Kinetics of Absorption of Oxygen into Aqueous Sodium Sulfite: Order in Oxygen

E. Alper, B. Abu-Sharkh
Chemical Engineering Department
King Fahd University
of Petroleum and Minerals
Dhahran 31261, Saudi Arabia

The kinetics of oxidation of sodium sulfite, which is catalyzed by cobalt ions, has received considerable attention in the chemical engineering literature; important findings were reviewed by Linek and Vacek (1981) and Doraiswamy and Sharma (1984). Interest in the absorption of oxygen in aqueous sulfite solutions arose mainly out of the desirability of using this system to study the performance characteristics of a variety of contactors. This system is especially appropriate for the determination of interfacial areas in industrial contactors as the required chemicals are cheap and noncorrosive.

In these investigations (Danckwerts and Rizvi, 1970; Alper, 1979, among others), air at nearly atmospheric pressure is often employed as the incoming gas so that the oxygen partial pressure is less than 0.21 atm. The same system may also seem convenient to measure the interfacial areas of gas-liquid contactors operating at elevated pressures which may result in oxygen partial pressures exceeding 1 atm. At this partial pressure range of oxygen there has been controversy about the order in oxygen.

Alper (1973) showed that the reaction is first order in oxygen for oxygen partial pressures exceeding 1 atm. Other researchers have also noted that the order of oxygen decreases from second order to first order as oxygen partial pressures increase to the 1 atm level (Linek and Mayrhoferova, 1970; Nyvlt and Kastanek, 1975; Onda et al., 1972). In recent studies at high oxygen partial pressures, the first-order dependency appears to be confirmed (Rice and Benoit, 1986; Botton et al., 1987). In a closely relevant study, Ahmad et al. (1987) report that order in oxygen is first order for the oxygen partial pressure range of 0.2 to 1 atm for ammonium sulfite oxidation. Botton et al. also concluded first-order dependency for the same pressure range. Neither of these two studies included experiments for the range of oxygen partial pressures of less than 0.21 atm. However, when the experimental results are extrapolated to zero oxygen concentration, they do not yield zero absorption rate, indicating that the order in oxygen is higher than one at low oxygen concentrations. However, order in oxygen should be known exactly for interfacial area determinations since the technique necessarily involves integration of absorption rate expressions along the column (Alper, 1979). It is therefore important to establish the order in oxygen exactly for a certain partial pressure range.

The aim of this investigation is to provide accurate substantial data in this respect. Other parameters, such as pH, sulfite concentration range, and Co^{++} concentration range were typical of those used in interfacial area determination experiments; they were not thoroughly investigated here since there appeared to be no controversy about their dependencies. Table 1 summarizes the conditions of the experiments. Under these conditions, the reaction is zero order in sulfite and *m*th order in oxygen.

If (Danckwerts, 1970):

$$1 + \left(\frac{B^0}{zC^*}\right) \gg \left[\frac{2D_c k_m [C^*]^{m-1}}{k_L^2(m+1)}\right]^{1/2} \gg 1 \tag{1}$$

then

$$R = [C^*]^{(m+1)/2}[2D_c k_m/(m+1)]^{1/2} \tag{2}$$

Since the gas-side resistance is negligible (because of low solubility of oxygen):

$$C^* = p/He \tag{3}$$

Hence

$$R = Kp^{(m+1)/2} \tag{4}$$

where

$$K = [2D_c k_m He/(m+1)]^{1/2} \tag{5}$$

and K is a function of cobalt ion concentration, pH, temperature, and ionic strength but does not depend on the oxygen par-

---

Correspondence concerning this paper should be addressed to E. Alper.

Table 1. Experimental Conditions

Temperature	298, 313 K
Total pressure	1–30 atm
O_2 partial pressure	0.14–4.2 atm
Incoming gas	Air (20.9% O_2)
Outgoing gas	14–20% O_2
Initial sulfite conc.	0.8 kmol/m^3, prepared using technical (95%) sodium sulfite
Cobalt chloride conc.	0.5–3 × 10^{-3} kmol/m^3
pH of solution	8.5, adjusted by adding concentrated H_2SO_4

tial pressure. Thus, Eq. 4 can be used conveniently to determine the order in oxygen while keeping everything else constant.

