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Oxidation of Sulphur Dioxide in Aqueous Solutions

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The sulphur dioxide oxidation reactions in aqueous solutions under mild conditions are examined. The kinetics of the oxidation of SO_2 to H_2SO_4 by various oxidants are described, the reaction mechanism is discussed, and its possible practical applications are indicated.
The bibliography includes 96 references.

CONTENTS

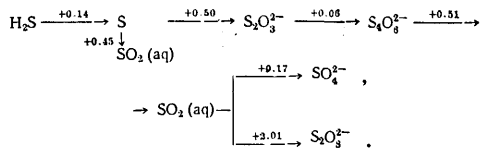
I. Introduction 1029
II. Catalytic and non-catalytic reactions involving the oxidation of SO_2 by various compounds 1030
III. Catalytic reactions involving the oxidation of SO_2 by molecular oxygen 1035
IV. Conclusion 1037

I. INTRODUCTION

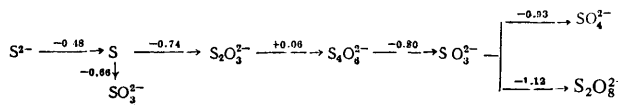
The SO_2 oxidation reactions under mild conditions are of interest from the theoretical point of view for the study of the detailed mechanism of the inner-sphere transformations of the substrate molecules. The study of such processes is important also from the practical point of view because they can be used to develop methods for the elimination of the highly toxic component (sulphur dioxide) from the waste gases generated in metallurgical and other industries. (The discharged sulphur dioxide is known to cause considerable damage in nature, to spoil buildings and equipment, and to cause their breakdown.) Although the SO_2 concentration in waste gases is usually low, its overall release throughout the world can be measured in hundreds of millions of tonnes. Therefore, together with the solution of the ecological problems, the utilisation of waste gases makes it also possible to obtain large amounts of sulphuric acid. The use of liquid-phase catalysts is desirable precisely in the oxidation of gas mixtures with a low SO_2 content where heterogeneous catalysts are ineffective.

Three types of reactions are characteristic of sulphur dioxide: reactions occurring without change (a), with decrease (b), and with increase (c) in the valence of sulphur. The oxidation state of sulphur in compounds varies from -2 to +6. In the schemes below, the oxidation-reduction potentials of the corresponding transitions between different sulphur compounds are indicated above the arrows (in V):[1]

(1) Acid solutions:



(2) Alkaline solutions:



The dissolution of SO_2 in water with formation of hydrates and sulphurous acid may serve as an example of reactions in which there is no change in the valence of sulphur:

$$H_2O + SO_2 \rightleftharpoons H_2SO_3 \overset{K_1}{\rightleftharpoons} H^+ + HSO_3^- \overset{K_2}{\rightleftharpoons} 2H^+ + SO_3^{2-}, \quad (1)$$

where $pK_1 = 1.92$ and $pK_2 = 7.2$.[1] The interaction of sulphur dioxide with bases and the salts of weak acids leads to salts of sulphurous acid.[2]

There is no direct proportionality between the total absorption of SO_2 and its partial pressure (above 1 atm), i.e. Henry's law is not applicable to the dissolution of SO_2 in water.[2] On the other hand, it has been established that the dependence of the solubility of SO_2 in water on pressure (up to 1 atm) is close to linearity. The solubility of SO_2 in sulphuric acid at pressures up to 1 atm obeys Henry's law. With increase in the H_2SO_4 concentration from 0 to 85%, the solubility of SO_2 gradually falls, while in more concentrated acid solutions it increases.[3]

The dissolution of SO_2 in water and sulphuric acid is widely used in chemical industry. The dependence of the solubility of sulphur dioxide on its partial pressure and also on temperature and acidity has been studied in detail,[3] which is important for the solution of practical problems in the manufacture of sulphuric acid. According to equilibrium (1), the solubility of SO_2 in water can be increased by lowering the H^+ concentration or by removing sulphite ions by oxidising them to sulphate ions. However, in the latter case the concentration of H^+ ions increases somewhat, since the H_2SO_4 formed is more ionised than sulphurous acid: this partly weakens the influence of the decrease in the sulphite concentration on the solubility of SO_2.[4]

The physicochemical principles of the sulphur dioxide extraction and concentration processes have been examined in greatest detail by Rozenknop,[2] who quotes the solubilities of SO_2 in water, in solutions of strong acids and bases as well as salts, and in heterogeneous systems and provides equations from which it is possible to calculate the temperature dependence of the vapour pressures of sulphur dioxide solutions.

The heats of the reactions occurring during the absorption of SO_2 have the following values:[2]

$$SO_2 + H_2O \rightleftharpoons H_2SO_3 + 26 \text{ kJ},$$
$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^- + 16 \text{ kJ}.$$

If the absorber is a base, then

$$H^+ + OH^- \rightleftharpoons H_2O + 56 \text{ kJ}.$$

If the absorber is the salt of a weak acid, then the heat of absorption of SO_2 is equal to the heat of ionisation of this acid.

The most suitable absorbers for sulphur dioxide are the following buffer solutions at fairly high pH:[5] (1) solutions of salts of a weak acid and a strong base (for example, sodium sulphite and bisulphite); (2) solutions of salts of a strong acid and a weak base (for example, basic aluminium sulphite); (3) solutions of salts of a weak acid and a weak base (for example, ammonium sulphite and bisulphite); (4) solutions of salts of weak acids in the presence of the free acid (sulphites and bisulphites in the presence of organic acids). Water is used to absorb SO_2 from gases when its concentration is $\geqslant 7$ vol.%; for more dilute gases, this method is uneconomical because of the large consumption of water and the expenditure of heat on desorption.[5]

The kinetics of the absorption of sulphur dioxide by solutions of ammonia and ammonium sulphite-bisulphite have been investigated[6] at 298 K and it has been established that, when SO_2 is absorbed by NH_3 solutions, the following rapid two-stage reaction takes place:

$$SO_2 + 2NH_3 \xrightarrow{H_2O} (NH_4)_2 SO_3,$$

while in solutions of ammonium sulphite an irreversible interaction of SO_2 with SO_3^{2-} ions occurs. The study of the kinetics of the absorption of sulphur dioxide by NH_4OH, NaOH, KOH, Na_2CO_3, and Na_2SO_3 solutions showed[7] that, with decrease in their concentration, the rate of absorption of SO_2 increases for all the absorbers except sodium sulphite. In this case the chemisorption process is limited by the diffusion of SO_2 in the liquid phase and the viscosity of these solutions increases linearly with their concentration. The order of the reaction with respect to SO_2 is close to zero.

The absorbers can be arranged in the following sequence in terms of decreasing SO_2 absorption rate constants (at 293 K):

$$NH_4OH\ (8.99) > KOH\ (5.126) > NaOH\ (5.078) > Na_2CO_3\ (4.931) > > Na_2SO_3\ (4.217\ m^3\ kmol^{-1}\ h^{-1}).$$

The equation for the rate of reaction for different compounds can be written in the general form

$$w = Ae^{-B\tau},$$

where τ is the time in min and A and B are constants which depend on the nature of the absorber and have the following values: 5.8521 and 0.0469 for Na_2SO_3; 6.314 and 0.0254 for Na_2CO_3; 6.6205 and 0.0173 for KOH; 7.3205 and 0.0151 for NaOH; 9.9144 and 0.0048 for NH_4OH.

