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The Mechanism of the Adsorption of Sulphur Dioxide on Carbonaceous Adsorbents

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The most important literature data concerning the mechanism of the adsorption of SO_2 and the influence of oxygen and water vapour on the latter are described systematically and analysed. The possible types of interaction between the components of the gaseous mixture and the surface of the carbonaceous adsorbent are discussed.
The bibliography includes 112 references.

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I. INTRODUCTION

During the last 10–15 years, increasing attention has been devoted to active search for new adsorbents in many world scientific centres. The reason for this is, on the one hand, the ease of their preparation as a result of favourable thermodynamic and kinetic factors governing adsorbent–adsorbate systems, and, on the other hand, their importance and the wide variety of their practical applications. The vigorous development of such research is to a large extent associated with the fact that it is directed to the solution of one of the most urgent problems in the development of modern society—the protection of the environment, in particular the elimination of sulphur oxides from gases.

The tendency towards an increase in the amount of waste sulphur oxides is manifested from year to year in connection with the expansion of the manufacture of heavy non-ferrous metals and sulphuric acid, the increase in the output of electric power stations operating on sulphur-containing fuels, etc. Thus the SO_2 waste (and the predicted amount of such waste) discharged into the atmosphere in the USA is characterised by the following data (million tonnes)[1]:

1966	1970	1980	1990	2000
28.6	36.6	61.0	86.5	126.0

The development of new methods for the extraction of sulphur dioxide from gases led to the appearance of carbonaceous and silicon-containing adsorbents, adsorbents based on metal compounds, and various ion-exchange resins. Many of these adsorbents have a high thermal stability, chemical resistance, effective characteristics as regards deformation and strength, etc.

The method for the elimination of sulphur dioxide from gaseous mixtures by means of various carbonaceous adsorbents has developed extensively at the present time. The extraction of SO_2 by carbonaceous adsorbents has attracted the attention of specialists by its relative simplicity, the ease of preparation of the adsorbents on an industrial scale, and the wide range of particle sizes and types of adsorbents. The elimination of SO_2 from gases by carbonaceous adsorbents is one of the procedures undergoing industrial tests. Studies on the applications of carbonaceous adsorbents for the sorption of SO_2 have been very numerous; a wide variety of methods and starting materials have been used for their preparation. Nevertheless, despite the different nature and types of these adsorbents, the adsorption of sulphur dioxide on them may involve the same process.

Studies in recent years have been characterised by a growth of interest in the mechanism of the sorption of SO_2 on various carbonaceous adsorbents and by a more far-reaching investigation of the properties of the latter. The number of studies on these lines has been increasing every year. However, the published data, scattered throughout numerous articles and journals, have not so far been reviewed systematically and analysed. In the present review, an attempt is made to fill the existing gap.

The review does not claim to cover the available data fully. Attention is concentrated on the mechanism of the adsorption of SO_2 and on the influence of various factors on this process.

II. GENERAL CHARACTERISTICS OF THE SORPTION OF THE COMPONENTS OF THE GASEOUS MIXTURE

The experimental data accumulated hitherto concerning the adsorption of SO_2 from gaseous mixtures by carbonaceous adsorbents have shown that the sorption process has many features which depend on the chemical composition of the gas to be purified. However, despite this, it is always possible to isolate a large group of typical primary or secondary reactions occurring when a gaseous mixture is passed through a layer of a carbonaceous adsorbent. One should also note that the general characteristics do not rule out the occurrence of specific individual elementary reactions of the components of the gaseous mixture.

The primary adsorption processes consist mainly in the sorption of the components of the gas stream via fundamental mechanisms[2,3] of the following types:

$$SO_2 \rightleftarrows SO_2^* , \quad (1)$$

$$H_2O \rightleftarrows H_2O^* , \quad (2)$$

$$^1/_2O_2 \rightleftarrows O^* , \quad (3)$$

where an asterisk denotes the sorbed state of the component.

Because of the occurrence of the three fundamental types of the primary interaction of the components of the gaseous mixture with the carbonaceous sorbent, the process involving the elimination of the desired component (sulphur dioxide) proceeds in two ways—via the primary

reaction (1) and via secondary interconversions of the sorption products[4,5]:

$$SO_2^* + H_2O^* \rightleftarrows H_2SO_3^* \quad , \tag{4}$$

$$H_2SO_3^* + O^* \rightleftarrows H_2SO_4^* \quad , \tag{5}$$

$$H_2SO_4^* + n\,H_2O^* \rightleftarrows (H_2SO_4 \cdot nH_2O)^* \quad . \tag{6}$$

It is frequently very difficult to determine the contribution of the adsorption step to the technological process. This is because modern technical procedures permit a reliable and fairly simple identification of only ionised products in the solid state (conductimetric, ESR, infrared spectroscopic, and other methods). As a rule, the role of the adsorbed product in the sorption process must be inferred from indirect data. However, there have been recently many studies where the formation of secondary compounds and their role in various sorption processes were analysed.

The adsorption capacity and catalytic properties of activated charcoals are known to depend not only on the specific surface but also on the nature of the distribution of pores with respect to their effective radii[6-8] and also on the chemical structure of the surface layer[9,10]. Dubinin's studies[11,12] showed that the activated charcoal is a conglomerate of irregularly joined hexagonal graphite prisms. During the preparation and activation of the charcoal, some of the rings are disrupted and ring residues, consisting of one or two carbon atoms, accumulate on the surface. Such atoms have unused valencies and form surface oxides on coming into contact with oxygen. The formation of surface oxides has been observed in numerous investigations[13-16]. It is also noteworthy that many investigators claim the existence of two types of surface oxides—acidic and basic oxides[17-19].

