This evidence excluded the possibility of a gas phase reaction according to hydrolysis reaction of N_2O_4 and since the nitrous acid would have decomposed to yield nitric oxide.

Mathematical Treatment

Physically in this mathematical treatment of the experimental results measured in two type of absorbers (the double stirrer cell and the bubbler cell), modeling of the mass transfer is based on the film model of Lewis and Whitman, using Fick's first law of diffusion:

$$D_{NO_2,g}\frac{d^2c_{NO_2}}{dx^2}=0\cdots(3)$$

With the boundary conditions:

for $x=0$, $\qquad c_{NO_2}=c^*_{NO_2}$

and $x=\delta_g$ $\qquad c_{NO_2}=c_{NO_2,\text{bulk}}$

Also an analogous equation is valid for the N_2O_4 species. The mass flow rate in terms of chemical NO_2^* species can be expressed as:

$$J_{NO_2^*}=J_{NO_2}+2J_{N_2O_4}\cdots(4)$$

Substituting $k_{g_i}={D_{i,g}}/{\delta_g}$, it follows for the rate of mass transfer:

$$J_{NO_2^*}=k_{g_{NO_2}}\left(C_{NO_2}-C_{NO_2^*}\right)+2k_{g_{N_2O_4}}\left(C_{N_2O_4bulk}-C_{N_2O_4^*}\right)\qquad\cdots(5)$$

In terms of the equilibrium constant, Substitute Eq (3) in Eq (5) yields,

$$J_{NO_2^*}=k_{g_{NO_2}}\left(C_{NO_2bulk}-C_{NO_2^*}\right)+2k_Pk_{g_{N_2O_4}}\left[\left(C_{NO_2bulk}\right)^2-\left(C_{NO_2^*}\right)^2\right]\qquad\cdots(6)$$

Across the interface, in the liquid side from the interface, in addition to diffusion, a chemical reaction occurs between N_2O_4 and H_2O, which described by the following differential equation:

$$D_{N_2O_4,L}\frac{d^2C_{N_2O_4}}{dy^2}-k\,C_{N_2O_4}=0\cdots(7)$$

With the boundary conditions,

for $y=0$, $\qquad C_{N_2O_4}=C_{N_2^*O_4}$

and $y=\delta_L$ $\qquad C_{N_2O_4}=C_{N_2O_4\text{bulk}}$

Solving the above equation and also taking into account the Hatta number, $Ha=\delta_L\left(k/D_{N_2O_4,L}\right)^{1/2}$, and applying $k_{N_2O_4,L}=D_{N_2O_4,L}\left(\delta_L\right)^{-1}$, an equation for the mass transfer rate is established:

$$J_{N_2O_4}=\frac{Ha}{\tanh Ha}\left[1-\frac{C_{N_2O_4}}{C_{N_2^*O_4}}\frac{1}{\cosh Ha}\right]\times k_{N_2O_4,L}C_{N_2^*O_4}\cdots(8)$$

For a fast chemical reaction Eq (8) may be simplified to:

$$J_{N_2O_4}=C_{N_2^*O_4}\left(k\,D_{N_2O_4,L}\right)^{1/2}\cdots(9)$$

The equilibrium at the gas/liquid interface as a condition of the film theory model, may be expressed according to Henry's law:

$$C_{N_2^*O_4}=H_{N_2O_4}P^*_{N_2O_4}\cdots(10)$$

Incorporating to the above assumption, the two film theory of mass transfer accompanied by a rapid pseudo-first order reaction in the liquid phase is applied, then the absorption rate per unit of surface area can be written as:

$$J_{N_2O_4}=H_{N_2O_4}P^*_{N_2O_4}\sqrt{k\,D_\ell}\cdots(11)$$

Note in above equation the value of rate constant (k) incorporate the molar concentration of N_2O_4 in water. Values of Hatta number, $\left[H_{N_2O_4}\sqrt{k\,D_\ell}\right]$, have been measured by several investigators using different laboratory absorbers (contactor). Accordingly, Hatta number had been measured in terms of temperature variation, different concentration of NO_2 and different initial concentration of nitric acid in the liquid phase.

