The less steep gradient could come from greater backmixing of the liquid or from channeling (radial velocity variations). The absence of any large effect of misalignment on the concentration drop at the feed inlet suggests that channeling in lower regions is the greater effect. This corresponds to the visual observations of channeling when $KMnO_4$ solution was added.

CONCLUSIONS

Vertical misalignment of foam and bubble fractionation columns can strongly affect their performance, even for slight departures from the true vertical. The sensitivity to misalignment is probably affected by flow rates, bubble diameters, and length-to-diameter ratio of the column. These factors were not investigated explicitly. It would appear that a number of cases of nonreproducibility of bubble-column performances can be explained by slight departures from true vertical alignment of the contactor.

Deckwer et al. (1973) reported experimentally derived backmixing coefficients for bubble columns, which varied abruptly at a certain point in the column. It may be that this phenomenon is also associated with effects of slight departures of the column from the vertical.

ACKNOWLEDGMENTS

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Remarks on the Rate of Formation of Bisulfite Ions in Aqueous Solution

SIEGFRIED BEILKE and DENNIS LAMB

Umweltbundesamt, Pilotstation
Frankfurt/Main, Germany

In 1964 a paper by Wang and Himmelblau was published in the *AIChE Journal* on the rate of formation of bisulfite ions in aqueous solution. The results of this work based on radioactive tracer techniques have been widely used in fields of both engineering and science. Apparently unknown to them at that time another work, one based on relaxation methods and conflicting drastically with theirs, had already been published by Eigen et al. (1961). It is the purpose of this note to point out this discrepancy and to shed new light on the rate at which physically dissolved SO_2 dissociates into HSO_3^- in aqueous solutions.

Both of the earlier studies made use of the same reaction for the formation of the bisulfite ion:

$$SO_2 + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H^+ + HSO_3^- \qquad (1)$$

For comparison purposes, the values of the forward rate constant k_1 and of the reverse rate constant k_{-1} are presented from the respective works in Table 1. As is readily apparent, we are not concerned about small deviations of possibly experimental origin, but rather about very large discrepancies of over 8 orders of magnitude which could have arisen only through false assumptions or fundamental differences in definition in one or the other of the two works. Whether the values of Wang and Himmelblau or those of Eigen et al. are used could therefore completely alter the interpretations of other experimental results. One example of this occurred recently in the interpretation of recent laboratory experiments by Beilke et al. (1975).

Since a decision as to which set of measurements one should accept, if either, requires an independent basis, some simple measurements were made in our own laboratory. The experimental setup is shown in Figure 1. A mixture of triply purified N_2 and traces of SO_2 were bubbled continuously through the two bubble columns connected in series. The first bubble column contained 40 or 70 ml of doubly distilled water, the second, the same volume of highly diluted H_2O_2 to oxidize and fix any SO_2 not absorbed in the first column. Measurements were made continuously of *p*H in the first column and specific conductivity in the second. The concentration of SO_2 in the source chamber was measured by having the gas mixture sucked through a conductivity cell (Hartmann and Braun), calibrated against the standard procedure of West and Gaeke (1956).

As the gas mixture contained no oxygen, the formation of $SO_4^=$ was excluded, leaving HSO_3^- and $SO_3^=$ as the

TABLE 1. COMPARISON OF MEASURED RATE CONSTANTS, APPROPRIATE TO 20°C

Rate constant	Wang and Himmelblau (1964)	Eigen et al. (1961)	Units
k	$(2.2) \cdot 10^{-2}$	$(3.4) \cdot 10^{6}$	s^{-1}
k_{-1}	1.6	$(2.0) \cdot 10^{8}$	$l\ mole^{-1}\ s^{-1}$

Correspondence concerning this note should be addressed to D. Lamb at the Desert Research Institute, University of Nevada System, Reno, Nevada 89507.

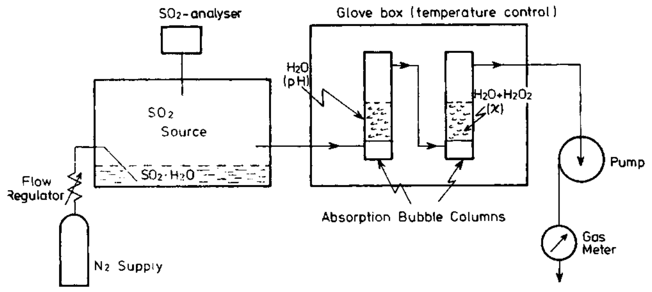

Fig. 1. The experimental setup used to observe the reaction of SO_2 with water.

