

Adsorption and Desorption of Bromine by Graphites

By

Wataru FUNASAKA, Makoto KAWANE, Tatsuo KONADA,
and Yoshio ASANO

Department of Industrial Chemistry

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Abstract

Isothermal adsorption and desorption of bromine by graphites and other carbonaceous compounds have been studied at 30°C or 80°C. The results were as follows:

- i. Quantity of bromine adsorbed decreases with charcoal, graphite, soot and pitch coke in order. With graphites, adsorptive capacity of natural graphite exceeds that of artificial graphite.
- ii. Effect of grain surface area upon quantity of adsorption is small with charcoal and graphite.
- iii. Plotting the adsorption process curve on a full logarithmic section paper, it is found to be inflected with graphite and to be straight with the other kinds. The positions of inflexion and the inclinations of the inflected lines are characteristic with graphites.
- iv. It is assumed that the point of inflexion and the inclination may be related to degree of graphitizing.

Introduction

Adsorption (more strictly, "sorption") of bromine by graphite has been studied by many investigators.

W. Rüdorff and others^{1,2)} have described that graphite in saturated bromine vapor keeps always 83.5% bromine in weight (atomic ratio, C:Br=8:1) as liquid within its expanded inter-crystal layers by adsorption. On the other hand, R. Juza³⁾, G. M. Schwab⁴⁾ and M. Goldsmith⁵⁾ have proved, by measuring the magnetic susceptibility, that almost all of adsorbed bromine will be in a molecular state with a few C-Br conjugate or ion-combinations, the latter being weakened in inverse proportion to adsorption. While graphite desorbs bromine into free air by exposure¹⁾, G.

Henning⁶⁾ has shown, as Rüdorff²⁾, through his X-ray diffraction experiments, that a shifting of laminar lattice distance, during adsorption and desorption, makes a part of bromine remain as "compounds". He has shown also that such combined bromine may be found over portions of incomplete crystallization and around crystal borders in natural graphite, and may be at combining portions in artificial graphite.

Measuring the hysteresis curves of isothermal adsorption and desorption of bromine by several carbonaceous compounds, especially by graphites, we have been able to gain some results to be reported here.

Effect of Grain Size

The experiments to check the effect of grain size on the quantity of adsorption were carried out as follows.

Put 1-2 g. weighed samples of definite grain size into weighing bottles with well fitted-in stoppers, coated inside with bromine resisting grease, such as of polytrifluorochloroethylene. Lay the bottles, keeping the stoppers half fitted, in a desiccator with tightly fixed lid, greased as mentioned above. Thin glass bulbs filled with bromine, at the bottom of the desiccator, were crushed with lead weights, by making them fall over the bulbs, under reduced pressure, to fill the desiccator with bromine vapor. Keep the desiccator, with samples in it, in a thermostat of 40°C., for about 10 hours. Then, uncover the desiccator to fit the stoppers of the weighing bottles tight rapidly. The quantity of bromine adsorbed was found by the weight increase of the sample, and the gas concentration was calculated from the difference

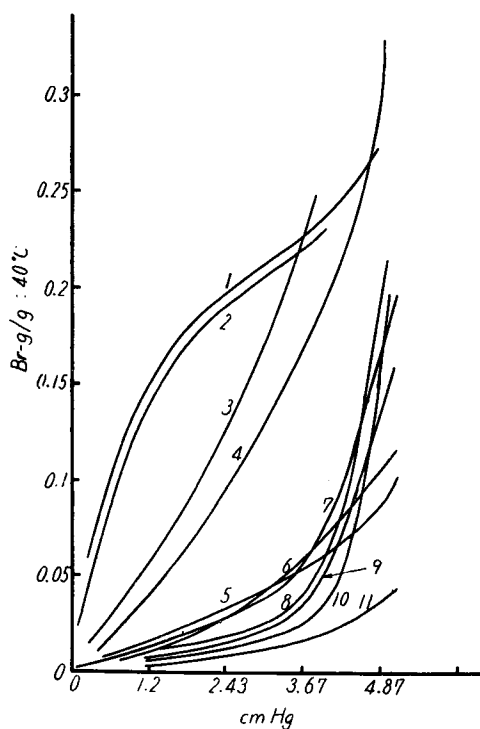


Fig. 1. Quantity of bromine (g./g. carbonaceous material) against pressure of bromine vapor.

