ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH. VIII. THE RELATION BETWEEN THE CATALYTIC ACTIVITY AND THE ADSORPTION.*

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In the previous paper(1) the behaviours of the chief constituents of Japanese acid earth in the catalytic action on naphthalene have been elucidated, and it has been noted that there exists the parallelism between their chemical compositions and catalytic activities. The present paper deals with the relation between their catalytic activities and adsorptive powers. The specimens of the acid earth used in the present investigation are the same as those mentioned in the previous paper and their general descriptions are here omitted.

The adsorptive power of the acid earth greatly depends upon the nature of adsorbates, i. e. upon their acidities or basicities, and therefore the catalytic activity on naphthalene was compared with adsorptive powers for neutral substances such as water, benzene, and naphthalene itself.

From the experiments described below on the adsorption of the various specimens of the acid earth for these neutral substances, it is concluded that the larger the surface area the greater is the catalytic activity. Therefore,

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(1) Inoue and Ishimura, This Bulletin, 9 (1934), 431.

if the catalysis does not take place on the whole surface uniformly but only on some particular parts, the active centres, then the distribution of these active centres on the surface is approximately equal for the various specimens of the acid earth, that is, the magnitude of the catalytic activity depends upon the surface area possessing active centres equally distributed but not on the number of the active centres on the equal surface area. On the other hand, the catalytic activity is closely connected with the chemical composition, as stated in the previous paper, so it may not be illogical to consider that the surface area is influenced by the chemical composition; the larger the ratio Al_2O_3/SiO_2 and the smaller the ratio $CaO+K_2O/SiO_2$, the greater is the surface area.

The Adsorption of Water. Six specimens of the earth were taken. Each of them was dried at 120°, powdered, and particles with mesh-size of 60–80 were sifted out, about 0.5 g. of which were taken into the weighing bottle, and heated at 300° in an electric furnace to a constant weight. The bottle was then put on a glass stand placed in a wide-necked bottle containing some distilled water in a thermostat of 25°. It was taken out at intervals and weighed. The amount of adsorbed water is plotted against time in Fig. 1. The letters assigned to the samples denote their order of the magnitude of the catalytic activity, earth A having the smallest activity and earth G the greatest as noted in the previous paper. Fig. 1 shows that a parallelism holds between the catalytic activity and both the adsorption velocity and capacity up to about 20 per cent. of water adsorbed.

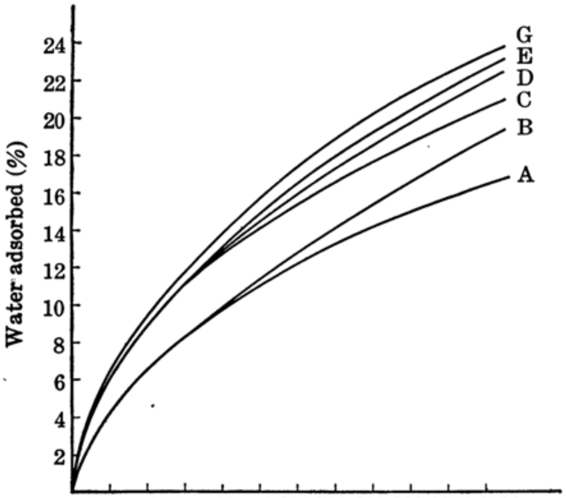

Fig. 1.

Adsorption velocity depends upon both the surface area and adsorption intensity, and so if adsorption intensity is constant the surface area only influences the velocity. The adsorption intensities of the acid earths for water may be taken constant after the whole surfaces are covered with several layers of water molecules. Since the amount of water sufficient to cover the whole surface of the earth in a monomolecular layer is about 2.5 per cent. of the weight of the dry earth, as will be shown in later communications, the adsorption intensities of the various specimens of the earth may be safely taken as constant after the amount of water several times as great as the above value has been adsorbed. However, the monomolecular film of water is not necessarily formed on the whole surface before the formation of any polymolecular layer begins(2) and, moreover, it cannot be admitted that layer adsorption only takes place all over the surface before there occurs capillary condensation even in the early stage of the adsorption under the experimental condition above mentioned. Yet if it is assumed that the distribution of radii of pores is of approximately the same probability for all specimens of the acid earth, then the adsorbed amount within certain limits can be regarded as collected on the surface by layer condensation only with a constant intensity, and therefore their adsorption velocities for water depend upon the surface areas only and the adsorbed amounts within those limits can be taken as measures of the surface areas, when the various specimens of the acid earth are taken into consideration in comparison with one another. Therefore it seems that the curves given in Fig. 1 can be interpreted as showing that the larger the surface area the greater is the catalytic activity.

