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Physicochemical aspects of the adsorption of sulfur dioxide by carbon adsorbents

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Abstract. Literature data on the chemistry of the adsorption of sulfur dioxide on carbon adsorbents are surveyed and described systematically. The influence of various factors (the nature of the carbon matrix, the activation method, the chemistry of the adsorbent surfaces, temperature, the composition of the gas stream, etc.) on the sorption of SO_2 by activated carbons and semicokes is examined. The possible ways in which sulfur dioxide interacts with the carbon surface are discussed. The bibliography includes 128 references.

I. Introduction

The protection of the environment from pollution is one of the most important and complex socioecological problems. Nowadays approximately 2.5 billion tonnes of pollutants are discharged into the atmosphere annually.[1] The oxides of carbon, nitrogen, and sulfur, dust, ammonia, and various hydrocarbons are massive pollutants of air. Among them, sulfur dioxide, which on entering the atmosphere is capable of forming sulfuric acid, constitutes the greatest hazard. The acid residues in the form of rain or smoke have a negative effect on human health and the flora and fauna and cause the disintegration of constructional materials. Sulfur dioxide is formed mainly by the combustion of fuel in thermal electric power stations. Nonferrous metallurgy and to a lesser extent the sulfuric acid industry and the regeneration of sulfur by the Klaus method are sources from which large amounts of SO_2 are emitted.

In 1980, major plants, involving solely the combustion of fuel, discharged about 145 million tonnes of SO_2 into the atmosphere in countries of the European Economic Community. In most of the industrially developed countries, governments have adopted measures designed to achieve a sharp reduction of the discharge of sulfur dioxide. The 1989 EEC directive prescribes a reduction in the evolution of SO_2 in three stages and specifies the control periods during which these stages must be completed:[2] 1993, 1998, and 2003 (Table 1). This will make it possible not only to solve the most important ecological problem but also to economise on valuable sulfur-containing raw material for the production of sulfuric acid and other chemical products.

Table 1. The volumes of SO_2 discharged into the atmosphere in EEC countries.

Country	SO_2 discharged in	SO_2 discharged (in 10^3 t) and the change in the latter relative to 1980 (%)		
	1980 / 10^3 t	1993	1998	2003
Belgium	530	318/−40	212/−60	159/−70
Denmark	323	213/−34	141/−56	106/−67
Germany	2225	1335/−40	890/−60	668/−70
Greece	303	320/+6	320/+6	320/+6
Spain	2290	2290/0	1730/−24	1440/−37
France	1910	1146/−40	764/−60	573/−70
Ireland	99	124/+25	124/+25	124/+25
Italy	2450	1800/−27	1500/−39	900/−63
Luxembourg	3	1.8/−40	1.5/−50	1.5/−50
The Netherlands	299	180/−40	120/−60	90/−70
Portugal	115	232/+102	270/+135	206/+79
Great Britain	3883	3106/−20	2330/−40	1553/−60

Depending on the conditions under which sulfur dioxide is evolved, different methods are applied to remove it from gas streams. One of the most rational and promising procedures involves processes whereby SO_2 is extracted by carbon adsorbents (activated carbons and semicokes), which make it possible to obtain sulfur dioxide in a form suitable for its subsequent use — as a gas enriched in SO_2, liquid sulfur dioxide, elemental sulfur, as well as sulfuric acid. A number of processes for the removal of SO_2 from effluent gases have been devised on the basis of carbon adsorbents.[3–8] Almost all of them have passed successfully through pilot and experimental-industrial tests and some have been introduced into industry.

Although the carbon adsorption method is already used in industry, the question of the chemistry of the interaction of sulfur dioxide with a carbon surface still remains open. The growing interest in this problem can be accounted for not only by its scientific importance[2] but also by the necessity to formulate the principal requirements which must be met by carbon adsorbents capable of extracting effectively sulfur dioxide from gas streams.

There are fairly numerous literature data on the adsorption of sulfur dioxide by carbon materials, but there are virtually no surveys devoted to a critical analysis of the experimental data. The review which we published earlier[9] as well as the attempt by

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Loskutov and Khlopotov[10] to survey the available data are incomplete and morally obsolete and do not reflect the entire depth of the problem. In the present review, we have attempted to fill the existing gap.

II. General characteristics of the adsorption of SO_2 by carbon adsorbents

1. The forms of the bond between SO_2 and the carbon surface

The study of the chemistry of the sorption of SO_2 by carbon adsorbents presupposes the elucidation of the nature of the stages involving the adsorption of sulfur dioxide from a complex gas mixture containing SO_2, O_2, N_2, CO_2, H_2O and other components with subsequent conversion of SO_2 into the final product as well as the establishment of the role played in these stages by individual components of the surfaces of the carbons and semicokes.

The transition of sulfur dioxide to the adsorbed state cannot occur immediately as a result of a single elementary step. The process involving the adsorption of a SO_2 molecule consists of a series of consecutive stages. The characteristics of the sorption process depend on the nature of the sorbent, the technological conditions of the sorption, and the chemical composition of the gas being purified. However, it is always possible to differentiate typical primary or secondary reactions occurring when the gas mixture passes through a layer of the carbon adsorbent.

The primary adsorption processes, occurring when SO_2, O_2, and water vapour are present simultaneously in the gas, can be described by the following equations:[11-21]

$$\tfrac{1}{2}O_2 \rightleftharpoons O_{ads},$$

$$SO_2 \rightleftharpoons SO_{2\,ads},$$

$$H_2O \rightleftharpoons H_2O_{ads}.$$

Next there is a possibility of secondary transformations of the adsorbed components:

$$SO_{2\,ads} + H_2O_{ads} \rightleftharpoons H_2SO_{3\,ads},$$

$$H_2SO_{3\,ads} + O_{ads} \rightleftharpoons H_2SO_{4\,ads},$$

$$H_2SO_{4\,ads} + nH_2O_{ads} \rightleftharpoons (H_2SO_4 \cdot nH_2O)_{ads}.$$

On real surfaces, particularly when activated carbons and semicokes are employed, a large set of sorbed forms usually arises. By no means all of them participate directly in the sorption of SO_2. Their influence on the adsorption of sulfur dioxide is manifested, in particular, by the fact that they alter in some way the properties of the carbon surface or simply block individual sections which constitute active centres for the adsorption of SO_2.

The hypothesis of the existence of two forms of bond between carbon dioxide and the carbon surface, each of which is characterised by a definite heat of adsorption and desorption temperature, has been put forward.[22-31] Analysis of the isobars for the desorption of SO_2 from carbon adsorbents leads to this conclusion. In virtually all cases, there are horizontal sections in the temperature range 100–150 °C (Fig. 1). At low temperatures (< 150 °C), the weakly bound sulfur dioxide, retained on the surface by van der Waals forces, is desorbed. The removal of this portion of SO_2 is achieved rapidly, in 10–20 min, which indicates a low energy of the bond between this form of sulfur dioxide and the surface (Fig. 2, curve *1*). If the temperature is raised to 200 °C, the amount of desorbed SO_2 hardly increases.

Above 200 °C, the strongly bound form of SO_2, retained by chemical forces, is desorbed. The chemical nature of the interaction of this portion of SO_2 with the surface is also indicated by the rate of desorption: the process takes place slowly and is completed in 50–90 min (Fig. 2, curve *2*).

This view on the forms of the bonds between sulfur dioxide and the carbon surface has been confirmed, on the one hand, by the heats of adsorption and, on the other, by the results of spectroscopic analysis. Thus the heat of adsorption of the part of sulfur dioxide weakly bound to activated carbons and semicokes is

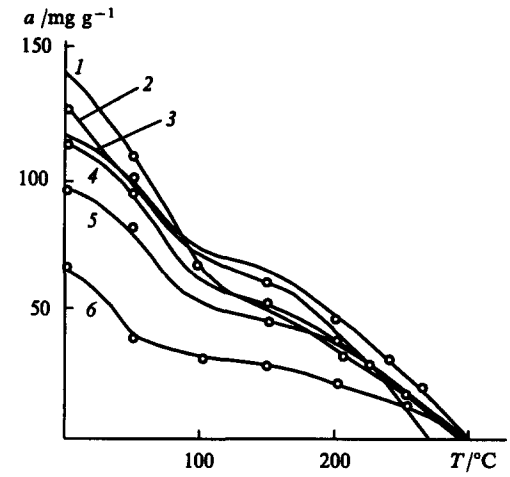


Figure 1. Isobars for the desorption of sulfur dioxide from carbon adsorbents: (*1*) SKT; (*2*) AR-3; (*3*) AG-5; (*4*) IGI; (*5*) KAD; (*6*) BAU.

in all cases less than 50 kJ mol^{-1}.[32-39] This makes it possible to claim that this component of the SO_2 is a physically adsorbed form, which is retained on the surface by dispersion forces. The presence of molecularly sorbed SO_2 on the surfaces of carbon adsorbents is indicated also by the existence of the 1350 cm^{-1} absorption band in the IR spectra of virtually all the Russian and foreign carbon materials saturated by sulfur dioxide.[40,41]

The strongly bound form of sulfur dioxide has a higher heat of adsorption (> 80 kJ mol^{-1}). In the IR spectra of activated carbons and semicokes, intense absorption bands in the region of 950, 1050, 1170, and 1250 cm^{-1}, associated with sulfur compounds having different degrees of oxidation,[40,41] correspond to this form. This makes it possible to postulate the occurrence of chemisorption processes.

The ratio of these two forms is determined, on the one hand, by the nature of the adsorbents and, on the other, by the adsorption conditions. The maximum degree of adsorption of sulfur dioxide in the physical form, not exceeding 50% of the overall degree of adsorption, is attained when SO_2 is sorbed from a dry oxygen-free gas. In all cases, the physical adsorption of SO_2 takes place and then, as a result of the chemical reaction with the surface compounds, a particular form of chemisorbed sulfur dioxide arises.