TABLE 2. EQUILIBRIUM DATA USED TO OBTAIN THE DISSOCIATION CONSTANT K_1 AT 25°C

P_{SO_2}, 10^{-6} atm	$[HSO_3^-]$, 10^{-4} mole l^{-1}	K_1, 10^{-2} mole l^{-1}
12.6	5.30	1.80
10.5	4.785	1.76
3.45	2.65	1.64
2.10	2.10	1.69
1.25	1.64	1.74
1.16	1.55	1.67
0.52	1.04	1.68

only ionic species of sulfur in solution. Furthermore, in the low pH range applicable to these experiments, the concentration of sulfite can be neglected compared with that of bisulfite so the trend with time of the measured pH must be due almost exclusively to the formation of HSO_3^- as SO_2 is absorbed by the solution. Designating the physically dissolved SO_2 as $SO_2 \cdot H_2O$, one obtains for the rate of formation of HSO_3^- by the reaction given in Equation (1)

$$\frac{d[HSO_3^-]}{dt} = k_1[SO_2 \cdot H_2O] - k_{-1}[H^+]\,[HSO_3^-] \qquad (2)$$

Because the solution must maintain its electroneutrality, it follows (in this lower pH range) that

$$[H^+] = [HSO_3^-] \qquad (3)$$

and

$$\frac{d[H^+]}{dt} = \frac{d[HSO_3^-]}{dt} = k_1[SO_2 \cdot H_2O] - k_{-1}[HSO_3^-]^2 \qquad (4)$$

The solution to Equation (4) has the form

$$[HSO_3^-] = \frac{A[HSO_3^-]_0 + k_1[SO_2 \cdot H_2O]\tanh(A \cdot t)}{A + k_{-1}[HSO_3^-]_0 \tanh(A \cdot t)} \qquad (5)$$

where

$$A = (k_1 k_{-1}[SO_2 \cdot H_2O])^{1/2} \qquad (6)$$

This solution assumes that $[SO_2 \cdot H_2O]$ is constant with time, a condition which is really true only in the extreme case of an infinite supply rate of SO_2 from the gas phase, in which case

$$[SO_2 \cdot H_2O] = H \cdot P_{SO_2} \qquad (7)$$

where $H = 1.24$ mole l^{-1} atm^{-1} is Henry's constant and P_{SO_2} is the measured incoming partial pressure of SO_2.

Assuming the validity of Equation (7) and using the values of k_1 and k_{-1} from Wang and Himmelblau, one obtains the trend to the HSO_3^- concentration shown in Figure 2 as the dashed curves for different values of P_{SO_2}. The corresponding curves from our own experimental measurements of pH are shown by the solid curves. The straight lines represent the supply rate of SO_2 from the gas phase as calculated from the measured values of P_{SO_2} and the volumetric flow of gas through the system. The fact that the measured trend of HSO_3^- formation follows the supply curve very closely early in each run is consistent with the measurements of electroconductivity in the second column which showed no measurable passage of the SO_2 through the first column.

It is readily apparent that the rate at which HSO_3^- is formed in our system is at least 6 times that in the system of Wang and Himmelblau. As the measurements at small times cannot be separated from the respective supply curves, the actual rates of HSO_3^- formation could be many times greater yet. This experiment can only provide qualitative evidence that the rate of formation found by Wang and Himmelblau may be too low. Additional qualitative evidence comes from the independent studies of Beilke et al. (1975), Penkett (1974), Hales (1974), and Harrison (1974). None of these observations can be used to say that the results of Eigen et al. are correct, only that more information on the rate of formation of HSO_3^- is desirable.

Even though the present technique is unsuitable for the measurement of reaction rates, it can be used to measure the equilibrium dissociation constant $K_1 = [H^+][HSO_3^-]/[SO_2 \cdot H_2O]$. By allowing the experimental runs to continue until the solution in the first wash bottle is saturated, the derivative in Equation (2) may be set equal to zero and the equilibrium constant calculated. When this is done, using the relationships in Equations (3) and (7) and the data in Table 2, the mean value $K_1 = (1.71 \pm 0.05) \cdot 10^{-2}$ mole l^{-1} is obtained. This is consistent with many of the works listed in Sillén (1964) and with the suggestion of McKay (1971), but over 30% higher than the value obtained by Wang and Himmelblau.

Continued efforts to obtain accurate kinetic and equilibrium data on the sulfur dioxide-water system would have significant impact on our understanding of, among other things, the scavenging of SO_2 from the atmosphere