Davtyan and coworkers[20,21] carried out a series of experiments in which they showed that surface oxides are formed on contact with oxygen (and water). They believe that these oxides do not constitute a separate, independent phase but are bound directly to the crystal lattice of the adsorbent. These surface compounds are formed because the energy liberated as a result of oxidation is insufficient for the removal of the oxide molecule from the surface. Reactions (4)–(6) proceed as follows. Sulphur dioxide molecules in the sorbed state interact with the initial adsorbent–oxygen or adsorbent–hydroxyl surface compound, which results in the formation of an activated surface complex having a definite chemical reactivity. If the energy of the system is sufficient for the removal of a species from the surface, the final product of the reaction

$$(H_2SO_4 \cdot n\,H_2O)^* \rightarrow H_2SO_4 + n\,H_2O \tag{7}$$

is formed directly via the activated surface complex. In certain studies, the formation of sulphuric acid is regarded as the primary stage of the gas purification process and it is suggested that the acid is formed before its sorption by the carbonaceous adsorbent[22,23]. We believe that such a process can occur only in the purification of the residual gases in the manufacture of sulphuric acid, containing a sulphuric acid mist[24].

The role of surface oxides in the sorption of SO_2 by carbonaceous adsorbents is probably really considerable[25,26]. However, analysis of numerous investigations shows (without going into the details of the mechanism of the primary step involving the sorption of the components of the gaseous mixture and of secondary processes) that the conventional subdivision of the extraction of SO_2 from industrial gases by sorption into two groups of processes [reactions (1)–(3) and (4)–(6)] is probably legitimate. One should bear in mind that, under certain conditions, reaction (4) is favoured over reaction (6).

In considering typical reactions of the second group [reactions (4)–(6)], the authors usually distinguish two temperature ranges in each of which a characteristic reaction takes place[27,28]. At low temperatures (up to approximately 200°C), sulphurous acid decomposes to SO_2 and water vapour via the reaction

$$H_2SO_3^* \rightarrow SO_2 + H_2O \quad . \tag{8}$$

This reaction is characteristic of the purification of gases which do not contain oxygen. However, under real conditions, an oxygen-free gaseous mixture is hardly ever encountered.

At temperatures above 200°C (approximately 350–450°C), the decomposition of the adsorbed sulphuric acid is most probable:

$$2H_2SO_4^* + C \rightarrow 2SO_2 + 2H_2O + CO_2 \quad , \tag{9}$$

as a result of which the adsorbent reduces the acid to sulphur dioxide with formation of carbon dioxide.

Reactions (8) and (9) were investigated in detail by Dratwa[29]. The experiments were performed using model gases with the following compositions:

I. $SO_2 + N_2$,

II. $SO_2 + N_2 + O_2$,

III. $SO_2 + N_2 + O_2 + H_2O$,

IV. $SO_2 + N_2 + H_2O$.

The concentration of nitrogen was kept constant and the concentrations of the remaining components of the gaseous mixtures were 5 vol.% SO_2, 10 vol.% O_2, and 18 vol.% H_2O. SO_2 was adsorbed at 110–120°C and the regeneration temperature was kept in the range 400–450°C. The results of these studies are presented in Fig. 1.

In the experiments on the $SO_2 + N_2$ (I) model gas, there is only physical adsorption of SO_2 by the activated charcoal. In the regeneration of the spent activated charcoal, the presence of SO_2 in the desorbed gas is detected over the entire temperature range from 20° to 200°C and the rate of evolution of SO_2 increases rapidly after heating the adsorbent above 100°C. The evolution of carbon dioxide is observed only in the temperature range which is not characteristic of the desorption of physically adsorbed SO_2.

The results of these experiments with the oxygen-containing model gas (II) are analogous to those analysed above. Here too an increase of temperature during adsorption is insignificant and SO_2 is mainly desorbed in the range between room temperature and 200°C. A considerable amount of CO_2 is formed together with SO_2. It follows from these data that sulphuric acid is not formed in the adsorption of SO_2 by carbonaceous adsorbents from an oxygen-containing gas.

In order to investigate the conditions under which SO_2 is vigorously oxidised to sulphuric acid, an experiment was performed on the model gas (III), which contains water vapour in addition to SO_2 and oxygen. Here an appreciable increase of temperature is observed following the adsorption of SO_2. The SO_2 content in the desorbed gas increases with increase of regeneration temperature: the evolution of SO_2 is initially observed above the adsorption temperature and is accompanied by the formation of a large amount of CO_2. These results (the high heat of the phase transition in the adsorption of SO_2, the shift of the temperature curve for the desorption of SO_2, and the vigorous formation of CO_2) can be explained by the fact that the simultaneous presence of oxygen and water vapour promotes the conversion of SO_2 into sulphuric acid.