As will be shown below, chemisorption represents the interaction of the adsorbed molecules of sulfur dioxide with basic

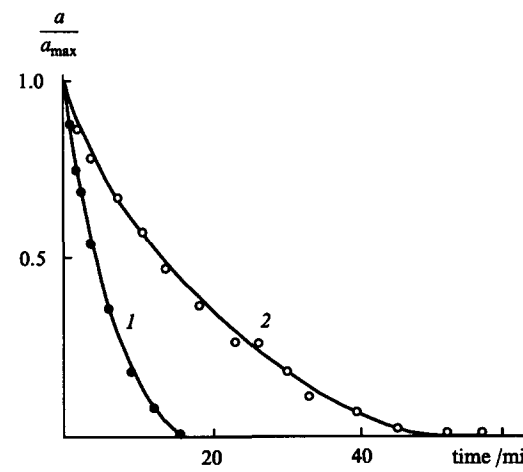


Figure 2. Kinetics of the desorption of sulfur dioxide from the activated carbon AR-3 at different temperatures (°C): (*1*) 150; (*2*) 350

oxygen-containing functional groups on the surfaces of carbon adsorbents, which results in the formation of an active complex of the type $C-SO_2$ with a definite chemical reactivity. If it is assumed that each chemisorbed SO_2 molecule occupies only one active centre, it is possible to estimate approximately the total number of primary active centres on the surfaces of adsorbents and the area occupied by the sulfur dioxide molecules. For example, the AR-3 activated carbon with a specific surface $S_{BET} = 730\ m^2\ g^{-1}$ can sorb sulfur dioxide from a dry oxygen-containing gas in the maximum amount $a = 125\ mg\ g^{-1}$, i.e. $2\ mmol\ g^{-1}$. The cross-sectional area of the SO_2 molecule (average diameter 3.38×10^{-10} m) is $S = 8.967 \times 10^{-20}\ m^2$. The overall area occupied by the chemisorbed SO_2 molecules is then

$$S_\Sigma = SaN_A = 8.967 \times 10^{-20} \times 2 \times 10^{-3} \times 6.02 \times 10^{23} = 108\ m^2,$$

which corresponds to 1/7 of the surface of the charcoal (N_A is the Avogadro number). The number of active centres per m^2 of the surface of the charcoal is

$$\frac{aN_A}{S_{BET}} = \frac{2 \times 10^{-3} \times 6.02 \times 10^{23}}{730} = 1.65 \times 10^{18}.$$

The factors which determine both the adsorption capacity of the adsorbents with respect to SO_2 as well as the process chemistry itself are of special interest from the technological point of view. Such factors may be the pore structure of the adsorbent, the quantitative and qualitative composition of the ash, and also the chemical nature of the surface. Furthermore, the process conditions may be of great importance: temperature, composition of the gas mixture, etc.

2. The influence of the pore structure of the adsorbents

One of the most important factors influencing the adsorption capacity of sorbents is known to be their pore structure.[42,43] It is to be expected that, in the case of purely physical adsorption and when all the micropores of the adsorbent are accessible to the given adsorbate, the adsorption capacity of carbon materials is greater the greater their porosity. This hypothesis has been tested experimentally[44-47] using as adsorbents both Russian and foreign industrial activated carbons of different origin and subjected to activation by different methods: SKT, AR-3, AG-3, AG-5, KAD-iodine, and BAU (Russia), Norit-2RL-Extra (the Netherlands), A-G (Poland), and experimental specimens of activated carbons IGI (Russia) and WJ-4 (Poland), the active coke K-14 (Poland), the semicokes PK-1 and PK-2 obtained by pyrolysis from brown coal from the Irsha-Borodinsk deposit, as well as the German carbon black of the Corax LHS type. The parameters of the porous structures of some of the adsorbents investigated are presented in Table 2.

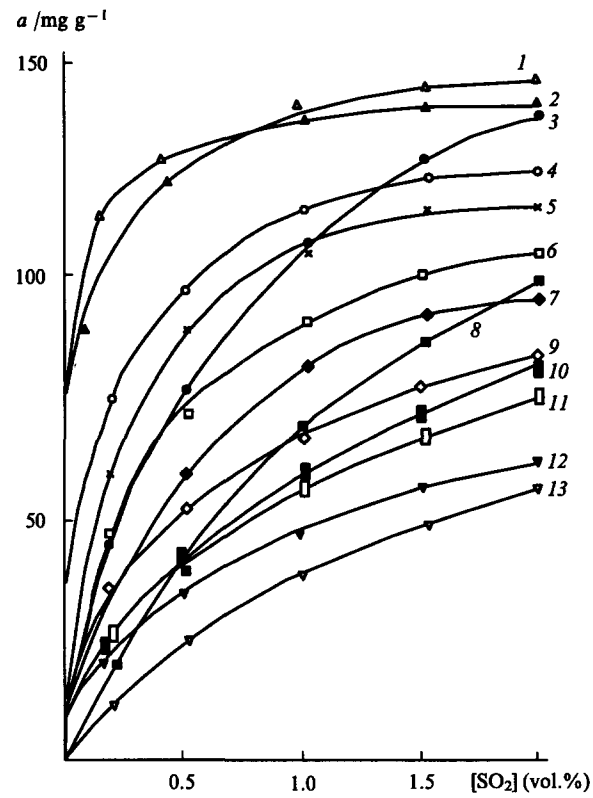


Figure 3. Sulfur dioxide adsorption isotherms on different carbon adsorbents at 25 °C; (*1*) PK-1; (*2*) PK-2; (*3*) SKT; (*4*) AR-3; (*5*) KAD; (*6*) IGI; (*7*) AG-5; (*8*) Norit; (*9*) K-14; (*10*) A-G; (*11*) AG-3; (*12*) BAU; (*13*) WJ-4.

Fig. 3 presents experimental data on the static adsorption of sulfur dioxide from a dry oxygen-free mixture at 25 °C. Among the Russian adsorbents, the highest capacity with respect to SO_2 over the entire range of concentrations investigated is shown by the brown coal semicokes PK-1 and PK-2 (curves *1* and *2*). The static adsorption capacities of these adsorbents at a sulfur dioxide concentration in the gas undergoing purification of 0.1 vol.%

Table 2. Characteristics of the porous structures of certain carbon adsorbents.

Parameter	Brand of adsorbent											
	SKT	AR-3	AG-3	AG-5	KAD	BAU	IGI	Norit	WJ-4	AG	K-14	Corax
Total pore volume /$cm^3\ g^{-1}$	0.98	0.70	0.74	0.56	0.70	1.5	0.81	1.09	1.81	0.92	0.43	0.14
Micropore volume /$cm^3\ g^{-1}$	0.51	0.33	0.30	0.27	0.29	0.23	0.40	0.60	0.46	0.28	0.16	0.04
Mesopore volume /$cm^3\ g^{-1}$	0.20	0.07	0.19	0.10	0.15	0.08	0.11	0.09	0.41	0.16	0.03	0.10
Macropore volume /$cm^3\ g^{-1}$	0.27	0.30	0.25	0.19	0.51	1.10	0.30	0.40	0.94	0.48	0.24	–
Specific surface area of mesopore /$m^2\ g^{-1}$	105	48	33	35	110	57	35	72	245	107	16	42
Total specific surface area /$m^2\ g^{-1}$	970	731	427	410	620	584	850	1550	1350	790	790	84
Limiting volume of adsorption space /$cm^3\ g^{-1}$	0.55	0.35	0.3	0.25	0.30	0.20	0.39	–	–	–	–	–
Characteristic energy of the adsorption of standard vapour/kJ mol^{-1}	21.7	20.1	21.3	20.4	19.7	25.5	19.6	–	–	–	–	–
Characteristic size of micropores /Å	5.6	5.9	5.6	5.9	6.1	4.8	6.1	–	–	–	–	–

are respectively 100 and 110 mg g^{-1}.[31] Among the activated carbons, the highest adsorption capacities are shown by SKT and AR-3 specimens (45.4 and 67.2 mg g^{-1} respectively),[31] whilst among the foreign carbon materials the Polish activated coke K-14 has the highest adsorption capacity (50.3 mg g^{-1}).

However, in all cases the adsorption capacities of the carbon sorbents investigated with respect to sulfur dioxide were not correlated with the parameters of their porous structure (the total pore volume, the volumes of the mesopores and micropores, and the limiting volume of the adsorption space W_0) and also with the specific surface. Nevertheless, Grzybek et al.[47] attributed the increased adsorption capacity of the K-14 coke to the presence in the latter of a definite number of supermicropores. This variety of pores has not been observed in the remaining adsorbents.

Thus the impression is created that the porous structures of carbon adsorbents of different origin and subjected to activation by different methods do not by themselves exert a decisive influence on their adsorption capacities with respect to sulfur dioxide.

However, this conclusion cannot be extended to carbon adsorbents obtained from a single initial material and using a single activation method. Semicoke formation has been achieved[48,49] by the thermal pyrolysis of brown coal from the Irsha–Borodinsk deposit at 500–800 °C without access of air. The adsorbents synthesised had specific surfaces ranging from 250 to 500 $m^2 g^{-1}$. Sulfur dioxide was adsorbed on the specimens obtained at 25 °C from a stream of nitrogen containing 1 vol.% of SO_2. The results are presented in Fig. 4, from which it follows that the adsorption capacity of the semicokes with respect to SO_2 is directly proportional to the specific surface area.

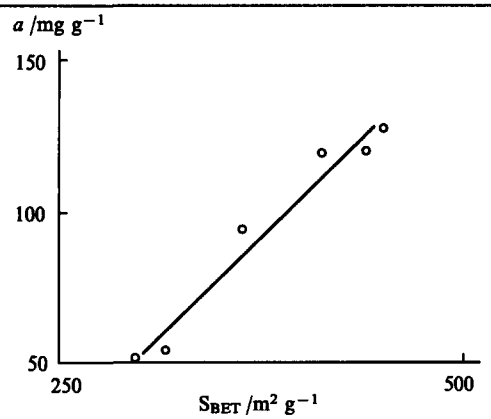


Figure 4. Dependence of the adsorption capacity of the semicoke PK-2 with respect to SO_2 on its specific surface area.

