GAS ABSORPTION AND OXIDATION IN DISPERSED MEDIA

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The absorption and subsequent liquid-phase reaction of oxygen was studied with two types of dispersion apparatus, the Venturi atomizer and the fritted-glass disperser. The systems studied in both devices included the absorption of atmospheric oxygen by catalyzed sodium sulfite solutions and the simultaneous absorption of atmospheric oxygen with nitrogen dioxide and with sulfur dioxide by water.

Very large values of the liquid-film mass transfer coefficient for oxygen absorption were measured in the atomization zone of the Venturi atomizer. Over-all recovery efficiencies were less than 2.3% for nitrogen dioxide but reached as much as 22% for sulfur dioxide. Oxidation efficiencies for sodium sulfite solutions ranged up to 80%, depending on the operating conditions.

The fritted-glass disperser gave recovery efficiencies of nitrogen dioxide as high as 90% from air containing 10% of the gas. The recovery efficiency decreased at low concentrations of nitrogen dioxide for both the Venturi atomizer and the fritted-glass disperser.

Fine dispersion of either the gas or liquid phase produces a large interfacial area for gas absorption and relatively high rates of mass transfer. Large mass transfer coefficients have been reported for the finely dispersed liquid phase in the Venturi atomizer(*3*). In this work, measurements were reported on the rates of absorption of sulfur dioxide and oxygen and the rate of desorption of carbon dioxide in the atomization zone. For carbon dioxide and oxygen the values of the liquid-film mass transfer coefficient were very large in the vicinity of the liquid injection and decreased rapidly with distance within the atomization zone. The high rates of carbon dioxide desorption suggested the present work, in which an attempt was made to define further the absorption process in the Venturi atomizer. The work was confined to processes involving oxygen absorption and subsequent chemical reaction in the liquid phase. If the oxygen in solution reacts chemically as rapidly as it is absorbed, the rate of absorption should be substantially increased.

Results are presented for two methods of dispersion: atomization in a Venturi throat and aeration through a porous fritted-glass cylinder. For the former, measurements are reported on rates of absorption of oxygen by pure water and by sodium sulfite solutions, as well as on the rates of oxygen absorption during the simultaneous absorption of nitrogen dioxide and sulfur dioxide. Mass transfer coefficients for oxygen were determined in each case as functions of distance near the point of liquid injection. This is the region of highest transfer rate. Over-all oxidation efficiencies for sodium sulfite solutions and recovery efficiencies for nitrogen dioxide and sulfur dioxide in the Venturi atomizer were also determined.

With the fritted-glass disperser, the gas phase is finely divided in the bulk liquid phase. This produces a large interfacial area per unit volume of gas and ensures intimate contact of all the gas with the liquid absorbent. Recovery efficiencies for nitrogen dioxide were determined for gas compositions up to 10% nitrogen dioxide. In addition, brief studies were made on sulfur dioxide recovery and sodium sulfite oxidation with this type of contactor.

EXPERIMENTAL

Two venturi sections were used in the work. The data for oxygen absorption by pure water were obtained in the Lucite venturi used previously for studies of carbon dioxide desorption (*8*). The throat diameter was approximately 1-1/8 in. and the throat length was 3 in. All other measurements were made in a Lucite venturi with a throat diameter of 1/4 in. and a throat length of 1/2 in. The gas velocity was 327 ft./sec. in the larger venturi throat and 300 ft./sec. in the smaller throat. Gas flow rates were measured upstream of the liquid injection venturi by a standard venturimeter. Nitrogen dioxide or sulfur dioxide was injected sufficiently far upstream to ensure a uniform composition at the gas-analysis point. Liquid was injected axially with a single stainless-steel hypodermic needle which had an inside diameter of 0.13 cm. Samples of the spray were collected with an impact tube at 0.45, 1.10, and 2.84 in. from the point of liquid injection in the larger venturi and at 0.25, 0.50, and 1.00 in. from injection in the smaller venturi.

The fritted-glass disperser was a relatively simple apparatus. The contacting element was a standard coarse-porosity Pyrex fritted-glass cylinder. The dimensions of the cylinder were 4 mm. I.D., 12 mm. O.D., and 19 mm. high. The base of the cylinder was sealed and gas passed only through the sides. The cylinder was located at the bottom of a liquid-filled column 43 in. high and 2-3/8 in. in diameter. The gas passed through the interstices in the fritted glass and bubbled up through two liters of liquid. It then passed to a column filled with standard sodium hydroxide and hydrogen peroxide for removal of any nitrogen dioxide or sulfur dioxide not absorbed in the first column.

Analytical Procedures. The gas phase in the venturi atomizer was analyzed for nitrogen dioxide, or sulfur dioxide, by passing a sample through a standard solution of sodium hydroxide containing hydrogen peroxide and measuring the remaining gas in the sample with a wet test meter. All the nitrogen dioxide, or sulfur dioxide, was absorbed in the sodium hydroxide and the excess hydroxide was determined by titration with standard hydrochloric acid. Total acid concentration in the liquid phase was determined by titration with standard sodium hydroxide. Nitrous acid was found by addition of an excess of potassium permanganate followed by back-titration with standard sodium thiosulfate. In the absorption of sulfur dioxide by water and of oxygen by sodium sul-

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Complete data are found in the Ph. D. thesis of L. B. Andersen, obtainable on microfilm from University Microfilms, Inc., Ann Arbor, Michigan.