Experimental Method

Figure 1 shows a diagram of the experimental set-up; pertinent details of the 300 cm^3 high-pressure reactor are given elsewhere (Alper and Palla, 1987). The stirrer speed was kept throughout at 200 rpm^{-1}, which ensured a known interfacial area. Selected experiments were also repeated at two other stirring speeds of 100 and 150 rpm^{-1} and no effect was observed, in accordance with Eq. 4. Some of the experiments at atmospheric pressure were also carried out in a 2 L fermenter (Biostat M, B. Braun, West Germany). The temperature of the liquid inside the reactor was maintained at either 298 ± 0.2 K or 313 ± 0.2 K. Air from a cylinder was always the inlet gas and the oxygen content of the gas leaving was measured using a paramagnetic oxygen analyzer (Servomex, U.K., model 540A). The flow rate of gas under working conditions was adjusted so that the outgoing oxygen compositions of 14 to 20.0% were obtained. Pseudo-steady-state conditions wer reached after 5–20 min. The final concentration of sulfite was determined iodimetrically and was between 0.35 and 0.77 kmol/m^3 depending on the Co^{++} concentration and the pressure.

Results and Discussion

The absorption rate of oxygen is given by:

$$RA = G_o\left(\frac{1 - y_o}{1 - y_i}y_i - y_o\right) \qquad (6)$$

where G_o is the molar gas flow rate of outgoing gas and y_i and y_o are mol fractions of oxygen in the incoming and outgoing gas streams, respectively. Noting that y_i is 0.209 and A is the cross-sectional area of the reactor; the absorption rate per unit interface, R, is obtained from the measured G_o and y_o values. The latter remained constant even though sulfite concentration decreased considerably, indicating that the absorption rate is independent of sulfite concentration, which corresponds to zero order.

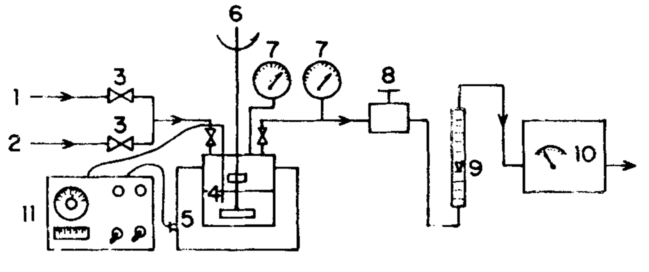

Figure 1. Experimental set-up.

1. Nitrogen
2. Air
3. Needle valves
4. 300 cm^3 Parr miniautoclave
5. Heating jacket
6. Magnetically coupled stirrer
7. Pressure gauges
8. Backpressure regulator
9. Flow meter
10. Paramagnetic oxygen analyzer
11. Automatic temperature controller

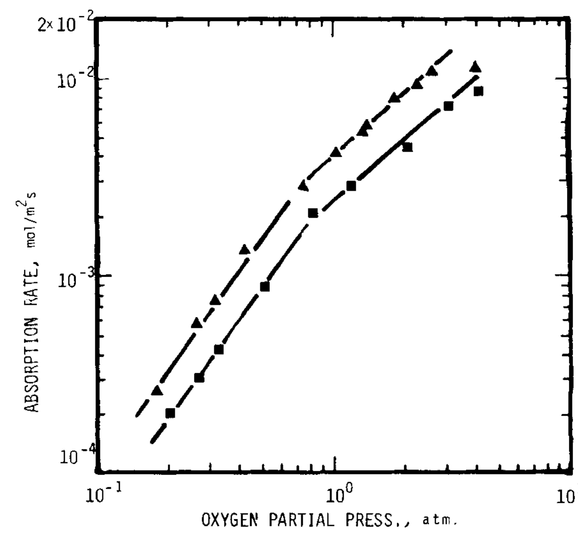

Figure 2. Oxygen absorption rate as a function of oxygen partial pressure.