Thus the specific surface of the carbon adsorbents affects their adsorption capacity with respect to SO_2, but only when the same initial material and the same chemical activation methods are used. An indirect confirmation of this conclusion has been obtained in a study of the influence of the chemistry of the surfaces of carbon materials on the adsorption of sulfur dioxide.[50,51]

3. The influence of the qualitative and quantitative composition of the ash

The qualitative and quantitative compositions of the ash in activated carbons may be extremely varied and depend as a rule on the nature of the raw materials used to prepare the adsorbents and on the method for their activation. The ash content in the industrial adsorbents ranges from 1 mass % to 17 mass % and the principal components of the ash are compounds of alkali and alkaline earth metals, nickel, iron, manganese, copper, etc. (Table 3).[52–55] Taking into account the high reactivity of sulfur dioxide, it was natural to expect that the presence of ash in carbon adsorbents exerts a definite influence on its adsorption. This was first noted in studies[44,46,55–57] in which only the qualitative conclusion was reached that the adsorption capacities of carbons with respect to sulfur dioxide increase with decrease in the ash content. This question has been investigated in greatest detail in a recent study employing Merck and C.Erba activated carbons subjected to complete or partial deashing.[55] The ash content in the charcoals varied from 0.12 mass % to 3.28 mass %. Sulfur dioxide was adsorbed in the temperature range 130–170 °C from a gas mixture with a composition similar to flue gas containing 0.2 vol.% of SO_2. The thermal desorption of SO_2 from the saturated adsorbent was achieved at 360 °C in a stream of nitrogen.

Figure 5 shows how the ash content in the carbons investigated, the adsorption temperature, and the number of 'adsorption–desorption' cycles influence the adsorption capacitites of the specimens with respect to sulfur dioxide. With increase in the duration of the operation (the number of cycles), the adsorption capacities fell in almost all the specimens. However, the capacities of the high-ash adsorbents fell, other conditions being equal, much faster than those of the low-ash specimens. Furthermore, the process was significantly influenced also by temperature: at 170 °C, a more marked decrease in adsorption capacity was observed than at 130 °C.

With increase in the duration of use, the parameters of the porous structures of the high-ash components were greatly impaired — in the first place, the number of micropores and mesopores diminished with a consequent decrease in the specific surface. For example, the specific surface of the C.Erba activated carbon containing 3.28 mass % of ash fell after 10 cycles by approximately 10% (from 835 to 750 $m^2 g^{-1}$). Similar but much less marked changes occurred in the low-ash specimens: during this period, S_{BET} for the C.Erba carbon subjected to preliminary deashing (down to 0.12 mass % of ash) diminished only from 850 to 835 $m^2 g^{-1}$, i.e. by 1.6%.

Activated carbons with an increased ash content are oxidised more readily than the low-ash carbon materials. Thus, in the

Table 3. Chemical composition of the ash in carbon adsorbents (mass %).

Brand of adsorbent	Na	K	Mg	Ca	Co	Ni	Fe	Mn	Cu	Zn	Cr	Al	Ash
SKT	0.09	0.22	0.06	0.51	0.0008	0.005	0.10	0.002	0.008	0.005	0.009	–	13.9
AR-3	0.15	0.20	0.10	0.55	0.001	0.003	0.58	0.01	0.01	0.003	0.005	–	12.0
AG-3	0.45	0.17	0.42	0.79	0.002	0.006	2.31	0.002	0.02	0.004	–	–	13.0
AG-5	0.39	0.15	0.25	0.60	0.001	0.003	1.72	0.008	0.02	0.004	–	–	10.5
KAD	0.08	0.03	0.05	0.40	0.001	0.002	0.26	0.001	0.004	0.002	–	–	12.6
BAU	0.21	0.35	0.53	3.16	0.001	0.001	0.05	0.004	0.025	0.002	–	–	4.5
IGI	0.28	0.16	0.12	0.83	0.001	0.004	1.23	0.007	0.003	0.003	–	–	17.8
Merc	0.074	0.54	0.031	0.027	–	0.003	0.006	0.002	0.003	–	–	0.089	1.8
C. Erba	0.12	0.64	0.057	0.033	–	0.005	0.02	0.004	0.004	–	–	0.051	3.2

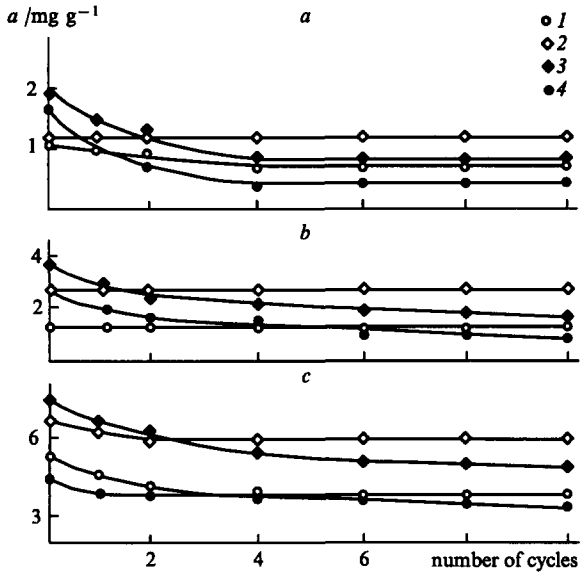


Figure 5. Dependence of the adsorption of sulfur dioxide {$[SO_2]_0 = 0.2$ vol.%} on the Merck and C.Erba activated carbons on the number of 'adsorption–desorption' cycles at 170 °C (*a*), 150 °C (*b*), and 130 °C (*c*) and for different ash contents (mass %): (*1*) 0.12; (*2*) 0.13; (*3*) 1.92; (*4*) 3.28.

thermal desorption stage at 360 °C, specimens containing more than 3 mass % of ash underwent appreciable oxidation accompanied by the partial surface combustion of the adsorbents and the evolution of CO_2 into the gas phase. The concentration of the bound oxygen in the high-ash carbons then increased by more than 20%, which naturally led to a sharp increase in the number of acid functional groups on their surface. A similar phenomenon is characteristic also of specimens containing 0.12 mass % to 0.13 mass % of ash, but, after similar 10 'adsorption–desorption' cycles, the concentration of oxygen on the surface increased by less than 2%. As will be shown below, the oxidised carbon should have *a priori* a lower adsorption capacity with respect to sulfur dioxide than the initial activated carbon.

Finally, the ash content itself in the low-ash adsorbents remains stable, like the sulfur content in the ash, during the above cycles, whereas in the high-ash specimens the above parameters increase from cycle to cycle. In all probability, this can be explained by the interaction of the adsorbed sulfur dioxide with individual components of the ash, which leads ultimately to the formation of stable compounds of the type of metal sulfates, which do not dissociate at the given temperatures and accumulate in the carbons.

Thus the presence of ash in the carbon adsorbents reduces the adsorption capacity with respect to SO_2 owing to the impairment of the parameters of the porous structure, a decrease in the specific surface, an increase in the degree of oxidation of the surface, and the conversion of the ash components to sulfates, which do not decompose in the course of regeneration and remain on the surface of the adsorbents, blocking the SO_2 specific adsorption centres.

4. The influence of the chemical nature of the adsorbent surfaces

The adsorption and catalytic properties of activated carbons and semicokes are to a large extent determined by the nature of their surfaces. Two types of surface functional groups of carbon materials are distinguished — acidic and basic.[58–62] Four groups of oxides with different acidities have been identified in oxidised carbons — carboxylic, lactone, phenolic, and carbonyl groups.[63] It has been suggested that these groups do not constitute a separate phase but are fragments of a single complex group of the type of phenolphthalein.[64] The question of the nature of the basic oxides on the carbon surface still remains open, although the hypotheses of the existence of chromene, quinonoid, benzopyrene, and pyrone structures have been put forward.[65–68]

Numerous investigations have been directed recently to the elucidation of the problem of the influence of the chemistry of the surfaces of carbon adsorbents on the adsorption of sulfur dioxide.[30,31,50,51,69–71] It was natural to suppose that basic surface groups are centres for the adsorption of SO_2 molecules. Treatment of the usual carbon adsorbents with air at high temperatures or with nitric acid is known to lead to the appearance of acid oxides on their surfaces and to a gradual disappearance of basic oxygen-containing groups.[72,73] The surfaces of the Merck[50] and AR-3 activated carbons and of the PK-2 semicokes[51] have been modified in this particular way, which made it possible to synthesise adsorbents with different contents of basic functional groups. These specimens were in fact used to identify the centres for the specific adsorption of SO_2.

