

MEASUREMENT OF INTERFACIAL AREA IN BUBBLE COLUMNS BY THE SULPHITE METHOD

V. NÝVL and F. KAŠTÁNEK

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchbát*

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The reaction rate constant and the reaction order with respect to oxygen and sulphite are determined in the paper from the rate of absorption of oxygen into aqueous sulphite solutions catalyzed by cobalt ions. The measurements were carried out in a mixed cell with quiescent liquid level. The utility of the results is discussed for the measurement of interfacial area in bubble columns.

The knowledge of the interfacial area is important both for design and calculation of chemical gas-liquid reactors. A most convenient method of determining this parameter is indirect evaluation from the absorption rates of a suitable model reaction. With regard to the various requirements put on such reaction (the knowledge of the reaction mechanism and kinetics, reasonable costs of the chemicals used for large-scale experiments) the choice is rather limited. The study of such model reactions has been the subject of numerous papers; the most significant ones are summarized in the monograph by Danckwerts¹. The often cited reaction is oxidation of sulphite ions by oxygen catalyzed by salts of heavy metals. The reaction scheme may be written as



Despite of the numerous studies, summarized and critically reviewed *e.g.* in the paper by one of the authors², the mechanism and kinetics of this reaction has not been fully comprehended. The issues of the discussions are quite principal and range from the reaction order with respect to both oxygen and sulphite to the effect of the catalyst and acidity of the solution on the reaction rate. On the other hand, the reaction is attractive because of the economy of large-scale experiment and non-corrosive solutions involved. From the so far published results it follows that the published kinetic data cannot be used safely to estimate interfacial area in a tested reactor. In fact, the kinetic data for the given sulphite solution should be obtained individually in a suitable test cell. The main reason for such precaution is the catalytic sensitivity of the reaction to heavy metals and organic compounds the presence and ratio of which are hard to reproduce experimentally.

This paper reports on the approach used for measurement of the interfacial area in bubble columns. The sulphite solution was prepared from an aqueous solution of sodium hydroxide saturated by pure gaseous SO_2 . The catalyst used was cobaltous sulphate. Identical solution and gas were used both in the test cell and the column.

EXPERIMENTAL

The test cell was a mixed vessel with a quiescent level of the batch³. The interfacial area of the level equalled $2.44 \cdot 10^{-2} \text{ m}^2$. The cell consisted of a metal cylinder (the inner diameter equal 0.176 m; height 0.250 m) coated inside by a baked silicon varnish. Around the circumference on the bottom there were rectangular $14 \times 30 \text{ mm}$ perspex glass baffles short enough not to reach the level of the batch. A 66 mm turbine impeller with six vertical $16 \times 13 \text{ mm}$ blades was also made of perspex glass. The constant temperature of the batch, held at 20°C , was achieved by immersing the cell into a thermostated bath. The cell was filled by 0.001 m^3 0.4M sulphite solution with the catalyst. Oxygen saturated by water vapour at 20°C was brought over the liquid level and the rate of oxygen absorption through the flat interface was measured. In order to protect the gas phase against the fluctuations of the surrounding atmosphere a dics of a diameter equalling approximately that of the test cell, provided with an opening for withdrawing the samples, was mounted just above the liquid level. The sampling was carried out by a pipette purged by nitrogen and the content of sulphite was determined by iodine titration. The frequency of revolution of the impeller could be varied between zero and 2.7 s^{-1} ; higher frequencies caused disturbances of the liquid level. The duration of the experiment was chosen so as to decrease the sulphite concentration by approximately 0.025M. Only two consecutive experiments were always performed with a single charge of the test cell. The initial pH of the solution was about 8.5. In order to determine the order of the reaction with respect to oxygen, the mole fraction of oxygen in mixture with nitrogen was varied between 0.2 and 1.0. The amount of oxygen absorbed, Q , was evaluated from the loss of sulphite: $Q = 1/2A (\text{kmol Na}_2\text{SO}_3/\text{s})$.