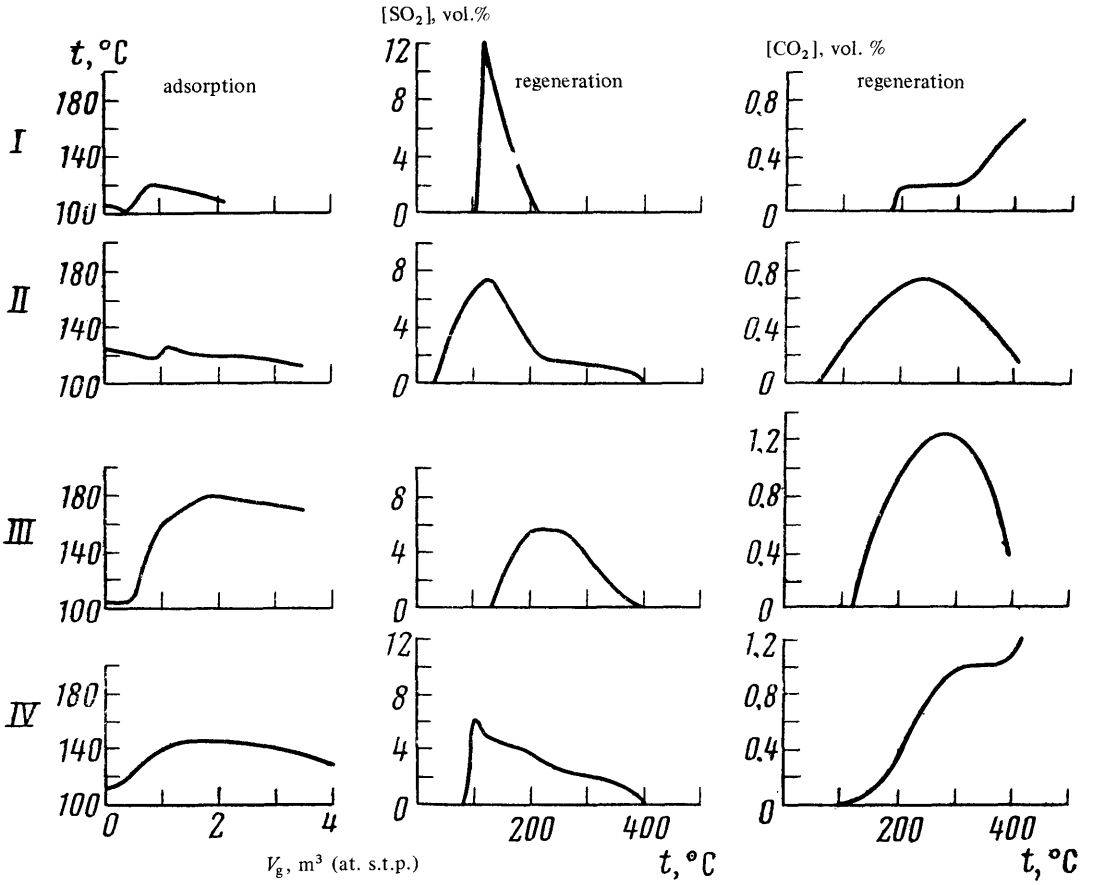


Figure 1. The influence of the composition of the initial gaseous mixture on the adsorption of sulphur dioxide and the regeneration of activated charcoal[29]; V_g (m^3 at s.t.p.)—amount of purified gas passed through the layer of adsorbent; t (°C)—regeneration temperature; $[SO_2]$ and $[CO_2]$ (vol.%)—concentrations of the components in the desorbed gas: I)–IV) model gases of different compositions.

In order to discover which reaction takes place in the presence of water vapour but in the absence of oxygen from the gases, the model gas (IV) was used. Here an appreciable increase of temperature was noted in the adsorption process and an extended SO_2 desorption curve (Fig. 1). Consequently in this case too there is extensive oxidation of SO_2 to sulphuric acid, probably by surface oxides. Similar results were obtained also in later studies[30].

The above classification of the reactions is naturally extremely arbitrary and in specific instances there is a possibility of particular departures from the proposed mechanism. Thus it has been stated[31] that the following reaction is possible in the adsorption of SO_2:

$$3SO_2^* \rightarrow S^* + 2SO_3^* \ . \qquad (10)$$

However, its occurrence is extremely doubtful.

One may note that the determination of the exact limits of the temperature ranges corresponding to the occurrence of the adsorption-catalytic processes is not only difficult but also controversial if one is dealing with specified carbonaceous adsorbents. Even for a particular type of activated charcoal, the temperature ranges where given sorption processes occur may be displaced as a function of the nature and amount of various impurities, the history of the active centres, etc.

It is noteworthy that, according to some data[32], free radicals are present on the surface of carbonaceous adsorbents. In the sorption of oxygen by an activated charcoal containing free radicals, the electrons of the latter become localised at oxygen molecules. These electronic states are stable, the corresponding species are rapidly chemisorbed and then activate the oxygen molecules[33,34]. Such a process on the surface of a carbonaceous adsorbent leads to the formation of the radical-ion O_2.[35] The occurrence of this stage may be represented by the reaction[36]:

$$R{\equiv}C^- + O_2 \rightarrow RCO_2^- \rightarrow R{\equiv}C \ldots O_2^- \ . \qquad (11)$$

If sulphur dioxide molecules appear on the surface of the charcoal, the following reactions may take place:

$$R{\equiv}C \ldots O_2^- + SO_2 \rightarrow R{\equiv}CO \ldots OSO_2 \ , \qquad (12)$$

$$R{\equiv}CO \ldots OSO_2 \rightarrow R{\equiv}C{-}O{-} + SO_3 \ , \qquad (13)$$

$$R{\equiv}C{-}O^- + SO_2 \rightarrow R{\equiv}C{-}O{-}SO_2 \ . \qquad (14)$$

It is noteworthy that, although the operation of this SO_2 sorption mechanism has been questioned by many specialists, the available experimental data are apparently consistent with this interpretation of the primary reactions.

The form of the bond between SO_2 and the surface of the carbonaceous material can have a marked influence on the primary SO_2 sorption processes. According to the hypotheses put forward by a number of investigators, two types of bond are formed between SO_2 and the carbon surface: a weak bond, which dissociates on slight heating in a stream of an inert gas (a_I) and a strong bond, the dissociation of which requires an increase of temperature (up to 300°C) as for surface oxides (a_{II}). Furthermore, these reactions are considerably influenced by the interaction of the surface with SO_2 and water vapour and by the ability of sulphur atoms to form hydrogen bonds[37,38].

We shall now consider the occurrence of the sorption processes from the theoretical standpoint based on the occurrence of reactions (1)–(3). The extent of adsorption of SO_2 on the activated charcoal obeys satisfactorily the Langmuir equation[30,31,39]:

$$a = \frac{a_m P}{P + b}, \tag{15}$$

where a_m is the degree of adsorption of SO_2 at equilibrium, P the partial pressure of SO_2, and b a constant, which depends on temperature and which can be calculated from the Arrhenius equation:

$$b = b_0 e^{-\frac{E^*}{RT}}, \tag{16}$$

where E^* is the heat of adsorption.

