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Physical Adsorption of Hydrogen Sulfide in Micropores of Zeolite and Activated Carbon

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Adsorption isotherms of hydrogen sulfide on zeolite and activated carbon were obtained by a gravimetric method at 20° and 30° in order to elucidate the thermodynamic properties of adsorption of hydrogen sulfide in micropores of zeolite and activated carbon. The Dubinin-Astakhov equation could be applied to these adsorption isotherms. The net differential heat of adsorption q and the differential molar entropy of adsorption ΔS were calculated from the adsorption isotherms by using the following equations: $q = E[(\ln a_0/a)^{1/n} + \alpha T/n\ (\ln a_0/a)^{1/n-1}]$ and $\Delta S = -\alpha E/n\ (\ln a_0/a)^{1/n-1}$. In all cases, q decreased with increasing degree of filling of micropores. It was considered that the micropores of zeolite and activated carbon are successively filled with hydrogen sulfide from the smallest pores to the largest ones. The differential molar entropy of adsorption became smaller with increase in the degree of filling. This entropy change suggests that hydrogen sulfide molecules are compactly filled in the micropores at the final stage of filling.

Keywords——hydrogen sulfide; microporous adsorbent; net differential heat of adsorption; differential molar entropy of adsorption; Dubinin-Astakhov equation

Hydrogen sulfide, which is often discharged into the atmosphere from paper-making factories, oil refineries, *etc.*, has a noxious odor and is toxic. We have studied the properties of various adsorbents which might be useful to remove hydrogen sulfide[1,2] and we also investigated the mechanism of adsorption of hydrogen sulfide on activated carbon.[3]

The present paper describes the thermodynamic properties of adsorption of hydrogen sulfide in micropores of zeolite and activated carbon on the basis of the net differential heat of adsorption and the differential molar entropy of adsorption.

Experimental

Materials——Hydrogen sulfide gas was of certified reagent grade (Seitetsu Kagaku Co.) and its purity was indicated to be 99.9%. Zeolite and activated carbon were commercial products, and their particle sizes were 1—16 mesh. Their physical properties are given in Table I.

Procedure for Adsorption——Adsorption isotherms of hydrogen sulfide on adsorbents were determined in an all-glass vacuum system similar to that described previously.[1] The adsorbent was dried at 110° for 1 hr at 1×10^{-3} Torr before use, and the decrease in the weight of adsorbent due to heating was corrected for. Equilibrium amounts of hydrogen sulfide adsorbed at pressures up to 500 Torr were measured by a gravimetric method by using a B.E.T. apparatus with a spring balance at 20° and 30°.

Results and Discussion

1. Adsorption Isotherms of Hydrogen Sulfide on Zeolite and Activated Carbon

Figure 1 shows adsorption isotherms of hydrogen sulfide on zeolite (Nos. 1 and 2) and activated carbon (Nos. 3 and 4) at 30° and at pressures up to 500 Torr. The adsorption isotherms of the zeolites rose sharply at about 100 Torr and then reached plateaux. However, the adsorption isotherms of the activated carbons rose gradually up to 500 Torr. It was con-

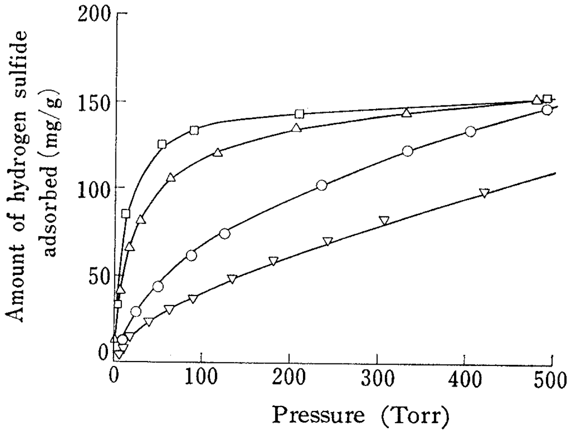

Fig. 1. Adsorption Isotherms of Hydrogen Sulfide on Adsorbents at 30°

□: No. 1 (molecular sieve 13X), △: No. 2 (molecular sieve 10 X), ○: No. 3 (activated carbon), ▽: No. 4 (activated carbon).