Few chemical processes are accompanied by a decrease in the valence of sulphur. The reactions of SO_2 with hydrogen sulphide and carbon monoxide may serve as examples:[2]

$$SO_2 + 2H_2S \rightarrow 2H_2O + 3S,$$
$$SO_2 + CO \rightarrow 2CO_2 + S.$$

Reactions occurring with increase in the valence of sulphur are most characteristic of sulphur dioxide. Thus sulphur dioxide combines with chlorine even in sunlight. The interaction of SO_2 with oxygen proceeds as a rule at a high temperature and in the presence of catalysts:[2]

$$2SO_2 + O_2 \xrightarrow{\text{catalyst}} 2SO_3.$$

In an aqueous medium, the oxidation of sulphur dioxide by compounds (ions) with a high oxidation-reduction potential is fairly rapid. In most cases, the process then proceeds with formation of sulphuric acid via a mechanism which we believe to involve the oxidative sulphonation of water[8] and subsequent regeneration of the reduced species Red by molecular oxygen:

$$\begin{array}{l} SO_2 + 2H_2O + Ox \rightarrow H_2SO_4 + Red + 2H^+, \\ Red + O_2 + 4H^+ \rightarrow Ox + 2H_2O, \\ \hline SO_2 + O_2 + 2H^+ \rightarrow H_2SO_4\ . \end{array}$$

The oxidation of SO_2 in aqueous solutions to sulphuric acid is very important for the extraction of sulphur dioxide from gases, but it has still been inadequately investigated.[9]

Numerous studies have been devoted to the high-temperature heterogeneous processes involving the oxidation of SO_2 to SO_3—the main method of synthesis of sulphuric acid.[10–15] On the other hand, the oxidation of SO_2 under mild conditions has been described in the literature to a much lesser extent, although it is attractive from the standpoint of economising on energy resources and leads to new possibilities for the investigation of the mechanism of catalysis by complex compounds and solutions.

II. CATALYTIC AND NON-CATALYTIC REACTIONS INVOLVING THE OXIDATION OF SO_2 BY VARIOUS COMPOUNDS

In aqueous media, the oxidation of sulphur dioxide by complex metal anions and molecular oxygen under the influence of homogeneous catalysts is fairly rapid with the formation of H_2SO_4. Table 1 indicates the metal ions (M^{n+}) which oxidise SO_2 to H_2SO_4 in aqueous solutions and also the energetic and kinetic characteristics of oxidation-reduction reactions of the type:

$$2M^n + SO_2 + 2H_2O \rightarrow 2M^{n-1} + H_2SO_4 + 2H^+.$$

Table 1. Kinetic and energetic characteristics of the processes leading to the oxidation of SO_2 to H_2SO_4 in aqueous solutions.

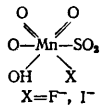
Ion	Active form of complex ion	T, K	Rate constant	E_a, kJ mol^{-1}	ΔS^*, J mol^{-1} K^{-1}	Refs.
Mn^{7+}	$MnO_3(OH)I^-$ (aq)	293	1.15×10^6 litre mol^{-1} min^{-1}	7.2	—178	[16]
Mn^{7+}	$MnO_3(OH)F^-$ (aq)	293	75.7×10^3 litre mol^{-1} min^{-1}	38.0	—92	[16]
Cr^{6+}	$CrO_3(OH)^-$ (aq)	298	18.0×10^4 litre mol^{-1} min^{-1}	---	—	[17, 18]
Cr^{6+}	$CrO_3(OH)I^{2-}$ (aq)	298—318	2.0×10^5 litre mol^{-1} min^{-1}	5.6	—	[17, 18]
Se^{4+}	$SeO_m(OH)_n I^{3-2m-n}$(aq)	293—323	7.2×10^4 litre^2 mol^{-1} min^{-1}	13.4	—	[18]
Hg^{2+}	HgX_n^{2-n}(Ac$^-$, NO_3^-)	303	0.5×10^2 litre^2 mol^{-2} min^{-1}	—	—	[19]
Fe^{3+}	$Fe(CN)_6^{3-}$ (aq)	298	0.52 litre^2 mol^{-2} min^{-1}	—	—	[20]
Cu^{2+}	$CuCl_2I^-$ (aq)	293—343	3.9×10^2 litre^2 mol^{-2} min^{-1}	32.6	—104.6	[21]
Cu^{2+}–Fe^{3+}	$CuFeCl_nI^{4-n}$ (aq)	293—353	3.6×10^3 litre^2 mol^{-2} min^{-1}	30.0	147.6	[22, 23]

Notation. T is the temperature, E_a the activation energy, and ΔS^* the activation entropy.

The oxidation of sulphur dioxide by manganese(VII), chromium(VI), and selenium(IV) compounds and $S_2O_8^{2-}$ has been studied in detail.[16–18,24,25] Thus potassium permanganate is readily reduced by sulphur dioxide in the presence of the F^-, I^-, or OH^- ions in accordance with the stoichiometric equation[16]

$$2MnO_4^- + 5SO_2 + 2H_2O \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+.$$

The reaction is of first order with respect to the oxidant, the reductant, and H^+ ions. It is believed that the rate-limiting stage of the process is inner-sphere redox decomposition of the intermediate complex incorporating all the reaction components:



Depending on the nature of the ligand-catalyst (OH^-, F^-, I^-), which effects electron transfer between the oxidant and the reductant, the rate of the process varies significantly: the activity of the ligands increases in the sequence $F^- < OH^- < I^-$. It is believed that the high activity of the I^- ion is due to the fact that it is a stronger nucleophile than the F^- and OH^- ions.[16]

Sulphur dioxide is oxidised by chromium(VI) in accordance with the equation

$$2CrO_4^{2-} + 3SO_2 + 4H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 2H_2O.$$

In the range of $HClO_4$ concentrations up to 10 M, the reaction is of first order with respect to Cr^{3+}, SO_2, and H_3O^+.[17,18] The proposed reaction mechanism includes the formation of the protonated form of chromium(VI) with subsequent addition to the latter of a SO_2 molecule. The stage in which the chromium(VI) complex of sulphur dioxide $CrO_3(OH)SO_2^-$(aq.) decomposes is rate-limiting:

$$\begin{gathered} SO_2 \overset{H_2O}{\rightleftharpoons} SO_2\,(aq), \\ CrO_4^{2-} + H_3O^+ \rightleftharpoons CrO_3\,(OH)^-\,(aq) + H_2O, \\ CrO_3\,(OH)^-\,(aq) + SO_2 \rightleftharpoons CrO_3\,(OH)\,SO_2^-\,(aq) + H_2O, \\ CrO_3\,(OH)\,SO_2^-\,(aq) \rightarrow CrO_3^- + HSO_3, \\ 2HSO_3 \rightarrow H_2SO_4 + SO_2. \end{gathered}$$

The rate of reaction is described by the equation

$$w = k \cdot [CrO_3\,(OH)\,SO_2^-\,(aq)].$$

The oxidation of sulphur dioxide by selenous acid[18]

$$H_2SeO_3 + 2SO_2 + H_2O \rightarrow Se + 2H_2SO_4$$

is greatly accelerated in the presence of proton-ligand catalysts. In the $H_2SeO_3 - HClO_4 - KI - H_2O$ system, the reaction is of first order with respect to Se^{4+}, SO_2, and KI; the order with respect to hydrogen ions is close to two. According to the reaction mechanism proposed,[18] hydrogen ions protonate the oxygen atoms in the SeO_3^{2-} anion after which the protonated forms form complexes with the dissolved sulphur dioxide and I^- ions:

$$\begin{gathered} SeO_3^{2-}\,(aq) + j\,H_3O^+ \rightleftharpoons SeO_m\,(OH)_n^{4-2m-n}\,(aq) + j\,H_2O, \\ SeO_m\,(OH)_n^{4-2m-n}\,(aq) + I^- \rightleftharpoons SeO_m\,I^{3-2m-n}\,(OH)_n\,(aq), \\ SeO_m I\,(OH)_n^{3-2m-n}\,(aq) + SO_2\,(aq) \rightleftharpoons SeO_m\,(OH)_n\,I\,(SO_2)^{3-2m-n}\,(aq). \end{gathered}$$

The redox reaction of the complexes $SeO_m(OH)_nISO_2^{3-2m-n}$(aq.) in stage (2) limits the rate of the process. The subsequent reduction of selenium(III) is rapid and is not reflected in the reaction kinetics:

$$\begin{gathered} SeO_m\,(OH)_n\,I\,(SO_2)^{3-2m-n}\,(aq) \rightarrow SeO_m\,(OH)_n\,(I^0)\,SO_2^{3-2m-n}\,(aq), \\ SeO_m\,(OH)_n\,(I^0)\,SO_2^{3-2m-n}\,(aq) \rightarrow Se^{3+} + I^- + HSO_3, \\ Se^{3+} + HSO_3 \rightarrow H_2SO_4 + Se^0. \end{gathered} \qquad (2)$$

The rate of reaction depends on the relative contents of the protonated forms Se(IV) – SeO^{2+}(aq.) and $SeOH^{3+}$(aq.) (κ_1 and κ_2 respectively) which exhibit the highest activity in the oxidation of sulphur dioxide:

$$w = (k_1\kappa_1 + k_2\kappa_2)\,[I^-]\,[SO_2],$$

where k_1 and k_2 are the partial rate constants.