A sample of the adsorbent (2–4 g) was saturated at 20 °C with sulfur dioxide in its mixture with nitrogen containing 0.3 vol.% of SO_2 until the attainment of a state of equilibrium. After equilibration, two-step thermal desorption of SO_2 from the carbon sorbents was carried out: initially the process was performed in a stream of nitrogen in the course of 3 h at 150 °C, after which the temperature was raised to 350 °C and the specimen

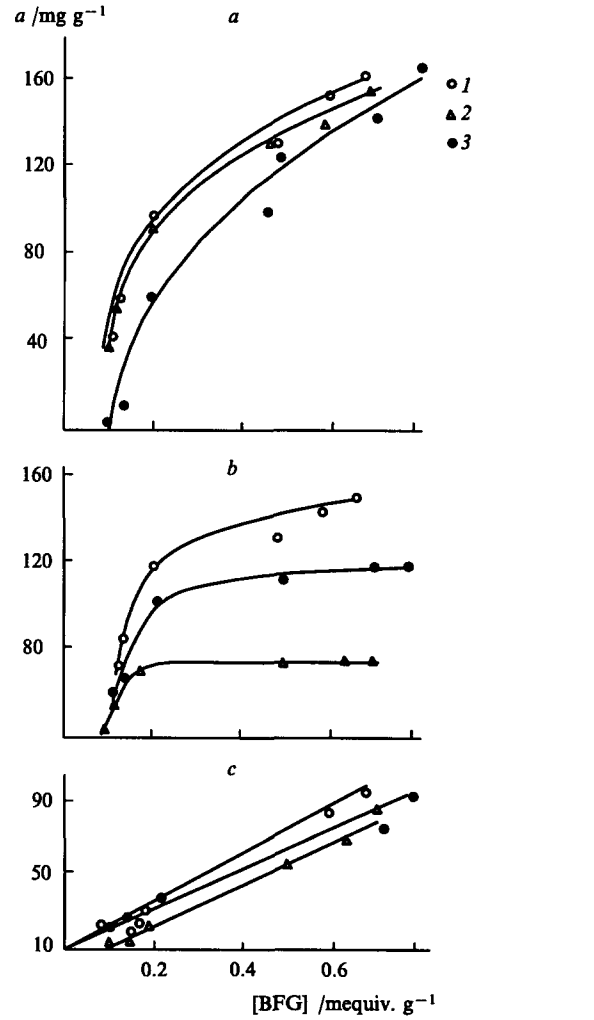


Figure 6. The influence of the concentration of basic functional groups (BFG) on the overall adsorption of sulfur dioxide on carbon adsorbents (*a*) and on the adsorption of SO_2 in the weakly bound (*b*) and strongly bound (*c*) forms at 25 °C {$[SO_2]_0 = 1$ vol.%}: (*1*) SKT; (*2*) Merck; (*3*) semicoke PK-2.

was subjected to a stream of nitrogen for 2 h. The SO_2 evolved was trapped in a Drechsel bottle filled with a 5% H_2O_2 solution. The sulfuric acid formed was titrated with 0.05 M NaOH solution in the presence of blue bromophenol.

The influence of the concentration of basic functional groups on the adsorption of sulfur dioxide by various adsorbents can be seen from Fig. 6. The presence of basic oxygen-containing groups on the surfaces of carbon adsorbents has a significant effect on their overall adsorption capacity with respect to SO_2: the amount of adsorbed SO_2 is proportional to their content (Fig. 6 *a*). Thus the AR-3 activated carbon, which has a low adsorption capacity (about 40 mg g^{-1}), has at the same time few basic oxygen-containing groups (0.090–0.127 mequiv. g^{-1}), while carbons with a high adsorption capacity (140–160 mg g^{-1}) are also characterised by a high content of basic surface oxides (0.500–0.660 mequiv. g^{-1}).

Figures 6 *b* and 6 *c* illustrate the influence the content of basic functional groups in the specimens on the adsorption of SO_2 in the weakly bound (a_1) and strongly bound (a_2) forms. The degree of adsorption of SO_2 in both forms increases in all cases with increase in the content of basic oxides. However, comparison of the relations in Figs 6 *b* and 6 *c* permits the conclusion that the adsorption of SO_2 in the strongly bound form is more sensitive to the presence of basic surface groups and hence to their acid–base characteristics than the adsorption in the weakly bound form.

Figure 7 shows how the concentration of basic oxides on the surface of Merck carbon affects the rate of sorption of SO_2. It is seen from the figure that the adsorption capacities of specimens containing few basic surface groups are low and are determined mainly by physical adsorption — equilibration occurs rapidly (after 20–30 min). At a high concentration of basic functional groups, the sorption of SO_2 is slow and equilibrium is attained only after 60–90 min. This demonstrates yet again that in this

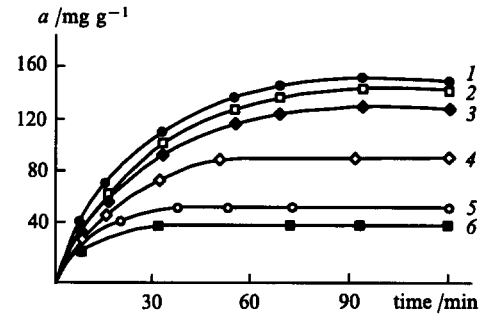


Figure 7. Kinetics of the adsorption of sulfur dioxide {$[SO_2]_0 = 0.3$ vol.%} on the activated Merck charcoal at 25 °C and at the following concentrations of the basic functional groups (mequiv. g^{-1}): (*1*) 0.685; (*2*) 0.610; (*3*) 0.493; (*4*) 0.190; (*5*) 0.116; (*6*) 0.112.

case adsorption includes also chemisorption: almost half of the adsorbed dioxide corresponds to the strongly bound SO_2.

Thus the concentration of basic functional groups on the surface of carbon materials determines their adsorption capacities with respect to SO_2. It has a stronger influence on the adsorption of sulfur dioxide in the strongly bound form (heat of adsorption > 80 kJ mol^{-1}). The amount of weakly bound sulfur dioxide (heat of adsorption < 50 kJ mol^{-1}) is influenced mainly by the structural characteristics of the adsorbents and in particular by their specific surface areas.

5. The influence of temperature

The question of the influence of temperature on the equilibrium adsorption capacities of carbon adsorbents has been thoroughly investigated.[20,21,39,74–87] The isotherms illustrated in Fig. 8 correspond to the first type in Brunauer's classification.[88] A steep

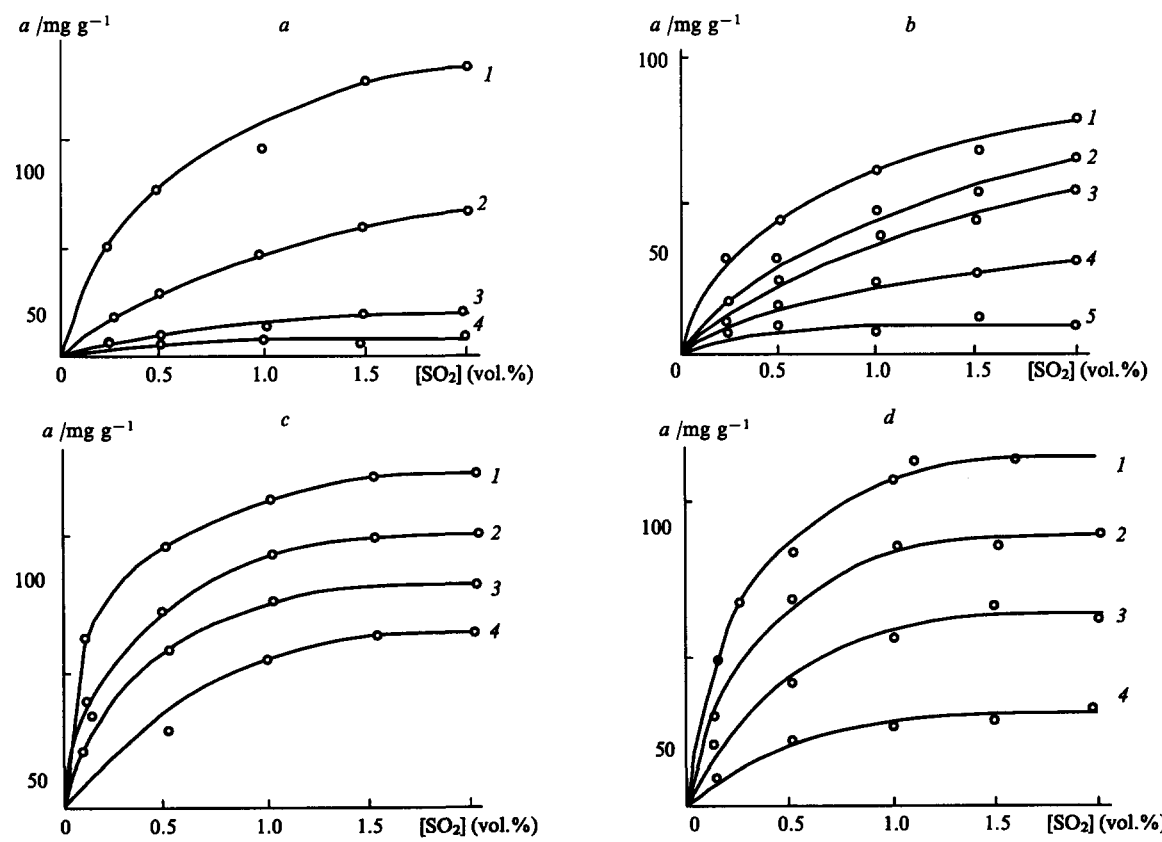


Figure 8. Isotherms for the adsorption of sulfur dioxide on the activated carbons SKT (*a*), BAU (*b*), AR-3 (*c*), and KAD (*d*) at different temperatures (°C): (*1*) 25; (*2*) 50; (*3*) 100; (*4*) 150.

rise in the isotherms in the region of relatively low SO_2 concentrations is characteristic of almost all the specimens. This means that carbon adsorbents can serve as an effective means for the extensive removal of sulfur dioxide from gases and can be used to treat gases with a low SO_2 content. With increase in temperature from 20 to 150 °C, the capacities of the adsorbents considered fall by 50%–90% when the SO_2 content in the initial gas mixture is about 1 vol.%. However, at low concentrations of sulfur dioxide (up to 0.5%) the adsorption capacity depends little on temperature, which shows that they would not be useful for the purification of gases with low concentrations and at an elevated temperature.

An increase in temperature has a negative effect on the overall amount of adsorbed sulfur dioxide.[22,24] However, the fraction of SO_2 retained on the carbon surface by chemical forces, i.e. as a result of the interaction with basic sulfurous groups, increases approximately by 10% as the temperature rises from 20 to 100 °C, after which it remains constant (Fig. 9). At temperatures above 50 °C, the fraction of chemisorbed SO_2 is in all cases greater than the fraction of the sulfur dioxide bound to the carbon adsorbents by dispersion forces and reaches 55% – 70%. Almost all the SO_2 adsorption isotherms on carbon adsorbents can be satisfactorily fitted by the Langmuir monomolecular adsorption equation[89] or by the Freundlich equation.[90]

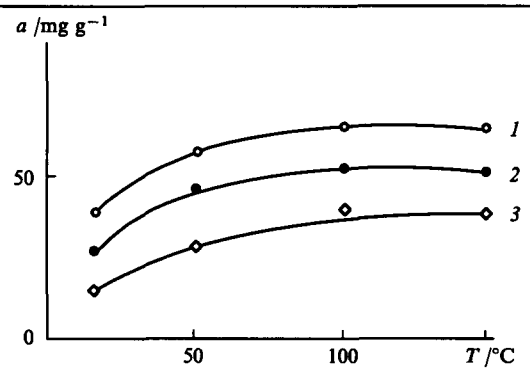


Figure 9. The influence of temperature on the ratio of the weakly and strongly bound forms of SO_2 on the surfaces of carbon adsorbents {$[SO_2]_0 = 1$ vol.%}: (*1*) SKT; (*2*) AR-3; (*3*) PK-2.