If it is assumed that $P \ll b$, Eqn. (16) can be replaced by Henry's law [Eqn. (17)], i.e. the degree of adsorption of SO_2 is directly proportional to its partial pressure:

$$a = \frac{a_m}{b} P. \tag{17}$$

SO_2 is oxidised to SO_3 on the surface of the activated charcoal and sulphuric acid is formed at a rate which is determined by the equation

$$\frac{d[H_2SO_4]}{dt} = k_I [SO_2^*] [O^*]^{0,5} [H_2O^*] - k_{II} [H_2SO_4^*], \tag{18}$$

where k_I and k_{II} are the rate constants for the forward and reverse reactions. The sulphuric acid formed on the surface fills internal pores, which enables the surface of the charcoal to participate in the oxidation process again. Thus the reverse reaction may be neglected in the adsorption of SO_2.[29]

We obtain from Eqns. (17) and (18)

$$\frac{d[H_2SO_4]}{dt} = k_I \frac{a_m a_{m_1} \sqrt{a_{m_2}}}{b\ b_1\ \sqrt{b_2}} P\ P_1\ P_2^{0,5}, \tag{19}$$

where the subscripts 1 and 2 refer to water and oxygen respectively.

During sorption, the values of a_m, a_{m_1}, and a_{m_2} are constant when the partial pressures of sulphur dioxide, water vapour, and oxygen are constant; the rate of formation of sulphuric acid in the catalytic region is likewise constant. The rate constant for the reaction is

$$k_I = k_{0I} e^{-\frac{E_{act}}{RT}}, \tag{20}$$

where E_{act} is the activation energy for the chemical reaction on the surface of the charcoal.

Having substituted in Eqn. (19) the adsorption rate constants defined by Eqn. (16), we obtain

$$\frac{d[H_2SO_4]}{dt} = {}'A e^{-\frac{E^*}{RT}}; \tag{21}$$

and the apparent activation energy E^* for the overall reaction now consists of the activation energy for the entire adsorption process and of the activation energy for the chemical reaction:

$$E^* = E^* + E_1^* + {}^1/_2 E_2^* - E_{act}. \tag{22}$$

When $(E^* + E_1^* + \frac{1}{2}E_2^*) > E_{act}$, the experimental data agree in this case with the calculated results[4] (Fig. 2). Data were obtained for two different types of activated charcoal: BKTs (continuous lines) and BKA (dashed lines). In the former case, the adsorbent particle size was varied for a constant contact time of 12 s and in the latter case the contact time was varied. The logarithm of the rate of adsorption of SO_2 ($cm^3\ kg^{-1}\ min^{-1}$) for constant SO_2, water vapour, and oxygen concentrations in the gaseous mixture is proportional to the reciprocal of temperature, in agreement with Eqn. (21). The apparent activation energy is 22 kcal $mole^{-1}$ for the BKTs charcoal and 14.6 kcal $mole^{-1}$ for the BKA charcoal. To a first approximation, E^* is comparable to the heat of adsorption.

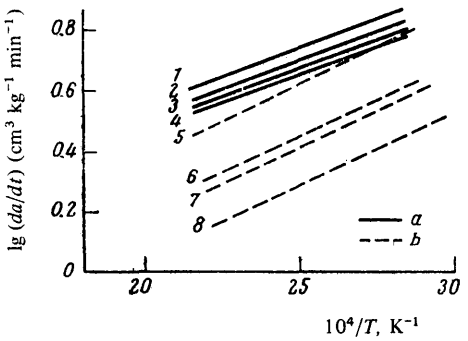


Figure 2. Temperature variation of the rate of adsorption of SO_2 on different activated charcoals in terms of the Arrhenius equation[4]: *a*) BKTs activated charcoal [particle size (mm): 1) 0.5–1.0; 2) 1–2; 3) 2–3; 4) 4–5]; *b*) BKA activated charcoal (particle size 2–3 mm). Contact time between the solid and gas phases (s): 1)–4) 12; 5) 5.4; 6) 8.6; 7) 13.0; 8) 22.0.

Measurements have been made[40] of the heat of adsorption of SO_2 on the "Aussig" coarsely porous charcoal at very low sulphur dioxide concentrations. The authors established that the minimum heat of adsorption is close to the heat of condensation of SO_2 (6.32 kcal $mole^{-1}$) and the maximum heat is 8.5 kcal $mole^{-1}$. The heat of adsorption of SO_2 on a finely porous activated charcoal reaches 10 kcal $mole^{-1}$.[41] However, the heats of adsorption of SO_2 on carbonaceous sorbents (coke, semicoke, and others) are lower than for activated charcoals, amounting to 6.5–8.0 kcal $mole^{-1}$.[42]

It is noteworthy that the heat of sorption of SO_2 on activated charcoal from a gaseous mixture containing oxygen and water vapour is much higher, reaching 14–16 kcal $mole^{-1}$.[43]

III. THE INFLUENCE OF OXYGEN

Real technological and ventilation gases as a rule contain oxygen[44,45]. Studies have shown that sulphur dioxide is in this case oxidised to the trioxide on the surface of carbonaceous adsorbents. In the presence of moisture, sulphur trioxide forms sulphuric acid [reactions (4)–(6)].

Thus the presence of oxygen and moisture must influence the mechanism of the process and hence its equilibrium and kinetic characteristics. The influence of oxygen on the sorption process was observed in the very first experiments designed to investigate the elimination of SO_2 from gases by an activated charcoal. However, systematic studies on these lines were undertaken only recently.

In 1956 Davtyan et al.[46] investigated the effect of oxygen in the gas phase in the adsorption of SO_2 on surfaces of different chemical types (adsorption from a mixture of SO_2 and O_2 in proportions of 2 : 1). The adsorbents investigated can be arranged in the following sequence in terms of their catalytic activity at low temperatures:

$$\text{activated charcoal} > V_2O_5 > \text{graphite} > Cr_2O_3 > Fe_2O_3.$$

It follows from Eqn. (19) that the rate of oxidation of SO_2 to sulphuric acid is proportional to the square root of the oxygen partial pressure. Under industrial conditions, the addition of oxygen to the gaseous mixture increases the degree of adsorption of SO_2[47] and the degree of purification of the gases[29] (Fig. 3). Here too SO_2 is apparently oxidised to sulphuric acid.

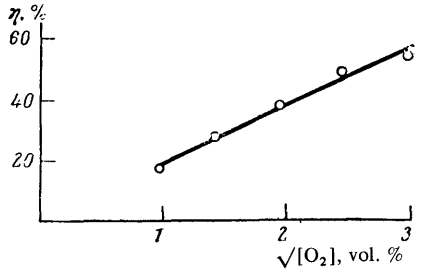


Figure 3. Variation of the degree of purification of the gases (η, %) with the initial concentration of oxygen in the gaseous mixture[29].