In order to determine the values of Hatta number from experimental results in the double stirred absorber, it is necessary to have reliable values for the diffusivities for NO_2 and N_2O_4. Theses values can be estimated using empirical equation proposed by

Gilliland (1934) for estimating the diffusivity in the gas phase, which is simply listed below:

$$D = \frac{0.0043T^{3/2}\sqrt{\frac{1}{M_A}+\frac{1}{M_b}}}{\left(V_A^{1/3}+V_B^{1/3}\right)^2 P} \cdots (12)$$

Whereas, the value of diffusivity of N_2O_4 in water may be calculated from many empirical equations listed in literatures e.g., Wilke's equation or Scheibel's equation or Othmer and Thaker's equation (Sherwood, 1975), but herein, the value of N_2O_4 diffusivity had been extracted from experimentally measured values done by (Dekker *et al*, 1959; Andrew and Hanson, 1961; Lefers and Von der Berg, 1982), which is equal to $1.4*10^{-5}$ cm/s.

Using the diffusion coefficients, it is possible to calculate the mass transfer coefficients ($k_{g,i}$, $k_{l,i}$) for the gas and liquid sides of the interface. They are determined from coefficients extracted by measuring model absorptions, e.g. of N_2O into $Ca(OH)_2$-solutions or $Mg(OH)_2$-solutions, a pure physisorption producing k_{l,N_2O} values and of SO_2 into NaOH-solution i.e. chemisorption with a fast chemical reaction yielding k_{g,SO_2} data.

Experimental results for absorption of N_2O into aqueous slurries of $Ca(OH)_2$ or $Mg(OH)_2$ show that the liquid-side mass transfer coefficient, k_l, can be correlated by the following equation (Sada *et al*, 1979),

$$k_{1,N_2O} = 3.53*10^{-5}\, n_1^{0.8} \cdots (13)$$

Where n_l is liquid-side stirring speed.

While, the gas-side mass transfer coefficient, k_{g,SO_2}, was correlated to the gas-phase stirring speed by the following equation (Sada *et al*, 1979),

$$k_{g,SO_2} = 14*10^{-6}\, n_G^{0.61} \cdots (14)$$

Furthermore, the obtained data may be converted to any kind of species by implementing the equation of Calderbank and Moo-Young (1961), using diffusion coefficients:

$$\frac{k_{g,SO_2}}{k_{g,i}} = \left(\frac{D_{g,SO_2}}{D_{g,i}}\right)^{2/3} \cdots (15)$$

$$\frac{k_{1,N_2O}}{k_{1,i}} = \left(\frac{D_{1,N_2O}}{D_{1,i}}\right)^{2/3} \cdots (16)$$

The rate of absorption is expressed as the equivalent moles of N_2O_4 absorbed per unit area of interfacial area per second, which is customarily on a macroscopic scale the following expression is adopted:

$$J_{N_2O_4} = \frac{\Delta C_{N_2O_4}}{A * t} \quad kmoles\ m^{-2} s^{-1} \cdots (17)$$

Where ΔC is the change in concentration of N_2O_4 through the run duration, t (time of exposure), and A is interfacial area for absorption.

Before calculating the rate of mass transfer a few manipulation had to be taken in advance. Preliminary, the measured data was the change in nitric acid concentration through run duration monitored by two different techniques (UV spectrophotometer and electrical conductivity meter). These changes were transferred to the changes in concentration of N_2O_4 species according to the following equation:

$$Number\ of\ moles\ of\ HNO_3 = \frac{\Delta C_{HNO_3}(wt\%) * \rho * V}{M.wt.} \cdots (18)$$

Then, make an advantage from the reaction of hydrolysis of N_2O_4 in the liquid phase. The rate of hydrolysis is given by Moll (1966) by the following equation,

$$\ln k = 16.38 - 3163/T \cdots (19)$$

From thermodynamic, the equilibrium constant of reaction (II) is given by:

$$k_p = \frac{[HNO_3][HNO_2]}{[N_2O_4][H_2O]} \cdots (20)$$

In addition, nitrous acid produced by reaction (II) was assumed to disproportionate into HNO_3, NO and H_2O according to reaction (III). Consequently, the amount of nitrous oxide was neglected as well as the concentration of water present as it is always greatly exceeds the nitrogen tetroxide, hence Eq (20) might rewritten as,

$$k_p = \frac{[HNO_3]}{[N_2O_4]} \cdots (21)$$

From these relation the moles of N_2O_4 species transferred to the liquid phase had been determined for further calculations to obtain the rate of mass transfer if this quantity had been divided on the interfacial area and run duration. The partial concentration of N_2O_4 ($C^*_{N_2O_4}$) at the gas-liquid interface may be deduced from Eqs (1), and (6)

$$J_{N_2O_4} = k_p k_{g_{N_2O_4}} \left[\left(C_{NO_2 bulk}\right)^2 - \left(C_{NO_2^*}\right)^2\right] \cdots (22)$$