The Adsorption of Benzene. The integral heats of wetting of the various specimens of the acid earth in benzene were compared by the method proposed by Berl and Andress(3) who have shown that the integral heats of wetting of porous materials such as active charcoals and silica gels can be taken as measures of their adsorptive powers and that ether isotherms for various charcoals are practically quantitatively related to the heats of wetting in benzene. The apparatus and manipulation were practically the same as those of Berl and Andress. The double wall was formed with two test-tubes of different sizes and a rubber stopper, and pure benzene (d_4^{25}, 0.8731) (10 c.c.) was poured into the inner tube fitted with a thermometer graduated to 0.1°. After the temperature became constant for about 5 minutes, the earth (sifted by a 200 mesh sieve and dried at 300° for one hour) (3.00 g.) was weighed out and rapidly put into the benzene, the thermometer being lifted meanwhile, and then serving as a stirrer. The change of temperature was recorded at the interval of one minute to 0.01°. In every case

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(2) In fact, the experiments to be described in the next communication seem to indicate that there remain some parts uncovered on the surface even in the neighbourhood of saturation.

(3) *Z. angew. Chem.*, **35** (1922), 722;

the mercury thread climbed to a maximum position within one minute and then gradually fell down. The sum of the rise and fall at the ends of the first two minutes was taken as a measure of the heat of wetting as proposed by the German authors. It is necessary to start each experiment at temperature not so different in order to keep all such heat measurements comparable. The results are shown in Table 1. In the fourth column, the catalytic activities on naphthalene measured by the yields of resinous matter are cited from the previous paper.(4)

Table 1.

Earths	Temperature changes	Means	Yields of resinous matter (g.)
A	0.84 0.89	0.87	1.65
B	1.53 1.57	1.55	1.82
C	1.71 1.74	1.73	1.86
D	1.71 1.93	1.82	1.90
E	2.38 2.19	2.29	2.10
F	2.63 2.66	2.65	2.23
G	2.87 2.59	2.73	2.60

The above results are quite analogous to those shown in Fig. 1; the catalytic activity goes parallel with the heat of wetting.

The heat evolved when solid is wetted by liquid is due to some surface phenomenon, but it is hardly conceivable that when liquid is stored in large pores it would give rise to the heat effect of measurable magnitude, hence the heat of wetting may be a function of both the intensity and capacity factors of adsorption,—whether it is the layer adsorption or the condensation in capillaries of molecular size or both—but not a function of the saturation capacity. A number of papers(5) have been published which show that the heat of wetting is a function of the surface area. It seems, however, that there must be an implied assumption that the surface is homogeneous or if heterogeneous there is no appreciable difference in the heat effect between the active and inactive parts(6) or, if any, it is negligible compared with the total heat evolved. The catalytically active parts on the surface of solid catalysts represent generally very small fraction of the total surface area(7) and

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(4) Loc. cit.

(5) Macy, *J. Phys. Chem.*, **34** (1931), 1397; Berl and Burkhardt, *Z. angew. Chem.*, **43** (1930), 332; Bartell and Fu, *Colloid Symposium Annual*, **7**, 135.

(6) Lamb and Coolidge found that the heats of adsorption of vapours are very nearly equal on inactive as on active charcoals of the same kind (*J. Am. Chem. Soc.*, **42** (1920), 1146).

(7) Rideal and Wright, *J. Chem. Soc.*, **127** (1925), 1352; Hoover and Rideal, *J. Am. Chem. Soc.*, **49** (1927), 122; Garner, Mckie and Knight, *J. Phys. Chem.*, **31** (1927), 644.

therefore even if the heat evolved on the adsorption of molecules directly held on these particular parts be much greater than on other parts or than of molecules localized on the upper parts of the adsorbed layers, their effect may be very small compared with the total heat quantity. Therefore the heat of wetting in general may be taken as an approximate measure of the surface area for the same kind of catalysts.

Thus the same conclusion may be attained from Table 1 that the larger the surface area the greater is the catalytic activity of the acid earth.

The values of the heat of wetting fall considerably as the drying temperature of the acid earth is raised. The temperature change due to the heat of wetting measured by the above-mentioned method is plotted against the drying temperature of earth F in Fig. 2. Each sample was dried at the required temperature for one hour. There may occur the sintering of catalyst mass causing the diminution of the surface area as temperature rises, yet at the same time more severe change of the surface may take place with the liberation of water, the nature of the acid earth thereby suffering the fundamental change as believed by many authors.(8)

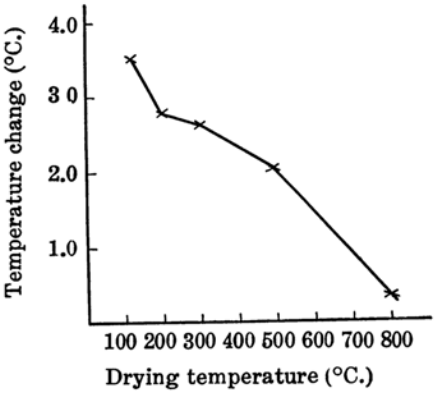

Fig. 2.