It has been observed that sulphur dioxide is rapidly oxidised by mercury(II) to sulphuric acid in the presence of $HClO_4$ (at a concentration of 2 – 8 M) with formation of metallic mercury.[19] The reaction orders with respect to Hg^{2+} and SO_2 are close to unity. According to Golodov and Panov,[19] the process includes the following stages:

$$\begin{gathered} HgX_n^{2-n}\,(aq) + SO_2\,(aq) \rightleftharpoons HgX_nSO_3^{2-n}\,(aq) + H_2O, \\ HgX_nSO_3^{2-n}\,(aq) \xrightarrow{2H_2O} Hg^0 + SO_4^{2-} + 4H^+ + n\,X, \\ X^- = Ac^-,\ NO_3^-. \end{gathered}$$

The oxidation of SO_2 by hydrogen peroxide in aqueous solution (ionic strength 1.0; pH 4 – 8) is of interest.[26,27] For example, it has been established that the reaction orders with respect to SO_2 and H_2O_2 are unity and that with respect to hydrogen ions varies from 1 in the pH range 4.5 – 6.5 to 2 in the pH range 6.5 – 8.0. The reaction is accelerated in the presence of proton donors (HA) in conformity with the mechanism of general acid catalysis. It is believed that the process mechanism includes the following stages:

$$\begin{gathered} HSO_3^- \overset{K}{\rightleftharpoons} SO_3^{2-} + H^+, \\ HSO_3^- + H_2O_2 \rightleftharpoons H_2O + HOOSOO^-, \\ HOOSOO^- + HA \rightarrow H_2SO_4 + A^- \end{gathered}$$

($HOOSOO^-$ is the monopersulphurous acid anion).

The rate of reaction is described by the equation

$$w = [H_2O_2]\,[SO_2]\,\{[H^+]/([H^+] + K)\}\,(k_1[H^+] + k_2[HA]),$$

where k_1 = 58 and k_2 = 720 litre^2 mol^{-2} s^{-1} at T = 285 K. The activation energy of the process is 37 ± 2 kJ mol^{-1} and the activation entropy is ~4 J mol^{-1} K^{-1}.

The oxidation of sulphur dioxide by sodium persulphate in the absence of catalysts,

$$Na_2S_2O_8 + SO_2 + 2H_2O \rightarrow Na_2SO_4 + 2H_2SO_4,$$

proceeds at low rates.[24,25] The reaction takes place vigorously when acted upon jointly by protic and ligand catalysts. It is believed that sulphur dioxide reacts in the form of HSO_3^- anions in the $Na_2S_2O_8 - HClO_4 - KI - SO_2 - H_2O$ and $Na_2S_2O_8 - HClO_4 - LiBr - SO_2 - H_2O$ systems, because it is known that the addition of the OH^- anion to SO_2 intensifies the reducing properties of the latter as a result of the increase in electron density in the donor orbital of the S atom.[28]

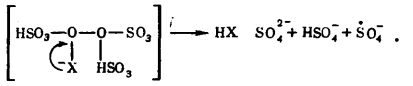
It has been suggested[28] that HSO_3^- anions are oxidised in the following way. The protonated form of the persulphate anion interacts initially with the halide ion X^-, i.e.

$$S_2O_7OH^-\,(aq) + X^- \rightleftharpoons [S_2O_7\,(OH)\,X]^{2-}\,(aq),$$

and the complex $[S_2O_7(OH)X]^{2-}$(aq.) then reacts with HSO_3^-:

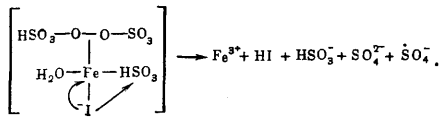
$$[S_2O_7\,(OH)\,X]^{2-}\,(aq) + HSO_3^- \rightleftharpoons [S_2O_7\,(OH)\,XHSO_3]^{3-}\,(aq).$$

In the rate-limiting stage, the active complex undergoes a redox reaction via the following mechanism:



It is believed[28] that the ligand (halide ion) gives up its electron to the peroxide linkage in the persulphate ion and then in the form X^0 oxidises HSO_3^-, being itself reconverted into X^-. Such electron redistribution takes place within the limits of the inner sphere of the complex.

The rate-limiting stage in the oxidation of HSO_3^- anions by persulphate anions in the presence of iron(III) is the reaction[25]



The iodide ion gives up its electron to the central atom of the complex, attacks the coordinated donor in the inner sphere, and is reduced to I. In its turn, Fe^{3+} transfers an electron to the peroxide linkage of the persulphate ion, as a result of which the latter is ruptured with subsequent decomposition of the complex. The reaction mechanism in the presence of iron(III) ions differs from that examined above in the fact that the metal in the complex facilitates the electron transfer from the iodide ion to the persulphate ion.

The oxidation of sulphite anions by the individual Fe^{3+} hexacyanoferrate(III) complex has also been investigated at 298 K.[20] The authors believe that the process proceeds as follows:

$$SO_3^{2-} + Fe(CN)_6^{3-} \rightleftharpoons Fe(CN)_6^{4-} + \dot{S}O_3^-,$$
$$Fe(CN)_6^{3-} + \dot{S}O_3^- \rightarrow Fe(CN)_5(CN\dot{S}O_3)^{4-},$$
$$Fe(CN)_5(CN\dot{S}O_3)^{4-} + H_2O \rightarrow Fe(CN)_6^{4-} + SO_4^{2-} + 2H^+.$$

The rate of reaction is described by the equation

$$\omega = k_M[M][SO_3^{2-}][Fe(CN)_6^{3-}],$$

where M is the Na^+ or K^+ ion, $k_{Na^+} = 0.52 \pm 0.02$ litre^2 mol^{-2} s^{-1}, and $k_{K^+} = 1.15 \pm 0.04$ litre^2 mol^{-2} s^{-1}. The oxidation of sulphite anions by hexacyanoferrate is weakly inhibited by molecular oxygen.

The liquid-phase oxidation of SO_2 by iron salts has been studied in acid solutions.[29] The increase in the $HClO_4$ concentration from 0.1 to 2.5 M leads to the formation in solution of the $SO_2.H_2O$ species, whose reactivity is low, as a result of which the rate of the process falls. The reaction orders with respect to SO_2 and Fe^{3+} are close to unity. The reaction mechanism presupposes the formation of the thionate radical HSO_3, which reacts with Fe^{3+} to form sulphate anions.

It has been observed[30] that Co^{3+} salts are more effective catalysts of the oxidation of sulphite ions than Fe^{3+} and Fe^{2+} salts. In the presence of cobalt nitrate, the concentration of sulphite ions at room temperature decreases by a factor of 7 in 3 h. A similar catalytic solution may be used to purify gases with a low SO_2 content.

The oxidation of sulphur dioxide by copper halides in the $CuCl_2-HCl-KI-H_2O$, $CuBr_2-HBr-KI-H_2O$, and $CuBr_2-LiBr-H_2O$ systems has been studied in greatest detail.[18,21,31] It takes place in accordance with the equation

$$2CuX_2 + SO_2 + 2H_2O \rightarrow 2CuX + H_2SO_4 + 2HX. \quad (3)$$

The reaction orders with respect to copper(II) and SO_2 were shown to be close to unity. Univalent copper increases the initial rate of the process by activating HSO_3^- anions (Figs.1 and 2).