6. The influence of oxygen

The influence of oxygen on the adsorption of sulfur dioxide was already noted in the very first studies devoted to the interaction of SO_2 with a carbon surface.[11,14,25,91–93] However, systematic investigations began only recently and this was associated with the appearance of the hypothesis that the chemical nature of the surfaces of the adsorbents affects SO_2 sorption process.

It was shown above that the sorption of SO_2 from an oxygen-free gas mixture includes chemisorption with formation of a stable chemical compound on the surface. The contribution of chemisorption, which does not exceed 45% – 70% of the total amount of the sorbed sulfur dioxide, is determined by the acid – base properties of the adsorbent and the adsorption temperature. Evidently the presence of oxygen in the gas phase should promote chemisorption and in all probability the degree of conversion of SO_2 should increase in parallel with increasing O_2 concentration in the gas.

The adsorption of sulfur dioxide on activated carbons in the presence of oxygen has been investigated in detail in a number of studies.[26,29,51,84,94–97,126] Fig. 10 illustrates the influence of the concentration of the oxygen in the gas stream on the adsorption capacities of the SKT and AR-3 carbons with respect to SO_2.[57,91] In all cases, sulfur dioxide is sorbed in the form of weakly bound (physically bound) and strongly bound (chemically bound) forms,

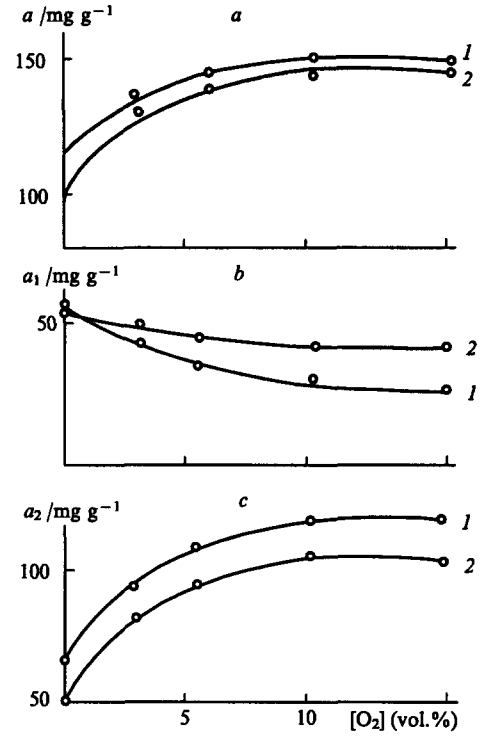


Figure 10. The influence of oxygen concentration in the gas mixture on the overall adsorption of sulfur dioxide by activated carbons (*a*) and on its physical (*b*) and chemical (*c*) adsorption at 25 °C {$[SO_2]_0 = 1$ vol.%} (*1*) AR-3; (*2*) SKT.

the fraction of the chemisorbed SO_2 depending to a large extent on the O_2 concentration in the gas and on the process temperature.

The adsorption capacities of sorbents increase with increasing O_2 content in the gas mixture. The degree of adsorption of SO_2 from a gas containing 10 vol.% of O_2 at 20 °C is approximately 30% greater than the degree of its adsorption from an oxygen-free gas mixture. A further increase in the O_2 content in the gas stream (above 10%) does not lead to an increase in the equilibrium adsorption capacity — virtually all the curves reach a plateau. In all cases, the increase in the adsorption capacities of carbons is caused exclusively by chemisorption processes. As can be seen from Fig. 10*b*, the amount of physically sorbed sulfur dioxide tends to decrease with increase in the O_2 concentration. As the adsorption temperature rises, this trend weakens and at 100–150 °C the quantity a_1 is almost independent of the O_2 concentration.

On the other hand, the amount of chemisorbed SO_2 increases with increase in the oxygen concentration in the gas mixture (Fig. 10*c*). At high temperatures, the $a_2 = f[O_2]$ relation is linear. At low temperatures, an increase in the oxygen content in the gas undergoing purification to above 10 vol.% hardly affects the adsorption of SO_2 in the strongly bound form.

According to a number of investigators,[51,96,97,126] such influence of the oxygen concentration on the adsorption of sulfur dioxide can be explained by the active sorption of oxygen by carbon adsorbents in the temperature range 0–150 °C. Physical adsorption of oxygen takes place initially, after which it is bound by chemical forces to the most active sections of the carbon's surface, i.e. it passes to the chemisorbed state. Basic oxides, which, as shown above, are centres for the specific adsorption of sulfur dioxide molecules, are formed as a result on the surfaces of activated carbons.[67,68,98,99] Thus the presence of oxygen in the gas mixture promotes an increase in the total number of SO_2 adsorption active sites, which naturally increases the adsorption capacities of activated carbons with respect to sulfur dioxide.

Table 4. Characteristics of the oxidised adsorbents.

Oxidation conditions		Content of oxygen-containing groups / mequiv. g^{-1}				
temperature /°C	O_2 concentration (vol.%)	carboxylic	lactone	phenolic	carbonyl	basic
SKT carbon sorbent						
Initial specimen		0.558	0.594	0.095	0.161	0.653
20	3.0	0.551	0.564	–	0.050	0.927
20	5.0	0.525	0.541	–	0.045	1.253
100	3.0	0.531	0.572	–	0.100	0.896
100	5.0	0.513	0.501	–	0.090	1.269
AR-3 carbon sorbent						
Initial specimen		–	–	0.125	0.100	0.744
20	3.0	–	–	0.104	–	0.986
20	5.0	–	–	0.080	0.020	1.334
100	3.0	–	–	0.100	0.025	0.951
100	5.0	–	–	0.075	0.030	1.395

In order to test this hypothesis, a series of experiments were performed in which the influence of the treatment of carbon adsorbents with oxygen on the chemical state of their surfaces was investigated.[51] The initial adsorbents were maintained for 2 h in a stream of nitrogen at 350 °C, after which they were cooled to the required temperature, continuing the passage of dried N_2 through them. After this, a measured amount of oxygen such that its content was 3 vol.% or 5 vol.% was introduced into the gas stream. The subsequent treatment of the adsorbents by the oxygen-containing mixture was carried out for 2 h at 20 or 100 °C. The conditions of the preceding experiments, in which there was no sulfur dioxide in the gas, were thus virtually reproduced.

After the adsorption of oxygen, the chemical state of the adsorbent surface was studied by the neutralisation method.[63] The results presented in Table 4 show that the initial AR-3 carbon possesses predominantly basic groups. The SKT activated carbon contains in addition an appreciable number of acid groups, mainly lactone and carboxy-groups.

Treatment of the adsorbents with nitrogen at 350 °C with subsequent adsorption of oxygen altered in all cases the chemical nature of the carbon surface: the surface acidic groups of virtually all types vanished and the number of basic groups, which constitute some of the sulfur dioxide adsorption centres, increased. The increase in the concentration of basic groups naturally increases the adsorption capacities of the carbons with respect to SO_2.

7. The influence of water vapour

The influence of water vapour on the sorption of SO_2 by carbon adsorbents has been the subject of numerous investigations.[13,20,22,23,26,100] An appreciable increase in the adsorption capacities of activated carbons in the adsorption of SO_2 from moist gas streams has been noted. The views of many investigators on this phenomenon reduce to the postulate that water, which has a considerable chemical affinity for the chemisorbed SO_2, abstracts it from the carbon surface and transfers it to the liquid phase. Thus the blocked SO_2 sorption active centres are liberated and can again participate in the process.

In all probability, a weak point in the above hypothesis is that water is regarded merely as an 'abstracting agent'. Furthermore, studies of the influence of water on the sorption of SO_2 have almost always been performed in the presence of O_2, which naturally has a definite effect on the course of the process itself. A study was therefore made[101] of the joint adsorption of sulfur dioxide and H_2O both in the absence of oxygen from the gas mixture and in its presence. The studies were performed by the thermal desorption method on SKT and AR-3 activated carbons and on the PK-2 semicoke. In another series of experiments, the saturated adsorbents were washed with distilled water and the content of H_2SO_3 and H_2SO_4 was then determined by titration.

a. The influence of water vapour on the adsorption of SO_2 from an oxygen-free mixture

Fig. 11 shows how water vapour influences the adsorption capacity of the SKT activated carbons.[101] The ratio of the contributions of physical adsorption and chemisorption in the sorption of SO_2 from a moist oxygen-free gas is determined not only by the nature of the adsorbent and the process temperature[95] but also by the water vapour content of the gas being purified. The appreciable increase in the adsorption capacity with increase in the H_2O content is due to the increase in the amount of chemisorbed sulfur dioxide (Fig. 11, curve *3*), since the physical adsorption of SO_2 (a_1) tends to diminish over the entire range of water vapour concentrations (curve *2*). This means that the presence of water on the surfaces of carbon adsorbents promotes the appearance of new centres for the chemical adsorption of SO_2.