Experimental Procedure

Apparatus

The experiments are carried out a double stirred cell type. A schematically diagram of the cell absorber is shown in Fig (1). While, the layout of the whole apparatus is shown in Fig (2). The apparatus is made of glass (Q.V.F) connected with flanges. The apparatus was mainly consisted from a generation section for generating nitrogen dioxide which leaded to the second section (absorber) passerby an adsorbing medium (silica gel) for driven out the moisture and an accumulator. The two absorbers were supplied with one entrance and one exit for the gas stream. To maintain the determination of the mass transfer rate of N_2O_4 in water and nitric acid solution at constant temperature, the cell had been immersed in a water bath that was in return connected to a chiller.

The nitrogen dioxide was generated from reacting copper of high purity with excess quantity of 98 % nitric acid. The excess quantity of nitric acid was introduced to accomplish a complete reaction and to prevent NO production. The concentration of nitrogen dioxide produced from the reaction is calculated based on the quantity of copper consumption according to the following reaction.

$Cu + 4HNO_3 \Leftrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

Different concentrations are attained through the experimental work to study the effect of NO_2 concentration by introducing different quantity of copper in the reaction flask of the generating unit. The generated quantity of NO_2 had been admitted to the accumulator that made of Q.V.F. until the whole quantity of copper has been diminished. Afterwards, the experiment has begun by maintaining a constant flow rate of dry air to passerby the chamber and carry over the gas to the absorber. Meanwhile, The average concentration of NO_2 in the inlet stream to the absorber had been carefully adjusted after enough experience. The generation section was consisted from a reaction vessel of 1-liter capacity connected to an outlet pipe leading directly to the accumulator across the drying column of silica gel. Before the run was conducted the water or the dilute nitric acid was introduced in the absorber, hence the absorber is considered as a semi-batch reactor. All the valves are of needle type and are made of Q.V.F. The absorber contactor as shown in Fig (2) is immersed in a cooled water bath, which connected to a chiller to maintain the temperature of the reaction in the absorber at the desired temperature.

The double stirred absorber was mainly consists of glass container of 35 cm length and 11 cm inside diameter supplied with one entrance and one exit for gas stream. One agitator had been implemented each phase. The two agitators were controlled separately. Ideal mixing had assumed if the gas phase stirrer is rotated at 1000-1200 rpm, which was accomplished by an electrical motor (Comtex E8). While, a magnetic stirrer (Aserle Company) stirred the liquid phase at 120-150 rpm. The advantage of this type of absorber is the exactly defined area of mass transfer, which is identical with the upper surface area of the liquid phase.

In order to monitor the absorption rates of N_2O_4 species from the gas phase to the liquid phase in both types of absorbers an electric conductivity probe was immersed inside the absorbers. In addition a sample from the liquid phase had been withdrawn periodically to analyze via Ultra Violet Spectrophotometer. Both measuring devices (the electrical conductivity meter and the UV spectrophotometer) had been previously correlated (calibrated) their readings quantitatively with known concentration of nitric acid solutions. A comparison had been made between the two readings and a mean value had been selected for further manipulations. Adding to that an acid-base titration method had performed from time to time for further checking for the acidity of the samples from the absorber.

Preliminarily, nitrogen dioxide had been generated in the reaction vessel by introducing certain amount of copper of high purity in the flask and pouring on it an excess amount of 98 % nitric acid to accomplish the reaction completely and to prevent production of NO. The nitrogen dioxide had been forced to accumulate with observing no condensation of the generating gas inside the leading pipes to the accumulator and the absorber and also inside the accumulator. The generated quantity of nitrogen dioxide had been calculated according to the consumed quantity of copper in the reaction vessel.