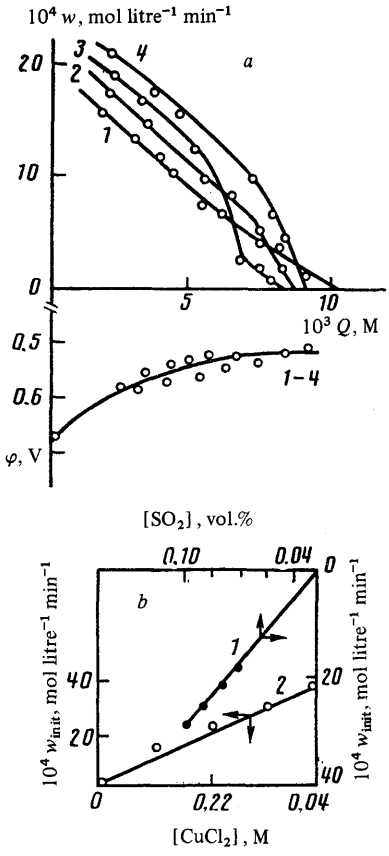


Figure 1. Oxidation of SO_2 by copper(II) chloride at 293 K, [HCl] = 4.8 M, and [KI] = 8×10^{-4} M: (a) dependence of the rate of oxidation w and of the potential of the system φ (calculated with respect to the hydrogen electrode potential) on the amount of SO_2 which has reacted for $[CuCl_2] = 0.02$ M and different initial SO_2 concentrations (vol.%) [(1) 0.062; (2) 0.076; (3) 0.086; (4) 0.103]; (b) dependence of the initial rate of oxidation on $[SO_2]$ (line 1) for $[CuCl_2] = 0.02$ M and on $[CuCl_2]$ (line 2) for $[SO_2] = 0.086$ vol.%.[18]

The reduction of Cu^{2+} to Cu^+ takes place in the inner-sphere redox decomposition of Cu^{2+} complexes with HSO_3^- anions via two parallel pathways:

(a) first pathway (X^- = halide ion):

$$CuX_mHSO_3^{1-m}(aq) \rightarrow HSO_3 + CuX_n^{1-n}(aq),$$
$$CuX_m^{2-m}(aq) + HSO_3 + H_2O \rightarrow H_2SO_4 + CuX_n^{1-n}(aq) + H^+;$$

(b) second pathway [associated with the activation of HSO_3^- anions by copper(I)]:

$$Cu_2X_{(n+m)}HSO_3^{2-m-n}(aq) \rightarrow 2CuX_n^{1-n}(aq) + HSO_3.$$

In the reduction of copper(II) by sulphur dioxide in the presence of iodide ions, there is a possibility of electron transfer to the central atom and the formation in the inner sphere of the ligand I^0, which oxidises the HSO_3^- anion to HSO_3:

(a) first pathway:

$$CuX_mI(HSO_3)^{m-}(aq) \rightleftharpoons CuX_m(I^0)(HSO_3)^{m-}(aq),$$
$$CuX_m(I^0)(HSO_3)^{m-}(aq) \rightarrow HSO_3 + CuX_n^{1-n}(aq) + I^-;$$

(b) second pathway [associated with the activation of HSO_3^- anions by copper(I)]:

$$Cu_2X_{(m+n)}I(HSO_3)^{1-m-n}(aq) \rightleftharpoons Cu_2X_{(m+n)}(I^0)(HSO_3)^{1-m-n}(aq),$$
$$Cu_2X_{(m+n)}(I^0)(HSO_3)^{1-m-n}(aq) \rightarrow HSO_3 + 2CuX_n^{1-n}(aq) + I^-.$$

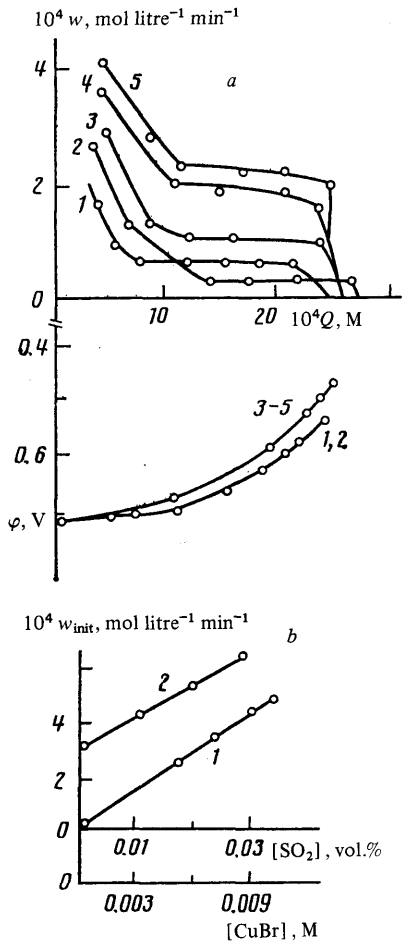


Figure 2. Oxidation of SO_2 by copper(II) bromide at 293 K, [HBr] = 6.0 M, and [KI] = 0.5 × 10^{-3} M: (a) dependence of the rate of oxidation w and of the potential of the system φ on the amount of SO_2 which has reacted for [$CuBr_2$] = 0.005 M and different initial SO_2 concentrations (vol.%) [(1) 0.017; (2) 0.023; (3) 0.028; (4) 0.032; (5) 0.035]; (b) dependence of the initial rate of oxidation on [SO_2] (line 1) for [$CuBr_2$] = 0.005 M and on [CuBr] (line 2) for [$CuBr_2$] = 0.003 M and [SO_2] = 0.028 vol.%.[18]

This scheme explains the catalytic action of the I^- ion (first order with respect to I^-), which served as a "mediator" in the electron transfer from SO_2 to Cu^{2+}. Bearing in mind that the reduction of copper(II) by sulphur dioxide in the $CuBr_2-LiBr-H_2O$ system in the presence of bromide ions alone, takes place at high concentrations of the latter, [Br^-] = 2–8 M and [Cu^{2+}] ≪ [Br^-], we suggest that homoligand copper(II) bromide complexes are the catalysts in this process. The activity of the chloride complexes in the SO_2 oxidation reactions has been observed only at a high sulphur dioxide concentration (100 vol.%).[32]

The rate of reduction of Cu^{2+} depends on the nature of the catalyst. The rate equation is[21]

$$w = (k_1 + k_2[Cu^+])[Cu^{2+}][SO_2],$$

where k_1 and k_2 are the rate constants for the first and second pathways respectively. Since the dependence of the rate of reduction of copper(II) by sulphur dioxide on the current copper(I) concentration is described by descending curves (Fig.1) of a non-autocatalytic character (the decrease in the rate of reaction as a result of the loss of Cu^{2+} is not compensated by its catalytic acceleration by the Cu^+ formed), one may conclude that the first pathway, unrelated to the activation of HSO_3^- anions by copper(I), makes the greatest contribution to the overall rate of the process. However, as a result of the existence of the second pathway, the kinetic curves do not obey a first-order equation with respect to CuX_2, while in the reduction of copper(II) bromide-iodide complexes, a "zero order" is observed over a large extent of the kinetic curves (Fig.2).[31]

Table 2. The activities of copper(II) halide complexes in the SO_2 oxidation reaction.[18,21,31]

Complex; system	k_1, litre mol^{-1} min^{-1}	k_2, litre^2 mol^{-2} min^{-1}	E_1, kJ mol^{-1}	E_2, kJ mol^{-1}	ΔS_1^*, J mol^{-1} K^{-1}	ΔS_2^*, J mol^{-1} K^{-1}
$CuBr_2I^-$ (aq); $CuBr_2$—HBr—KI—H_2O	$5.2\cdot10^2$	$7.7\cdot10^5$	28.8	46.0	—101	0.4
$CuCl_2I^-$ (aq); $CuCl_2$—HCl—KI—H_2O	$3.9\cdot10^2$	$1.7\cdot10^4$	32.6	24.7	—105	—90
$CuBr_3^-$ (aq)	$0.5\cdot10^{-2}$	4.5	44.0	40.0	—52	—5
$CuBr_2$ (aq); $CuBr_2$—LiBr—H_2O	$0.1\cdot10^{-2}$	0.5	—	—	—	—

Notation. k_1 and k_2 are the partial rate constants for the reaction, E_1 and E_2 are the apparent activation energies, and ΔS_1^* and ΔS_2^* are the activation entropies for the first and second pathways respectively.