Preparation of the solution. About 0.8M solution of sodium hydroxide was saturated by gaseous sulphur dioxide up to pH about 8.5. A large 250 l batch of the solution was prepared and the hydroxide used was all of the same production number. After neutralization the solution was mixed by nitrogen.

Analysis. The sulphite concentration was analyzed by adding a surplus of iodine solution and subsequent titration of excess iodine by sodium thiosulphate using starch⁴. The concentration of cobaltous sulphate was determined by polarography in 2.5M ammonia and 0.1M ammonium chloride solutions. Possible disturbing effect of oxygen was removed by adding a concentrated solution of sulphite. Standard solutions of cobaltous sulphate were calibrated by titration with 0.05M solution of ethylenediaminetetraacetic acid in urotropine using xylene orange. The polarographic analysis was very rapid and reliable; the error did not exceed $\pm 5\%$. In view of the low concentrations of the cobaltous salt (10^{-7} – 10^{-3} kmol/m^3) the error of determination is quite satisfactory. The equilibrium concentration of oxygen in the sulphite solution was determined on the assumption⁵ that it is equal to the equilibrium concentration of oxygen in corresponding sulphate solution. The analysis of the oxygen content was carried out by a method⁶ consisting in iodometric titration of iodine released by manganese(III) salt produced by oxidation of manganese(II) salt by the dissolved oxygen. A high-sensitivity and high-resistance pH meter equipped with a glass electrode was used to measure the acidity of the solution. A calomel electrode served as a reference electrode. The calibration was made by a borax buffer solution.

Physical properties of the system are summarized in Table I. *Measurement.* The kinetics of the oxidation was measured under the following conditions: $c(\text{CoSO}_4) = 5 \cdot 10^{-6}$ – 10^{-4} kmol/m^3 , $c(\text{Na}_2\text{SO}_4) = 0.3$ – 0.4 kmol/m^3 , $\text{pH} = 8.44$ – 8.54 , $y(\text{O}_2) = 0.2$ – 1.0 , $T = 293.15 \text{ K}$, $c(\text{Na}_2\text{SO}_3) = 0.20$ – 0.45 kmol/m^3 ; within this sulphite concentration range the reaction with respect to sulphite is reported^{3,7–10} to be of zero order. This finding was verified experimentally by measuring the rate of absorption in bubble columns. The results of the measurements are summarized in Tables II and III. The measurement of the rate of absorption in a bubble column with per-

forated distribution plate was carried out at three superficial velocities of gas and batchwise operation with respect to liquid. The column and plate characteristics are: $D = 152$ mm, $d = 1.6$ mm, $F_0 = 2.9\%$. The same solution and gas were used for the measurement as those in the test cell. All metal parts of the equipment were coated by baked silicon varnish; the gadgets used

TABLE I
Measured Physico-Chemical Properties of the Systems

$c(\text{Na}_2\text{SO}_3)$ kmol/m ³	t °C	$\mu \cdot 10^3$ kg/m s	$D(\text{O}_2) \cdot 10^{9a}$ m ² /s	$c^+(\text{O}_2) \cdot 10^4 b$ kmol/m ³
0.0	20.0	1.005	2.27	13.60
0.2	20.0	1.210	1.89	10.77
0.4	15.0	1.405	1.60	9.16
0.4	20.0	1.239	1.85	8.37
0.4	25.0	1.103	2.12	7.68
0.4	30.0	0.978	2.41	7.06
0.6	20.0	1.265	1.80	7.36

^a Computed from the Nernst-Einstein relation. ^b Valid for pressure $P(\text{O}_2) = 1.01 \cdot 10^3$ N/m².

