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Adsorption of Hydrogen Sulfide on Activated Carbon

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Adsorption-desorption isotherms of hydrogen sulfide on activated carbon were obtained by a gravimetric method at 20°, 30°, and 40° in order to elucidate the mechanism of adsorption. Hysteresis loops of the isotherms were observed and it was confirmed that only extremely small amounts of hydrogen sulfide were chemisorbed. The Dubinin-Astakhov equation could be applied to these adsorption isotherms of hydrogen sulfide ($E=2580$—2748, $n=2$). Isosteric heats of adsorption of hydrogen sulfide on activated carbon Nos. 2 and 3 in the range of W/W_0 0.07—0.6 were less than twice the value of the heat of condensation ($\Delta H_0=4.43$ kcal/mol) and that of activated carbon No. 4 was more than twice the value of the heat of condensation. It was observed that activated carbon Nos. 2—4 consisted mainly of micropores smaller in radius than 15 Å. These results suggest that adsorption of hydrogen sulfide in micropores of activated carbon resulted in volume filling, that hydrogen sulfide was mainly physisorbed, and that high isosteric heat of adsorption in some cases, such as No. 4, was not attributable to chemisorption, but to the small size of the micropores.

Keywords——hydrogen sulfide; mechanism of adsorption; application of Dubinin-Astakhov equation; isosteric heat of adsorption; micropore structure; physisorption

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 for the removal of hydrogen sulfide.[2,3]

The present paper describes the mechanism of adsorption of hydrogen sulfide on the basis of application of the Dubinin-Astakhov equation[4] to the adsorption isotherm, isosteric heat of adsorption, and pore size distribution.

Experimental

Materials——Hydrogen sulfide gas was certified reagent grade (Seitetu Kagaku Co.) and its purity was indicated to be 99.9%. Activated carbon and zeolite were commercial products, and their particle sizes were 4—8 mesh.

Procedure for Adsorption——Adsorption-desorption isotherms of hydrogen sulfide on adsorbents were determined in an all-glass vacuum system similar to that described previously.[2] 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 using a B.E.T. apparatus with a spring balance at 20°, 30°, and 40°. The amount of adsorption is proportional to the difference in extension of the spring balance before and after adsorption. Spring balance extensions were measued with the aid of a cathetometer.

Isosteric Heat of Adsorption——The isosteric heat of adsorption was calculated from the adsorption isotherms at three different temperatures (20°, 30°, and 40°) by means of the Clausius-Clapeyron equation.[5]

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[2] S. Tanada and K. Boki, *Chem. Pharm. Bull.*, 22, 2703 (1974).

[3] K. Boki, *Nippon Eiseigaku Zasshi*, 32, 482 (1977).

[4] V.A. Astakhov, M.M. Dubinin, and P.G. Romankov, *Theo. Osn. Khim. Tekhn.*, 3, 292 (1969); M.M. Dubinin and V.A. Astakhov, "Molecular Sieve Zeolite II," ed. by E.M. Flanigen and L.B. Sand, Academic Press, Inc., London, 1971, p. 69.

[5] V. Ponec, Z. Knor, and S. Cerny, "Adsorption on Solids," (English translation edited by B.A. Smith and N.G. Adams), Butterworths, London, 1974, pp. 310—311.

From the equation $(\partial \log p/\partial 1/T)_{A,n_s} = -q_{st}/2.3\,\boldsymbol{R}$ (q_{st}, isosteric heat of adsorption; $\boldsymbol{R}$, gas constant; A, a constant surface area; n_s, a constant amount of gas adsorbed), the isosteric heat of adsorption was calculated from the slope of plots of log p *vs.* $1/T$, for a constant amount of gas adsorbed. The plots of log p *vs.* $1/T$ were linear over the temperature range from 20° to 40°. The values of p and T were read from the measured adsorption isotherms.