Calculations and experimental results have shown that complexes with a definite composition of the inner sphere exhibit the highest activity in the reduction of copper(II) by sulphur dioxide. It follows from Table 2 that copper(II) halide complexes can be arranged in the following sequence in terms of their activities:

$$CuBr_2I^-(aq) > CuCl_2I^-(aq) > CuBr_3^-(aq) > CuBr_2(aq).$$

The activation energy for the first stage, which makes the greatest contribution to the overall rate of the process, increases on passing from the bromide-iodide complexes to the chloride complexes and further to the bromide complexes, which is consistent with the reaction rate constants.

The highest activation entropy ($\Delta S_2^{\neq} = 0.4$ J mol^{-1} K^{-1}) has been observed for the most active complex $CuBr_2I^-$(aq.) in the $CuBr_2-HBr-KI-H_2O$ system, indicating a high probability of the optimum orientation of the species at the instant of collision.

An appreciable catalytic acceleration of the oxidation of SO_2 by Cl^- and Br^- anions has been observed in a study[33] where the effect of certain anions and cations (Na^+, K^+, NH_4^+, Ca^{2+}, SO_4^{2-}, HCO_3^-, NO_3^-, F^-, Cl^-, Br^-) on the rate of oxidation of sodium sulphite was investigated. A significant cationic effect was not observed and Cl^- and Br^- ions showed an activity at concentrations above 1×10^{-3} M. The insignificant influence of the nature of the cation (Na^+, K^+, NH_4^+) on the oxidation of sulphite anions has also been noted in another study.[34]

It has been observed that the addition of iron chloride to the $CuCl_2-HCl-KI-H_2O$ system significantly increases the rate of oxidation of sulphur dioxide.[22,23] Kinetic and spectroscopic data have led to the conclusion that in the presence of chloride and iodide ions copper(II) and iron(III) form the heteronuclear complexes $CuFeCl_mI^{4-m}$(aq.), which are more active in the reaction with sulphur dioxide than the individual copper and iron complexes. The calculated stability constant of the heteronuclear complex is $\alpha = [Cu^{2+}-Fe^{3+}]/[Cu^{2+}][Fe^{3+}] = 10$.

The reduction of heteronuclear copper(II) and iron(III) complexes by sulphur dioxide also proceeds via two pathways. The reaction by the first pathway, which makes a greater contribution to the overall rate of the process, involves the inner-sphere oxidation-reduction decomposition of these complexes with the HSO_3^- anion in accordance with the equation[22,23]

$$CuFeCl_mIHSO_3^{3-m}(aq) + H_2O \rightarrow CuFeCl_n^{1-n}(aq) + H_2SO_4 + I^- + H^+. \quad (4)$$

The reaction via the second pathway is accelerated as a result of the activation of HSO_3^- anions by copper(I).

The kinetic equation describing the reduction of heteronuclear complexes is

$$w = [Cu^{2+}][Fe^{3+}]^{0.5}[SO_2](k_1 + k_2[Cu^+]),$$

where k_1 and k_2 are the rate constants for the first and second pathways respectively.

An attempt has been made to establish the composition of the heteronuclear complexes corresponding to the formula $CuFeCl_nI^{4-n}$ by the method of isomolar series [continuous variations (Editor of Translation)] (Fig.3).[22,23] The fact that the rate of reaction is a maximum for the ratio $[CuCl_2]:[FeCl_3] = 1:1$ suggested that one Cu^{2+} ion is bound to one Fe^{3+} ion in the active complex.

The existence of heteronuclear complexes in the $CuCl_2-FeCl_3-HCl-KI-H_2O$ system has been confirmed by calorimetric molar ratios and relative yield methods.[23] The formation of heteronuclear complexes is also indicated by the decrease in the intensity of the EPR signal of the $CuCl_2-HCl-KI-H_2O$ solution after the addition of $FeCl_3$ to the latter, demonstrating a decrease in the concentration of the $CuCl_2$ salt as a result of the formation of a heteronuclear complex which does not generate an EPR signal.[23]

In reaction (4), two individual complexes (copper and iron halides) exhibit a synergistic effect. A similar effect has also been observed in the oxidation of sulphur dioxide in aqueous solution by mixtures of manganese and iron salts. The most pronounced effect has been attained in a solution containing 1×10^{-4} M manganese acetate and 1×10^{-6} M iron chloride.[35]

The reason for the acceleration of the S(IV)–S(VI) oxidation is apparently the replacement of the two-stage electronic oxidation of SO_2 by the individual complexes under these conditions by a two-electron single-stage reaction, i.e. the redox process becomes synchronous.

Analysis of the experimental and literature data[18,21-25,31] leads to the conclusion that the reduction of metal complexes by sulphur dioxide proceeds via the formation of an intermediate–the metal complex with the hydrogen sulphite anion, in which the inner-sphere electron transfer from S^{4+} to M^{n+} takes place. It has been established that the components of systems incorporating metal complexes, sulphur dioxide, water, and ligands react in stoichiometric proportions, which rules out a chain mechanism of the reaction.[18,21-25,31]

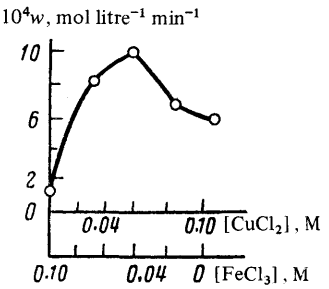


Figure 3. Dependence of the initial rate of reaction on the ratio $[CuCl_2]$: $[FeCl_3]$ at 293 K; [HCl] = 4.8 M; [KI] = 8×10^{-4} M; $[SO_2]$ = 0.58 vol.%.[23]

The electrochemical oxidation reactions of sulphites and SO_2, which readily occur on platinum and graphite anodes, are also of theoretical and practical importance. Thus the study of the anodic oxidation of H_2SO_3 on a platinum electrode showed that the overall rate of the process is determined by the oxidation of the reductant by oxygen from the water adsorbed electrochemically on platinum.[36] The process mechanism can be described by the following scheme:

$$Pt + H_2O - 2e \rightarrow PtO + 2H^+,$$
$$PtO + SO_3^{2-} \rightarrow Pt + SO_4^{2-},$$
$$PtO + SO_2 + H_2O \rightarrow Pt + H_2SO_4.$$

The rate of oxidation of sulphite anions falls appreciably as the bond between oxygen and the surface is strengthened.[37]

In order to increase the rate of reaction, the activation of the surface of the platinum is essential. It has been observed that the electrocatalytic activity of platinum in the presence of potassium iodide is several times higher than that of platinum merely coated by the SO_2H species.[38] It is assumed that the I_{ads} species on the surface participate in electron transfer across the interface. Apparently, both in the homogeneous systems described before and on the surface of electrode-catalysts, the mechanism of catalysis by the $I^0 + I^-$ pair is similar.

The adsorption of H_2SO_3 on electrodes used as electrocatalysts has also been studied in detail.[39-43] The electrochemical oxidation of sulphur dioxide on platinum–gold alloys and on organic metal complexes deposited on pyrographite or carbon black has been described.[44-46] One of the interesting applications of the electrochemical oxidation reaction involves its use in the thermoelectrochemical sulphuric acid method of preparation of hydrogen.

Studies in recent years have shown that not only platinum and platinum–carbon electrodes but also metalloporphyrin electrodes can be used as electrode-catalysts.[47–49]

The electrochemical oxidation of sulphur dioxide, which does not require oxidants, is apparently of interest for the elimination of SO_2 from gases.[50]

III. CATALYTIC REACTIONS INVOLVING THE OXIDATION OF SO_2 BY MOLECULAR OXYGEN

Studies on processes involving the oxidation of sulphur dioxide by molecular oxygen in the presence of homogeneous catalysts and water are of practical interest.

$$SO_2 + {}^1/_2O_2 + H_2O \xrightarrow{\text{catalyst}} H_2SO_4.$$

This reaction has been used since the past century for the preparation of H_2SO_4 by the familiar chamber method which has been described in many publications (see, for example, Amelin and Yashke[51]). However, a mechanism fundamentally different from the classical mechanism has been proposed comparatively recently.[52] All the versions of the traditional mechanism of the chamber process postulate the involvement of sulphuric acid in the form of nitrosylsulphuric acid in the sulphur dioxide oxidation step,[51] although under the experimental conditions the maximum rate of reaction in acid solutions is observed in the absence of H_2SO_4, an increase in the H_2SO_4 concentration inhibiting the reaction.[52]