TABLE II
Rate of Pure Oxygen Absorption in the Test Cell at 20°C

$c(\text{CoSO}_4) \cdot 10^5$ kmol/m ⁴	pH	Rate of absorption $Q \cdot 10^9$, kmol/s	k_1, s^{-1}	
			computed from Eq. (6)	experimental value Eq. (4)
0.5	8.44	7.17	61.3	66.57
0.5	8.44	7.18	61.3	66.8
1.0	8.44	9.98	122.6	129.24
1.0	8.44	9.12	122.6	107.72
5.0	8.4	21.71	613.1	610.8
5.0	8.4	22.79	613.1	673.1
10.0	8.4	29.25	1 226.1	1 108.8
10.0	8.4	28.33	1 226.1	1 040.1
1.0	8.54	11.33	163.5	166.4
1.0	8.54	10.60	163.5	145.7
5.0	8.54	24.97	817.7	807.9
5.0	8.54	24.13	817.7	754.5
10.0	8.54	35.07	1 635.4	1 594.4
10.0	8.54	35.24	1 635.4	1 609.6

were made of polyethylene. The bubble column was equipped by a cooling coil and the experiments showed no effect of the presence of such cooling device on the course of the porosity along the height in comparison with the experiments when no coil was present within column. It will be therefore assumed that the presence of the cooling coil does not change the structure of the heterogeneous mixture.

RESULTS AND DISCUSSION

The reaction order. From the slopes, $\alpha = (n + 1)/2$, of the curves in Fig. 1 it is apparent that the reaction in our system is of the first order with respect to oxygen for higher oxygen concentration in the gas phase (*i.e.* near the liquid level), or of the second order for low oxygen concentrations. The results further indicate that the transition between the two orders is rather sharp and occurs at the oxygen concentration equalling $c(\text{O}_2) = 3.75 \cdot 10^{-4} \text{ kmol/m}^3$. These results are in good agreement with those of Linek^{3,9,10}. This author though reports a somewhat higher oxygen concentration corresponding to the change of the reaction order. The transition to the first order in higher oxygen concentration range is in accord with the findings of other authors^{5,11,12} except those of Onda and coworkers¹³. The later authors

TABLE III
Rate of Oxygen Absorption in the Test Cell at 20°C and pH 8.54

Gas phase oxygen concentration, %	$c(\text{CoSO}_4) \cdot 10^5$ kmol/m^3	Rate of absorption $Q \cdot 10^9, \text{ kmol/s}$	Reaction order
83.3	5.0	22.35	1
83.3	5.0	21.271	1
62.5	5.0	16.241	1
62.5	5.0	16.111	1
33.3	5.0	7.41	2
33.3	5.0	7.29	2
20.0	5.0	3.66	2
20.0	5.0	3.39	2
83.3	10.0	29.851	1
83.3	10.0	29.57	1
71.4	10.0	26.20	1
71.4	10.0	26.14	1
58.8	10.0	21.79	1
58.8	10.0	20.50	1
40.0	10.0	13.39	2
40.0	10.0	14.27	2
20.0	10.0	5.13	2

report gradual transition between the two different reaction orders. The data of Reith¹⁴ showing the reaction to be of the second order with respect to oxygen may be explained by decreased solubility of oxygen in concentrated solution and by measurement at increased temperature. For the below described experimental technique of measuring the interfacial area it is further essential that starting from a certain limiting interfacial oxygen concentration the order of the reaction between oxygen and the sulphite solution prepared as described be of the first order; when using pure oxygen under atmospheric pressure this condition is always met.

The reaction rate constant. The dependence of the reaction rate constant on catalyst concentration and to some extent also on pH was examined experimentally (Fig. 2). Fig. 2 plots the reaction rate *versus* catalyst concentration in the form

$$R = k[c(\text{CoSO}_4)]^{1/2} \quad (2)$$

for the catalyst concentration $5 \cdot 10^{-6} - 1 \cdot 10^{-4} \text{ kmol/m}^3$. The experimental data on the rate of oxygen absorption as a function of pH were fitted by the following

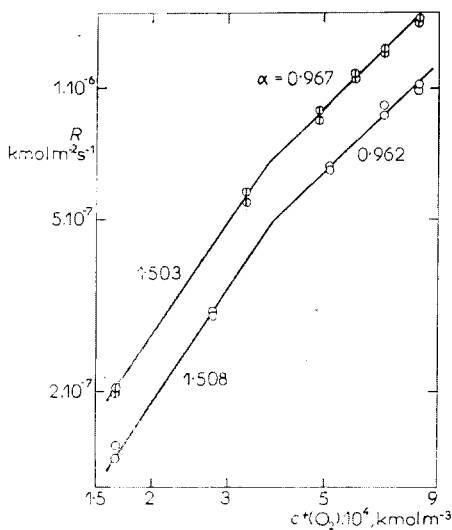


FIG. 1

Rate of Oxygen Absorption in the Test Cell as a Function of Concentration of the Dissolved Oxygen

- $c(\text{CoSO}_4) = 5 \cdot 10^{-5} \text{ (kmol/m}^3\text{)}$,
- $c(\text{CoSO}_4) = 1 \cdot 10^{-4}$.

