LOW-COST EXPERIMENTS IN MASS TRANSFER

Part 5. Desorption of Ammonia from a Liquid Jet

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The rate of gas-liquid mass transfer, absorption or desorption, is controlled by diffusional (film) resistances in the gas and liquid phases. The overall resistance is the sum of the two film resistances. If one film resistance is much larger than the other, the mass transfer rate is controlled mainly by the larger resistance. As discussed in the standard texts, such as Geankoplis,[1] the controlling resistance depends on the solubility of the transferring gas in the liquid phase. For some typical solute gases transferring between air and water at ambient conditions, controlling resistances are

Controlling resistance	*Solute gases*
Liquid diffusion	Oxygen, carbon dioxide (sparingly soluble)
Liquid and gas diffusion	Sulfur dioxide (moderately soluble)
Gas diffusion	Ammonia, hydrochloric acid gas (highly soluble)

Previous papers in this series[2,3] have described some simple undergraduate-level experiments with liquid-phase control, using oxygen or CO_2 as the transferring gas.

It is also desirable to study cases in which mass transfer is controlled by the gas phase, but as the above table indicates, the highly water-soluble gases are hazardous substances. Some years ago, students at McMaster University operated a packed-absorption tower in which an ammonia/air mixture was scrubbed with water. Much care was needed in the control of the ammonia stream to make up the gas mixture, and there was sometimes trouble with leaking valves on the ammonia gas cylinder. Eventually the experiment was discontinued for safety reasons.

This paper describes a replacement experiment that was recently developed in which ammonia is *desorbed* from an aqueous solution into a stream of air. This is inherently safer since the ammonia levels in the gas phase are limited by the ammonia concentration in the aqueous feed solution. The experiment does not require pure ammonia gas. The objective of the experiment is to measure mass transfer coefficients for the desorption of ammonia from a liquid jet, at different liquid flow rates and for different jet lengths. Recommended time for the experiment is two laboratory periods of three hours.

EXPERIMENT DESCRIPTION

The schematic flow diagram is shown in Figure 1. The main items of equipment are mounted on a vertical wooden panel about four to six feet from floor level. The feed solution is a 1.5 mol/L standardized solution of ammonia in water that can be made up by the laboratory technician prior to the experiment. This concentration was chosen as a compromise to balance the needs for rapid rates of mass transfer (favored by higher concentration) and safety (favored by lower concentration). At ambient temperatures, the equilibrium mol fraction ammonia in the gas phase above this solution is between 2% and 3%. Accurate values are available from the literature[4] for the temperature of the experiment.

The ammonia solution is fed from an overhead reservoir through a stainless steel needle valve and rotameter to a desorption cell. Typically, the feed liquid flow is in the range

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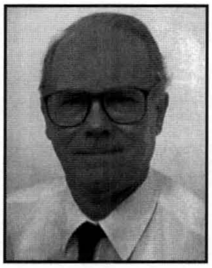

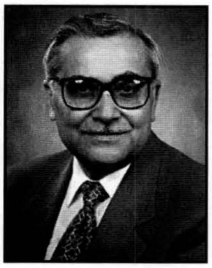

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of 50 to 300 mL/min. The desorption cell consists of a vertical 15-cm section of 5-cm internal diameter glass tubing, closed at each end by rubber stoppers. The feed solution enters the top of the cell through a glass nozzle of internal diameter 1.4 mm, which can be made easily by a glassblower from standard glass tubing. The free jet of solution falls from this nozzle to a collector tube (see Figure 1) located at a measured distance (L) below the nozzle. The collector tube should be slightly larger in diameter than the jet; an internal diameter of about 2.5 mm is recommended. At steady state, the liquid level in the collector tube should come right up to the open end, and there should not be any gas entrainment. This control can be quite easily achieved by means of a manually adjustable overflow leg, as shown in Figure 1. Some lateral adjustment of the positions of the jet and the collector can be made by hand, since the tubes are held by a rubber stopper that has some flexibility. The variation of jet length can be achieved by extending or retracting the jet nozzle between experiments.