The $SO_2-H_2O-HNO_3-O_2$ system has been investigated at 363–448 K and SO_2 pressures from 2×10^5 to 8×10^4 Pa.[52] The authors believe that the active oxidising species (oxygen transferring agent) is the nitronium ion NO^+ and it is postulated that the oxygen transfer to sulphurous acid molecules is effected not by the free nitronium ions but by their complexes with sulphite ions. The sulphur dioxide oxidation mechanism is described by the scheme:

$$SO_2 + H_2O \rightleftharpoons H_2SO_3 \rightleftharpoons H^+ + HSO_3^-,$$
$$HNO_3 + H^+ \rightleftharpoons H_2NO_3^+ \rightleftharpoons NO_2^+ + H_2O,$$
$$HSO_3^- + NO_2^+ \rightleftharpoons HSNO_5,$$
$$HSNO_5 + H^+ \rightarrow H_2SN^+O_5 \rightarrow (H_2SO_4)N^+O,$$
$$(H_2SO_4)N^+O \xrightarrow{HSO_3^-;\ O_2} H_2SO_4 + (HSO_3^-)N^+O \rightarrow HSNO_5.$$

Sulphur dioxide is oxidised by molecular oxygen under similar conditions in an aqueous medium using particles of activated charcoal as the catalyst, although it is assumed that in this case the process proceeds via a mechanism different from that of the oxidation of SO_2 in the presence of metal complexes.[53] The reaction is of first order with respect to the catalyst suspended in solution and with respect to molecular oxygen. The order with respect to SO_2 varies from 0 to 2 and the rate of the process is independent of the pH of the solution.[54]

In a study of the kinetics of the oxidation of sulphur dioxide by molecular oxygen in aqueous solutions containing vanadium salts, it has been established that in this case V^{5+} ions initiate the chain reaction:[55]

$$VO_2^+ + SO_3^{2-} + 2H^+ \rightleftharpoons VO^{2+} + \dot{S}O_3^- + H_2O.$$

The process then develops in accordance with the scheme

$$\dot{S}O_3^- + O_2 \rightarrow \dot{S}O_5^-,$$
$$\dot{S}O_5^- + SO_3^{2-} \rightarrow SO_5^{2-} + \dot{S}O_3^-,$$
$$SO_5^{2-} + SO_3^{2-} \rightarrow 2SO_4^{2-}.$$

Chain termination takes place as a result of radical recombination. The equation describing the rate of formation of sulphuric acid is

$$w = k([O_2][SO_2][V]^{1/4})/[H_2SO_4]^2.$$

The oxidation of sulphur dioxide by molecular oxygen in aqueous solutions containing $Fe_2(SO_4)_3$ has been investigated in the absence and presence of V^{4+}.[56] In the former case, a chain reaction mechanism is also postulated:

$$Fe^{3+} + SO_3^{2-} \rightarrow Fe^{2+} + \dot{S}O_3^-,$$
$$\dot{S}O_3^- + O_2 \rightarrow \dot{S}O_5^-,$$
$$Fe^{2+} + \dot{S}O_5^- \rightarrow Fe^{3+} + SO_5^{2-},$$
$$SO_3^{2-} + SO_5^{2-} \rightarrow 2SO_4^{2-}.$$

The rate of reaction is expressed by the equation

$$w = 4.32 \times 10^7 \exp(9625/RT)[SO_2].$$

V^{4+} ions lower the rate of reaction because they interact with the $\dot{S}O_5^-$ radical-ions, diminishing their concentration.

The oxidation of sulphur dioxide by molecular oxygen in the presence of iron salts has also been studied by Freiberg,[57] who established that the reaction order with respect to Fe^{3+} increases from 0 to 1 with decrease in $[Fe^{3+}]$. The oxidation of sulphur dioxide by Fe^{3+} ions competes with its catalytic oxidation by molecular oxygen at $[Fe^{3+}] > 2 \times 10^{-3}$ M. The author quotes two equations describing the variation of the overall rate of reaction with increase in pH and in the sulphur dioxide concentration.

In contrast to Bronikowski,[56] Freiberg[57] postulates a non-radical mechanism of the oxidation of sulphur dioxide:

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \rightleftharpoons 2H^+ + SO_3^{2-},$$
$$Fe(OH)^{2+} + H^+ \rightleftharpoons Fe^{3+} + H_2O,$$
$$Fe^{3+} + HSO_3^- \rightleftharpoons Fe(HSO_3)^{2+},$$
$$Fe(HSO_3)^{2+} + SO_3^{2-} \rightleftharpoons Fe(HSO_3)(SO_3),$$
$$Fe(HSO_3)(SO_3) + O_2 + H_2O \rightarrow Fe(OH)^{2+} + 2HSO_4^-,$$
$$Fe(HSO_3)(SO_3) + Fe^{3+} + H_2O \rightarrow 2Fe^{2+} + HSO_4^- + HSO_3^- + H^+.$$

Lunak et al.[58] likewise adhere to the view that the oxidation of sulphur dioxide by molecular oxygen in the presence of copper(II), iron(III), cobalt(III), nickel(II), and manganese(II), salts cannot be described by a radical-chain mechanism and propose an associative mechanism, according to which relatively stable complexes are formed between sulphite anions and the catalyst. The possibility of the formation of complexes between S(IV) and M^{x+} in the oxidation of SO_2 by molecular oxygen has also been indicated by Beilke and Gravenhorst.[59]

It has been established[58] that the oxidation of sulphur dioxide by molecular oxygen is of first order with respect to SO_2 over a wide range of concentrations of the latter. The catalytic action of transition metal ions on the reaction decreases in the sequence

$$Fe^{2+} \simeq Co^{2+} > Mn^{2+} \simeq Cu^+,\ Cu^{2+} \gg Fe^{3+} \simeq Co^{3+} \gg Ni^{2+}.$$

In the oxidation of SO_2 by molecular oxygen in the presence of Fe^{2+} in the pH range 0.8–5.0 in solutions, the reaction has an induction period whose duration increases with increase in the acidity of the medium.[60] It has been observed that, in the oxidation of sulphur dioxide by molecular oxygen, the addition of Mn^{2+} and Fe^{3+} has a comparatively small influence on the rate of the process.[61] On the other hand, other investigators regard manganese(II), iron(III), and also cobalt(II) compounds as promising catalysts of this reaction.[62–66] It has been established that iron and

manganese salts are active in a comparatively acid medium, while cobalt salts are active only in an alkaline medium. The maximum activity is observed at pH ~3.4 (Fe), 4.1 (Mn), and 9.0 (Co).[62,63] A radical-chain mechanism of the catalytic oxidation of SO_2 has been proposed in the above studies. In the oxidation of sulphur dioxide in acid solutions, the chains are short (n = 1, 2) and the reaction order with respect to SO_2 is close to or greater than unity and that with respect to the catalyst is less than unity. In alkaline solutions, the chains are lengthened and the reaction order is 1.5 with respect to SO_2 and 0.5 with respect to the catalyst.

It has been suggested[64] that the oxidation of SO_2 by molecular oxygen in the presence of $MnSO_4$ proceeds in accordance with the scheme

$$SO_2 + H_2O \rightleftharpoons H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \rightleftharpoons 2H^+ + SO_3^{2-},$$

$$\left.\begin{aligned} Mn^{3+} + HSO_3^- &\rightarrow Mn^{2+} + \dot{H}SO_3 \\ Mn^{3+} + HSO_3^- &\rightarrow Mn^{2+} + \dot{H}SO_5 \end{aligned}\right\} \text{initiation},$$

$$\left.\begin{aligned} \dot{H}SO_3 + O_2 &\rightarrow \dot{H}SO_5 \\ \dot{H}SO_5 + HSO_3^- &\rightarrow HSO_5^- + \dot{H}SO_3 \end{aligned}\right\} \text{chain propagation},$$

$$\left.\begin{aligned} \dot{H}SO_5 + \dot{H}SO_3 &\rightarrow;\quad 2\dot{H}SO_5 \rightarrow;\quad 2\dot{H}SO_3 \rightarrow \\ \dot{H}SO_3 + Mn^{3+} &\xrightarrow{H_2O} H_2SO_4 + Mn^{2+} + H^+ \end{aligned}\right\} \text{chain termination},$$