1. Active carbon, 110-130 mesh
2. Active carbon, 90-110 mesh
3. Pitch coke, 130-170 mesh
4. Pitch coke, 110-130 mesh
5. Petroleum coke, 110-130 mesh
6. Pitch coke, 90-110 mesh
7. Artificial graphite #5, 110-130 mesh
8. Natural graphite (Ceylon), 110-130 mesh
9. Artificial graphite #5, 90-110 mesh
10. Natural graphite (Ceylon), 90-110 mesh
11. Petroleum coke, 90-110 mesh

between the quantities of original and total adsorbed bromine.

In spite of its tolerable error, this method seems to be worthy of recommendation for a handy process to compare the quantities of adsorption under the same condition with several samples, changing both temperature and bromine concentration. Fig. 1 shows the results gained with some carbonaceous materials of 90-170 mesh. Quantities of bromine adsorbed by active carbon, pitch coke and petroleum coke increase proportionally to their bromine pressure increase. In the case of graphite, a rapid adsorption increase at and above 0.30-0.35 g./l. Br_2 (3.7-4.2 cm. Hg Br_2) is also observed.

Effect of grain size, or effect of apparent surface area of grain, increases from active carbon to pitch coke through graphite in turn. It may be deduced that the effect of grain size will increase from active carbon with characteristic active center and capillar adsorptive capacity to those with additional factors for surface adsorption.

Measurement of Adsorption and Desorption

Fig. 2 shows the measuring device used. Variation of sample weight during

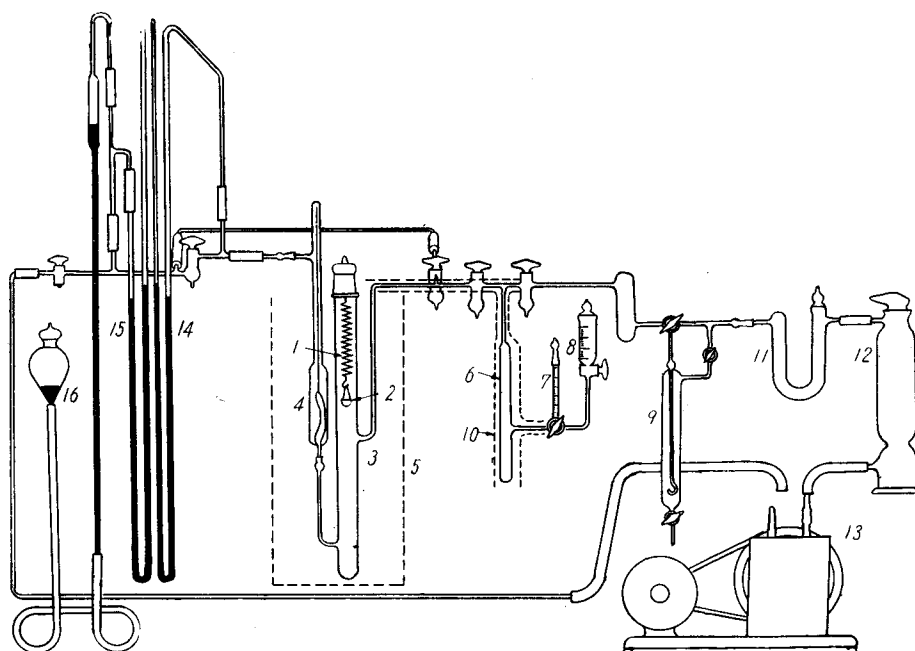


Fig. 2. Measuring device.