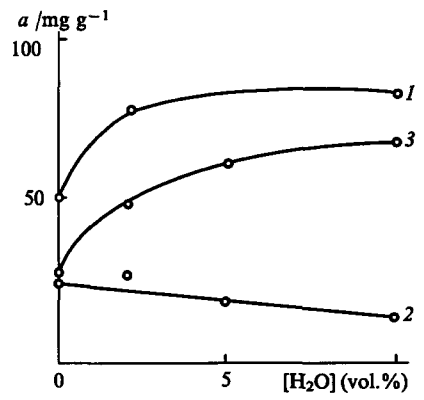


Figure 11. Dependence of the adsorption of sulfur dioxide from an oxygen-free mixture on the activated carbon SKT on the concentration of water vapour adsorption in the gas at 50 °C: (*1*) overall adsorption; (*2*) physical adsorption; (*3*) chemisorption.

The results of the chemical analysis of aqueous extracts, obtained as a result of the washing of saturated adsorbents with water, indicate the presence of sulfuric and sulfurous acids (Fig. 12). The amount of sulfur dioxide washed off the adsorbent in the form of sulfuric acid increases slightly with increase in the concentration of water vapour in the gas. On the other hand, the content of sulfurous acid increases to a much greater extent. This permits the conclusion that in the presence of water vapour the

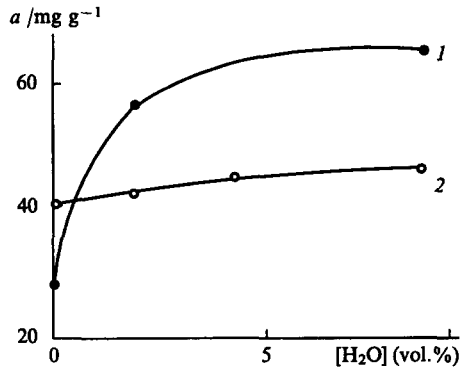


Figure 12. The influence of the concentration of water vapour on the composition of the aqueous extract from the carbon SKT saturated with sulfur dioxide at 50 °C: (*1*) sulfurous acid; (*2*) sulfuric acid.

degree of oxidation of sulfur dioxide to the trioxide does not increase. In all probability, the increase in the amount of chemisorbed SO_2 and hence the overall increase in the adsorption capacity of the carbons are induced by other chemical causes, which have a bearing on the presence of water on the surfaces of the adsorbents.

The mechanism of the adsorption of water vapour on activated carbons has been examined in detail.[58,102,103] It has been established that the adsorption capacity of a carbon in relation to water vapour depends greatly on the number of chemically bound oxygen atoms present on the surface as part of the composition of acidic surface oxides, which play the role of primary adsorption centres for water molecules. At low equilibrium pressures, adsorption is ensured mainly by the formation of hydrogen bonds between the water molecules and the primary adsorption centres. The adsorbed water molecules are secondary adsorption centres, which may include other molecules as a result of the formation of hydrogen bonds. With increase in pressure, the probability of adsorption increases as a consequence of the increase in the number of secondary absorption centres , i.e. the adsorbed molecules themselves.

Bearing in mind the ability of sulfur atoms to form hydrogen bonds,[127] one may postulate that in the case under consideration the preliminary adsorption of water on the carbon surface results in the appearance of a second variety of adsorption centre, namely adsorbed H_2O molecules, which may retain sulfur dioxide with the aid of hydrogen bonds. Thus, in the presence of water vapour in the gas phase, there are two types of active centres for SO_2 molecules on the carbon adsorbents: basic surface groups[30,50,51] and the protons of the sorbed water molecules, capable of forming hydrogen bonds with sulfur dioxide.[23,26] It is natural to postulate that an increase in the concentration of adsorbed water entails also an increase in the number of centres of the second type, which means an increase also in the total number of SO_2 adsorption centres. As a result, the adsorption capacities of the carbon adsorbents with respect to sulfur dioxide increase when the latter is sorbed from a moist gas.

However, one must not forget the possibility of the interaction of some of the sorbed H_2O molecules with the sulfur dioxide chemisorbed on the basic surface centres, resulting in the formation of sulfuric acid.[11] The molecules of the latter do not in all probability form strong bonds with the active centres and may be displaced to other sections of the adsorbent surface by virtue of diffusion, liberating the active centres for further oxidation of SO_2. A slight increase in the amount of sulfuric acid formed in the adsorption process with increase in the H_2O concentration (Fig. 12, curve *1*) can be explained by the fact that each active centre of the first type participates repeatedly in the oxidation process.

The sulfur dioxide bound by hydrogen bonds to the adsorbed water is not in the oxidised state and may be washed off the surfaces of the adsorbents with water in the form of sulfurous acid. This accounts for the marked increase in the H_2SO_3 concentration with increase in the concentration of H_2O (Fig. 12, curve *2*). On the other hand, under thermal desorption conditions, SO_2 may be removed from the surface only at temperatures in excess of 200 °C. This is in fact the reason why the quantity a_2 increases with increase in the concentration of H_2O (Fig. 11, curve *3*).

In conclusion, we may note that the influence of temperature on the adsorption capacities of carbon adsorbents is less marked than the influence of the concentration of water vapour. This can be explained by the partial compensation for the decrease in adsorption capacity with increase in temperature by the increase in the content of water vapour in the gas stream.

b. The influence of water vapour on the adsorption of SO_2 from a mixture containing oxygen

Analysis of literature data shows that the adsorption capacities of carbon adsorbents in the sorption of SO_2 from a gas containing simultaneously oxygen and water vapour are higher than in all the preceding cases. Fig. 13 shows how the concentration of water vapour influences the adsorption capacity of the AR-3 activated carbon and its components (a_1 and a_2) at 50 °C and a constant oxygen concentration of 5 vol.%.[101] With increase in the water vapour content in the gas being purified, the capacity of the adsorbent with respect to SO_2 also increases over the entire range of H_2O concentrations solely as a result of the chemisorption of sulfur dioxide (a_2). The fraction of SO_2 bound to the carbon surface by physical forces diminishes steadily.

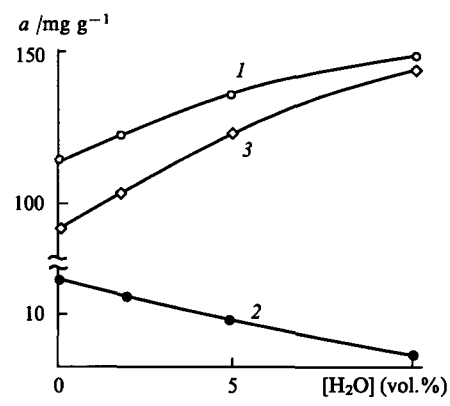


Figure 13. Dependence of the adsorption of sulfur dioxide from a gas containing 5 vol.% O_2 on the carbon AR-3 on the concentration of water vapour at 50 °C: (*1*) overall adsorption; (*2*) physical adsorption; (*3*) chemisorption.

According to the results of the chemical analysis of the solutions formed when the saturated adsorbents are washed with water, the liquid phase contains sulfurous and sulfuric acids (Fig. 14). The fraction of sulfurous acid in the wash waters ranges from 15% to 45% depending on the system parameters and increases with increasing concentration of water vapour.[128] On the other hand, the concentration of H_2O in the gas being purified hardly affects the content of sulfuric acid. In all probability, the high H_2SO_3 content in the wash waters can be accounted for by a deficiency of oxygen in the system, which prevents more complete oxidation of sulfur dioxide.

The results of the study of the influence of the oxygen concentration on the sorption of sulfur dioxide from a moist gas are presented in Fig. 15. They show that the amount of the oxidised product, washed off the adsorbents in the form of H_2SO_4, increases with increase in the O_2 content. At an oxygen concentration of 10 vol.% in the gas being purified, virtually complete oxidation of SO_2 is already attained: only sulfuric acid is present in the solution formed.

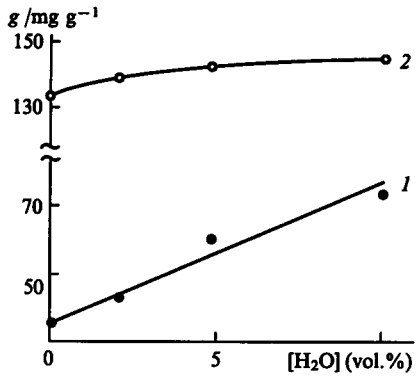


Figure 14. The influence of the concentration of water vapour on the composition of the aqueous extract from the carbon AR-3 saturated with sulfur dioxide at 50 °C in a gas containing 5 vol.% of O_2 (*1*) sulfurous acid; (*2*) sulfuric acid.

As in all the previous cases, an increase in temperature has a negative effect on the adsorption capacity, although this is manifested to a much smaller extent because the chemical component of the adsorption process is less subject to the influence of temperature.

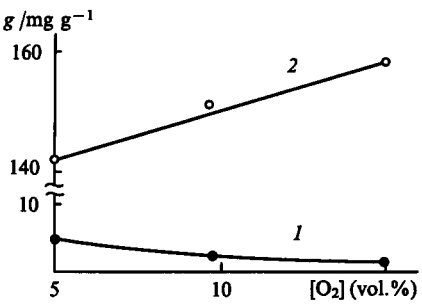


Figure 15. The influence of the concentration of oxygen on the composition of the aqueous extract from the carbon SKT saturated with sulfur dioxide at 50 °C in a gas containing 10 vol.% of H_2O: (*1*) sulfurous acid; (*2*) sulfuric acid.

III. The nature of the active centres for the adsorption of SO_2 on carbon adsorbents

1. Infrared spectroscopic study of the interaction of SO_2 with carbon adsorbents

IR spectroscopy is one of the few methods of physicochemical analysis which make it possible to assess quantitatively the nature of the processes occurring in the sorption of sulfur dioxide by optically opaque bodies such as carbon adsorbents, to discover the possible reactions between the components of the gas mixture, and also to identify the final products and the sites of the specific adsorption of SO_2 molecules.