Pore Size Distribution——The pore size distribution curves of three kinds of activated carbons in the range of 7.5 to 300 Å were obtained by the method of Dollimore and Heal,[6] which applies the Kelvin equation to the adsorption isotherm of nitrogen on adsorbent at −195.8°, the calculation being performed on a FACOM 203-28S computer (Fujitsu Co., Ltd.) using a FORTRAN program.[3]

Results and Discussion

1. Adsorption-Desorption Isotherms of Hydrogen Sulfide on Adsorbents

Adsorption isotherms of hydrogen sulfide on activated carbon (Nos. 2—6) and zeolite (No. 1) at 30° and at pressures up to 500 Torr are shown in Fig. 1. The adsorption isotherms of activated carbon were dissimilar in form to that of zeolite. The adsorption isotherms of activated carbon (Nos. 2—6) rose gradually up to 500 Torr. However, the adsorption isotherm of zeolite rose sharply at about 50 Torr and then reached a plateau. The amount of hydrogen sulfide adsorbed on zeolite up to about 150 Torr was larger than those on activated carbon Nos. 2—4, and the results were similar to those previously obtained for hydrogen sulfide on activated carbon and zeolite at pressures up to 200 Torr.[3] It was concluded that zeolite (No. 1) and activated carbon (Nos. 2—4) were the preferred adsorbents for removing hydrogen sulfide in the ranges of low and high pressure, respectively.

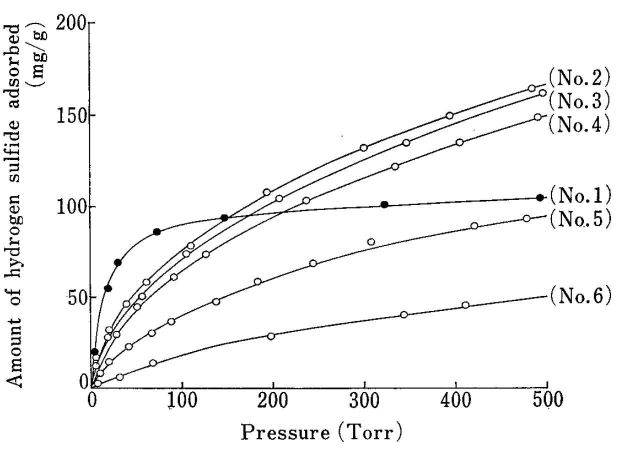

Fig. 1. Adsorption Isotherms of Hydrogen Sulfide on Adsorbents at 30°

No. 1: zeolite, Nos. 2—6: activated carbon.

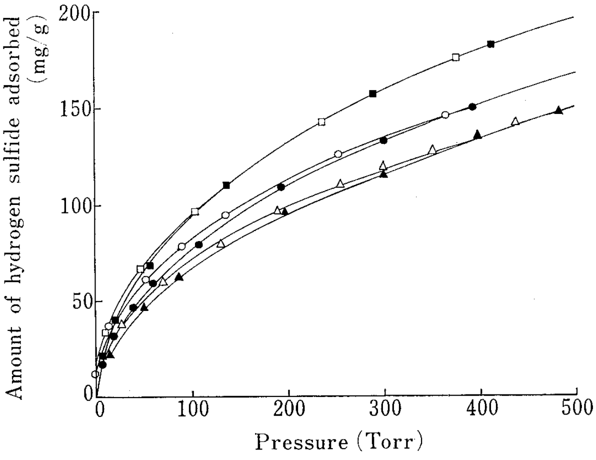

Fig. 2. Adsorption–Desorption Isotherms of Hydrogen Sulfide on Activated Carbon No. 2

■: adsorption and □: desorption at 20°, ●: adsorption and ○: desorption at 30°, ▲: adsorption and △: desorption at 40°.

In order to obtain information on desorption in connection with the regeneration of activated carbon used, the adsorption-desorption isotherms of hydrogen sulfide on activated carbon Nos. 2—4 were obtained and are shown in Figs. 2—4. The sizes and shapes of the hysteresis loops of the adsorption-desorption isotherms at 30° were similar to those at 40°, as shown in Figs. 2—4. The hysteresis loop of activated carbon No. 2 was limited to the range of 0 to 100 Torr (Fig. 2), while the size of the hysteresis loop of activated carbon No. 3 decreased (Fig. 3), and the hysteresis loop of activated carbon No. 4 disappeared (Fig. 4) as the temperature was lowered from 30° to 20°. The results obtained showed that the hysteresis phenomena were

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6) D. Dollimore and G.R. Heal, *J. Appl. Chem.*, **14**, 109 (1964).