The reaction had commenced vigorously and a gaseous of heavy concentration of nitrogen dioxide had driven out to the accumulator of 10-liter capacity passerby an adsorder column of silica gel to driven out the moisture from the gaseous stream. Different concentrations were attained through the experimental work to study the effect of NO_2 concentration in the gas stream. This was accomplished by introducing different amounts of copper in the reaction vessel. The reaction between copper and nitric acid had been commenced until the whole quantity of copper had been diminished completely.

Meanwhile, the experiment had begun by admitting a constant flow rate of dry air to enter the accumulator to driven out the equilibrium gaseous mixture of NO_2/N_2O_4 leading it directly to the absorber. The flow rate of the air was 0.575 l/min in the double stirred adsorber. The runs were lasted for 30 minutes.

The quantity of generated NO_2 had been averaged over run duration. In other wards the concentration of NO_2 in the inlet stream to the absorber had been calculated from the generated quantity of NO_2 which averaged over the whole quantity of air that entering the apparatus through run duration.

For the calculation of the rates of mass transfer of the transporting species in the double stirred absorber, the area of mass transfer has a well-defined area. The average concentration of NO_2 in the inlet stream to the absorber had been carefully adjusted after thorough experimental trials had been carried out. The runs had conducted in different concentrations of NO2, which takes 58, 87, and 116*10-6 kmol/m3.