Fig. 16 presents typical IR spectra of the Russian industrial activated carbons SKT, AR-3, and BAU, as well as a cellulose-based carbon adsorbent after their evacuation to a residual pressure of 10^{-4} mm Hg at 350 °C for 2 h.[40,41,104–107] In virtually all cases, weak absorption bands at 1750 and 1710 cm^{-1} and also moderately intense bands at 900 and 725 cm^{-1} are observed in the spectra of the activated carbons. Evidently the 1750 and 1710 cm^{-1} bands may be assigned to the stretching vibrations of the carbonyl groups.[108]

The 1600 cm^{-1} band is attributed to the C=O structures, in which the bond length is greater and the bond multiplicity is smaller than in the carbonyl groups absorbing at higher frequencies.[109] Similar structures are formed with participation of the π

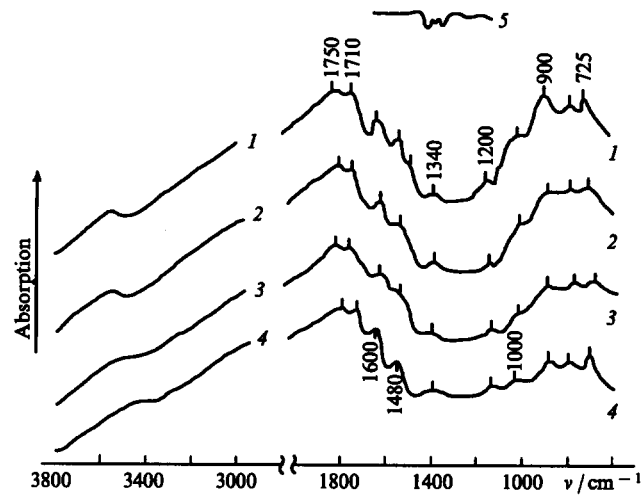
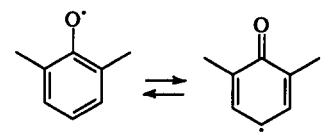


Figure 16. IR spectra of activated carbon evacuated to a residual pressure of 10^{-4} mm Hg at 350 °C: (*1*) AR-3; (*2*) SKT; (*3*) BAU; (*4*) KAD-iodine; (*5*) gaseous SO_2.

electrons of condensed aromatic systems. In all probability, they can be assigned to the radical-ion structures C⁻=O, which are intermediate forms on the way to the formation of carbonyl groups strongly bound to the carbon surface.[104,106,107,110]



The absorption bands in the range 1340–1480 cm^{-1} are characteristic of the deformation vibrations of the COOH groups.[111] The assignment of the bands in the range 1110–1130 cm^{-1} gives rise to difficulties. The band with a frequency of about 1120 cm^{-1}, observed in the spectrum of oxidised carbon black and graphite oxide, has been assigned[112–114] to the stretching vibrations of the C–OH bond, while the similar band (1065 cm^{-1}) in the spectrum of graphite oxide has been assigned[115] to the stretching vibrations of the C–OH enolic group. Finally, the absorption in the range 1000–1180 cm^{-1} is characteristic of the stretching vibrations of the C–O bond.[108]

Cooling of the adsorbents in a stream of air after preliminary evacuation at 350 °C leads to the appearance of intense absorption bands at 1800–1830, 1750–1770, 900, 725, and 1230–1250 cm^{-1} in the IR spectra of the specimens (Fig. 17, curve *2*). The presence of doubled bands (at 1830 and 1770 cm^{-1}) in the region of the deformation vibrations of the carbonyl groups C=O and also of intense bands at 900 and 725 cm^{-1} indicates the

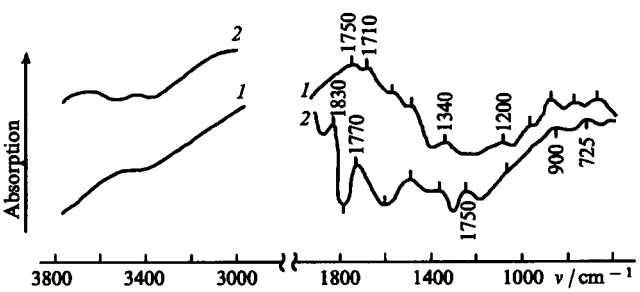
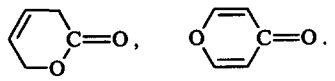


Figure 17. IR spectra of the activated carbon BAU evacuated to a residual pressure of 10^{-4} mm Hg at 350 °C (*1*) and subjected after this procedure to cooling in air to 20 °C (*2*).

dehydration of the carboxy-groups and the formation of cyclic aromatic systems with participation of π electrons.[106]

The intense 1250 cm^{-1} absorption band is characteristic of the vibrations of the C–O–C groups. This means that the most probable form of the basic surface oxides, formed on oxidation of the carbon in a stream of air, comprises unsaturated lactones, in particular α- and γ-pyrones or their derivatives:



Thus IR spectroscopic analysis confirms indirectly the existence on the surface of carbon adsorbents, in an anion-exchange form, of the pyrone structures predicted by Voll and Boehm.[67,68]

Analysis of the IR spectra of activated charcoals and semicokes saturated by sulfur dioxide from complex gas mixtures permits the conclusion that the adsorption of SO_2 on various carbon adsorbents proceeds via a single mechanism. The physical adsorption of sulfur dioxide, which does not require the presence on the surface of any kind of active centre, is accompanied by the appearance of absorption bands within the comparatively narrow range 1330–1360 cm^{-1} and at 1150 cm^{-1} (Fig. 18).

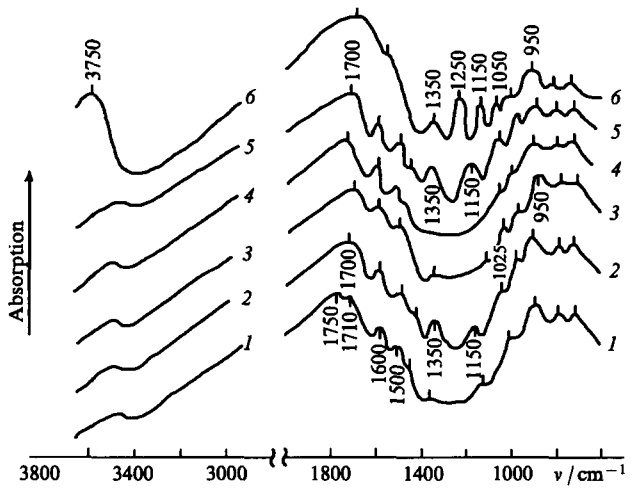


Figure 18. IR spectra of the activated carbon AR-3: (*1*) after evacuation to 10^{-4} mm Hg at 350 °C; (*2*) after saturation with sulfur dioxide at 50 °C; (*3*) after evacuation at 20 °C; (*4*) after saturation with sulfur dioxide at 100 °C; (*5*) after preliminary adsorption of SO_2 at 20 °C and subsequent saturation with oxygen; (*6*) after preliminary adsorption SO_2 and O_2 at 20 °C and subsequent saturation with water vapour.

Another portion of the sulfur dioxide is chemisorbed on particular active centres. The bathochromic shift of the 1740 cm^{-1} band, which is characteristic of the stretching vibrations of the carbonyl group, after the adsorption of SO_2 (to 1700 cm^{-1}) and also the fact that the C=O bond remains perturbed also after the removal of the physically sorbed SO_2 indicate that the surface carbonyl groups, playing the role of an electron donor, actually participate in the chemisorption of sulfur dioxide.

One cannot rule out also the interaction of SO_2 with the surface OH groups. Since the change in the stretching vibration frequency of the OH groups of the adsorbents persists also after the removal from the surface of weakly bound sulfur dioxide, one may postulate that SO_2 does not form hydrogen bonds with these groups. At the same time, the positions of the absorption bands of the OH groups and their appreciable half-width indicate the existence of a hydrogen bond. The only explanation of this may be the interaction of the adsorbed SO_2 with the surface hydroxy-groups involving the formation of bisulfites. However, judging from the intensity of the 1075 cm^{-1} band in the spectrum, the contribution of such interaction is low.

After the adsorption of sulfur dioxide in the presence of water vapour, a broad intense band at 3600 cm^{-1} as well as a moderately intense band in the range 1045–1073 cm^{-1} appear in the IR spectra of virtually all the adsorbents. These refer respectively to the vibrations of the OH groups of the adsorbed water and of the S–O bisulfites. It is natural to postulate that sulfurous acid is formed on the surfaces of the adsorbents as a result of the interaction of sulfur dioxide with the adsorbed water molecules.

The adsorption of the molecular form of SO_2 may not involve solely the formation of a physical bond with the surface. There is also a possibility of strong adsorption, observed for example, on the SKT and BAU activated carbons. It has been noted[116] that SO_2 is capable of forming molecular complexes with pyridine, triethanolamine, and triethylamine, in which sulfur dioxide exhibits the properties of an electron pair acceptor. The absorption bands corresponding to the S–O vibrations, undergo a bathochromic shift in the spectra of such complexes compared with the absorption bands of the free molecule. The surface O^{2-} ions may serve as electron donors in the formation of a complex with the adsorbed SO_2.[117,118]

$$C....O^{2-} + SO_2 \longrightarrow C....SO_3^{2-}.$$

The presence of oxygen in the gas leads to the oxidation of the chemisorbed SO_2 with formation of sulfate ions:

$$C....SO_3^{2-} + \tfrac{1}{2}O_2 \longrightarrow C....SO_4^{2-}.$$

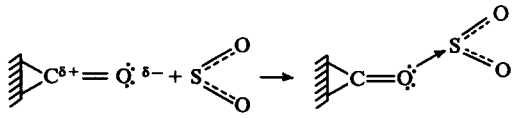
The spectrum of the SO_4^{2-} ions depends to a large extent on the presence of water vapour in the system.

Thus the study of the IR spectra has shown that the strength and nature of the interaction of sulfur dioxide with the surfaces of carbon adsorbents are determined both by the chemical nature of the latter and the composition of the gas mixture. Part of the SO_2 is then sorbed as a result of dispersion (physical) forces in the form of molecularly adsorbed sulfur dioxide. This process, which is not related to the presence on the surface of particular active centres, is accompanied by the appearance of absorption bands in the comparatively narrow range 1330–1360 and at 1150 cm^{-1}.