$$\left.\begin{aligned} \dot{H}SO_5 + Mn^{2+} &\rightarrow HSO_5^- + Mn^{3+} \\ 2Mn^{2+} + HSO_5^- &\xrightarrow{2H^+} 2Mn^{3+} + HSO_4^- + H_2O \end{aligned}\right\} \text{regeneration of } Mn^{3+} \text{ ions},$$

$$Mn^{2+} \rightarrow Mn^{3+} \quad \text{autoxidation}.$$

The scheme also includes other reactions, for example:

$$HSO_5^- + HSO_3^- \rightarrow 2HSO_4^-.$$

A radical-chain mechanism of the oxidation of SO_2 by molecular oxygen has been likewise proposed for catalysis by Co^{2+} [67] and Fe^{2+} [68] ions. The reaction catalysed by Fe^{2+} has an induction period whose duration increases with increasing acidity of the medium.[69] In aqueous solutions at pH 8.5, the catalytic action of Co^{2+} ions is 12 times stronger than that of Cu^{2+} ions.[67] The reaction orders with respect to O_2, Co^{2+}, and SO_2 are respectively 0, 0.5, and 1.5, while in another study[70] a reaction order with respect to O_2 equal to unity has been quoted for analogous conditions.

The oxidation of sulphur dioxide by molecular oxygen in the presence of copper(I, II) halides has been studied in the $CuCl_2-HCl-KI-H_2O$ and $CuBr_2-KI-H_2O$ systems.[71,72] It was found that the process consists of two stages: the reaction involving the reduction of copper(II) by sulphur dioxide in accordance with Eqn.(3) and the reaction in which copper(I) is oxidised by molecular oxygen:

$$4CuX + O_2 + 4HX \rightarrow 4CuX_2 + 2H_2O. \qquad (5)$$

The rate of oxidation of sulphur dioxide by molecular oxygen can in general depend on the ratio of the rate constants for reaction (3) and (5), while under the conditions of the experiments of Golodov et al.[72] it is described by reaction (5).

Fig.4[71,72] presents typical kinetic and potentiometric curves for the oxidation of SO_2 by molecular oxygen. There are two sections on these curves: non-stationary and stationary. Along the non-stationary section, Cu^{2+} is reduced via reaction (3). Under stationary conditions, equilibrium is established between the reactions involving the reduction of Cu^{2+} by sulphur dioxide [reaction (3)] and the oxidation of Cu^+ by molecular oxygen [reaction (5)]. In order to increase the overall rate of oxidation of sulphur dioxide by molecular oxygen, it is necessary to use factors accelerating the oxidation of Cu^+ to Cu^{2+}, which is then rapidly reduced to Cu^+. Calculations have shown[71,72] that the $CuCl_3^{2-}$(aq.) complex in the $CuCl_2-HCl-KI-H_2O$ system and the $CuBr_3^{2-}$(aq.) complex in the $CuBr_2-HBr-KI-H_2O$ system have the highest activity in the reactions where Cu^+ is oxidised by molecular oxygen.

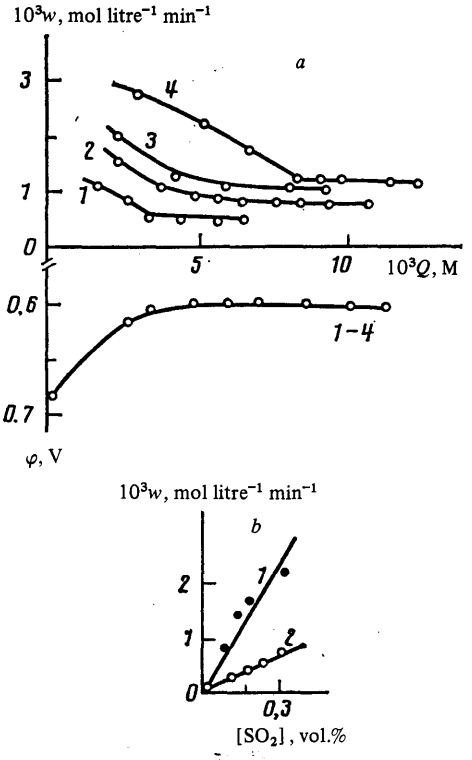


Figure 4. Oxidation of SO_2 by molecular oxygen at 293 K, $[CuCl_2]$ = 0.02 M, [HCl] = 4.8 M, [KI] = 8×10^{-4} M, and $[O_2]$ = 20 vol.%: (a) dependence of the rate of reaction and of the oxidation-reduction potential of the system on the amount of SO_2 which has reacted at different SO_2 concentrations (vol.%) [(1) 0.06; (2) 0.14; (3) 0.17; (4) 0.26]; (b) dependence of the initial (line 1) and stationary (line 2) rates of reaction on $[SO_2]$.[71]

The rate of oxidation of Cu^+ by molecular oxygen is described by the equation

$$w = k_{st}[Cu^+]_{st}[SO_2][O_2],$$

where k_{st} and $[Cu^+]_{st}$ are respectively the rate constant and the concentration of Cu^+ in the stationary region.

Iodide ions do not influence the oxidation of Cu^+. Thus the highest activity in the oxidation of sulphur dioxide by molecular oxygen is shown by copper chloride-iodide complexes. Along the non-stationary section, the reaction is of first order with respect to Cu^{2+}, SO_2, and I^-, while along the stationary section it is of first order with respect to Cu^+, SO_2, and O_2.[71,72] The addition of iron chloride to the $CuCl_2-HCl-KI-H_2O$ system greatly increases the rate of reaction along the non-stationary and stationary sections.[23]

The results of the study by Hegg and Hobbs[73] also show that catalysis by mixtures of iron, copper, and manganese salts leads to a tenfold increase in the rate of oxidation of sulphur dioxide by molecular oxygen compared with the rate of oxidation in the presence of a one-component catalyst alone. The oxidation of SO_2 by molecular oxygen in the presence of copper(I, II) halides and variable-valence metal salts (Mn, Fe) is inhibited by phenolic antioxidants and chelating additives[74] and also by surfactants.[75]

Studies on sulphur dioxide oxidation processes in air are of great theoretical and practical interest.[61,76,77] It has been observed that SO_2 is oxidised in air via several pathways:[61] (a) non-catalytic oxidation by molecular oxygen; (b) oxidation by molecular oxygen in the presence of metallic catalyst particles; (c) oxidation by O_3, H_2O_2, and SO_2; (d) oxidation in the presence of NH_3 acting as a neutralising agent.

The contributions of the principal mechanisms of the oxidation of SO_2 in air to the overall conversion of sulphur dioxide have been examined.[77] The overall contribution of the photochemical formation of excited sulphur dioxide molecules and of their interaction with O_2, O_3, and H_2O_2 as well as the reaction of SO_2 with the $\dot{O}H$, $\dot{R}O_2$, and $\dot{H}O_2$ radicals reaches 9%. The liquid-phase oxidation in the water droplets in clouds reaches 35%. The rate of this process is influenced by the pH of the drops, by the presence of metal ions (Fe and Mn), and by the presence of oxidants other than O_2 (O_3, H_2O_2). The contribution by the gas-phase oxidation of SO_2 with subsequent removal of sulphates from the atmosphere in the form of aqueous solutions is 50% of the overall balance. The remaining SO_2 is removed in the form of solid deposits.