Co^{++} conc. at 298 K: ▲ 5 × 10^{-4} kmol/m^3, ■ 2 × 10^{-3} kmol/m^3

Figures 2 and 3 show the results at various Co^{++} concentrations and at two temperatures. Special attention was given to the experiments where oxygen partial pressure was around 0.2 atm since they would correspond to interfacial area determination experiments at about atmospheric pressure with air. Results confirm that the reaction is second order at the oxygen partial

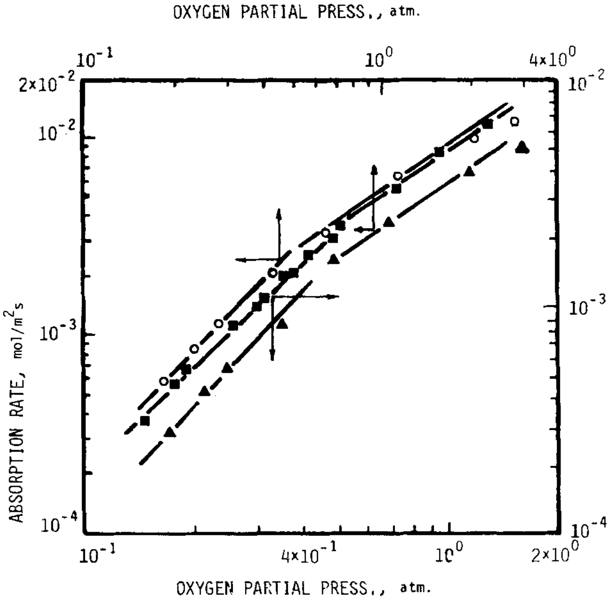

Figure 3. Oxygen absorption rate as a function of oxygen partial pressure.

Co^{++} conc.: ○ 5 × 10^{-4} kmol/m^3 at 313 K, ▲ 2 × 10^{-3} kmol/m^3 at 313 K, ■ 3 × 10^{-3} kmol/m^3 at 298 K

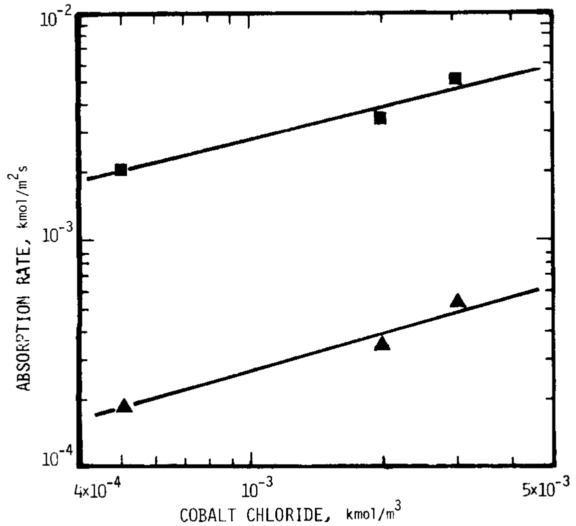

Figure 4. Oxygen absorption rate as a function of Co^{++} concentration.

O_2 partial pressure: ▲ 0.2 atm, ■ 1.0 atm at 298 K

pressure range of 0.2 atm since the slope of the straight line in a logarithmic scale plot is about 1.5, in accordance with Eq. 4; this can be seen in Figures 2 and 3. At oxygen partial pressures substantially higher than 0.2 atm, the order in oxygen appears to be first order. When the oxygen partial pressure is further increased, the dependency on the oxygen partial pressure decreases rapidly. However, the reason for the latter is that at very high pressures, the lefthand side of inequality Eq. 1 is no longer satisfied, so that sulfite is depleted near the interface. Then the conditions do not conform to the pseudofirst-order reaction and the absorption rate is less than would be predicted from Eq. 4. This behavior is evident in Figures 2 and 3.

From the experimental data it appears difficult to decide the exact range of partial pressure of oxygen where the change in order takes place. In addition, this should also depend on the temperature since the solubility of oxygen strongly depends on it. Although reporting results in terms of the dissolved oxygen concentration would seem more appropriate, this would require an accurate estimation of the Henry's law constant. Further, the practical information required is in terms of oxygen partial pressure and therefore the results are presented here only as function of the latter.

Figure 4 shows the plots of absorption rate as a function of Co^{++} concentration at oxygen partial pressures of 0.20 atm and 1 atm on a logarithmic scale. The linear regression analysis of these data yielded slopes of 0.45 and 0.53 for experiments at 0.2 and 1.0 atm, respectively, indicating that the intrinsic reaction rate is proportional to Co^{++} according to Eq. 4.