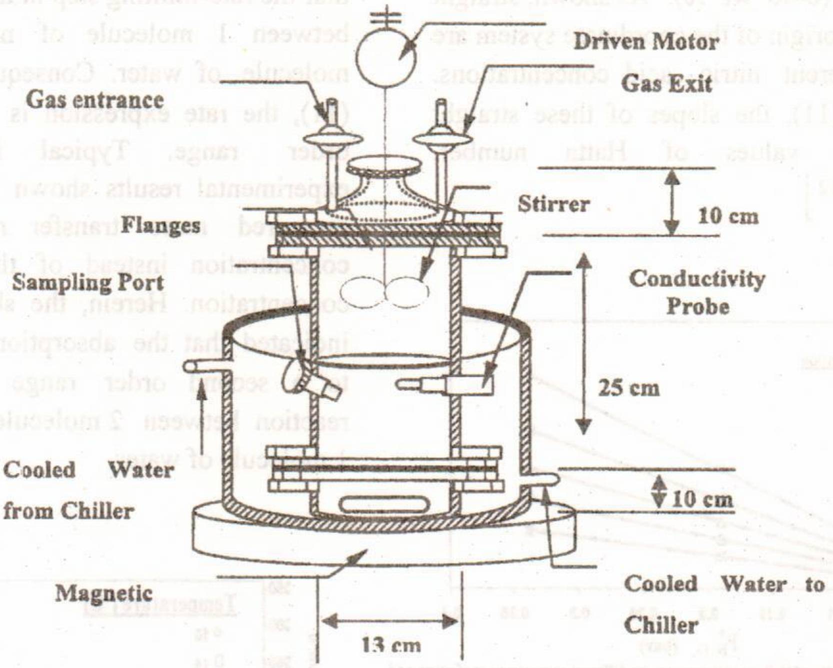


Fig (1) Schematic drawing of the double stirring type cell absorber

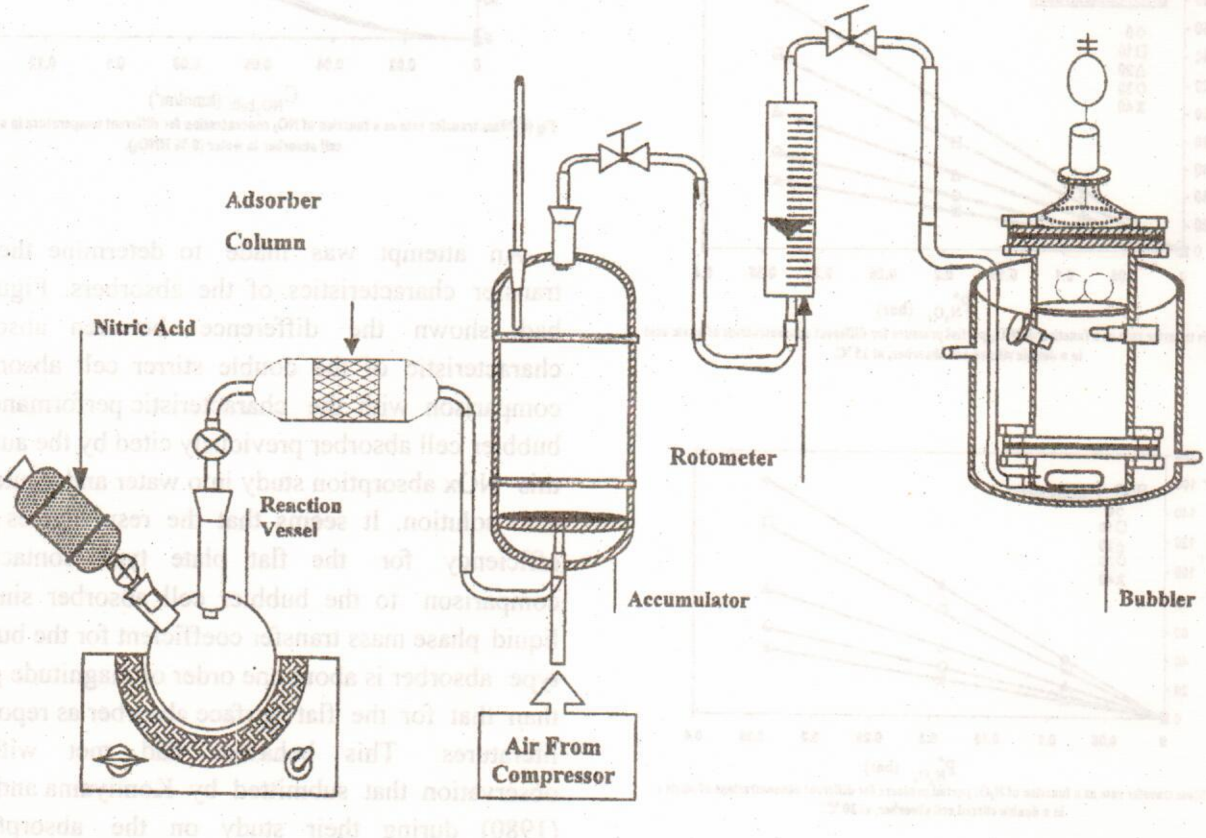


Fig (2) Layout of the apparatus which consists mainly from the generating unit, accumulator and double stirrer type absorber

Results and Discussion

The measured rate for transfer of N_2O_4 are shown in Figs (3) to (5) for the double stirrer cell absorber at different temperature (10, 15, and 20 °C) and nitric acid concentration (0-40 wt %). As shown, straight lines through the origin of the coordinate system are observed for different nitric acid concentrations. According to Eq (11), the slopes of these straight lines yield the values of Hatta number, $\left[H_{N_2O_4}\left(kD_{N_2O_4,l}\right)^{1/2}\right]$.

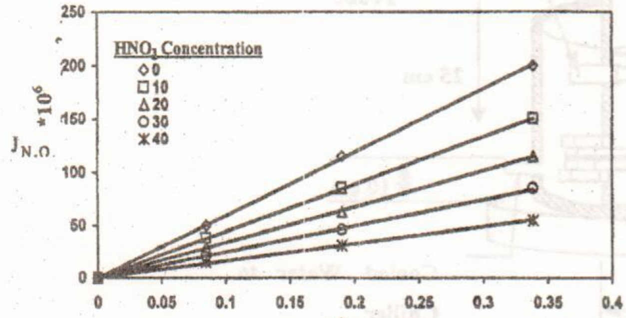


Fig (3) Mass transfer rate as a function of N_2O_4 partial pressure for different concentrations of nitric acid in a double stirred cell absorber, at 20 °C.

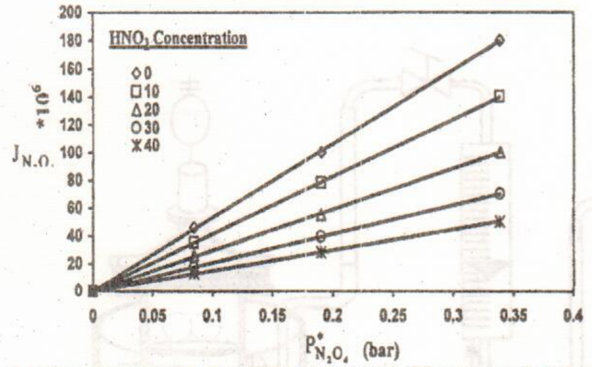


Fig (4) Mass transfer rate as a function of N_2O_4 partial pressure for different concentrations of nitric acid in a double stirred cell absorber, at 15 °C.