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fite solutions, sulfite ion was determined by addition of an excess of standard iodine solution and back-titration with standard sodium thiosulfate. Similar procedures, where applicable, were used with the fritted-glass absorber.

The quantity of oxygen absorbed in the atomization zone of the venturi atomizer with simultaneous absorption with nitrogen dioxide was found from the difference between the concentration of nitric acid and nitrous acid. In the over-all reaction of oxygen with nitrogen dioxide and water

$$n\,NO_2 + \frac{n}{2}H_2O + x\,O_2 = \left[\frac{n}{2} - 2x\right]HNO_2 + \left[\frac{n}{2} + 2x\right]HNO_3 \qquad (1)$$

and

$$\text{moles oxygen absorbed} = x = \frac{\text{moles } HNO_3 - \text{moles } HNO_2}{4} \qquad (2)$$

This calculation assumes that there is no escape of nitric oxide formed by decomposition of nitrous acid in the very short time in the atomization zone. This is reasonable, since decomposition of the acid in the liquid phase is slow (*1*) and oxygen can be absorbed sufficiently rapidly to oxidize any nitric oxide formed. The oxygen absorbed with sulfur dioxide was found from the amount of sulfuric acid formed. The oxygen absorbed by sodium sulfite solutions was found from the difference between the initial and final sulfite concentrations.

The Spray Zone. In order to calculate values for the liquid-film mass transfer coefficient in the venturi atomizer, it was necessary to determine the absorption volume occupied by the spray. The dimensions of the spray zone at a gas velocity of 300 ft./sec. were measured visually with calipers from the outside of the transparent throat. Within 1 in. of liquid injection the spray zone was found to be a straight-sided truncated cone. The cross-sectional diameter at the injection point was 0.051 in., and at 1 in. from injection it was 0.22 in. The shape of the spray zone should depend on the properties of the liquid, the size and shape of the injection nozzle, and the relative velocity between the liquid and the gas. It should be independent of the size of the venturi throat, so long as no wall impingement occurs. The absorption volume determined in this manner is not analogous to the absorption volume in conventional absorption equipment. It is useful, however, in calculating the absorption coefficient for comparison of the systems studied.

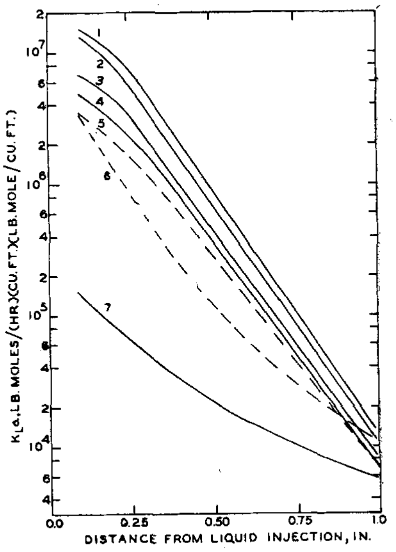

FIG. 2. COEFFICIENT K_La FOR OXYGEN ABSORPTION BY SODIUM SULFITE SOLUTIONS: CATALYST, 0.01M $CoSO_4$; GAS VELOCITY, 300 FT./SEC. EXCEPT AS NOTED.

	Solution	Liquid rate, ml./min.
1	0.0100M Na_2SO_3	300
2	0.0100M Na_2SO_3	200
3	0.0100M Na_2SO_3	100
4	0.0100M Na_2SO_3	50
5	0.050M Na_2SO_3	50
6	0.025M Na_2SO_3	50
7	Pure water	95.2, velocity, 327 ft./sec.

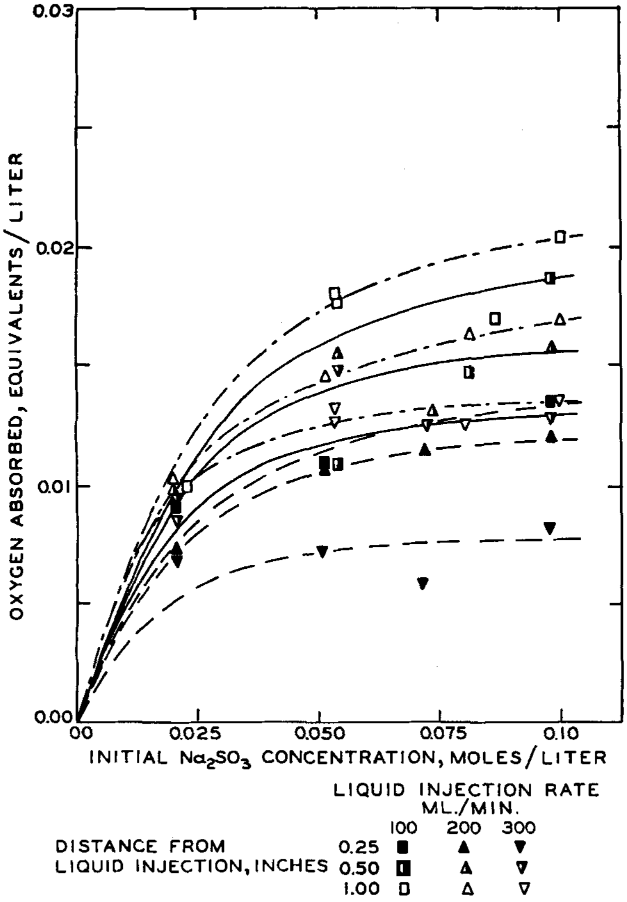

FIG. 1. EFFECT OF SULFATE CONCENTRATION ON RATE OF OXYGEN ABSORPTION IN THE VENTURI ATOMIZER.