It is therefore concluded that for conditions relevant to interfacial area determinations, this complicated oxidation reaction behaves as zero order in sulfite and first order in Co^{++}. However, the order in oxygen is not unique and for the temperature range of 298 to 313K it is apparently second order when air is employed at atmospheric pressures and first order if the oxygen partial pressure exceeds 0.21 atm considerably. Therefore if one uses the air—SO_3^{--}-Co^{++} system for interfacial area determinations at elevated pressures, care should be exerted about the correct order in oxygen. In this respect, the data presented here in Figures 2 and 3 may be useful for guidance.

Notation

A = gas-liquid interfacial area (cross-sectional area of stirred cell, m^2
B^o = concentration of sulfite ions in bulk of liquid, kmol/m^3
C^* = concentration of dissolved oxygen at interface in equilibrium with bulk liquid, kmol/m^3
D_c = diffusivity of dissolved oxygen, m^2/s
He = Henry's law constant, atm · m^3/kmol
k_L = physical liquid-side mass transfer coefficient, m/s
k_m = pseudo mth-order reaction rate constant, m^3/kmol)$^{m-1}$ · s^{-1}
m = order of reaction with respect to oxygen
p = partial pressure of gas in bulk of gas, atm
R = average rate of absorption per unit area of gas-liquid interface, mol/m^2 · s
z = number of moles of sulfite reacting with each mole of oxygen

Literature Cited

Ahmad, N., I. Eroglu, and T. Gurkan, "Factors Affecting the Kinetics of the Heterogeneous Oxidation of Ammonium Sulfite," *Can. J. Chem. Eng.*, **65**, 50 (1987).

Alper, E., "The Kinetics of Oxidation of Sodium Sulfite Solution," *Trans. Inst. Chem. Engrs.*, **51**, 159 (1973).

———, "Measurement of Effective Interfacial Area in a Packed Column Absorber by Chemical Methods," *Trans. Inst. Chem. Engrs.*, **57**, 65 (1979).

Alper, E., and M. A. Palla, "Oxidation of Aqueous Sodium Sulfide Solutions Containing Fine Activated Carbon at Elevated Temperatures," *Chem. Eng.*, **35**, 37 (1987).

Botton, R., D. Cosserat, and J.-C. Charpentier, "A New Laboratory Apparatus for the Study of Gas-Liquid Reactions and the Simulation of Reactors: The Gas-Lift Bubble Column," *Int. Chem. Eng.*, **27**, 243 (1987).

Danckwerts, P. V., *Gas-Liquid Reactions,* McGraw-Hill, New York (1970).

Danckwerts, P. V., and S. F. Rizvi, "Design of Gas Absorbers. II," *Trans. Inst. Chem. Engrs.*, **49**, T129 (1971).

Doraiswamy, L. K., and M. M. Sharma, *Heterogeneous Reactions,* **2**, Wiley, New York (1984).

Linek, V., and J. Mayrhoferova, "The Kinetics of Oxidation of Aqueous Sodium Sulfite Solutions," *Chem. Eng. Sci.*, **25**, 787 (1970).

Linek, V., and V. Vacek, "Chemical Engineering Use of Catalyzed Sulfite Oxidation Kinetics for the Determination of Mass Transfer Characteristic of Gas-Liquid Contactors," *Chem. Eng. Sci.* **36**, 1747 (1981).

Nyvlt, V., and F. Kastanek, "Measurement of Interfacial Area in Bubble Columns by the Sulfite Method," *Coll. Czech. Chem. Commun.*, **40**, 1853 (1975).

Onda, K., H. Takeuchi, and Y. Maeda, "The Absorption of Oxygen into Sodium Sulfite Solution in a Packed Column," *Chem. Eng. Sci.*, **27**, 449 (1972).

Rice, F. G., and E. L. Benoit, "An Experimental Pressure Response Method to Measure Gas-Liquid Kinetics," *Chem. Eng. Sci.*, **41**, 2629 (1986).

Manuscript received Jul. 30, 1987, and revision received Jan. 6, 1988.