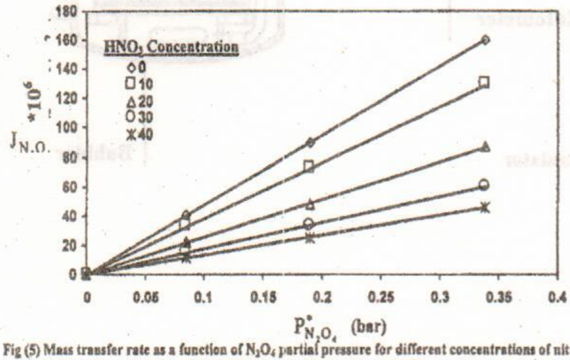


Fig (5) Mass transfer rate as a function of N_2O_4 partial pressure for different concentrations of nitric a in a double stirred cell absorber, at 10 °C.

A straight line through these results direct proportionality between $J_{N_2O_4}$ and $C^*_{N_2O_4}$. Therefore, nitrogen tetroxide is the only species, which dissolves and reacts more rapidly. In all these figures the linear relation between the absorption rate and nitrogen tetroxide bulk concentration suggests very strongly that the rate-limiting step in the process is the reaction between 1 molecule of nitrogen tetroxide and 1 molecule of water. Consequently, according to Eq (11), the rate expression is corresponding to a first order range. Typical interpretation of the experimental results shown in Fig (6) represents the measured mass transfer rate in terms of NO_2 concentration instead of the hypothetical species concentration. Herein, the shapes of the results had indicated that the absorption rates are corresponding to a second order range as expected, i.e. is the reaction between 2 molecule of nitrogen dioxide and 1 molecule of water.

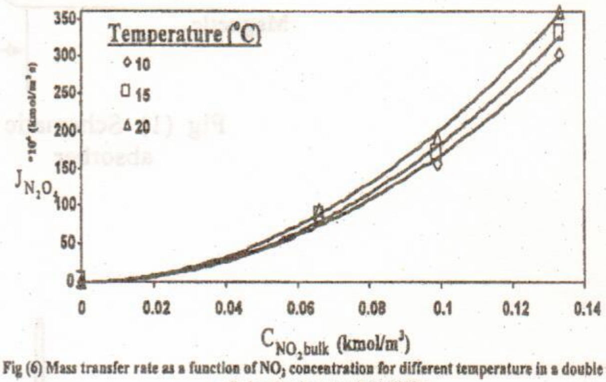
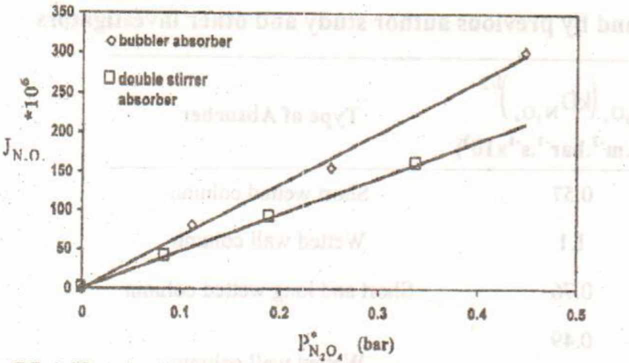


Fig (6) Mass transfer rate as a function of NO_2 concentration for different temperature in a double stirred cell absorber in water (0 % HNO_3).

An attempt was made to determine the mass transfer characteristics of the absorbers. Figure (7) had shown the difference between absorption characteristic of the double stirrer cell absorber in comparison with the characteristic performance of a bubbler cell absorber previously cited by the author in this NOx absorption study into water and dilute nitric acid solution. It seems that the results gives poorer efficiency for the flat plate type contactor in comparison to the bubbler cell absorber since the liquid phase mass transfer coefficient for the bubbling type absorber is about one order of magnitude greater than that for the flat surface absorber as reported in literatures. This behavior had met with the observation that submitted by Komiyama and Inoue (1980) during their study on the absorption of nitrogen oxides into water via two different types of absorbers (flat surface type and bubbler type).



g (7) Typical Comparison shows the difference in characteristic absorption between the bubbler absorber and the double stirrer absorber at 10 °C and 0 % concentration of nitric acid (water).