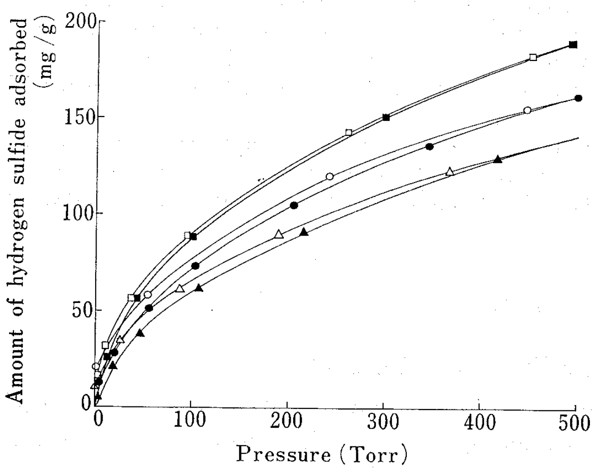

Fig. 3. Adsorption–Desorption Isotherms of Hydrogen Sulfide on Activated Carbon No. 3

■: adsorption and □: desorption at 20°, ●: adsorption and ○: desorption at 30°, ▲: adsorption and △: desorption at 40°.

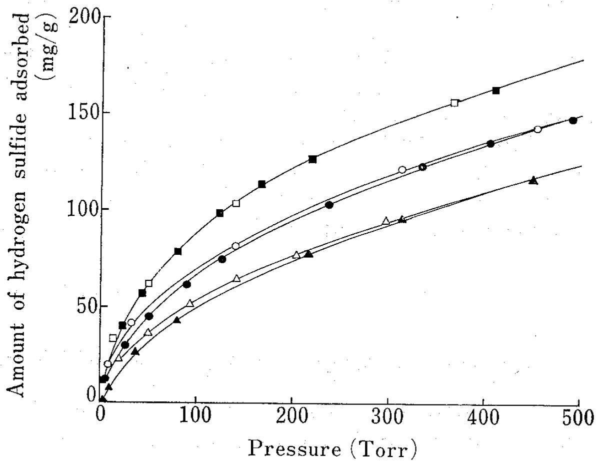

Fig. 4. Adsorption–Desorption Isotherms of Hydrogen Sulfide on Activated Carbon No. 4

■: adsorption and □: desorption at 20°, ●: adsorption and ○: desorption at 30°, ▲: adsorption and △: desorption at 40°.

temperature-dependent, and that the hysteresis loops increased in size with increasing temperature. After evacuation at 20°, 30°, and 40°, and at 1×10^{-3} Torr for 2 hr, small amounts of hydrogen sulfide were retained on activated carbon (No. 2, 10.3—12.5 mg/g; No. 3, 8.0—11.0 mg/g; No. 4, 8.2—8.9 mg/g). The lower the temperature of adsorption, the smaller were the amounts of hydrogen sulfide retained on the activated carbon after evacuation. The results of evacuation suggest that hydrogen sulfide was mainly physisorbed though an extremely small amount of hydrogen sulfide was chemisorbed on activated carbon Nos. 2—4. Thus, these activated carbons can be easily regenerated by pumping out hydrogen sulfide adsorbed.

2. Application of the Dubinin-Astakhov Equation to Adsorption Isotherms

Dubinin and Astakhov[4] reported a thermodynamic equation for adsorption that is well fitted to express the characteristics of gas adsorption by a porous adsorbent on the basis of the potential theory of Polanyi.[7]

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

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

$$(q_{st})_{1/e} = \Delta H_0 + E \qquad (3)$$

where W is the filled volume of the adsorption space, W_0 the limiting volume of the adsorption space, A the decrease of free energy of adsorption, E the characteristic energy of adsorption, n a small integer, $\boldsymbol{R}$ the gas constant, T the absolute temperature, p_s the saturated vapor pressure, p the equilibrium pressure, $(q_{st})_{1/e}$ the isosteric heat of adsorption at the characteristic point ($W/W_0 = 1/e = 0.368$), and ΔH_0 the heat of condensation.

Figures 5—7 show the application of the Dubinin-Astakhov equation to adsorption isotherms on activated carbon Nos. 2—4 at 20°, 30°, and 40°. Linear relationships were found between log W and A^2, as shown in Figs. 5—7. The Dubinin-Astakhov equation is suitable for adsorption isotherms which indicate the volume filling of micropores.[4] Therefore, it appears that the adsorption of hydrogen sulfide on activated carbon Nos. 2—4 resulted in volume filling of the micropores (pore radius$<$15 Å).[4] This is consistent with the results that activated carbon Nos. 2—4 consisted mainly of micropores smaller in radius than about 15 Å, as shown in Fig. 8. The limiting volume of the adsorption space (W_0) and the characteristic

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7) M. Polanyi, *Verh. Dtsch. Phys. Ges.*, **16**, 1012 (1914).