ABSORPTION IN THE VENTURI ATOMIZER

Nukiyama and Tanasawa(*5*) describe the mechanism of atomization of a liquid when it is injected into a high-velocity air stream. At the gas velocities used in this work, the liquid is atomized by the formation and subsequent shattering of attentuated, twisted filaments and thin, cuplike films. These filaments and films are initially available for absorption. Subsequently more or less spherical droplets are formed which have less surface area per unit volume of liquid than the attenuated films and filaments.

The mass transfer coefficient was calculated(*3*) from the slope of the curve of oxygen absorbed as a function of the absorption volume, which was determined from the original data of oxygen absorbed as a function of distance from injection, illustrated in Figure 1. This slope, measured in gram-moles/(liter) (cubic inch), was multiplied by the liquid injection rate and divided by the driving force across the liquid film to give the liquid-film mass transfer coefficient, K_La. The driving force is the difference between interfacial oxygen concentration and the bulk concentration. The interfacial concentration was assumed to be in equilibrium with the oxygen in the gas. The bulk concentration was taken as zero, since the chemical reaction consumed all the oxygen. The coefficient is the transfer rate per unit absorption volume per unit driving force.

The scatter of the data can be attributed to variations in the spray under otherwise identical conditions. The present measurements were all made within 1 in. of the point of injection, closer than in any of the previous work. The values of the coefficient K_La for oxygen absorption by catalyzed sodium sulfite solutions, shown in Figure 2, are initially much larger than those for absorption of the gas by pure water. The values for sodium sulfite decrease rapidly with distance until they are nearly equal to those for pure water at 1 in. from liquid injection.

Curves similar to those in Figure 1 were drawn through the original data for oxygen absorption with nitrogen dioxide and with sulfur dioxide. The data scattered like those for sodium sulfite. The values of the coefficient K_La for oxygen absorption with nitrogen dioxide are shown in Figure 3 and for oxygen absorption with sulfur dioxide, in Figure 4.

The high initial mass transfer coefficients for oxygen absorption by pure water can be attributed to the large initial interfacial area, high relative gas-liquid velocity, and great liquid turbulence. The rapid decrease in the absorption rate is caused by the decrease in interfacial area as the films and filaments shatter into spherical droplets, to the decrease in the relative velocity as the droplets are accelerated to the gas velocity, and to the decrease in liquid turbulence as the droplets pass downstream. When oxygen reacts in solution, the rate of chemical reaction is another factor to be considered. If the reaction is sufficiently rapid, there will be no build-up of dissolved oxygen and the absorption rate will be at a maximum. For slower reactions, a combination of diffusion and reaction rate will determine the rate of absorption. Slow reactions result in the same rate of absorption as when no chemical reaction occurs in the short time available in the Venturi apparatus.

In the oxidation of sodium sulfite solutions, the rapid removal of dissolved oxygen by reaction produces much larger values for the coefficient K_La than in the case of absorption by pure water. The value of K_La for oxygen absorption by a 0.025 M sodium sulfite solution at 0.1 in. from liquid injection is 5,200,000 lb. moles/(hr.)(cu. ft.)(lb. mole/cu. ft.) for a liquid rate of 100 ml./min. This is to be compared with K_La for absorption by pure water of 160,000 at aproximately the same liquid and gas rates. An additional factor influences the decrease in oxygen absorption rate by sodium sulfite solutions. As the sodium sulfite is oxidized, its concentration decreases and the rate of chemical consumption of oxygen consequently decreases. In the ultimate case all the sodium sulfite is oxidized, and the final absorption rate would approach that for absorption by pure water. Thus the value of the mass transfer coefficient for 0.025 M sodium sulfite solution is only twice as great as that in water at 1.0 in. from the point of injection. The values of the coefficient K_La decrease similarly for other initial sodium sulfite concentrations. Thus apparently the same factors which operate to decrease the rate of oxygen absorption by pure water also control the rate of absorption by sodium sulfite solutions. Such a situation can be explained by postulating that initially during atomization, in the region of filaments and films there is no significant physical resistance to absorption and therefore the absorption rate is controlled by the chemical reaction. Later, when the droplets have been formed, the diffusional resistance controls. This transition must occur rapidly, within 1 in. of the point of liquid injection.

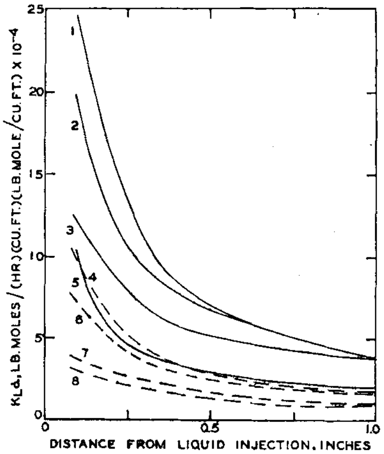

Fig. 3. Coefficient K_La for Oxygen Absorbed Simultaneously with Nitrogen Dioxide.