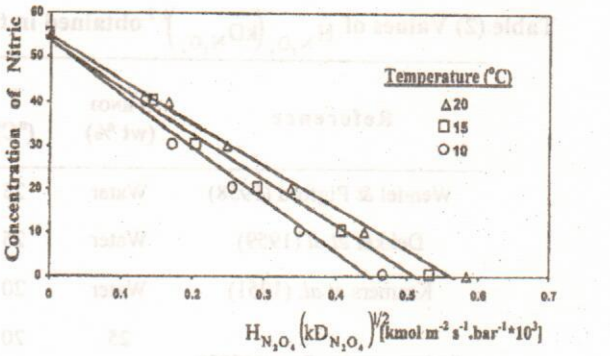


Fig (8) $H_{N_2O_4}(kD_{N_2O_4})^{1/2}$ as a function of nitric acid concentration at different absorption temperature in a double stirrer absorber.

Figure (8) interprets the values of Hatta number, $H_{N_2O_4}(kD_{N_2O_4})^{1/2}$, in terms of nitric acid concentration and absorption temperature for the double stirrer cell absorber, as well as the results are summarized in Table (1). This figure advocate that values of Hatta number $H_{N_2O_4}(kD_{N_2O_4})^{1/2}$ decreases with increasing acid strength (i.e., the Henry's constant decreases with increasing acid strength). As well as, the decrease of the pseudo-first order reaction rate constant (k) as the concentration of "free" water becomes relatively small in more concentrated nitric acid.

Moreover, this decrease in the Hatta number with the ionic strength was incorporated with the findings of Hoftyzer and Kwanten (1972), as they relate the ionic strength on $(H_{N_2O_4})$ in dilute nitric acid with henry's constant by the following equation:

$$\left(H_{N_2O_4}\right)_{nitric\,acid} = \left(H_{N_2O_4}\right)_{water} \exp(-0.075I) \cdots (23)$$

Where (I) is the ionic strength.

Table (1) Experimentally determined values of $H_{N_2O_4}(kD_{N_2O_4})^{1/2}$ [kmol m^{-2} s^{-1}.bar^{-1}*10^3] for double stirrer cell absorber.

Concentration of HNO$_3$ (wt %)	Temperature (°C) 10	15	20
0	0.5941	0.5310	0.4734
10	0.4443	0.4130	0.3810
20	0.3380	0.2950	0.2560
30	0.2483	0.2050	0.1770
40	0.1633	0.1480	0.1352

From the range of the studied concentration of nitric acid, Fig (8), it can be concluded that the decrease in Hatta number values with increase in acid strength is mainly attributed to the decrease in Henry constants with increase in ionic strength.

Comparison with other workers, Table (2) had summarized the obtained values of Hatta number carried out by different investigators and that of this study. It was noted that the results of the double stirred absorber implemented in this study are of the same order of magnitude as those of Lefers and Van den Berg (1982), Wendel and Pigford (1958) and Dekker et al, (1959) whom also employed a laboratory absorber (wetted column). On the other hand, It is striking that the figures are substantially lower than of Miller (1987) who used an industrial-scale absorber. A contributing factor to these differences was the omission of the reverse driving force term for equilibrium liquid phase reaction (hydrolysis of tetroxide). The back-reaction effect is particularly important if the contact times are short and HNO2 decomposition incomplete.

In this investigation, the inclusion of the driving force limits not only would increase the values of Hatta number but also would moderate the sharp drop found in the studied range of initial concentration of nitric acid (0-40 wt %). Also, the entire small-scale test done by the workers except that reported by Lefers and Van den Berg (1982) used nitrogen rather than air as a feed gas diluent. While, the presence of oxygen in the plant gases may contribute to enhanced N2O4 mass transfer by liquid phase HNO2 oxidation.