- | | |
|--|-----------------------------|
| 1. Spring balance, quartz | 2. Boat |
| 3. Adsorption and desorption tube | 4. Spoon gauge |
| 5. Thermostat | 6. Bromine evaporation tube |
| 7. Burette | 8. Bromine reservoir |
| 9. Bromine catcher (saturated sodium carbonate solution) | |
| 10. Steam heater | 11. Active carbon |
| 12. Active carbon | 13. Vacuum pump |
| 14-15. Hg-manometer | 16. Hg-reservoir |

adsorption and desorption was observed with a quartz spring balance, whose available and maximum loads were 1 g. and 2 g., respectively, and sensitivity 0.2 mg., suspended in the adsorption cylinder.

The sample was put in a glass dish of 100–150 mg. capacity, hung at one end of the spring. All the measurements were made at 30°C., keeping the adsorption cylinder within a water thermostat.

The pressure of bromine was measured with a mercury barometer, using a glass spoon gauge, sensitivity 2 mm. Hg, as a zero indicator.

The grease applied over ground parts of the adsorption cylinder was of Dow's silicone at normal temperature zone, and of polytrifluorochloroethylene at high temperature zone. Even these materials, however, could not resist long.

The samples were sieved to be retained between 170 and 200 mesh, and were dried for several days at 150°C. Bromine was redistilled before use.

As the samples expanded very rapidly during adsorption, we could only take into the sampling dish 100–200 mg. of them, equivalent to 60% of the dish cavity in volume, and put the whole in the adsorption cylinder. Under enough air-tight conditions, the cylinder was evacuated by a rotating vacuum pump sufficiently. So much bromine as would exert an expected pressure by vaporization was taken into an evaporation tube out of a bromine burette. Evaporation of

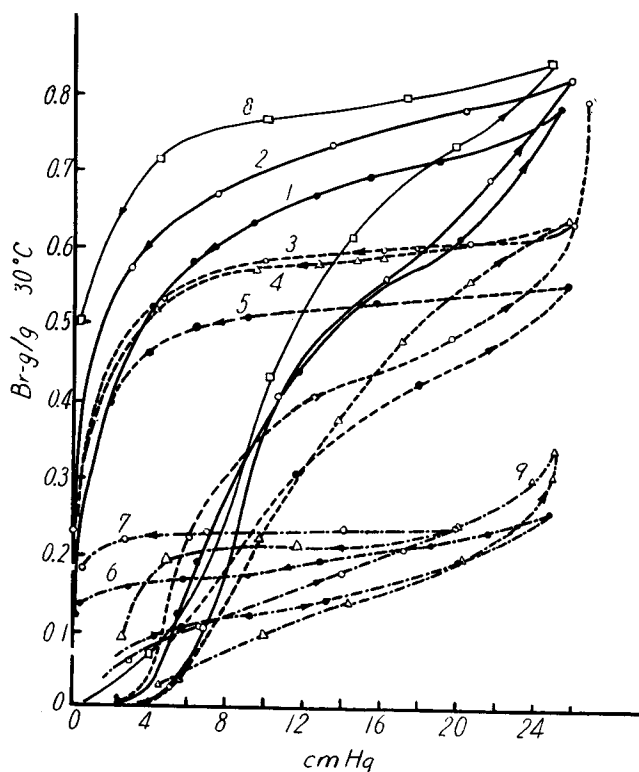


Fig. 3. Adsorption and desorption curve.

1. Natural graphite (Ceylon), 170–200 mesh
2. Natural graphite (Korea), 170–200 mesh
3. Japanese artificial graphite A, 170–200 mesh
4. Acheson's graphite, 170–200 mesh
5. Japanese artificial graphite B, 170–200 mesh
6. Petroleum coke, 170–200 mesh
7. Pitch coke, 170–200 mesh
8. Charcoal, 170–200 mesh
9. C-4 soot, 170–200 mesh

the bromine, by steam heating, was followed by saturation of the tube with the vapor. The quantity of bromine adsorbed was measured, after an hour, with a travelling microscope. And, at the same time, the pressure of bromine was measured. This procedure was repeated several times up to the apparent saturated pressure of bromine to be gained. During this operation, condensation of bromine inside the tube was observed very frequently, when its quantity exceeded a certain limit.