At very low (5%) and very high (95%) oxygen partial pressures, a smaller amount of sulphuric acid is obtained than in the case where the oxygen and sulphur dioxide partial pressures are equal (50%) for a given oxidation time[21]. However, the authors note that the amount of oxidised product can reach a limiting value after a specific time interval whatever the oxygen partial pressure. The formation of the limiting amount of the oxidised product on the charcoal is slow, which can be evidently accounted for by the rôle of diffusion in micropores. Only part of the adsorbed sulphur dioxide is then oxidised. On this basis, the authors conclude that "oxides" weakly bound to the charcoal surface and involved in equilibrium with the oxygen in the gas phase take part in the catalytic SO_2 oxidation process; these catalytically active "oxides" are readily removed by evacuation for 1 h at 20°C.[48] They consist of chemisorbed oxygen with a low activation energy and occupying about 10% of the entire surface of the charcoal[49,50]. Apart from these "oxides", weakly bound to the activated charcoal surface, Davtyan and Tkach[21] believe that none of the individual surface oxides of the charcoal are involved in the catalytic oxidation of sulphur dioxide.

A similar view has been developed also in other investigations[51,52] in the discussion of the adsorption of SO_2 by an activated charcoal from a nitrogen–oxygen–sulphur dioxide mixture. However, in this case the SO_2 concentration did not exceed 4 vol.% and the yield of the oxidised product, i.e. sulphur trioxide, was 50% of the adsorbed SO_2; the dynamic capacity of the charcoal proved to be 250 mg g^{-1}.

The sorption of SO_2 from a dry gas on activated SKT charcoal at 26°C consists of two processes: physical adsorption (77%) and chemisorption (23%).[53] With increase of temperature to 150°C, the amount of SO_2 chemisorbed from the dry gas hardly changes. This confirms yet again the hypothesis of the presence of a limited and constant number of active centres on the surface of the charcoal.

One should note that the degree of oxidation of SO_2 on carbonaceous adsorbents with a low surface activity (semicoke, coke, etc.) is insignificant[5]. The degree of oxidation of SO_2 on the semicoke obtained from brown coal at the pyrolysis temperature (650°C) is 10–12, 5–6, 3–4, and 2–3 wt.% of the total amount of adsorbed SO_2 at 25°, 75°, 100°, and 150°C respectively. The degree of adsorption of SO_2 (its equilibrium concentration in the gas–air mixture is 3 vol.%) is 148, 52, 48, and 26 mg g^{-1} at the temperatures stated.

It is noteworthy that, despite the different surface activities of activated charcoal and semicoke, the rate of acid formation increases in both cases during the first 10 min and is then stabilised[5,46] (Fig. 4). This can probably be explained by the identical mechanism of the interaction of SO_2 with the carbon surface.

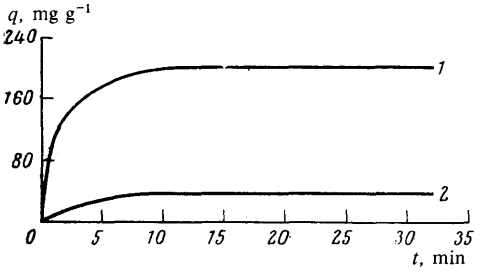


Figure 4. Kinetic curves for the increase in the weight of sulphuric acid on activated charcoal (curve *1*) and brown coal semicoke (curve *2*) in the adsorption of SO_2 from a gas–air mixture[5,46] at 20°C.

It has been claimed[23,29] that the oxidation of SO_2 on a carbon surface, for example on activated coke, is possible only in the presence of water vapour. The reaction

$$SO_2^{\bullet} + {}^1/_2O_2^{\bullet} + H_2O \rightarrow H_2SO_4^{\bullet} \qquad (23)$$

then occurs.

This view is adhered to also in other investigations[54,55], where the adsorption of SO_2 on carbonaceous adsorbents with a low surface activity was likewise investigated. The

degree of oxidation of SO_2 on semicoke at an adsorption temperature of 100°C for a moist gaseous mixture containing 2, 5, 10, and 15 vol.% of water vapour is 4–5, 5–6, 7–8, and 10–11%.[5] The degree of oxidation is higher in all cases for the moist gas than for the dry gas.

According to some workers[54-59], the oxidation of SO_2 on a carbon surface proceeds in the temperature range 20–120°C, while on heating the saturated adsorbent in a stream of inert gas above 220°C, sulphuric acid is reduced by carbon in the adsorbent via reaction (9) with regeneration of SO_2 and renewal of the carbon surface. However, this evidence has been disproved by subsequent investigations of the adsorption of SO_2 in the temperature range 50–300°C.[60] The spent charcoal was regenerated at temperatures up to 950°C. The authors noted the sorption of SO_2 up to 300°C, but physical adsorption of SO_2 was not observed at 250° and 300°C (Table 1).

Table 1. Variation of the degree of adsorption of SO_2 at different temperatures[60] (charcoal regeneration temperature 950°C).

Adsorption temp., °C	Degree of sorption of SO_2, mg g^{-1}		
	overall	chemisorption	physical adsorption
150	12.4	10.4	2.0
150	11.1	8.3	2.3
150	11.8	8.2	3.6
150	10.8	8.2	2.6
150*	9.3	7.2	2.1
150**	3.6	2.9	1.0
300	10.8	10.8	nil
250	10.5	10.5	nil
100	17.8	9.9	7.9
50	41.3	9.3	32.0

*Regeneration temperature 650°C
**Regeneration temperature 500°C

We may note that the amount of chemisorbed SO_2 at temperatures in the range 50–300°C changes insignificantly. In the regeneration of the charcoal in the temperature range 650–950°C, particles of elemental sulphur were observed on the cold surfaces of the column. Hence the authors concluded that, in the adsorption of SO_2 at 50–300°C, the chemisorbed sulphur dioxide is converted into elemental sulphur in the regeneration stage.