energy of adsorption (E) were estimated by extrapolation of the intercept to $A^2=0$ and from the slope, respectively, of the straight line obtained by the least-squares method. The results obtained are shown in Table I. The limiting volumes of the adsorption spaces of activated carbon Nos. 2—4 were 0.3332—0.3368 ml/g, and their characteristic energy was 2580—2748 cal/mol. When the exponent n is 2, the relation between E and ΔH_0 has been reported to be $E=2/3\Delta H_0$.[8] The heat of condensation of hydrogen sulfide ($\Delta H_0=4.43$ kcal/mol) was evalu-

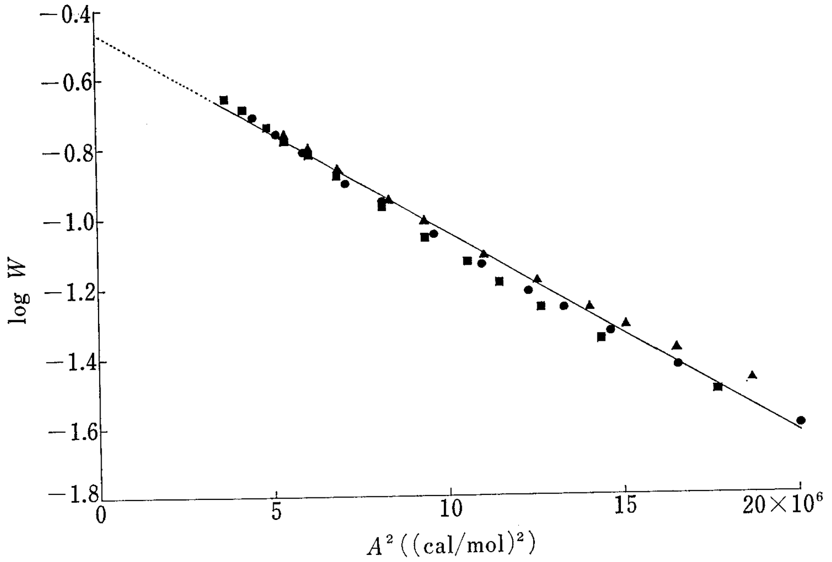

Fig. 5. Application of the Dubinin–Astakhov Equation to the Adsorption Isotherms of Hydrogen Sulfide on Activated Carbon No. 2

■: 20°, ●: 30°, ▲: 40°.

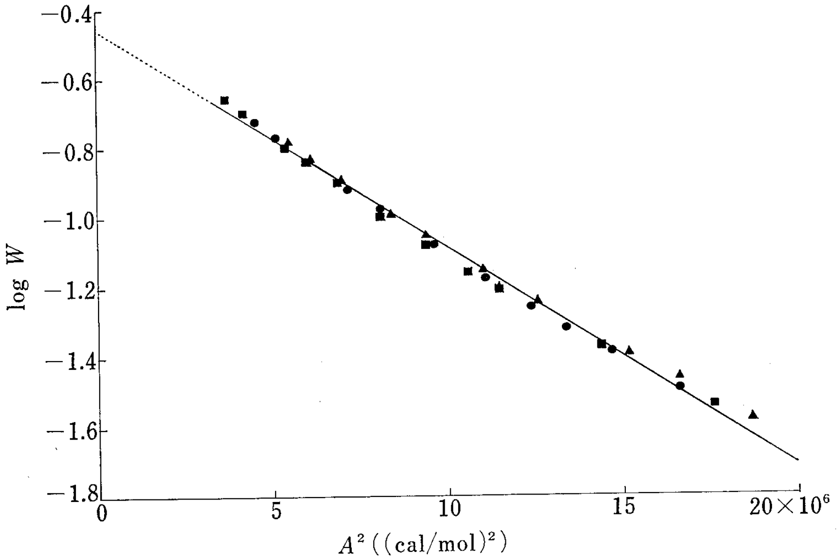

Fig. 6. Application of the Dubinin–Astakhov Equation to the Adsorption Isotherms of Hydrogen Sulfide on Activated Carbon No. 3

■: 20°, ●: 30°, ▲: 40°.