	Gas composition	Liquid rate, ml./min.
1	10% NO_2	300
2	10% NO_2	200
3	10% NO_2	100
4	10% NO_2	50
5	8% NO_2	50
6	6% NO_2	50
7	4% NO_2	50
8	2% NO_2	50

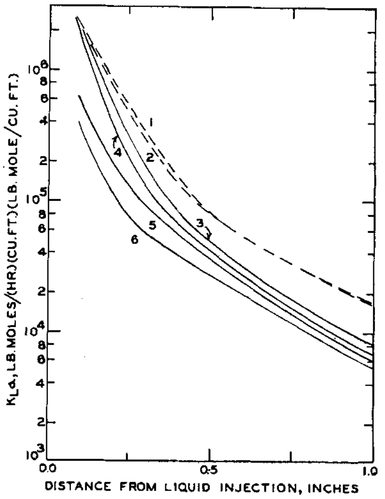

Fig. 4. Coefficient K_La for Oxygen Absorbed Simultaneously with Sulfur Dioxide: Catalyst, 0.01M Manganous Sulfite.

	Gas composition	Liquid rate, ml./min.
1	0.2% SO_2	300
2	0.3% SO_2	300
3	0.1% SO_2	300
4	0.1% SO_2	200
5	0.1% SO_2	100
6	0.1% SO_2	50

This mechanism also affects the results of the oxygen–nitrogen dioxide absorption. The nitrogen dioxide must diffuse into the liquid before it reacts with dissolved oxygen. Thus the rate of oxygen absorption will depend on the rate of nitrogen dioxide absorption, as well as on the rate of intermediate reactions:

$$2\,NO_2\,(aq.) + H_2O = HNO_3\,(aq.) + HNO_2\,(aq.) \qquad (3)$$

$$2\,HNO_2\,(aq.) = NO\,(aq.) + NO_2\,(aq.) + H_2O \qquad (4)$$

$$NO\,(aq.) + \frac{1}{2}\,O_2\,(aq.) = NO_2\,(aq.) \qquad (5)$$

In dilute solutions nitrogen dioxide reacts immediately once it enters the liquid phase. The values for the coefficient K_La for oxygen absorption vary more with initial nitrogen dioxide concentration than they do with initial sodium sulfite concentration, an indication that the rate of oxygen absorption depends in part on the rate of nitrogen dioxide absorption. In general, the values in this case are lower than for sodium sulfite oxidation. The method of calculation of K_La is based on an assumed zero concentration of oxygen in the liquid phase because of rapid chemical reaction. Where the values of K_La for oxygen absorption with nitrogen dioxide fall below those for pure water under otherwise similar conditions, the assumption is no longer correct, because the value of K_La for oxygen absorption into pure water should be the minimum. Thus if the chemical reaction is slow, the oxygen concentration in the bulk of the liquid is not zero, because oxygen does not react as fast as it is absorbed. Since the values for the coefficient K_La for oxygen absorption with nitrogen dioxide actually fall below those for absorption by pure water, the reactions involved must be too slow to use the oxygen as rapidly as it is absorbed. The rate of nitrogen dioxide absorption does not completely control the rate of oxygen absorption, since there is still an oxygen deficiency. Apparently the nitrous acid decomposition and oxidation are the controlling reactions for oxygen absorption. This discussion assumes that there is no appreciable reaction between oxygen, nitrogen dioxide, and water vapor in the gas film, a reasonable assumption considering the short time available for the reaction and subsequent diffusion of nitric acid into the liquid.

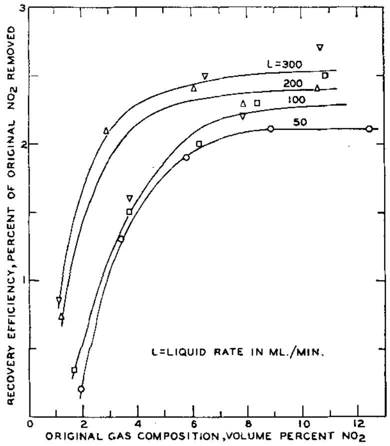

Fig. 5. Effect of Gas Composition on Recovery Efficiency for Nitrogen Dioxide in the Venturi Atomizer.

A case where the chemical reactions are less complex, the absorption of oxygen with sulfur dioxide in the presence of a catalyst, should provide further information on this point. Sulfur dioxide dissolves in water to give sulfurous acid in solution. Here the chemical reaction is rapid, but the sulfur dioxide must be absorbed before the oxygen can react in solution. The values for the coefficient K_La for oxygen absorption with sulfur dioxide are initially between those for sodium sulfite and for nitrogen dioxide. The mass transfer coefficients fall off rapidly with distance to the same magnitude as those for sodium sulfite solutions. Initially the rate of reaction requires more oxygen than in the nitrogen dioxide case, but less oxygen is consumed than in the absorption by sodium sulfite solutions. For sodium sulfite oxidation the solute must diffuse outward to react with the oxygen diffusing inward from the surface if mixing is not complete within the droplet. For sulfur dioxide–oxygen absorption, both constituents must be absorbed by the liquid, but they can react immediately without further diffusion through the liquid. In this case, if the liquid droplet lacks circulation, the diffusion of sodium sulfite becomes controlling for a fast reaction.

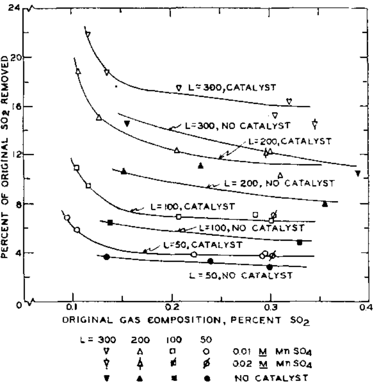

Fig. 6. Effect of Gas Composition and Catalyst on the Over-all Recovery Efficiency for Sulfur Dioxide in the Venturi Atomizer.