Chemical analysis of the regenerated charcoal showed that the adsorbent still contains a considerable amount of sulphur (0.68–2.03 wt.%). On this basis, one may conclude that the restoration of the initial adsorption capacity of the charcoal cannot be attributed to its liberation from sulphur. In this case, there is surface migration of sulphur from the initial adsorption centres and the formation of new centres as a result of the evolution of CO and CO_2 (observed in the regeneration of the charcoal).

The decrease of the SO_2 content in the desorbed gas during the regeneration of the charcoal can be explained by the following reactions[61]:

$$SO_2 + C \rightarrow CO_2 + {}^1/_2S_2 \quad , \tag{24}$$

$$CO_2 + C \rightarrow 2CO \quad . \tag{25}$$

The appearance of CO as a product at 250–300°C (and naturally also up to 700°C, since the adsorbent is sintered above this temperature) cannot be attributed solely to these reactions, since the rate of reaction (25) is insignificant under these conditions[62]. It is more likely that an oxygen-exchange reaction takes place between SO_2 and the charcoal, analogous to the well known reaction between CO_2 and charcoal[63]. In this case, an intermediate oxygen complex is formed and may be desorbed in the form of CO or converted into a more stable oxygen compound[13,64,65].

The only oxygen compound found at 300°C is CO; CO_2 was detected together with CO only at 600–650°C. In contrast to this, when carbon interacts with oxygen, the ratio of CO and CO_2 increases with temperature[2,66].

The combustion of carbon is known to yield CO and CO_2 from intermediate oxygen complexes with the carbonyl and lactone structures respectively[67,68]. It has been shown by infrared absorption spectroscopy[69,70] that these structures arise when carbon interacts with oxygen at room temperature. During vacuum heat treatment up to a higher temperature, a large amount of CO_2 is formed and the concentration of the complexes with the lactone structure decreases faster than that of the complexes with the carbonyl structure. It was observed[69,70] that CO appeared initially at 150°C in the regeneration of the charcoal after the adsorption of SO_2; there were no traces of CO up to 500°C. The sulphur content in the charcoal increased with increase of the number of adsorption–desorption cycles. The authors therefore suggested that the presence of sulphur on the surface of charcoal affects either the relative accessibility of peripheral regions, which can give rise to the carbonyl or lactone structures, or the relative thermal stabilities of these complexes after their formation.

Furthermore, CO_2 can be evolved also when the reaction

$$SO_2 + 2CO \rightarrow 2CO_2 + {}^1/_2S_2 \tag{26}$$

takes place[61]. Stagy et al.[60] investigated this reaction at 550°, 500°, and 350°C. A gaseous mixture containing 0.5 vol.% SO_2 and 2 vol.% CO in a stream of helium passed through a layer of the adsorbent; the experimental results are presented in Table 2.

Table 2. Material balance in the SO_2–C (1) and SO_2–CO–C (2) systems*.

Temp., °C	$10^5 c_1$, mole min^{-1}		Duration of expt., min	$10^5 c_2$, mole min^{-1}			
	SO_2	CO		SO_2	CO	CO_2	COS
650	4.5	nil	420	traces	1.0	8.8	traces
600	4.5	nil	130	traces	0.5	1.8	traces
550	4.5	17.0	15	0.4	8.9	8.6	0.2
550	4.5	17.0	195	0.4	8.2	7.7	0.4
500	4.5	17.0	240	traces	6.6	10.6	1.2
350	4.5	17.0	330	traces	4.6	9.6	3.4

* c_1 and c_2 are the SO_2, CO, CO_2, and COS concentrations in systems (1) and (2) respectively.

Comparison of the results obtained for the above two systems (SO_2–activated charcoal and SO_2–CO–activated charcoal) shows that the presence of CO appreciably altered the mechanism of the formation of elemental sulphur. It follows from Table 2 that the absence of a loss of carbon from the activated charcoal is characteristic of the SO_2–CO–C system. In the SO_2–C system at 600°C,

more than 50% of the oxygen bound in SO_2 was still retained in the layer of activated charcoal. However, in the SO_2–CO–C system at 550°C oxygen was essentially not retained. Evidently the presence of CO fully suppressed the formation of the oxygen complex on the surface of the activated charcoal.

At 550°C, the ratio of CO and SO_2 was approximately 2, confirming the occurrence of reaction (26). However, when the temperature was reduced to 350°C, the ratio of CO and SO_2 rose to 2.8 and 75% of the total sulphur was detected in the form of carbonyl sulphide. Thus carbon monoxide reacted under these conditions with the sulphur–oxygen surface complex.

Despite the apparent simplicity of the mechanism described above for the reaction of SO_2 on a carbon surface during adsorption and desorption, there are data throwing doubt on its validity. There exist different views concerning the details of the process. Some workers observed the oxidation of SO_2 during adsorption on a dry adsorbent from a dry gas[38,46], while others assumed that the oxidation is possible only in the presence of water[2,16]. According to one group of investigators[22], all the adsorption centres are catalytically active in the reactions, while others[23] believe that only some are active.

Furthermore, there exist experimental data which cannot be accounted for at all in terms of this mechanism. This applies to the amount of carbon dioxide appearing in the desorption of SO_2 via reaction (9). According to Dratwa et al.,[4] its amount is 80–120% relative to the stoichiometric composition based on reaction (9). The increase of the amount of CO_2 can be explained by the desorption of part of the surface carbon oxides. On the other hand, the decrease of the amount of CO_2 relative to stoichiometry can be attributed only to the fact that not all the chemisorbed SO_2 is oxidised to SO_3 at a temperature in excess of 220°C, where SO_2 is formed from SO_3 via reaction (9) according to the mechanism described: in fact ordinary desorption of strongly bound sulphur dioxides takes place to some extent.