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[8] K. Kawazoe, V.A. Astakhov, and T. Kawai, *Seisan Kenkyu*, **22**, 491 (1970).

ated by fitting the Clausius-Clapeyron equation to the data[9] and it agreed well with the literature value ($\Delta H_0 = 4.46$ kcal/mol).[10] In this study the relation between the characteristic energy and the heat of condensation was also found to be $E = 2/3\Delta H_0$ at $n = 2$. The relation between the isosteric heat of adsorption (q_{st}) and W/W_0 (the dimensionless parameter W/W_0 expressing the degree of filling of micropores) is shown in Fig. 9. According to (3), the isosteric heat of adsorption at a characteristic point ($W/W_0 = 0.368$) is equal to the sum of the heat of condensation and the characteristic energy. This relation could be roughly applied to activated carbon Nos. 2 and 3. However, the isosteric heat of adsorption of activated carbon

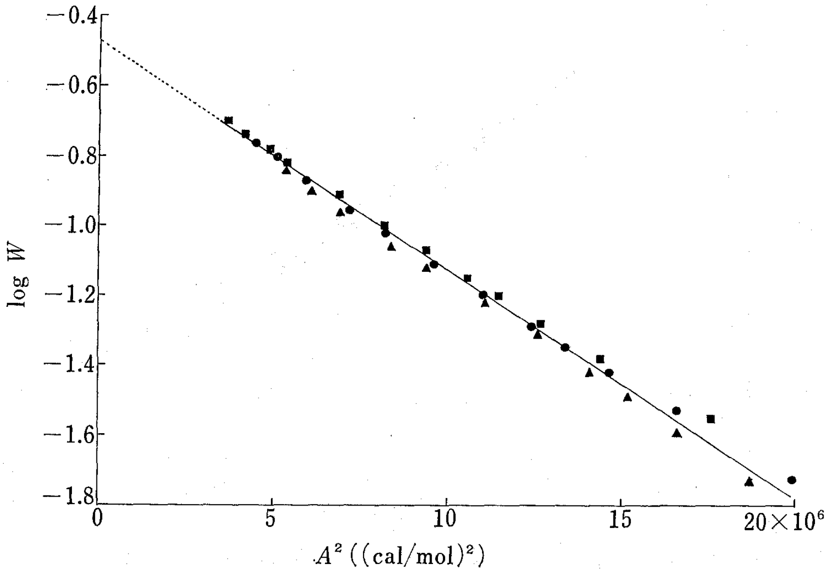

Fig. 7. Application of the Dubinin–Astakhov Equation to the Adsorption Isotherms of Hydrogen Sulfide on Activated Carbon No. 4

■: 20°, ●: 30°, ▲: 40°.

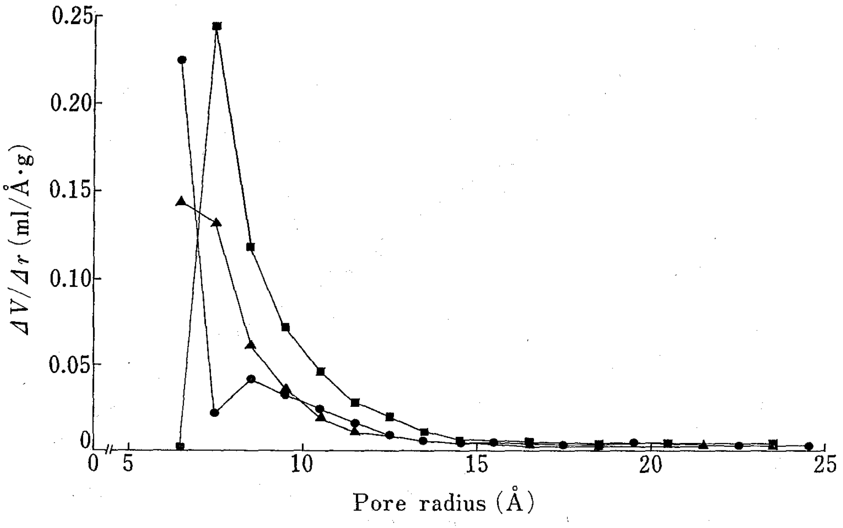

Fig. 8. Pore Size Distribution Curves of Activated Carbon Nos. 2—4

▲: No. 2, ■: No. 3, ●: No. 4.

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9) Chemical Society of Japan (ed.), "Kagaku Binran Kisohen II," (Handbook of Chemistry II) 2nd, Maruzen, Tokyo, 1975, p. 706.

10) R.C. Reid and F.K. Sherwood, "The Properties of Gases and Liquids," McGraw-Hill, New York, 1966, p. 157.