Recovery of Gases. The application of the venturi atomizer to the removal of a constituent from the gas phase may now be considered. In the present work the recovery efficiencies for nitrogen dioxide and for sulfur dioxide were determined, based on the composition of the effluent from the cyclone following the atomizer. The recovery efficiency for nitrogen dioxide was low, as shown in Figure 5. The efficiencies decreased from approximately 2.3% for 10% nitrogen dioxide in the gas phase to less than 1% for 1% nitrogen dioxide. This decrease is expected on the assumption that the chemical reaction controls the absorption rate (*6*). Use of the venturi atomizer for the recovery of a substantial portion of nitrogen dioxide from the gas phase does not appear feasible because the reaction is too slow. The use of an oxidation catalyst gave no improvement in recovery efficiency. Apparently the oxidation reaction does not control the absorption of nitrogen dioxide in dilute solution.

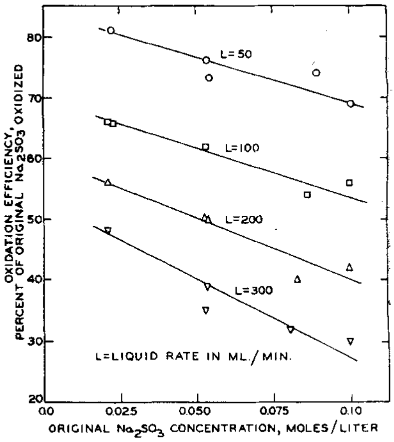

Fig. 7. Efficiency of Oxidation of Sodium Sulfite Solution in the Venturi Atomizer.

The recovery efficiencies for sulfur dioxide were substantially higher than those for nitrogen dioxide, as shown in Figure 6. The efficiency increased at lower sulfur dioxide concentrations; the recovery increased in the presence of an oxidation catalyst, 0.01 *M* manganous sulfate. An increase in the concentration of the catalyst to 0.02 *M* had no appreciable effect. Efficiencies varied from 4 to 22% with liquid rate and sulfur dioxide concentration in the gas. These are sufficient to make the method of some commercial interest.

A number of factors contribute to the low recovery efficiencies in the venturi atomizer. In order to achieve fine atomization it is necessary to maintain a high gas velocity in the throat. In the present work the liquid supplied to contact the gas varied from 2.1 to 12.8 gal./1,000 cu. ft. of gas. Some of the droplets impinged on the wall

Table 1.—Comparison of Absorption in the Atomization Zone with Over-all Absorption in the Venturi Atomizer

Oxygen Absorption

Initial Na_2SO_3 concentration, moles/liter	Liquid rate, ml./min.	Oxygen absorbed, equiv./liter		Ratio of atomization zone to over-all absorption
		Atomization zone	Cyclone effluent	
Pure H_2O	95.2	4.2×10^{-4}	5.6×10^{-4} (saturated)	0.75
0.021	100	0.0099	0.0141	0.70
0.054	100	0.0176	0.0292	0.60
0.054	300	0.0127	0.0209	0.61
0.100	100	0.0204	0.0555	0.31
0.100	200	0.0170	0.0418	0.41
0.099	300	0.0137	0.0297	0.46

Simultaneous Nitrogen Dioxide—Oxygen Absorption

Initial gas composition, vol. %NO_2	Liquid rate, ml./min.	Oxygen absorbed, equiv./liter		NO_2 absorbed, moles/liter		Ratio of atomization zone to over-all absorption	
		Atomization zone	Cyclone effluent	Atomization zone	Cyclone effluent	O_2	NO_2
1.7	100	0.0004	0.0010	0.0016	0.0042	0.40	0.38
1.1	300	0.0003	0.0016	0.0003	0.0022	0.19	0.14
6.3	100	0.0029	0.038	0.0083	0.090	0.08	0.09
6.5	300	0.0020	0.015	0.0027	0.037	0.13	0.07
8.4	100	0.0020	0.052	0.0116	0.132	0.04	0.09
7.9	300	0.0007	0.012	0.0037	0.040	0.02	0.09
10.9	100	0.0063	0.083	0.0171	0.191	0.08	0.09
10.7	300	0.0010	0.018	0.0048	0.068	0.06	0.07

Simultaneous Sulfur Dioxide—Oxygen Absorption

Initial gas composition, vol. % SO_2	Liquid rate, ml./min.	Oxygen absorbed, equiv./liter		SO_2 absorbed, moles/liter		Ratio of atomization zone to over-all absorption	
		Atomization zone	Cyclone effluent	Atomization zone	Cyclone effluent	O_2	SO_2
0.104	100	0.0017	0.0024	0.0034	0.0080	0.71	0.43
0.117	300	0.0013	0.0015	0.0026	0.0060	0.87	0.43
0.116	100	0.0021	0.0023	0.0036	0.0077	0.91	0.47
0.135	300	0.0011	0.0013	0.0019	0.0059	0.85	0.32
0.286	100	0.0020	0.0026	0.0070	0.0144	0.77	0.49
0.320	300	0.0010	0.0019	0.0039	0.0123	0.53	0.32

as they passed downstream and some settled out. The higher liquid rates necessary to ensure thorough contact of all the gas with the liquid resulted in greater wall impingement, with resultant decrease in interfacial area. Very low liquid rates gave little impingement, but not all the gas was brought into contact with the liquid. Because of the high linear velocities in the throat, the time of contact with the liquid is very short and the time of contact in the zone of high interfacial area and turbulence is even less. These difficulties of course do not exist in large venturi atomizers where impingement on the wall and settling do not occur.