The mechanism of the oxidation of sulphur dioxide in the atmosphere in the presence of metal ions includes the following stages:[78]

$$SO_3^{2-} + M^{+} \rightleftharpoons \dot{S}O_3^{-} + M \quad \text{initiation},$$

$$\left.\begin{aligned} &\dot{S}O_3^{-} + O_2 \rightleftharpoons \dot{S}O_5^{-},\\ &\dot{S}O_5^{-} + HSO_3^{-} \rightleftharpoons HSO_5^{-} + \dot{S}O_3^{-} \quad (pH \lesssim 7)\\ &\dot{S}O_5^{-} + SO_3^{2-} \rightleftharpoons SO_5^{2-} + \dot{S}O_3^{-} \quad (pH \gtrsim 7) \end{aligned}\right\} \text{chain propagation},$$

$$\left.\begin{aligned} SO_3^{2-} + HSO_5^{-} &\rightleftharpoons HSO_4^{-} + SO_4^{2-} \quad (pH \lesssim 7)\\ SO_3^{2-} + SO_5^{2-} &\rightleftharpoons 2SO_4^{2-} \quad (pH \gtrsim 7) \end{aligned}\right\} \text{oxidation},$$

$$\left.\begin{aligned} &\dot{S}O_3^{-} + \dot{S}O_5^{-} \rightleftharpoons S_2O_8^{2-} + O_2\\ &\dot{S}O_5^{-} + \text{inhibitor} \rightleftharpoons \text{inactive product} \end{aligned}\right\} \text{destruction of radicals}.$$

In conclusion, we shall consider the photochemical oxidation of sulphite anions. This reaction in the absence and presence of molecular oxygen has been described in detail.[79] Sulphates are formed in the absence of O_2 as a result of the oxidation of monothionic acid HSO_3, which is the primary product in the irradiation of the sulphite products by visible light,

$$SO_3^{2-} + H_2O \xrightarrow{h\nu} SO_3^{-} + H + OH^{-},$$
$$SO_3^{-} + H^{+} \rightarrow HSO_3 \ (H^{+}\text{—from water}),$$
$$HSO_3 + H + H_2O \rightarrow H_2 + H_2SO_4.$$

In the presence of molecular oxygen, sulphates are formed in accordance with the equation

$$HSO_3 + O_2 + SO_3^{2-} \rightarrow 2SO_4^{2-} + H.$$

Thus the photochemical activation of SO_2 leads to the formation of sulphuric acid vapour in the atmosphere.[80] The acid is then removed from air with rain drops—this is the main pathway leading to the natural elimination of SO_2 from the atmosphere.[81]

It follows from the present review that at the present time there is no unanimous view concerning the mechanism of the oxidation of SO_2 in aqueous solutions; radical-chain and associative mechanisms have been proposed. The adherents of the radical-chain mechanism believe that radicals may be formed in the interaction of sulphite anions with metal ions in accordance with the equation

$$SO_3^{2-} + M^{n+} \rightleftharpoons \dot{S}O_3^{-} + M^{n-1}$$

or as a result of the reactions[55,56,83]

$$2HSO_3^{-} \rightleftharpoons S_2O_5^{2-} + H_2O,$$
$$S_2O_5^{2-} \rightleftharpoons \dot{S}O_3^{-} + \dot{S}O_2^{-}.$$

The associative mechanism includes the formation of relatively stable complexes between sulphite anions and the catalyst.[58,84]

Analysis of the literature data shows that the stoichiometry of the oxidation of sulphur dioxide by metal complexes, i.e.

$$SO_2 + 2M^{n+} + 2H_2O \rightarrow H_2SO_4 + 2M^{n-1} + 2H^{+}$$

is satisfied, which rules out the chain reaction pathway.

It is most likely that the oxidation of sulphur dioxide by metal complexes proceeds via the formation of an intermediate compound of M^{n+} with the hydrogen sulphite anion formed via reaction (6), because the HSO_3^{-} anion is a more active electron donor than SO_2:[82,85]

$$SO_2 + H_2O \rightleftharpoons H_2SO_3 \rightleftharpoons HSO_3^{-} + H^{+}. \qquad (6)$$

The subsequent reactions in the system can be represented by the following scheme:

$$HSO_3^{-} + M^{n+}(aq) \rightleftharpoons MHSO_3^{n-1}(aq) + H_2O, \qquad (7)$$

$$MHSO_3^{n-1}(aq) \rightleftharpoons M^{n-1}(aq) + HSO_3, \qquad (8)$$

$$M^{n+}(aq) + HSO_3 + H_2O \rightarrow H_2SO_4 + M^{n-1}(aq) + H^{+}. \qquad (9)$$

The HSO_3^{-} anion interacts via reaction (7) with the metal complex, whereupon the intermediate $MHSO_3^{n-1}$(aq.) appears and then undergoes the inner-sphere redox reaction (8) with the formation of monothionic acid HSO_3. The possibility of the formation of HSO_3 during the reaction has also been pointed out in other studies.[86,87] In the next stage [reaction (9)], monothionic acid is oxidised rapidly to H_2SO_4.

The oxidation of SO_2 via a chain mechanism is also possible in processes with photochemical and radiochemical activation of the molecules of sulphur dioxide and molecular oxygen.[88–90]

IV. CONCLUSION

The problem of the search for and study of effective catalysts of the oxidation of sulphur dioxide to sulphuric acid, including liquid-phase oxidation, continues to be of interest. Special interest attaches to the elucidation of the process mechanism and of the influence of a number of factors on the kinetics of individual stages of the complex reaction, which promotes the development of promising and economical catalysts.

According to Dorfman,[82] the optimum system for the liquid-phase oxidation of sulphur dioxide by molecular oxygen should contain

the following components: (1) electron donors capable of intensifying the electron-donating function of the sulphur dioxide molecule; (2) halogens which interact with the donor orbital of the SO_2 molecule; (3) a polar solvent and a metal ion which give rise to stable compounds together with a halogen cation or halide anion and increase thereby the dipole moment of the halogen molecule; (4) a variable-valence metal ion, which reacts rapidly with molecular oxygen. The $CuCl_2-HCl-KI-H_2O$ and $CuCl_2-FeCl_3-HCl-KI-H_2O$ systems satisfy these features.[21,23]

The liquid-phase oxidation of SO_2 to H_2SO_4 has already found a practical application: the use of homogeneous catalysts for the elimination of the sulphur dioxide impurity from waste gases in various industries has been described.[91,92] Tests on catalysts based on copper and iron halide salts have shown that, for a high space velocity of the effluent gas (12 000 h^{-1}), the degree of conversion reaches 98% and the residual content of sulphur dioxide is 0.003 to 0.01 vol.%.[92] The 50% acid obtained, containing copper and iron complexes, can be used for the treatment of oxidised copper ores, which makes it possible to reduce the consumption of commercial sulphuric acid. Furthermore, the elimination of toxic sulphur dioxide from the effluent gas greatly improves the ecological position.

The choice of the method for the extraction and processing of sulphur dioxide is determined mainly by its concentration in the gas. Comparatively concentrated, with $[SO_2] > 4\%$, effluent gases in the non-ferrous metallurgy—roasting, converter and water jacket gases—can be used to manufacture sulphuric acid by the chamber or contact (in the presence of vanadium catalysts) method. Data have been published recently concerning the possibility of using heterogeneous catalysts also for gases at low concentrations.[2,93]

The temperature range of the operation of vanadium catalysts is in the region of high temperatures (400–600 °C). Practice has shown that their activity falls during use as a function of the nature of the sulphur-containing raw material, the degree of purification and variations in the concentration of sulphur dioxide, and the temperature range and the presence of catalyst poisons—arsenic and fluorine.[94,95] Gases with a low sulphur content (from 1 vol.% SO_2 upwards) have been utilised in recent years by employing non-stationary conditions.[96]

As shown above, the catalytic oxidation of SO_2 to H_2SO_4 in aqueous solutions takes place successfully also at a much lower SO_2 concentration in the effluent gases and under these conditions the method becomes economically viable. On comparing the liquid-phase homogeneous and heterogeneous catalytic methods for the oxidation of SO_2, it is possible to note the following advantages of the former: (1) homogeneous oxidation of SO_2 proceeds under mild conditions and does not require additional energy expenditures; (2) certain catalysts, for example, solutions of copper(II) halide salts, do not require additional elimination of arsenic and fluorine from the gas: F^- ions increase the rate of oxidation of SO_2 and As^{3+} is readily oxidised by copper(II); (3) waste water, containing active metal ions (Cu^{2+}, Fe^{3+}, Mn^{4+}, Mn^{7+}), can be used for the sanitary purification of gases.

Among the disadvantages of the method, one should include the corrosion activity of the catalytic solutions, the high concentration of halides in certain systems, the need to eliminate metal ions from the H_2SO_4 obtained, and the low final concentration of this acid (50 wt.%).

Thus the study of the processes leading to the oxidation of SO_2 to sulphuric acid in aqueous solutions is not only of theoretical interest but also helps to solve the problem of the purification of effluent gases.

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