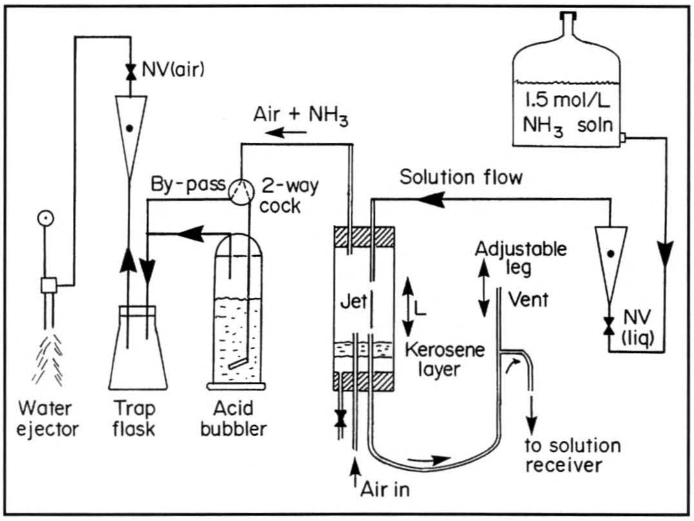

Figure 1. *Schematic flow diagram.*

It is inevitable that some drops of solution will occasionally spill over the collector tube, and for this reason a few mL of kerosene are placed at the base of the cell to provide a mass-transfer barrier. There is also provision to occasionally drain off any large amount of spilled ammonia from the base of the cell, as shown. The main liquid flow leaving the cell still contains most of the ammonia feed, and it is collected in a receiver for reuse. It is important to avoid the use of copper or brass in any of the valves or lines handling ammonia solution since these metals are slowly attacked by aqueous ammonia; this is apparent from a blue coloration of the solution with cuprous ammonium salts.

A continuous flow of atmospheric air is drawn through the cell, entering from the bottom. The exit air, containing desorbed ammonia gas, leaves the cell from the top. During the preliminary adjustment of the system it flows through a bypass line to a trap, and then to a rotameter, needle valve, and water aspirator (ejector). The air flow is adjusted to a fixed value (typically between 1 and 5 L/min) by means of the needle valve and rotameter. The system should be run for three to four minutes at the adjusted liquid and gas flows, to reach a steady state before gas analysis is begun.

The air leaving the cell contains a small amount of ammonia, typically no more than 1 mol%. Analysis is carried out by a semi-continuous chemical method, by scrubbing with dilute hydrochloric acid. Before the experiment, a standard fritted-glass bubbling tube is filled with a known volume (typically 100 mL) of 0.01 mol/L dilute hydrochloric acid, with a few drops of methyl red indicator, and is connected to the system, as shown in Figure 1. The gas analysis is begun by turning a 2-way cock to divert the exit gas through the bubbling tube. As the cock is turned, a stopwatch must be started. Because of the large gas-liquid interfacial area produced at the bubbler, the absorption of the ammonia from the gas phase is extremely efficient and it reacts stoichiometrically with the acid. After sufficient time has elapsed, all the acid will be consumed and the pH of the liquid in the bubbler will rise sharply, accompanied by a change in the methyl red color from pink (acid) to yellow (alkaline). The color change occurs over a period of 1-2 s, which is much smaller than the neutralization time of 100 s. At the above endpoint, the stopwatch is stopped and read, and the gas flow is then diverted to the bypass.

The rate of mass transfer is calculated from the moles of acid neutralized in the bubbler, and the neutralization time

$$m' = V_A c_A / t_N \qquad (1)$$

The molar concentration of ammonia in the exit gas from the desorption cell can be obtained from the mass transfer rate and the gas flow rate

$$c_2 = m' / Q_G \qquad (2)$$

At the end of each experiment, the liquid and gas flows are shut off and the bubbler is removed for rinsing with distilled water.

EXPERIMENTAL PLAN

A typical plan for two 3-hour laboratory periods calls for measurement of the mass transfer coefficient at three different jet lengths (for example, 3, 5, and 7 cm) and three or four different flow rates within the operating range. In addition, at least some of the experiments should be replicated with different concentrations of acid in the bubbler. Changes in c_A would affect t_N but would not be expected to affect the value of k_g obtained at the same liquid flowrate and jet length. Because of time constraints, the jet diameter and the air flowrate are the same in all experiments.