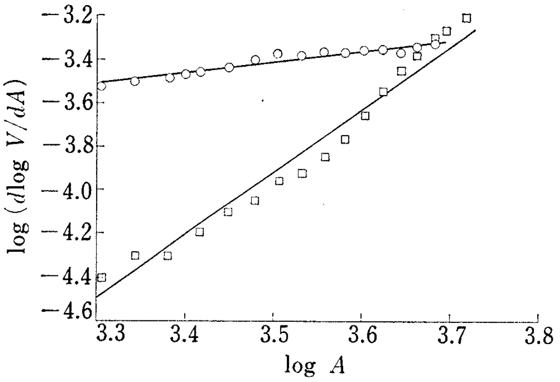

Fig. 2. Determination of n Value for Hydrogen Sulfide Adsorbed on Adsorbents

□: No. 1. ○: No. 3.

cluded that zeolite (Nos. 1 and 2) are preferred adsorbents for removing hydrogen sulfide in the range of low pressure.

2. Thermodynamic Properties of Adsorption of Hydrogen Sulfide

Dubinin and Astakhov[4] reported a thermodynamic equation for adsorption well fitted to express the characteristics of gas adsorption by a porous adsorbent on the basis of the potential theory of Polanyi.[5]

$$W = W_0 \exp[-(A/E)^n] \qquad (1)$$

$$A = \boldsymbol{R}T \ln(p_s/p) \qquad (2)$$

where W is the filled volume of the adsorption space, W_0 is the limiting volume of the adsorption space, A is the decrease of free energy of adsorption, E is the characteristic energy of adsorption at the characteristic point ($W/W_0=1/e=0.368$), n is a small integer, $\boldsymbol{R}$ is the gas constant, T is the absolute temperature, p_s is the saturated vapor pressure, and p is the equilibrium pressure.

The value of n was 2 for the adsorption of hydrogen sulfide on activated carbon.[3] However, since n is an adjustable parameter, there is no special reason why it should be an integer.

$$W/W_0 = V/V_0 \qquad (3)$$

where V (ml/g) is the volume of gas adsorbed at STP. If we substitute Eq. (3) into Eq. (1) and differentiate Eq. (4) in the logarithmic form

$$\log V = \log V_0 - A^n/2.303E^n \qquad (4)$$

we obtain

$$\log(d \log V/dA) = \log(-n/2.303\,E^n) + (n-1)\log A \qquad (5)$$

From the slopes of the straight lines obtained by the least-squares method, as shown in Fig. 2, the values of n were determined. The results obtained are listed in Table I. Figures 3 and 4 show the application of the Dubinin–Astakhov equation to adsorption isotherms on zeolite and activated carbon, respectively, at 20° and 30°. Linear relationships were found between log W and $A^{3.86}$ and between log W and $A^{1.49}$ for zeolite (No. 1) and activated carbon (No. 3), respectively. Similar linear relationships for other adsorbents were found between log W and A^n (No. 2; $n=2.85$, No. 4; $n=1.11$). The Dubinin–Astakhov equation is suitable for adsorption isotherms which correspond to the volume filling of micropores.[4] Therefore, it

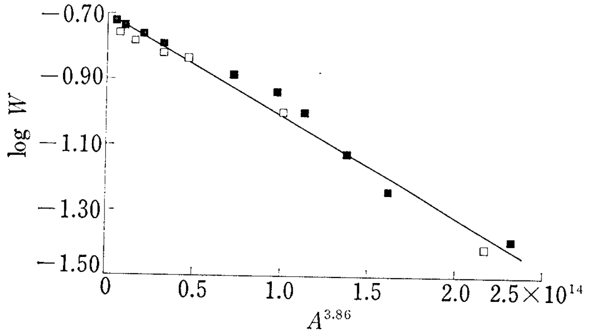

Fig. 3. Application of the Dubinin–Astakhov Equation to the Adsorption Isotherms of Hydrogen Sulfide on Adsorbent No. 1

■: 20°, □: 30°.