Oxidation Processes. Although complete removal of a constituent from the gas phase appears to be impossible with the venturi atomizer, its use for absorbing oxygen from an air stream to oxidize an oxygen-deficient solution appears feasible. In this case it is not necessary to remove all or even a substantial part of the oxygen from the gas, nor must all the gas necessary for atomization come into contact with the liquid. Figure 7 shows the oxidation efficiencies of sodium sulfite solutions containing an oxidation catalyst. In this case the liquid rate is a major factor. Lower liquid rates give higher initial surface-volume ratios, less impingement, and higher oxidation efficiencies. Efficiencies as high as 80% were obtained with 0.025 *M* sodium sulfite original concentration.

Absorption in the Atomization Zone Compared with Over-all Absorption. It is of interest to compare with the over-all absorption the absorption that occurs in the very short time in the atomization zone up to 1 in. from liquid injection. In this way the effectiveness of the unique feature of the venturi atomizer can be determined for gas absorption. The remainder of the apparatus other than the atomization zone resembles a spray chamber. If the atomization zone does not accomplish a large share of the absorption, there is little point in using the venturi atomizer. Table 1 gives representative ratios of the absorption at 1 in. from injection to the over-all absorption. It is not possible to calculate the relative times, because of the unknown acceleration characteristics of the liquid particles and because of ultimate wall impingement, but there is certainly a factor of at least two hundred between the over-all time and that up to 1 in. In the case of the absorption of oxygen by pure water 75% of saturation was reached within 1 in. of liquid injection. For oxygen absorption into sodium sulfite solutions, from 30 to 70% of the total absorption occurs in the atomization zone. The solutions with lower initial concentrations give a higher proportion of oxidation in the atomization zone, because of the approach to complete oxidation in the atomization zone by the dilute solutions.

For nitrogen dioxide absorption, the atomization zone contributes much less to the total absorption. In general, less than 10% of the total absorption occurs within 1 in. of the liquid injection; thus, the unique characteristics of the venturi are of little use in nitrogen dioxide absorption. In sulfur dioxide–oxygen absorption the atomization zone is again significant. From 50 to 90% of the total oxygen is absorbed within 1 in., and from 30 to 50% of the sulfur dioxide is absorbed in the same region. It is interesting to note that in the atomization zone a greater proportion of oxygen is absorbed than of sulfur dioxide. This indicates the value of the venturi for the absorption of slightly soluble gases.

ABSORPTION IN THE FRITTED-GLASS DISPERSER

The fritted-glass disperser was studied as another means of obtaining phase dispersion and large interfacial absorption area. The high recovery efficiencies for nitrogen dioxide with this device indicate possible industrial applications in place of the conventional bubble-cap trays. The unique feature of the fritted-glass absorber is the high rate of gas absorption during bubble formation.

In the absorption of nitrogen dioxide from a gas containing 2.7% nitrogen dioxide in the fritted-glass disperser, an eightfold decrease in liquid volume causes *only* a 10% decrease in the amount of nitrogen dioxide absorbed in a 2-hr. period, as shown in Figure 8. This decrease is caused in part by the higher concentrations of acid in the smaller liquid volume. Thus most of the nitrogen dioxide absorption occurs during the bubble formation in or near the fritted-glass surface. Only a small portion occurs as the bubbles rise through the liquid. The rate of absorption of nitrogen dioxide is nearly constant when air is the diluent, as shown in Figure 9. An increase in air rate decreases the recovery efficiency only slightly. A fourfold increase from 0.05 to 0.2 cu.ft./min. reduces the recovery efficiency by only 2%, as shown in Figure 10, and yet allows only one fourth the contact time for the gas within the fritted glass. The substitution of pure oxygen for air improves the recovery of nitrogen dioxide in a 2-hr. period by 6%. Absorption of nitrogen dioxide with nitrogen as the diluent is 18% less than with air. Thus oxidation has some influence on absorption but is not the controlling factor.

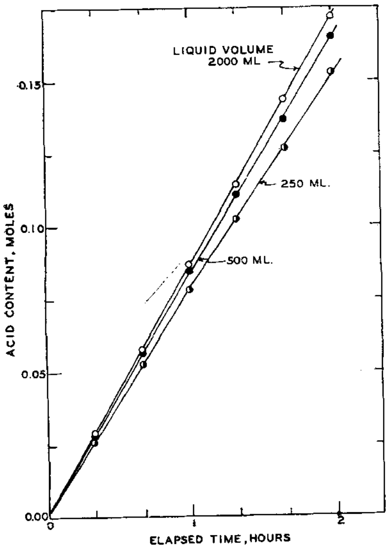

Fig. 8. Effect of Liquid Volume on Nitrogen Dioxide Absorption in the Fritted-Glass Disperser; Gas Rate, 0.05 cu.ft./min.; Gas Composition, 2.7% NO_2.

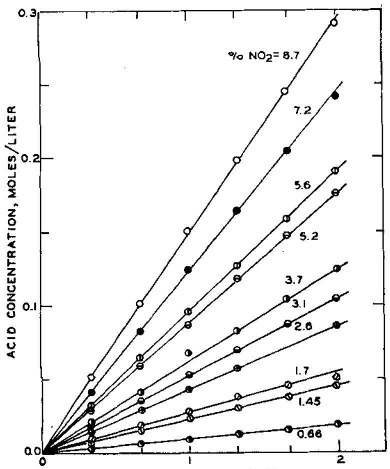

Fig. 9. Absorption of Nitrogen Dioxide from Air in the Fritted-Glass Disperser at a Gas Rate of 0.05 cu.ft./min.