An average time of 15 to 20 minutes is spent on each experiment, with students working in groups of two. Although the mass-transfer measurement itself takes only one to three minutes, additional time is needed for adjustment of the operating conditions and for achieving steady state. Also, from time to time the ammonia-feed reservoir has to be refilled. Goggles and gloves should be worn by the students when they are handling the ammonia and acid solutions, *e.g.,* when they are recharging the bubbler. The ammonia levels in the ambient air are low, but minor discomfort may be experienced if there is not adequate ventilation in the laboratory.

CALCULATION OF MASS-TRANSFER COEFFICIENTS FROM DATA

The mass-transfer rate, m', is the product of the mass-transfer coefficient, the interfacial area, and the concentration driving force

$$m' = k_g A\left(c^* - c_2\right) \tag{3}$$

The terms m' and c_2 have already been obtained through Eqs. (1) and (2). The interfacial area A can be calculated from the jet length, L, and the orifice diameter, d. For precise work, allowance should be made for the acceleration of the jet due to gravity. But for short jets and high velocities (keeping in mind that this is only an undergraduate-level experiment), the acceleration effect can be ignored. Therefore, we use

$$A = \pi d L \tag{4}$$

The equilibrium concentration of ammonia in the gas phase, c*, can be obtained from standard sources.[4] For 1.5 mol/L ammonia in the solution, the values of c* at 20°C and 25°C are, respectively, 0.837 and 1.076 mol/m^3; these values are less than 0.1% of the liquid phase concentration, illustrating the very high solubility of ammonia. The back-concentration term is taken as c_2 (calculated from Eq. 2), based on the assumption that the gas space within the cell is "well mixed." This was found to give consistent results, and it is reasonable to expect that the combined effects of gas and liquid flow would result in a well-mixed gas phase in the cell.

Rearranging Eq. (3), the mass transfer coefficient can be obtained from known data as

$$k_g = m' / \left[A\left(c^* - c_2\right)\right] \tag{5}$$

EQUATIONS FOR PREDICTION OF MASS-TRANSFER COEFFICIENT

The conditions of the experiment do not correspond exactly to any of the commonly available predictive equations because little is known about the hydrodynamic conditions in the gas space in the cell. It is thought that the gas is circulating due to the action of the liquid jet and the throughflowing stream of gas, and the flow is likely to be weakly turbulent. There are two simple equations that can at least provide an approximate comparison with the data.

HIGBIE PENETRATION MODEL[5]

This well-known equation is based on the simple concept of unsteady diffusion into the gas phase during the "contact time," τ, for which the liquid is exposed to the gas. In using this equation, it is assumed that the gas film adjacent to the liquid jet is moving down with it at the same velocity, namely

$$U = Q_L / \left(\pi d^2/4\right) \tag{6}$$

The contact time between liquid and gas is L/U, or

$$\tau = \pi d^2 L / \left(4 Q_L\right) \tag{7}$$

According to the penetration model,

$$k_g = 2\left(D_g / \pi\tau\right)^{0.5} \tag{8}$$

where D_g is the molecular diffusivity of ammonia in air, which can be estimated from the method of Fuller, *et al.,* as cited in Perry's *Handbook.*[6] Values of D_g at 20°C and 25°C are, respectively, 2.36×10^{-5} and 2.43×10^{-5} m^2/s. Equation (8) can also be expressed in dimensionless form as

$$Sh_L = 1.128\left(Re_L\, Sc\right)^{0.5} \tag{9}$$

where the Sherwood and Reynolds numbers are based on jet length. Equations (8) and (9) can only be regarded as approximate for the present case, since they assume that the gas is moving down at the same velocity as the liquid jet; no allowance is made for a developing boundary layer or the effects of turbulence in the bulk gas flow.

BOUNDARY-LAYER MODEL[7]

As an alternative to the penetration model, it could be assumed that the air is dragged down in a developing laminar boundary layer adjacent to the interface, with ammonia diffusing through the boundary layer. For this case

$$Sh_L = 0.664\, Re_L^{0.5}\, Sc^{1/3} \tag{10}$$

In this work, Re_L is always well below the critical value of 500,000 at which there is a transition to turbulent flow in the boundary layer. But the use of Eq. (10) is also open to criticism since it was developed for a flat plate, whereas the interface in this case is cylindrical. Moreover, the bulk gas may be turbulent, which could affect the boundary layer.

RESULTS AND DISCUSSION

Figure 2 shows 12 directly measured mass-transfer coefficients from a typical student project,[8] plotted against jet velocity on a linear scale. It can be seen that k_g always increases with the velocity and in general it decreases with increasing jet length.