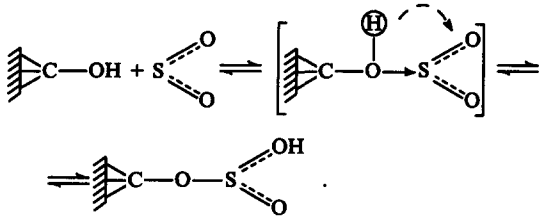
Another portion of sulfur dioxide is bound to the surface by stronger (chemical) forces. This chemisorbed SO_2 is converted on the surfaces of activated carbons and semicokes into sulfur compounds with different degrees of oxidation.

2. The chemistry of the adsorption of SO_2 from a dry oxygen-free mixture

It was shown above that the amount of sulfur dioxide chemisorbed from a dry gas is directly proportional to the concentration of basic functional groups on the carbon surface. At the same time, spectroscopic data indicate unambiguously the existence of pyrone structures on carbons having basic properties. One can therefore postulate that the centres for the specific sorption of SO_2 molecules from a dry oxygen-free mixture are basic oxygen complexes or more precisely, the carbonyl groups of pyrone derivatives. By virtue of the presence of the electron lone pair on the oxygen atom, the carbonyl group possesses weakly basic properties and interacts chemically with sulfur dioxide, which exhibits in this instance the properties of a Lewis acid:



The slight change in the vibration frequency of the OH groups on virtually all activated carbons and semicokes after the removal of the physically adsorbed SO_2 indicates the involvement in the process of surface hydroxy-groups:



(2)

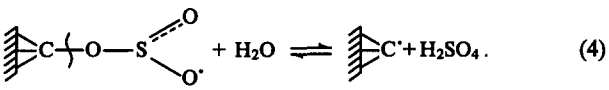
The formation of sulfite compounds on the surfaces of carbon adsorbents has been confirmed also by the existence of absorption bands at 1070, 1025, and 950 cm^{-1} in the IR spectra of all the adsorbents.

Thus the strongly bound form of SO_2 may be regarded as the intermediate sulfite compound $C-OSO_2$, in which the sulfur retains the +4 oxidation state. The amount of heat evolved in this process should not be large. Indeed, the isosteric heats of adsorption are 25–63 kJ mol^{-1} depending on the type of adsorbent. At low temperatures, the final product of the adsorption-catalytic process remains on the adsorbent surface and blocks the active sites. At fairly high temperatures, the chemisorbed SO_2 passes to the gas phase in the form of sulfur dioxide.



(3)

When the carbon adsorbent saturated with sulfur dioxide comes into contact with water, the chemisorbed SO_2 is abstracted from the surface in the form of sulfuric acid:



(4)

The process proceeds at room temperature and is accompanied by the transfer of electrons from the sulfur atom to the oxygen atoms and the reduction of the surfaces of the adsorbents with formation of electronic defects of the type of oxygen vacancies.

3. The chemistry of the adsorption of SO_2 from a dry oxygen-containing mixture

If O_2 is present in the gas phase during the adsorption of sulfur dioxide by carbon adsorbents, then not only chemically but also physically adsorbed oxygen participates in the oxidation of SO_2. Detailed study of the catalytic properties of carbon in the oxidation reactions of various substances led to the conclusion that the process proceeds via a radical-chain mechanism.[119–123] In conformity with this hypothesis, oxygen radical-ions are formed in the first stage of the process as a result of the transfer of electrons from heteroatoms via conjugated bonds to physically sorbed O_2:

$$O_{2,g} \longrightarrow O_{2,ads} + \bar{e} \longrightarrow O_2^{-}. \quad (5)$$

The next oxidation stage determines the order of the reaction with respect to oxygen (0.5) and the overall rate of the process:

$$O_2^{-} + \bar{e} \longrightarrow 2O_2^{-} + 2\bar{e} \longrightarrow 2O^{2-}. \quad (6)$$

The sources of electrons for the formation of superoxides are structural nitrogen atoms and the CN groups, which enter the lattice of the carbon adsorbents, as well as variable-valence metals (M) introduced into the adsorbents to activate and modify them:[121, 124, 125]

$$\equiv N \rightleftharpoons \equiv N^{+} + \bar{e},$$

$$M^{n} \rightleftharpoons M^{(n-1)} + \bar{e}.$$

The oxygen radical-ion structures (O^{-} and O_2^{-}) the existence of which on the surfaces of activated carbons and semicokes is confirmed by the presence of an intense 1600 cm^{-1} absorption band in the IR spectra, actually initiate the conversion of SO_2 into SO_3:

$$C....O_2 + \bar{e} \longrightarrow C....O_2^{-} + \bar{e} \longrightarrow C....2O^{-} + SO_2 \longrightarrow \longrightarrow C....O...OSO_2 \longrightarrow C....O^{-} + SO_3, \quad (7)$$

$$C....O^{-} + SO_2 \longrightarrow C....O—SO_2 \longrightarrow C....O_2^{-} + \bar{e} \quad (8)$$

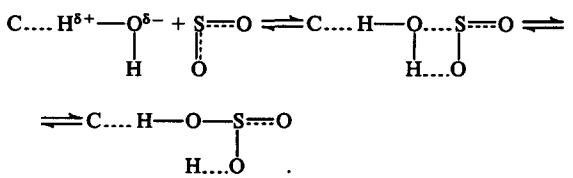
etc.

Another part of SO_2 enters into reactions (1) and (2) with the basic surface oxides of the carbon adsorbents, namely with the carbonyl groups of the pyrone structures and also with the surface hydroxyls, which is indicated by the presence of the 1075 and 1025 cm^{-1} absorption bands characteristic of sulfides in the IR spectra of virtually all activated carbons saturated with sulfur dioxide in the presence of O_2. Furthermore, after the desorption of the weakly bound SO_2, a change in the OH group vibration frequencies is observed in the adsorbents.

Thus the centres for the adsorption of sulfur dioxide from dry oxygen-containing mixtures are the oxygen radical-ions O^{-} and O_2^{-} as well as the carboxy- and hydroxy-groups of the pyrone structures.

4. The chemistry of the adsorption of SO_2 from a moist oxygen-containing mixture

If the gas streams contain water vapour and oxygen, then, apart from the centres in which reactions (1) and (2) as well as (7) and (8) occur, additional centres for the adsorption of sulfur dioxide appear on the surfaces of carbon adsorbents. The latter are the protons of the preadsorbed H_2O molecules.[23, 26] The appreciable increase in the adsorption capacities of carbons and semicokes under these conditions is due to the formation of hydrogen bonds between SO_2 and the water molecules sorbed beforehand. Sulfurous acid appears on the surfaces of the adsorbents as a result:



However, the role of water vapour does not reduce solely to the formation of new active centres for the adsorption of sulfur dioxide. In all probability, some of the H_2O molecules react during adsorption on the carbon surface with the chemisorbed sulfur dioxide (in the form of either SO_3 or SO_3^{2-}), forming sulfurous and sulfuric acids. The acids do not form a strong bond with the active centres and are displaced by diffusion to other sections of the surfaces of the adsorbents, liberating the active centres for further chemisorption of new SO_2 molecules. Thus each active centre can participate repeatedly in the adsorption process.

In the presence of oxygen, sulfurous acid is oxidised to sulfuric acid, i.e.

$$H_2SO_3 + \tfrac{1}{2}O_2 \rightleftharpoons H_2SO_4,$$

which is in fact the final product of the adsorption of sulfur dioxide on carbon adsorbents. The presence of H_2SO_4 on the surface has also been confirmed by IR spectroscopic analysis (there are absorption bands at 1160 and 1240 cm^{-1} in the IR spectrum).

IV. Conclusion

Summarising, one may say that the adsorption of sulfur dioxide on carbon adsorbents from gas mixtures of different composition is an adsorption-catalytic process, which consists of several stages and leads to the formation of compounds of sulfur in different oxidation states. The adsorption of sulfur dioxide occurs only on adsorbents in an anion-exchange form; oxidised carbon hardly adsorbs SO_2.

Two types of bonds between sulfur dioxide and the carbon surface are distinguished — a weak bond which is characterised by a heat of absorption < 50 kJ mol^{-1} and may be ruptured at a temperature < 150 °C, and a strong bond (heat of adsorption > 80 kJ mol^{-1}) ruptured at temperatures above 200 °C. The weak bond is due to van der Waals forces and corresponds to the physical adsorption of SO_2. The strong bond is formed as a result of chemical interaction between sulfur dioxide and the surface compounds and corresponds to the chemisorption of SO_2. In the latter case, the most likely centres for the specific adsorption of sulfur dioxide are surface carbonyl and hydroxy-groups of the pyrone structures and their derivatives, which have basic properties, the oxygen radical-ions (O^- and O_2^-), as well as the protons of the adsorbed water molecules.

The degree of oxidation of the adsorbed SO_2 depends on the nature of the adsorbent, the process temperature, and also the presence of O_2 in the gas mixture. Sulfur dioxide is partly oxidised to SO_3 also when SO_2 is sorbed from a dry oxygen-free gas. This is ensured by the oxygen weakly bound the carbon surface and forming part of the composition of the basic surface functional groups. The presence of water vapour in the gas phase promotes an increase in the adsorption capacity as a result of the formation of a strong hydrogen bond between the molecules of the pre-adsorbed water and SO_2, but the amount of oxidised sulfur dioxide does not increase under these conditions.

The removal of the reaction products from the adsorbent surfaces can be achieved by heating the adsorbents in a stream of an inert gas or by washing with water. The liberated active centres can again participate in the process.

The carbon adsorbents employed in the processes involving the removal of sulfur dioxide from industrial and ventilation gases must satisfy the following principal requirements:

— they must have an extensive pore structure;

— they must exist in the anion-exchange form, i.e. they must possess basic properties;

— they must contain an appreciable amount of structural nitrogen;

— as far as possible, they must include in their composition catalysts for the oxidation of sulfur dioxide to the trioxide.

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