The recovery efficiencies for nitrogen dioxide in the fritted-glass absorber, shown in Figure 11, are substantially higher than those for a bubble-cap column at atmospheric pressure, as reported by Peters(*6*). The efficiency decreases from 90% at a gas composition of 10% nitrogen dioxide in air to 89% at 3% nitrogen dioxide and then falls off to 80% at 1% nitrogen dioxide. This decrease with concentration agrees with the theory proposed by Peters(*6*). The high concentrations of nitrous acid found here were not found in the bubble-cap column. About 20% of the total acid was in the form of nitrous acid, but in the bubble-cap column the concentration of nitrous acid was negligible. With nitrogen as the diluent gas, the same concentration of nitrous acid was found. The decrease in efficiency at higher gas concentrations with nitrogen as the diluent, as shown in Figure 11, is not readily explained. It may be caused in part by a greater build-up of nitrous acid which retards the reaction of nitrogen dioxide with water. This would also explain the substantially lower recovery efficiencies when nitrogen is the diluent instead of air. There was no difference between nitrogen and air in the bubble-cap column.

The differences between the fritted-glass absorber and the bubble-cap column may be explained on the basis of gas- and liquid-film reactions. Peters made a theoretical analysis of the kinetics of the bubble-cap absorber, assuming that chemical reactions controlled, and concluded that the gas-film reaction predominates. The nitrogen dioxide reacts in the gas film with water vapor and oxygen and gives nitric acid and some nitrous acid. The nitric acid condenses into a mist and diffuses into the liquid. Any nitrous acid formed may decompose and react with oxygen; a small portion may diffuse into the liquid. This nitrous acid and any formed in solution will be oxidized by dissolved oxygen so that the nitrous acid concentration in the liquid is negligible.

In the fritted-glass absorber, on the other hand, because of the greater interfacial area and more complete contact of the gas with the liquid, the rate of absorption of nitrogen dioxide is greater; therefore the liquid-film reactions are more important. Nitric and nitrous acids form in the liquid phase, and oxygen must be absorbed to oxidize the nitrous acid. Decomposition of nitrous acid is slower in the liquid phase than in the gas phase, and the concentration of nitrous acid remains at a high value.

The higher over-all rate of absorption of nitrogen dioxide in the fritted-glass absorber compared with that in the bubble-cap column can be attributed to the more rapid reaction of nitrogen dioxide in the liquid phase compared with that in the gas phase.

Effect of Liquid-Phase Additives on Nitrogen Dioxide Absorption. Catalysts or inhibitors for nitrous acid decomposition, as well as oxidation catalysts, have no appreciable effect on the over-all acid content or nitrogen dioxide recovery. There is a slight effect on the nitrous acid concentration, as shown in Figure 12. Boric acid and potassium nitrate were used as the catalysts for nitrous acid decomposition(*4*). Manganous sulfate is an oxidation catalyst and phenol is both an oxidation and decomposition inhibitor. In the presence of these agents the

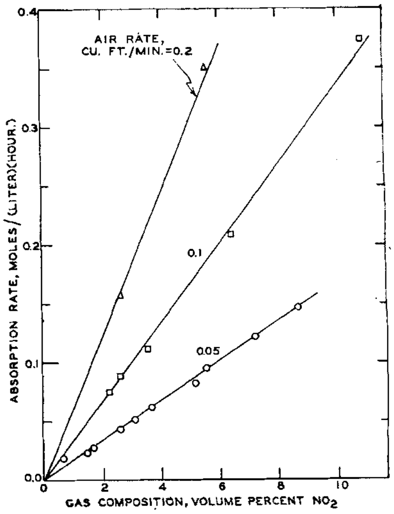

Fig. 10. Effect of Gas Rate and Gas Composition on the Absorption Rate of Nitrogen Dioxide in the Fritted-Glass Disperser.

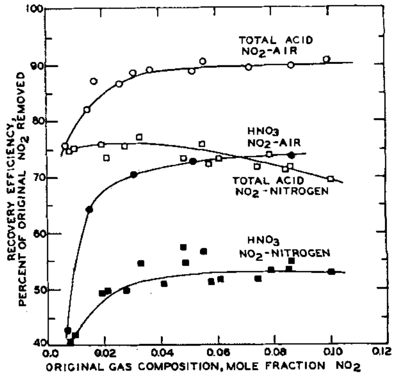

Fig. 11. Recovery Efficiency for Nitrogen Dioxide in the Fritted-Glass Disperser: Gas Rate, 0.05 cu.ft./min.

total acid curves are essentially the same as in their absence. The nitrous acid concentration is lower in the presence of the catalysts and higher in the presence of phenol, as expected. Thus, although a catalyst has some effect on the nitrous acid content of the solution, it has no effect on the total acid content or over-all recovery of nitrogen dioxide from air mixtures. With nitrogen as a diluent, however, the decomposition and oxidation of nitrous acid does have an effect on the over-all recovery. Above a critical minimum rate the decomposition of nitrous acid apparently does not influence the over-all recovery of nitrogen dioxide from dilute gases in the fritted-glass disperser.