The results can be expressed in dimensionless form by conversion to Sherwood number, which can then be compared with the model Eqs. (9) and (10). The Schmidt number is essentially constant (≈0.65) except for minor effects of temperature between different experiments.

Therefore, a plot of Sherwood number versus Reynolds number allows the data to be compared with the two model equations, as shown in Figure 3. Both models predict that $Sh_L \propto Re_L^{0.5}$, so they appear on the log-log scale as two parallel straight lines, which are shown dashed. The data points fall between the two predictions; lower than the penetration theory but higher than the boundary layer prediction.

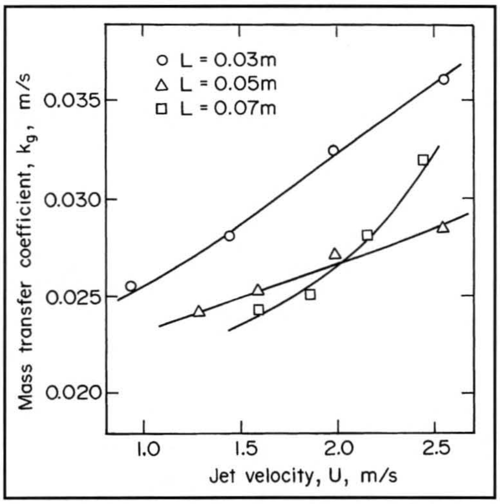

Figure 2. *Effect of jet velocity and jet length on mass transfer coefficients.*

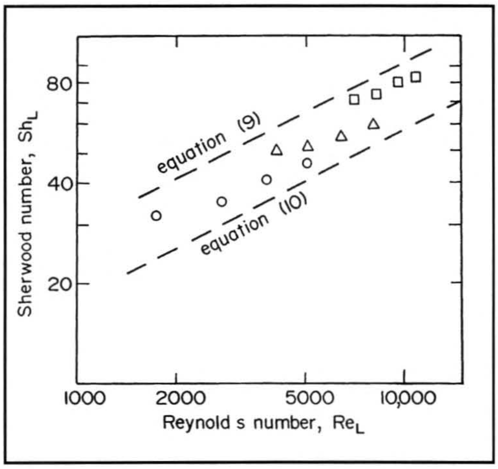

Figure 3. *Dimensionless plot of data showing comparison with Eqs. (9) and (10). Symbols are the same as in Figure 2.*

When students are confronted with a case like this in which the results do not agree very well with the "theoretical predictions," they are apt to find fault with the experiment and the accuracy of their data. But when an analysis of measurement errors is done, the measurement accuracy for k_g is found to be better than ±10%. Then a question for the students is: why are there deviations of 30% or more between the results and the models?

The students are encouraged to discuss ways in which their actual experiment departs from the sets of idealizing assumptions built into the two simple theoretical models. The curvature of the jet surface and the complex and probably turbulent gas-flow patterns in the cell have already been mentioned. If the theoretical treatment could be "fine tuned" to account for these effects, better agreement could be expected, but that would take us into the realm of graduate research.

This low-cost experiment can be set up with normal laboratory glassware and fittings. It provides students with a reasonably accurate method of measuring gas-film controlled mass-transfer coefficients that can then be compared with simple (though approximate) theoretical predictions.

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NOMENCLATURE

A	interfacial area, m^2
c_A	initial concentration of acid in bubbler, mol/m^3
c_2	concentration of ammonia in exit gas, mol/m^3
c^*	equilibrium concentration of ammonia in gas, mol/m^3
D_g	molecular diffusion coefficient of ammonia in air, m^2/s
d	jet diameter, m
k_g	mass transfer coefficient, m/s
L	jet length, m
m'	mass transfer rate, mol/s
Q_G	air flow rate, m^3/s
Q_L	water flow rate, m^3/s
Re_L	Reynolds number, $\rho UL / \mu$
Sc	Schmidt number, $\mu / \left(\rho D_g\right)$
Sh_L	Sherwood number, $k_g L/D_g$
t_N	time to neutralize acid in bubbler, s
U	jet velocity, m/s
V_A	volume of acid in bubbler, m^3

Greek Symbols

μ	viscosity of air, Pa.s
ρ	density of air, kg/m^3
τ	contact time, s

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