The heats of wetting of various materials other than the acid earth were compared by the same method. All of the samples are the same as those described in the previous paper.(9) The data are tabulated in Table 2,(10) in which the catalytic activities are also quoted from the previous paper.

It would be impossible to compare the surface areas of these substances of widely different natures by the heats of wetting, because their adsorption intensities for benzene would be greatly different from one another, though it is noticed that such substances as active charcoal and silica gel generally accepted as of very large surface areas evolve the larger heat quantities. There can be denoted no relationship between the heat of wetting and the catalytic activity given in Table 2.

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(8) Kobayashi, Yamamoto and Bito, *J. Soc. Chem. Ind. Japan*, **32** (1929), 298B; Kameyama and Oka, ibid., **32** (1929), 94B; Isobe, *Sci. Papers of Inst. Phys. Chem. Research, Japan*, **14** (1930), 229.

(9) Loc. cit.

(10) In case of voluminous substances such as active charcoal and diatomaceous earth 1.5 g. were taken and the observed values of the temperature change were doubled.

Table 2.

Subst.	Earth F	Earth F treated with HCl	Bentonite	Bentonite treated with HCl	Caoline	Clay I	Diatom. earth	Bauxite	Active charcoal	Silica gel a	$Al(OH)_3$ b
Temp. Change	2.65	3.18	2.93	2.11	0.45	1.02	0.91	5.13	6.80	6.60	4.57
Yields of resinous matter	2.23	2.33	0.25	2.89	0.81	0.33	0.22	0	0	0.03	0.02

As for bentonite, the surface area suffers little change by the treatment with hydrochloric acid, while its catalytic activity is increased greatly owing to the removal of poisons from the surface as suggested in the previous publication. In the case of the acid earth, its chemical composition and consequently its catalytic activity as well as its surface area is increased by a small degree by the same treatment.

The Adsorption of Naphthalene. Naphthalene has a very small vapour pressure at ordinary temperature and it will take a very long time for it to saturate adsorbents, while the complication of the apparatus and the difficulty of manipulation would be accompanied in experiments at high temperatures. A rigorous temperature regulation is not needed in the present experiment, since what is required is not the correctness of values but only relative adsorptive powers. So the experiment was carried out at room temperature as follows. About 0.5 g. of each acid earth (sifted by a 200 mesh sieve and dried at 300° for one hour) is weighed in a weighing bottle of the same size, put in a desiccator of sulphuric acid ($d = 1.84$), and left to stand for 7 days, and then a dish containing naphthalene, dried beforehand on sulphuric acid of the same specific gravity, is placed at the centre of the desiccator. Naphthalene is slowly adsorbed by the earth. The weighing bottle is taken out at intervals and weighed. The amount adsorbed is plotted against time as shown in Fig. 3. The increase or decrease in the weight of the earth due to the difference between the vapour pressure of the acid earth and that of sulphuric acid is negligible as a blank test has shown.

The magnitude of the surface area of the acid earth is of the order of about 10 square metres per gram as will be shown in later communication and it is very probable that the adsorbed naphthalene forms a monomolecular

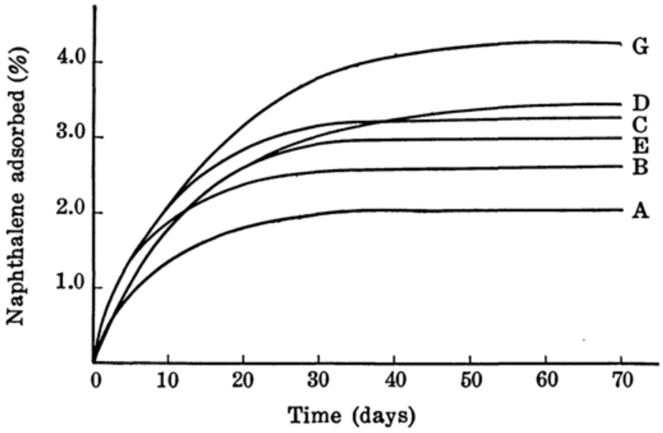

Fig. 3.

film on the surface,(11) if its molecular dimensions and the amounts adsorbed by the acid earths are taken into consideration.(12) Therefore, the surface areas of the earths may be roughly measured by the saturation capacities for naphthalene. Fig. 3 shows that the surface area goes parallel with the catalytic activity (with one exception of the earth designated E). Thus the author has come here again to the same conclusion.