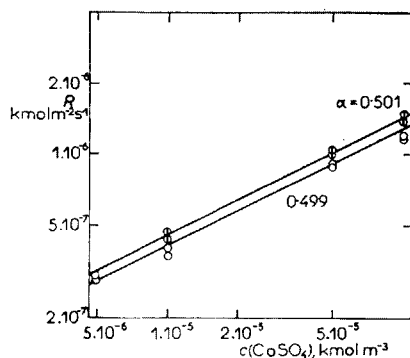


FIG. 2

Rate of Oxygen Absorption in the Test Cell as a Function of Catalyst Concentration

- pH 8.44, □ pH 8.54.

equation recommended by Linek^{3,7-10}

$$R = k[\text{pH} - 7.9 + 0.04(T - 273.15)]^b, \quad (3)$$

where b was put equal to unity. Substituting our experimental mean absorption rates for the pairs of pH equal 8.44 and 8.54 and catalyst concentrations $1 \cdot 10^{-5}$, $5 \cdot 10^{-5}$ and $10 \cdot 10^{-5}$ kmol/m³ into Eq. (3) the obtained values of the exponent amounted to 1.9, 1.36 and 2.76. In the following we took for b the average value of 2.0.

From the analysis of the dependence of R^2 on $c(\text{CoSO}_4)$ (the data taken from Table II) it follows that the rates of absorption may be described by the well-known formula for a second-order reaction

$$(Ra) = a(D(\text{O}_2) k_1)^{1/2} c^+(\text{O}_2). \quad (4)$$

This indicates that under the prevailing experimental conditions the effect of the liquid-side mass transfer coefficient, k_L , may be neglected.

From the experimentally found relations (Eqs (2), (3)) showing

$$R \sim (c(\text{CoSO}_4))^{1/2} [f(\text{pH})]^2, \quad (5)$$

and Eq. (5) it follows that for a given temperature one can find an expression enabling for instance the calculation of the reaction rate constant for an arbitrary pH and catalyst concentration from a known value of the reaction rate constant for selected standard conditions. This approach, spare for the value of the exponent over the function $f(\text{pH})$, is formally identical with that of Linek. Then where $f(\text{pH})$ is given

$$k_1 = k_1^0 [c(\text{CoSO}_4)/c^0(\text{CoSO}_4)] [f(\text{pH})/f(\text{pH})^0]^4 \quad (6)$$

by Eq. (3) and the values k_1^0 , $c^0(\text{CoSO}_4)$ and $f(\text{pH})^0$ are the standard values the choice of which is arbitrary within the range of applicability of the empirical correlations (2) and (3) (the validity of Eq. (3) is assumed within 7.8–9.1 pH ref.^{3,7-10}). For the selected standard values: $(\text{pH})^0 = 8.5$, $c^0(\text{CoSO}_4) = 5 \cdot 10^{-5}$ kmol/m³ the standard reaction rate constant, k_1^0 , amounts to 730.7 s⁻¹, which in turn served to evaluate the reaction rate constants for individual experimental conditions. The values of k_1 computed from Eq. (6) are compared with those evaluated from the rate of absorption data using Eq. (4). The comparison is shown in Table II.