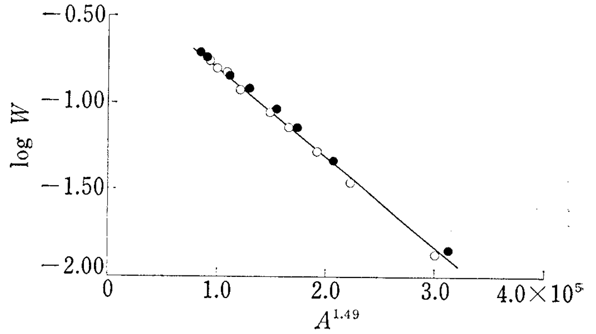

Fig. 4. Application of the Dubinin–Astakhov Equation to the Adsorption Isotherms of Hydrogen Sulfide on Adsorbent No. 3

●: 20°, ○: 30°.

appears that the adsorption of hydrogen sulfide on zeolites (Nos. 1 and 2) and activated carbons (Nos. 3 and 4) resulted in the volume filling of micropores.

Bering *et al.*[6] formulated, in thermodynamic terms, the qualitative differences between adsorption on non-porous and microporous adsorbents. It was shown that the basic equation describing adsorption on a non-porous adsorbent is the Gibbs equation, while the equation describing adsorption in micropores is the Gibbs–Duhem equation.[7] According to Bering *et al.*[8] and Dubinin,[7] it is possible to write the following expressions for the net differential heat of adsorption q (equal to the variation in the differential molar enthalpy of adsorption ΔH with a minus sign) and for the differential molar entropy of adsorption ΔS

$$q = -\Delta H = A - T[(\partial A/\partial T) + \alpha(\partial A/\partial \ln a)_T] \tag{6}$$

$$\Delta S = (\partial A/\partial T)_\theta + \alpha(\partial A/\partial \ln a)_T \tag{7}$$

where α is the coefficient of thermal expansion of the adsorbate, a is the amount adsorbed (mmol/g), and θ is the degree of filling of micropores ($\theta = a/a_0$; a_0 is the limiting amount adsorbed).

These equations are valid for adsorption in micropores under the condition $(\partial A/\partial T)_\theta = 0$.[8] Therefore, from Eqs. (6) and (7) we have

$$q = -\Delta H = A - \alpha T(\partial A/\partial \ln a)_T \tag{8}$$

$$\Delta S = \alpha(\partial A/\partial \ln a)_T \tag{9}$$

From Eq. (1) $W/W_0 = \theta = a/a_0 = exp[-(A/E)^n]$, we obtain

$$(\partial A/\partial \ln a)_T = E/n\,(\ln a_0/a)^{\frac{1}{n}-1} \tag{10}$$

and substituting this into Eqs. (8) and (9), we obtain expressions for the net differential heat of adsorption q and for the differential molar entropy of adsorption ΔS whose range of applicability is restricted by the thermodynamic criteria $\Delta S < O$ and $(\partial A/\partial T)_\theta = 0$.[8]

$$q = E[(\ln a_0/a)^{\frac{1}{n}} + \alpha T/n\,(\ln a_0/a)^{\frac{1}{n}-1}] \tag{11}$$

$$\Delta S = -\alpha E/n\,(\ln a_0/a)^{\frac{1}{n}-1} \tag{12}$$

Figure 5 shows the net differential heats of adsorption calculated from Eq. (11) for different temperatures and amounts adsorbed; the finding that q is independent of temperature substantiates Eq. (8). The larger the n value of the Dubinin–Astakhov equation (Table I), the larger was the net differential heat of adsorption at the same degree of filling of micropores. A molecule is in translation, and it is considered that the heat of adsorption increases with a decrease in the degree of freedom in its translation. The fact that the larger the n value, the larger was the net differential heat of adsorption can be consistently explained by assuming

TABLE I. Physical Properties of Adsorbents Used, Limiting Volume of Adsorption Space, Characteristic Energy of Adsorption ,and n Value of the Dubinin–Astakhov Equation

Adsorbent No.	Specific surface area (m^2/g)$^{a)}$	Micropore volume (ml/g)$^{b)}$	Total pore volume (ml/g)$^{c)}$	W_o (ml/g)	E (cal/mol)	n
1	429.7	0.186	0.250	0.1975	4634	3.86
2	479.2	0.225	0.287	0.2110	4175	2.85
3	958.6	0.395	0.557	0.5122	2029	1.49
4	1922.5	0.631	0.790	0.9225	1152	1.11

a) Ar gas-B.E.T. method.
b) Micropore volume is the volume at pore radii less than 15.5 Å.
c) Total pore volume is the volume at $p_e/p_s=1.0$ (adsorption isotherm of nitrogen).