For measurement of desorption, the apparatus was evacuated with a water pump until 30 mm. Hg pressure was gained, and with a rotating vacuum pump, with a bromine adsorber, until the lowest pressure value for the pump suction was gained. But it was very difficult to measure the quantity of residual bromine at such a low pressure range, since it was fluctuated very much by any slightest pressure change.

While adsorption and desorption velocity is large for initial 15-20 minutes, it decreases to an almost constant value within 50-60 minutes, and then it shifts to an equilibrium state very gradually.

Though it takes 1 or 2 days to get complete equilibrium⁶⁾, we only plot every reading at an hour later, on the assumption that it is an apparent stable value. The results of the measurements are shown in Fig. 3.

It is noteworthy that natural graphite expands its volume rapidly at the bromine pressure 8-12 cm.

Considerations

The quantity of bromine adsorbed by graphite has been proposed as a measure of degree of graphitizing. The results can be arranged in order according to the quantity of bromine adsorbed, as charcoal > natural graphite A (Korea, flake) > natural graphite B (Ceylon, flake) > Acheson's artificial graphite > Japanese artificial graphite A > Japanese artificial graphite B > C-4 soot > pitch coke > petroleum coke (Great Lake). Though adsorptive capacities differ very much among the members owing to their carbon properties, the order seems to coincide with that determined by other methods.

Hysteresis curves can be classified into three categories. They take an S-form in common, and it is most evident with those for graphites. Freundlich's isothermal equation is regarded to be applicable to low pressure and low temperature adsorption by these materials.

Although hysteresis curves can be classified in three types, they can also be classified in four patterns by plotting them on a full logarithmic section paper (the results are shown in Fig. 4), as charcoal, natural graphite, artificial graphite and pitch coke. Adsorption process of graphite is presented by an inflected line with different positions of inflexion. Moreover, their inclinations might be classified in two

groups, natural and artificial graphites, and the inclinations for the latter run parallelwise. Curves for charcoal and pitch coke run straight. The quantity of adsorption by charcoal is large and that by pitch coke is small. Inclination of the adsorption curve for charcoal is large and that for pitch coke is small.

Adsorption process by natural graphite is expressed with an inflected straight line, whose point of inflexion lies at about 9 cm. Hg bromine pressure. So it may be easily imagined that two types of adsorption, differing in their mechanism, are in contact at the point of inflexion. On the other hand, it takes a rapid volume increase at about 8-12 cm. Hg pressure.

Supposing the existence of capillar diameter can be calculated with Kelvin's equation, as

$$D = \frac{4.V.\gamma.\cos\theta}{R.T.\ln(p_0/p)}$$

- where V : molecular volume, 47 cm³/mole,
 γ : surface tension, 40 dyne/cm., 30°C.
 p_0 : saturated vapor pressure, 26.4 cm. Hg, 30°C.
 p : bromine vapor pressure, 9 cm. Hg,
 R : 8.31×10⁷ erg/°K, mole,
 T : 303.2°K,
 θ : angle of contact.

If θ be 0°, $D \approx 3 \times 10^{-8}$ cm., corresponding to the laminar lattice distance of perfect graphite crystal, 3.41Å.

According to the Rüdorff's study on X-ray diffraction, the laminar lattice distance