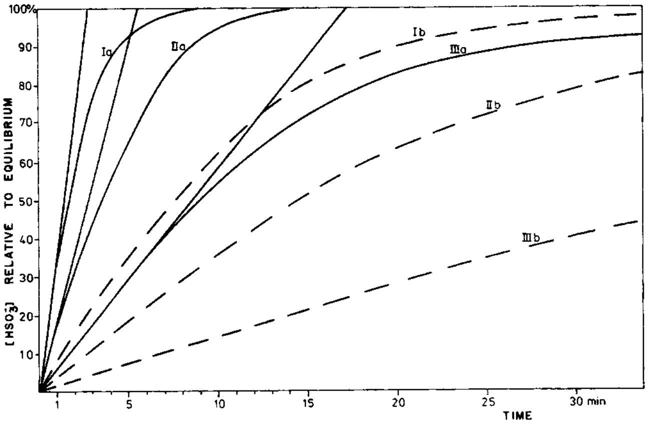

Fig. 2. The formation of HSO_3^- as a function of time at 25°C. Solid straight lines indicate the molar supply of SO_2 corresponding to the associated solid curves (a), which represent the measured concentration of HSO_3^- (expressed as a fraction of the equilibrium value). The dashed curves (b) represent the trends calculated according to Equation (5) using the rate constants of Wang and Himmelblau under the following conditions:

curves I: $P_{SO_2} = 12.6 \times 10^{-6}$ atm
II: $P_{SO_2} = 3.45 \times 10^{-6}$ atm
III: $P_{SO_2} = 0.52 \times 10^{-6}$ atm

by rain and cloud droplets, an important environmental consideration at present.

NOTATION

H = Henry's constant for SO_2, mole l^{-1} atm^{-1}
k_1 = forward rate constant for dissociation, s^{-1}
k_{-1} = reverse rate constant for dissociation, l mole^{-1} s^{-1}
K_1 = equilibrium constant for dissociation, mole l^{-1}
p_{SO_2} = partial pressure of SO_2, atm
t = time, s

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Polymer Moment Equations for Distributed Parameter Systems

CHARLES E. WYMAN

Process Technology Department
Monsanto Company, Springfield, Massachusetts 01051

For conventional material balance problems in chemical engineering, either a mole or mass balance for the system is sufficient to characterize the concentration of the various components of interest. However, for polymerization systems, molecular weight determination of the product is generally necessary in addition to predicting the polymer concentration in order to assess the utility of a particular reactor scheme. For batch and continuous stirred-tank reactors, methods have been applied which allow satisfactory evaluation of performance; but for tubular reactors the method predominately used is to predict instantaneous molecular weights at any point in the tube and weight the contribution to the overall molecular weight according to the conversion that occurs at that point (Cintron-Cordero et al., 1968; Wallis, 1973). By neglecting diffusion and summing the weighted contributions over the reactor length for each radial position, the flow average or cross-sectional average molecular weight parameters at any distance down the tube are determined. Alternatively, a method has been developed based on the continuous blending approach which accounts for diffusion and predicts conversion as well as number and weight average chain lengths (Kwon and Evans, 1973).

This paper will show that by extending the derivation of mass and mole balances to other concentration systems, moment equations are derived which allow exact prediction of molecular weight characteristics in homopolymer systems in which both convection and diffusion are important. The derivation is general so that as many moments as are desirable can be calculated, but no more calculations are required than the previous methods to get the equivalent amount of information. This work follows the general format of Bird, Stewart, and Lightfoot (1960).

DERIVATION OF MATERIAL BALANCE EQUATIONS

It can be shown that for a concentration c_{ij} of type i and species j that a material balance gives

$$\frac{\partial c_{ij}}{\partial t} + \nabla \bullet \mathbf{N}_{ij} = R_{ij} \tag{1}$$

where $\mathbf{N}_{ij}$ is a flux of type i, species j with respect to stationary coordinates while R_{ij} is the reaction rate. Now, $\mathbf{v}_i$ is defined by

$$\mathbf{v}_i = \sum_{j=1}^{N} \frac{c_{ij}\mathbf{v}_j}{c_i} \tag{2}$$

The flux of species j with respect to velocity $\mathbf{v}_i$ for a binary system is

$$\mathbf{J}^*_{ij} = c_{ij}(\mathbf{v}_j - \mathbf{v}_i) = -c_i D_{AB} \nabla x_{ij} \tag{3}$$

while that with respect to $\mathbf{v}_1$ is

$$\mathbf{J}_{ij} = c_{ij}(\mathbf{v}_j - \mathbf{v}_1) \tag{4}$$

It can be shown that

$$\mathbf{J}_{ij} = \frac{c_i(c_1 - c_{1j})}{c_1(c_i - c_{ij})} \mathbf{J}^*_{ij} \tag{5}$$

The flux with respect to stationary coordinates is

$$\mathbf{N}_{ij} = c_{ij}\mathbf{v}_j = c_{ij}\mathbf{v}_i - c_i D_{AB} \nabla x_{ij} \tag{6}$$

again for binary diffusion where

$$x_{ij} = \frac{c_{ij}}{c_i} \tag{7}$$

But it is desirable to reference all stationary coordinate fluxes relative to the same velocity $\mathbf{v}_1$. From (3) and (5)

$$\mathbf{J}_{ij} = \frac{-c_i(c_1 - c_{1j})c_i}{c_1(c_i - c_{ij})} D_{AB} \nabla x_{ij} \tag{8}$$

C. E. Wyman is with the Department of Chemical Engineering University of New Hampshire, Durham, New Hampshire 03824.