The presence of oxygen in the gas causes not only a change in the nature of the process but also leads to a decrease of the overall rate of adsorption. This can be clearly seen in Fig. 5 from a comparison of the kinetic curves characterising the rate of adsorption of SO_2 by SKT-2 charcoal grains at an initial concentration of 1 vol. %, at 20°C, and for different amounts of oxygen in the inert gas (nitrogen).[30]

IV. THE INFLUENCE OF WATER

The influence of water on the sorption properties of activated charcoals can be manifested both in the gas phase and directly in the adsorbent itself. The sorption of water vapour by the activated charcoal or the desorption of water from the latter not only accompany the sorption of other vapours and gases but, as a rule, constitute an important factor, determining the kinetics (and hence also the dynamics) of the adsorption. It has been shown in a number of studies[73–76] that the equilibrium capacity of the activated charcoal with respect to sulphur dioxide depends to a large extent on the moisture content in the system.

The moisture present in the activated charcoal grains constitutes an intermediate diffusion medium in which the volatile component is transferred between the gas phase and the solid substance of the activated charcoal. Consequently the gas–activated charcoal system consists of three phases in the presence of moisture; the equilibrium compositions of the phases and the kinetics of the interphase exchange are determined by the content and nature of the water in the activated charcoal.

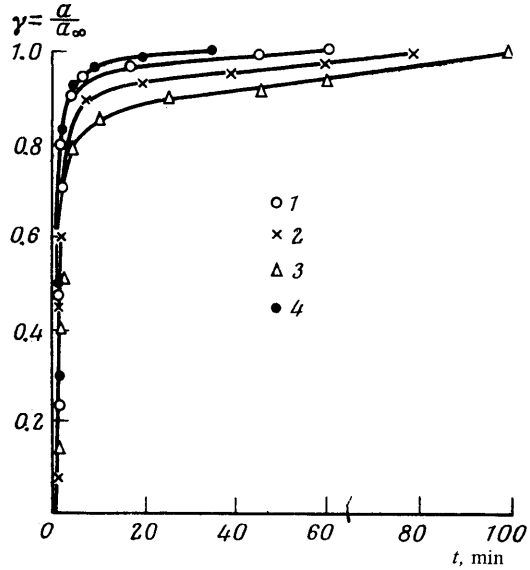


Figure 5. The influence of the oxygen content on the kinetics of the adsorption of SO_2 by SKT-2 charcoal[30]; initial SO_2 concentration 1 vol.%; temperature 20°C; oxygen content in the gaseous mixture (vol.%): 1) 3; 2) 5; 3) 15; 4) no oxygen.

The influence of the moisture content in the activated charcoal on the sorption of SO_2 was noted for the first time in 1917 in a study of the sorption properties of wood charcoal[77]. It was found that the overall sorption of SO_2 by the moist charcoal greatly exceeds the value for the dry charcoal. Somewhat later a similar effect was observed also for activated charcoals obtained from different starting materials, for example coconut, sugar, etc.[78] In the 1950s and 1960s, several patents were issued abroad for a method of synthesis of sulphuric acid using moist charcoal[79–88]. Widely known methods for the elimination of sulphur dioxide from industrial gases, such as the Lurgi[89–92], Hitachi[93,94], and West-Vaco[95,96] methods, are based on this principle.

The influence of charcoal saturated beforehand with moisture on the adsorption of SO_2 has been investigated comprehensively. It has been established that moisture has a significant effect on the nature and shape of the isotherm (Fig. 6), particularly at low partial pressures of sulphur dioxide in the gaseous mixture[48]. The degree of adsorption of SO_2 increases sharply with increase of the moisture content in the charcoal. Furthermore, it has been found that the amount of sulphuric acid obtained initially increases almost linearly with increase of the moisture content in the charcoal, reaches a maximum only in the presence of a moisture content of 300 mg g^{-1}, and then decreases sharply (Fig. 7).[48] The descending branch of the curve corresponds to saturation of the adsorbent

micropores with water. Similar effects were observed also on other activated charcoals for different initial SO_2 concentrations[19].

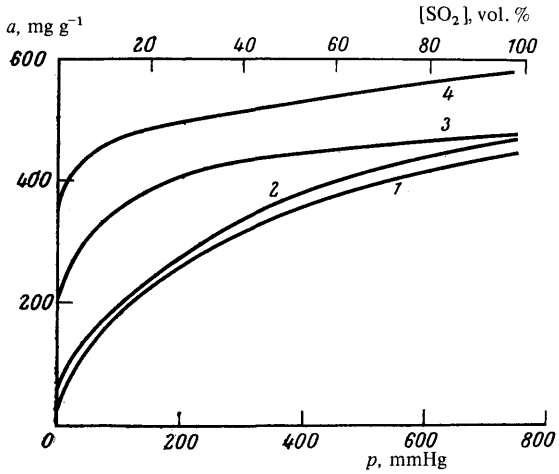


Figure 6. SO_2 adsorption isotherm at room temperature on activated charcoals with different moisture contents[48] (mg H_2O per gram): 1) 0; 2) 1.98; 3) 13; 4) 19.6.

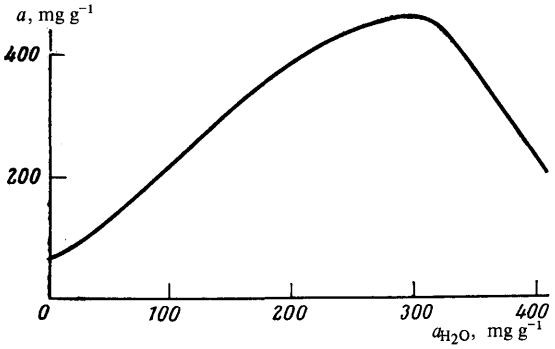


Figure 7. Variation of the degree of sorption of SO_2 at 20°C on activated charcoal with the amount of moisture adsorbed beforehand[48].

It has been suggested[37] that there are two types of interaction between SO_2 molecules and the carbonaceous adsorbent. The first is due to a weak bond between them, which may be broken on heating the adsorbent in a stream of an inert gas up to 100°C. This interaction makes a contribution a_I to the overall degree of adsorption. The second interaction is characterised by a strong bond, which is not dissociated up to 200°C. It makes a contribution a_{II} to the total sorption of SO_2. This hypothesis was also confirmed in a study of the adsorption of SO_2 on activated charcoal from a moist gas (Fig. 8).[97] With increase of the concentration of water vapour in the gas, a_I diminishes, while a_{II} passes through a maximum. The diametrically opposite effects of water vapour on a_I and a_{II} indicate the presence on the charcoal surface of adsorption centres of two types, involved in different kinds of surface interactions during the adsorption of sulphur dioxide and water vapour.