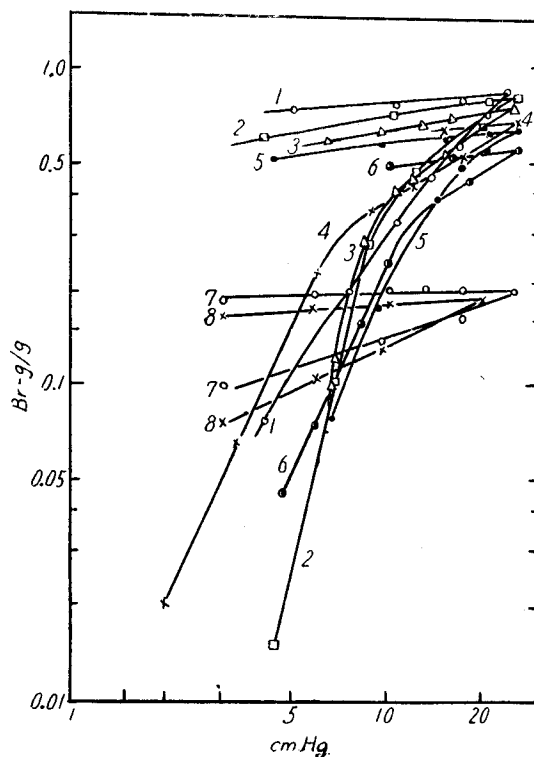


Fig. 4. Adsorption and desorption curve, plotted on a logarithmic section paper.

1. Charcoal
2. Natural graphite (Korea)
3. Natural graphite (Ceylon)
4. Acheson's graphite
5. Japanese artificial graphite A
6. Japanese artificial graphite B
7. Petroleum coke
8. Pitch coke

of graphite with bromine adsorbed is 7.05\AA , and the diameter of bromine ion is 3.96\AA .

Therefore, it may be said that bromine invasion into laminar lattice starts at about 9 cm. Hg pressure, and overcome of coagulation power of bromine molecule against van der Waals' force between laminar lattices then invites swelling of graphite by bromine invasion.

Because of the difference in life histories, artificial graphite is not to be compared with natural graphite from the same point of view. But it is very interesting that three kinds of artificial graphites have the same tendency, differing only in their adsorptive capacities and positions of inflexion. The positions of inflexion situate themselves in order, as Acheson's graphite at 7 cm. Hg < natural graphite at 9 cm. Hg < Japanese graphite B at 11.5 cm. Hg < Japanese graphite A at 14 cm. Hg. According to the results of the electrolysis of sodium chloride solution in which they are used as anode, the severeness of disintegration increases from Acheson's graphite to Japanese graphite A through Japanese graphite B in order. Electrical resistance is inverse. Both grain growth, measured by electron microscopic study, and graphitizing become worse in the same order mentioned above.

The position of inflexion, as considered in the case of graphite, is supposed to the dimensions of van der Waals' force between two laminar lattices, and the points of inflexion are considered to have some relations to graphitizing. At the same time, they are presumed to be effected by binding materials and by the arrangement of axis of graphite grain.

It is observed that the inclination of the adsorption curves for and the quantity of bromine adsorbed by charcoal and pitch coke differ very much in spite of the similar straight line adsorption curves, and that the effect of surface area on adsorption is much more evident with pitch coke than with charcoal.

The result is supposed to be derived from the discrepancies of their activity centers and their capillar adsorptive capacities, having the same mechanism.

Referring to the full logarithmic adsorption curves, position of inflexion, inclination of the curve and quantity of adsorption might be related to one another on the assumption that each member of the serial samples represents each step of

- i. the increase of crystallinity,
- ii. the increase of grain size,
- iii. the change of laminar lattice distance of hexagonal planes from 3.7\AA to 3.4\AA approximately and
- iv. the shifting from the two-dimensional structure to the three-dimensional structure in regularity,

in the mixture arrangement, in which graphite structure factors exist continuously from amorphous state to perfect graphite crystal.

Desorption curves, as shown in Fig. 3, have more parallel portions to the pressure axis with artificial graphites than with natural products. This indicates the less tendency of artificial graphites to adsorb bromine than that of natural products. But this can be seen only with pitch coke, not with charcoal.

Conclusion

Isothermal adsorption and desorption of bromine by graphites have been studied to find the followings.

i. Quantity of bromine adsorbed decreases with charcoal, graphite, soot and pitch coke in order. With graphites, adsorptive capacity of natural graphite exceeds that of artificial graphite.

ii. Effect of grain surface area upon quantity of adsorption is small with charcoal and graphite.

iii. Plotting the adsorption process curve on a full logarithmic section paper, it is found to be inflected with graphite and to be straight with the other kinds. The positions of inflexion and the inclinations of the inflected lines are characteristic with graphites.

iv. It is assumed that the point of inflexion and the inclination may be related to degree of graphitizing.

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