Table I. Limiting Volume of Adsorption Space, Characteristic Energy of Adsorption, n Value of the Dubinin–Astakhov Equation, and $(q_{st})_{1/e}$ vs. (ΔH_0+E) Relation

Activated carbon No.	W_0 (ml/g)	E (cal/mol)	n	$(q_{st})_{1/e}$ vs. (ΔH_0+E) (kcal/mol)
2	0.3368	2748	2	6.23≒(7.18)
3	0.3472	2629	2	6.50≒(7.16)
4	0.3332	2580	2	8.90>(7.01)

$(q_{st})_{1/e}$ was obtained from the plot of q_{st} vs. W/W_0 in Fig. 9.

No. 4 was about 2 kcal/mol larger than the sum of ΔH_0 and E (Table I). The isosteric heat of adsorption of activated carbon No. 4 was larger than those of activated carbon Nos. 2 and 3 in the range of W/W_0 0.07—0.6. The isosteric heat of adsorption of hexane on small-pore activated carbon was considerably larger than that on nonporous activated carbon;[11] it has already been suggested that the isosteric heat of adsorption on activated carbon micropores whose dimensions are comparable to those of the molecules being adsorbed is larger than that on nonporous activated carbon.[12] Figure 8 expresses the increment of pore volume corresponding to a differential increase in pore radius. Activated carbon No. 4 consisted mainly of micropores with radii of less than 7.5 Å. Curve No. 2 exhibited a monotonous decrease with increase in pore radius. Curve No. 3 had a maximum at a radius of 7.5 Å, and activated carbon Nos. 2 and 3 consisted mainly of pores in the broad range of radii from 6.5 to 15 Å. It was observed that the larger the isosteric heat of adsorption, the larger the pore volume at radii of less than 6.5 Å. The results seem to indicate that the increase of isosteric heat of adsorption was mainly attributable to the difference in micropore radius of the activated carbons. If the isosteric heat of adsorption does not exceed twice the value of the heat of condensation, the process is defined as physical adsorption.[13] The isosteric heats of adsorption of activated carbon Nos. 2 and 3 were less than twice the value of the heat of condensation in the range of W/W_0 0.07 to 0.6, and therefore, hydrogen sulfide seems to be physisorbed on them in this range. According to the above definition,[13] hydrogen sulfide seems to be chemisorbed on activated carbon No. 4 in the range of W/W_0 0.07 to 0.35. However, the bulk of hydrogen sulfide is physisorbed; only an extremely small amount is chemisorbed. Isosteric heats of adsorption on most activated carbons fall smoothly from an initial high value to one close to the heat of condensation,[14] and therefore, in the range of less than W/W_0 0.06 only an extremely small amount of hydrogen sulfide seems to be chemisorbed on activated carbon Nos. 2—4. The results of applying the Dubinin-Astakhov equation to adsorption isotherms and isosteric heat of adsorption indicate that adsorption of hydrogen sulfide in micropores of activated carbon results in volume filling and involves mainly physisorption.

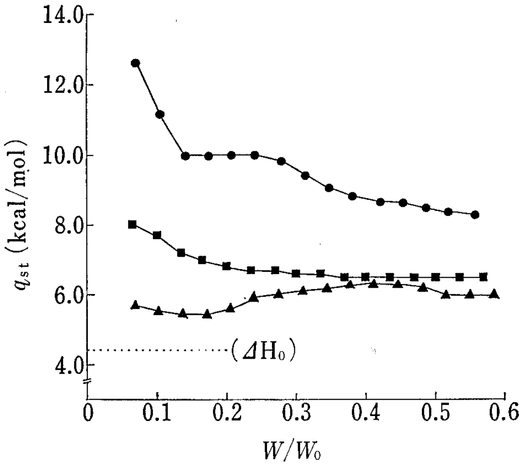

Fig. 9. Isosteric Heat of Adsorption vs. W/W_0

▲: No. 2, ■: No. 3, ●: No. 4.

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[11] N.N. Avgul, G.I. Berezin, A.V. Kiselev, and I.A. Lygina, *Zh. Fiz. Khim.*, **30**, 2106 (1956).

[12] M.M. Dubinin, *Chem. Rev.*, **60**, 235 (1960).

[13] W.J. Jones and R.A. Ross, *J. Chem. Soc.*, **1968**, 1787.

[14] E.A. Flood (ed.), "The Solid-Gas Interface," Vol. 2, Marcel Dekker, Inc., New York, 1967, p. 1016.