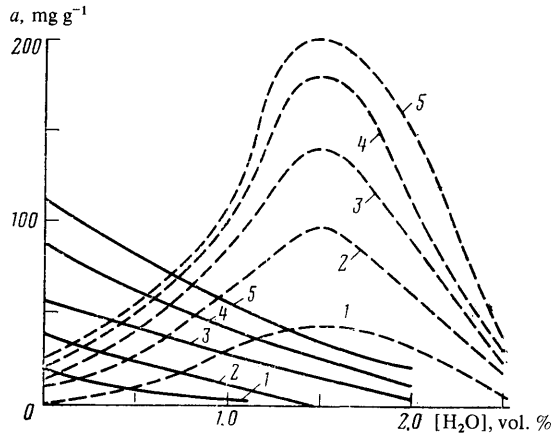


Figure 8. Variation of the degree of sorption of SO_2 [a_I (continuous lines) and a_{II} (dashed lines)] on SKT-2 charcoal with the concentration of water vapour at 25°C for different SO_2 concentrations[97] (vol.%): 1) 0.2; 2) 0.5; 3) 0.8; 4) 1.2; 5) 1.6.

Analysis of the experimental data leads to the following conclusions. The primary active centres in the adsorption of water on carbonaceous adsorbents are known to be oxygen complexes formed on the charcoal as a result of its activation. In the absence of such complexes, there is virtually no adsorption of water on the charcoal[11-16,98]. It is also known that oxygen complexes on the surface of charcoal serve as adsorption centres for sulphur dioxide too[19-23,46,48-53,99]. Under these conditions, the adsorption of SO_2 on active oxygen complexes is mainly in the nature of physical adsorption[40,43,100,101].

The water molecules adsorbed on the oxygen centres of the charcoal surface at water vapour pressures close to 0.5 of the saturation pressure are associated with one another via hydrogen bonding, which results in the coverage of the charcoal surface by isolated patches of condensed phase. The hydrogen atoms in the adsorbed water molecule, which are capable of forming hydrogen bonds, then serve as new adsorption centres and fresh portions of water are adsorbed by them. As a result, the number of adsorption centres in the given range of water vapour pressures increases sharply[97]. This mechanism is in fact used to account for the characteristic concave form of the water vapour adsorption isotherms on carbonaceous adsorbents with a sharp rise in the region of vapour pressures greater than 0.5 of the saturation pressure[98,102].

Sulphur is one of the elements capable of association via hydrogen bonding[103-105]. Thus the addition of SO_2 to the charcoal surface may proceed via the hydrogen of the adsorbed water. Since both water and sulphur dioxide molecules have strong dipoles, the strength of the bond formed may be greater than in the adsorption of SO_2 on silica gel via hydrogen bonding with the surface hydroxyls[106-109].

Thus the adsorption centres of the first type in the adsorption of SO_2 on charcoal from moist air are the oxygen complexes on the adsorbent surface. The adsorption centres of the second type in the adsorption of SO_2 from a moist gas are the protons of the adsorbed water molecules (hydrogen bonds). The above mechanism has been recently confirmed[97,110,111].

In the industrial synthesis of sulphuric acid, it is important to achieve the complete oxidation of SO_2 on carbonaceous adsorbents. Thus it has been stated[55] that, in order to attain the required degree of oxidation of SO_2 to SO_3, the contact time between the gas and the charcoal must be 10–20 s if the adsorbent temperature is maintained at the same time in the range 65–80°C; below 60°C, the reaction is strongly retarded. The concentration of the sulphuric acid obtained does not exceed 20% when the purified gas and water flow directly through the layer of adsorbent.

In a recently published study[112], carried out on a semi-industrial scale with the aim of purifying the residual gases in the manufacture of sulphuric acid, the influence of the regeneration time of the activated SKT-2 charcoal and of the amount of wash liquid on the concentration of the sulphuric acid formed was investigated (Fig. 9). In these experiments, the charcoal was wetted with the sulphuric acid solution obtained as a result of the adsorption of SO_2 before each adsorption–desorption cycle (apart from the first cycle, where the charcoal was wetted with water). The maximum concentration of sulphuric acid was 17% (SO_2 content in the gaseous mixture 0.2 vol.%, temperature 30–40°C).

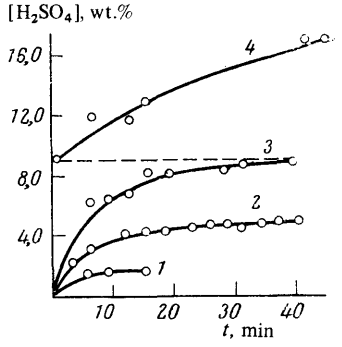


Figure 9. Variation of the concentration of the sulphuric acid formed with the regeneration time for dry charcoal (curve *1*), charcoal saturated with moisture after a single cycle (curve *2*), after two cycles (curve *3*), and after four cycles (curve *4*)[112]; SKT-2 charcoal; temperature 30–38°C.

There are data showing that, in the adsorption of SO_2, it is possible to obtain a 40% concentration of the acid[20]. However, in this case the gaseous mixture must contain 20 vol.% SO_2 and 80 vol.% O_2.

Thus the results presented above show that the sorption of sulphur dioxide by carbonaceous adsorbents is a complex physicochemical process, the rate of which and the absolute degree of adsorption of SO_2 depend not only on the composition of the gaseous mixture and the specific surface of the adsorbent, but also on its catalytic activity in relation to the oxidation of SO_2 to SO_3. The latter is in its turn determined by the specific properties of the adsorbent, for example, by the coverage of its surface by surface oxides, by the presence of the appropriate catalysts, and other factors.

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