Table (2) Values of $H_{N_2O_4}\left(kD_{N_2O_4}\right)^{1/2}$ obtained in this study and by previous author study and other investigators

Reference	C_{HNO3} (wt %)	T (°C)	$H_{N_2O_4}\left(kD_{N_2O_4}\right)^{1/2}$ (kmol.m^{-2}.bar^{-1}.s^{-1}x10^3)	**Type of Absorber**
Wendel & Pigford (1958)	Water	25	0.57	Short wetted column
Dekker *et al* (1959)	Water	25	1.1	Wetted wall column
Kramers *et al*, (1951)	Water	20	0.76	Short and long wetted column
Lefers, vanden Berg (1982)	25	20	0.49	Wetted wall column
	40	20	0.18	
	67	30	1.54	
Miller (1987)	28.5	38.5	1.88	Bubble-cap
	8.5	37.5	2.38	
Reference	C_{HNO3} (wt %)	T (°C)	$H_{N_2O_4}\left(kD_{N_2O_4}\right)^{1/2}$ (kmol.m^{-2}.bar^{-1}.s^{-1}x10^3)	**Type of Absorber**
Miller (1987)	58	31	0.82	Sieve-tray column
	39.5	33	0.86	
	18	33	1.45	
	11	31	2.38	
Werner *et al*, (1990)	60	25	0.02	Double stirrer
	50	25	0.10	
	30	25	0.29	
	15	25	0.47	
This study	40	20	0.17	Double stirrer cell
	30	20	0.248	
	20	20	0.34	
	10	20	0.44	
	water	20	0.58	
Nahidh *et al*, (2000)	40	20	0.20	Bubbler cell
	30	20	0.32	
	20	20	0.54	
	10	20	0.69	
	Water	20	0.80	

The initial concentration of nitric acid, which was previously contributed to the increase of the ionic strength that was mainly, affected the Henry coefficients. Whereas, absorption temperature was mainly affected the composition of the equilibrium mixture of the two gases NO2 and N2O4. Similarly, the concentration of NO2 in the gas phase had same effect on the equilibrium mixture, which accordingly increase the concentration of the hypothetical molecule at the interface.

From these experimental results it can be concluded that NO2 and N2O4 are transferred in continuous equilibrium with each other from the gas phase to the gas-liquid interface. In the liquid phase N2O4 is preferentially absorbed with dilute nitric acid (0-40 %) where the absorption is accompanied by a rapid pseudo-first order reaction between N2O4 and water. The study had shown that low absorption temperature results low mass transfer rate, which strictly attributed to the influence of absorption temperature on the rate of hydrolysis of N2O4 although the absorption temperature counter effect on

N2O4 solubility as well as on gas equilibrium. In contrary, Lefers and Van der Berg (1982) had arrived to a conclusion that the hydrolysis reaction can be neglected and that N2O4 dissolves physically in the liquid phase where the solubility of N2O4 in concentrated nitric acid (60-80 %) had decreases strongly with increasing temperature.

Conclusions

From the experimental results the following conclusion may be attributed:

NO2 and N2O4 are transferred in continuous equilibrium with each other from the gas phase to the gas-liquid interface. In the liquid phase N2O4 is preferentially absorbed.

The rate of removal of the nitrogen dioxide is increased with increasing the absorption temperature. This was attributed to the increase in the rate of hydrolysis of N2O4 although the rise in temperature would decrease the Henry coefficients, which means lesser degree in solubility with temperature rise. However, the experimental results had shown increase in the overall rate of mass transfer with temperature, which ascertained the majority of the chemical reaction rate in comparison to the rate of mass transfer of the concern system.

Nomenclature

Symbol	Definition	Units
A	Interfacial area	m^2
C	Concentration	$kmol/m^3$
C^{*}_{N2O4}	Concentration of hypothetical species	$kmol/m^3$
D	Diffusion coefficient	m^2/s
H	Henry constant	bar^{-1}
Ha	Hatta number	$kmol\ m^{-2}bar^{-1}s^{-1}$
I	Ionic strength	-
J	Mass transfer rate	$kmol\ m^{-2}s^{-1}$
K	Rate Constant	s^{-1}
k_g, k_l	Mass transfer coefficient in gas and liquid phase respectively	m/s
k_p	Equilibrium constant	-
M	Molecular weight	kmol/kg
N	Concentration in normality	N
n_G	Gas phase stirring speed	rpm
n_L	Liquid phase stirring speed	rpm
P	Pressure	bar
P^*	Partial pressure	bar
T	Temperature	^oK
T	Time	s
V	Volume	m^3
V_A,V_B	Molar volumes of gas at normal boiling point	cm^3/mol

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