As has been stated in the previous paper, the catalytic activity is almost entirely destroyed by the addition of about 3 per cent. of sodium hydroxide or lime. The surface area and consequently the amount of adsorbed naphthalene, however, will not change greatly as long as pores are not blocked up by the added matter. If, on the contrary, the amount added is large enough to block up some of small pores, then the diminution of the surface will occur, manifested by the decrease in the amount of adsorbed naphthalene. Plots given in Figs. 4 and 5 are in close agreement with the above speculation. There are three breaks in every curve, which seems to be unavoidable under the experimental condition mentioned above, since the temperature of the laboratory and the vapour pressure of naphthalene rose gradually as the experiment extended from the 8th of December, 1930, to the 4th of April, 1931.

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(11) It is improbable, however, that a perfect monomolecular film is always formed, for in the course of the adsorption of naphthalene the colour of the earths turns gradually from light yellow to brownish black, indicating that at room temperature there occurs already the catalytic action.

(12) The dimensions of naphthalene molecule are 8.68 by 6–7 by 3×10^{-8} cm. (Adam, The Physics and Chemistry of Surfaces, 1930, p. 95). A calculation shows that the area to be covered by 0.02 g. of naphthalene is 17.0–58.8 square metres according to the orientation of the molecules on the assumption of a packed monomolecular layer.

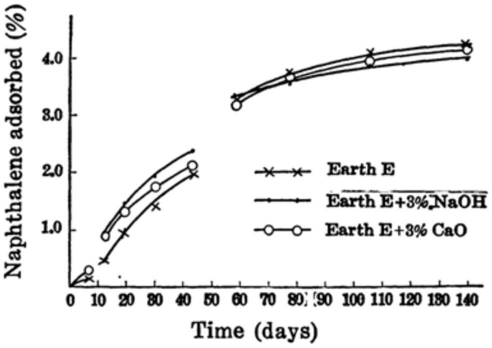

Fig. 4.

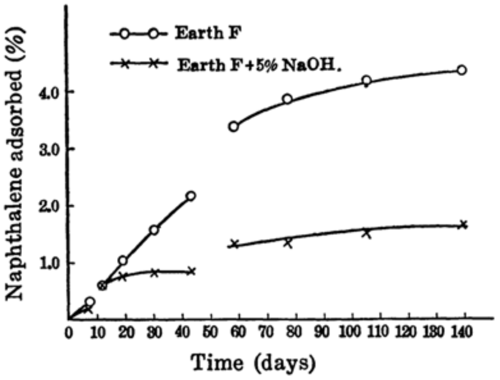

Fig. 5.

Fig. 6 shows the curves of the adsorbed amount plotted against time for several substances together with that for earth F. The substances are the same as those given in Table 2. The amount adsorbed by active charcoal is about ten times as great as that by the earth, and the surface of the former is also about ten times as large as that of the latter, as will be shown in later paper. It is very probable therefore that the surface areas of several materials of widely different natures also can be compared with one another by the saturation capacities for naphthalene. A close parallelism is observed also between the data given in Table 2 and Fig. 6.

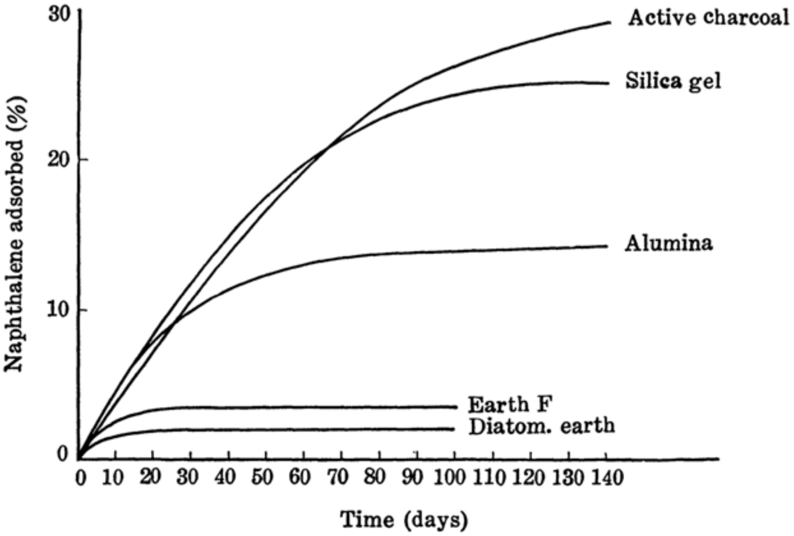

Fig. 6.

Summary.

(1) The catalytic activity of Japanese acid earth on naphthalene has been compared with its adsorptive powers for water, benzene, and naphthalene.

(2) The relations between the adsorptive powers and the surface area of the earth have been discussed.

(3) It has been concluded that the larger the surface area the greater is the catalytic activity and therefore the magnitude of the catalytic activity depends upon the surface area possessing active centres equally distributed but not on the number of the active centres on the equal surface area.

(4) The influence of the chemical composition of the earth on its surface area has been suggested.

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