The measurement of the interfacial area. In accord with the conclusions regarding the rate of absorption in the test cell one must find a region of catalyst concentration

where the rate of absorption is independent of the hydrodynamic conditions if the reaction is to be utilized for evaluation of the interfacial area. In such a region the reaction must be fast enough for one could assume $D(\text{O})_2 k_1 \gg k_1^2$ and the validity of

$$\log(Ra) = k + 1/2(\log c(\text{CoSO}_4)). \quad (7)$$

Fig. 3 is a log-log plot of the amount of oxygen absorbed *versus* catalyst concentration in a 152 mm bubble column. For the concentration of the catalyst exceeding $2.5 \cdot 10^{-5} \text{ kmol/m}^3$ up to 10^{-3} kmol/m^3 the evaluated slope equals 0.5. The condition of applicability of Eqs (1)–(6) for the calculation of the interfacial area are thus met within this concentration range. A detailed review of the experiments and results of interfacial area in bubble columns is given in the thesis of Nývlt².

CONCLUSIONS

The results of this study may be summarized as follows: Oxidation of aqueous sulphite solutions by oxygen catalyzed by cobaltous salts is suitable for determining the interfacial area in bubble columns. The investigations of the kinetics of this reaction in solutions prepared as described above essentially confirm the findings of Linek^{3,7-10}. For the use of the method for chemical engineering purposes it appears necessary to examine the reaction kinetics on a suitable test cell of known interfacial area on the system prepared by some standardized routine (the order of reaction with respect to sulphite and oxygen) as well as to determine the region of catalyst concentration where the effect of the hydrodynamic regime both in the test cell and

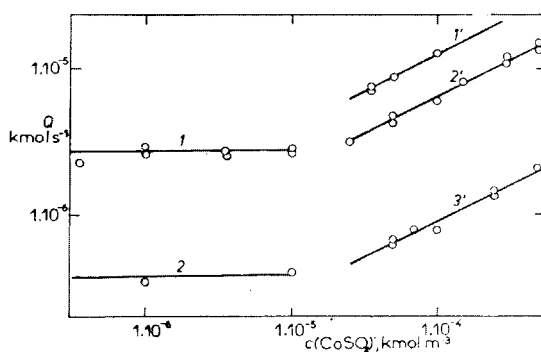


FIG. 3

Rate of Oxygen Absorption in a Bubble Column as a Function of Catalyst Concentration for $h = 0.6 \text{ m}$

1, 2' $v = 0.085 \text{ ms}^{-1}$, 2, 3' $v = 0.02 \text{ ms}^{-1}$, 1' $v = 0.18 \text{ ms}^{-1}$.

the reactor are comparable. In our case the lower bound of the concentration range was

$$c(\text{CoSO}_4) \geq 2.5 \cdot 10^{-5} \text{ kmol/m}^3.$$

The magnitude of the interfacial area in our case could be assessed from the equations (1), (3), (4), (6). However, the temperature in large-scale equipment is usually difficult to control and keep on the standard value ($t^0 = 20^\circ\text{C}$). Eq. (6) may then be multiplied by the correction factor on the changed temperature: $K_t = \exp [(-E/R) \cdot (1/T - 1/T_0)]$, $E = 1.4 \cdot 10^4 \text{ kcal/kmol}$, (the temperature range about 288.15 to 306.15°K)^{3,7-10}.

LIST OF SYMBOLS

a	specific interfacial area (m^{-1}) related to a unit volume of liquid
$c^+(i)$	equilibrium concentration of component i in liquid (kmol/m^3)
$c(i)$	concentration of component i (kmol/m^3)
d	diameter of opening in distributing plate
$D(i)$	diffusion coefficient of component i in liquid (m^2/s)
D	column diameter (m)
E	activation energy
$f(\text{pH})$	function in Eq. (3)
F_0	plate free area (%)
h	clear liquid height on plate (m)
k, k', k''	constants
k_1	reaction rate constant (s^{-1})
k_L	liquid-side mass transfer coefficient (m/s)
n	reaction order
Q	rate of oxygen absorption (kmol/s)
R	mean rate of absorption (kmol/s m^2)
Ra	mean rate of absorption related to a unit volume of liquid (kmol/s m^3)
R	gas constant
t	duration of experiment (s)
T	Kelvin temperature (K)
T_0	standard temperature
v	superficial velocity of gas in column (m/s)
$y(i)$	mole fraction of component i
α	slope
μ	viscosity

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