that the n value signifies the extent of decrease in the degree of freedom, in molecular translation, due to adsorption. A similar interpretation of the n value has been suggested by Kawazoe *et al.*[9]

In all cases, the net differential heat of adsorption decreased with increasing degree of filling of micropores. According to the potential theory developed by Dubinin *et al.* the micropores of adsorbent are successively filled from the smallest pore to pores of large dimensions.[10] If the micropores of zeolites (Nos. 1 and 2) and activated carbons (Nos. 3 and 4) are consecutively filled with hydrogen sulfide from their smallest pores to their large pores, it is considered that the net differential heat of adsorption is larger for small pores, that is, at a smaller degree of filling than at a large degree of filling, because the smaller the pore dimensions, the larger is the decrease in the degree of freedom of hydrogen sulfide. The results obtained can be interpreted on the basis of the considerations described above.

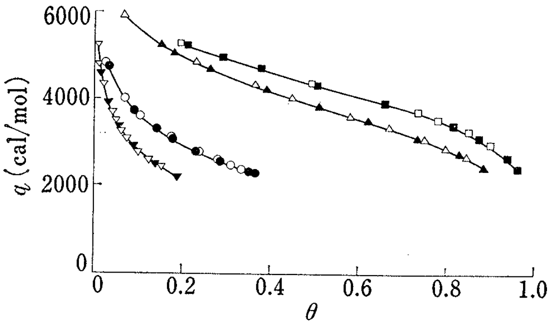

Fig. 5. Dependence of Net Differential Heat of Adsorption of Hydrogen Sulfide on Adsorbents upon the Degree of Filling

■: No. 1 at 20°, □: No. 1 at 30°, ▲: No. 2 at 20°, △: No. 2 at 30°, ●: No. 3 at 20°, ○: No. 3 at 30°, ▼: No. 4 at 20°, ▽: No. 4 at 30°.

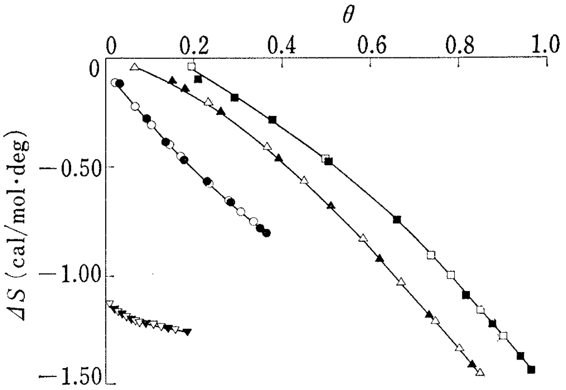

Fig. 6. Dependence of Differential Molar Entropy of Adsorption of Hydrogen Sulfide on Adsorbents upon the Degree of Filling

■: No. 1 at 20°, □: No. 1 at 30°, ▲: No. 2 at 20°, △: No. 2 at 30°, ●: No. 3 at 20°, ○: No. 3 at 30°, ▼: No. 4 at 20°, ▽: No. 4 at 30°.

The net differential heat of adsorption is closely related to the pore dimensions, that is, the degree of filling of micropores. It is, therefore, considered that when the dependence of the net differential heat of adsorption on the degree of filling is small, the micropore dimensions of the adsorbent are roughly the same. The fact that the dependence of the net differential heat of adsorption on zeolite (Nos. 1 and 2) upon the degree of filling is smaller than that of activated carbon (Nos. 3 and 4) can be explained by assuming that the zeolites consist of pores of approximately equal dimensions and that the activated carbons have pores of different dimensions, that is, they fill from the smallest pores successively to pores of a certain size.

Figure 6 shows the dependence of differential molar entropy of adsorption of hydrogen sulfide on zeolite (Nos. 1 and 2) and on activated carbon (Nos. 3 and 4) upon the degree of filling. The symbols denote the experimental points corresponding to the isotherms of adsorption at temperatures of 20° and 30°. The results obtained indicate that the relationship between ΔS and θ is independent of temperature (Eq. (9)). On transition from the normal liquid to the liquid adsorbate, entropy always decreases. The differential molar entropy of adsorption became smaller with increase in the degree of filling . This entropy change suggests that the hydrogen sulfide molecules are compactly filled in the micropores at the final stage of filling, that is, in pores of large dimensions.

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