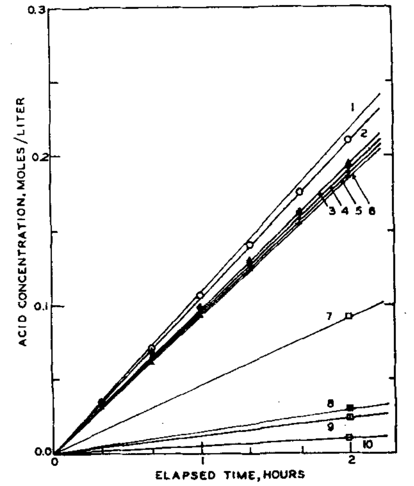

FIG. 12. EFFECT OF CATALYSTS AND SODIUM HYDROXIDE ON THE ABSORPTION OF NITROGEN DIOXIDE FROM AIR IN THE FRITTED-GLASS DISPERSER: GAS RATE, 0.05 CU.FT./MIN.; GAS COMPOSITION, 5.8% NO_2.

Total acid	Nitrous acid
1 With excess NaOH, 100% recovery	7 For phenol
2 With a stoichiometric quantity of NaOH	8 For H_3BO_4
3 With no catalyst	9 For KNO_3
4 Two runs: 0.01*M* KNO_3; 0.01*M* H_3BO_3	10 For $MnSO_4$
5 With 1*M* $CaCl_2$	
6 Two runs: 0.01*M* phenol, 0.01*M* $MnSO_4$	

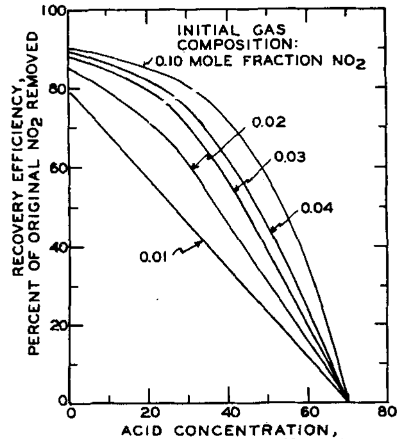

FIG. 13. EFFECT OF ACID CONCENTRATION ON RECOVERY EFFICIENCY FOR NITROGEN DIOXIDE AT VARIOUS GAS COMPOSITIONS IN THE FRITTED-GLASS DISPERSER; GAS RATE, 0.05 CU.FT/MIN.

Effect of Nitric Acid Concentration on Nitrogen Dioxide Recovery. As the nitric acid concentration of the solution increases, the reversibility of the reactions of nitrogen dioxide with water becomes important, until, at 15.4 *M* (69.6%) nitric acid, the rate of the forward reaction [Equation (3)] becomes insignificant compared with the reverse reaction, and no more nitrogen dioxide reacts with water at atmospheric pressure. The recovery efficiency thus becomes zero in 15.4 *M* nitric acid. This was verified experimentally, and the curves of Figure 13 show the decrease in recovery efficiency with acid concentration in the fritted-glass absorber. These efficiency data were used to calculate an over-all efficiency for a multistage absorber by the method of Sherwood and Pigford(*7*). For a four-stage countercurrent fritted-glass absorber with 10% nitrogen dioxide gas entering at the bottom of the tower and water entering at the top, assuming that all the nitric oxide is oxidized between stages, the over-all recovery efficiency for nitrogen dioxide is 99.7%. If the entering gas is 1% nitrogen dioxide, the over-all efficiency is 98.6%. With 30% acid entering at the top and 10% nitrogen dioxide in the gas, the over-all efficiency is 96.9%. These efficiencies are higher than those reported for bubble-cap columns at atmospheric pressure.

Other Reactions. In the absence of a catalyst in the absorption of 2 to 17% sulfur dioxide from air, the oxidation in solution is not rapid enough to prevent build-up of sulfur dioxide to the saturation point where no more sulfur dioxide is absorbed. At higher concentrations of sulfur dioxide in the gas, saturation is reached more readily. When an oxidation catalyst is present, the build-up is less pronounced. Previous work at very low sulfur dioxide concentrations (0.325%) in the gas showed that the catalyzed oxidation of sulfur dioxide is sufficiently rapid to prevent any build-up in solution.

The absorption of nitrogen dioxide by a solution containing an excess of sodium hydroxide over the amount necessary to react with all the nitrogen dioxide supplied in a 2-hr. period resulted in 100% recovery. The gas rate was 0.05 cu.ft./min. and the composition was 5.8% nitrogen dioxide. Chambers and Sherwood found a decrease in absorption by sodium hydroxide solutions in a wetted-wall column compared with absorption by pure water(*2*). In such a device the gas-film reaction predominates and the sodium hydroxide in solution lowers the vapor pressure of water. In the fritted-glass absorber the liquid-film reaction predominates because of the high interfacial area available for absorption.

COMPARISON OF THE VENTURI ATOMIZER AND THE FRITTED-GLASS DISPERSER

The two methods of gas-liquid contact used in this work cannot be compared in all respects. The initial rate of absorption is higher in the venturi atomizer, but the time of contact during which high absorption rates exist is much greater for the fritted-glass disperser. The over-all contact of the gas with the liquid is better in the disperser; consequently it is more effective for the recovery of a constituent from the gas phase. The shorter contact time in the venturi atomizer may be advantageous in a case where it is desired to stop a specific reaction after a short time. The use of a fritted disperser for nitrogen dioxide absorption appears to be promising.

Further work is planned on other fritted materials suitable for commercial absorbers of this type, such as sintered stainless steel. While the studies reported here were all made at atmospheric pressure, even higher recovery efficiencies for nitrogen dioxide would be expected at elevated pressures.

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