# *The Activation Energy of Bromine Absorption by Carbonaceous Materials**

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The object of the present work, which forms a part of the investigation of the transfer of substances in and through carbonaceous materials, is to study the rate of absorption of bromine by carbonaceous materials, especially its temperature dependence.

It is well known that graphite absorbs several substances such as bromine or metal halides, forming so-called lamellar compounds1). The rate of the absorption is known to be rather rapid. It has been reported that, in the case of bromine absorption, equilibrium was established within several hours, even at room temperature2). As the absorption by carbonaceous materials contains a process by which the reactant molecules are taken up into the crystal structure of graphite, these experimental results suggest that the reactant molecules may diffuse or move rather easily through graphite layers in the lamellar compounds. Thus, a study of the rate of absorption (viz., the rate of the formation of lamellar compounds) will give useful information on the behavior of the reactant molecules in the lamellar compounds.

Preliminary experiments on this subject which have been reported on previously3) show that the fractional absorption, plotted against the square root of time, gives a characteristic S-form, and that the rate and the saturation concentration of the absorbed bromine depend strongly upon the degree of graphitization of the materials. All the experiments were carried out at 0°C.

In the present paper, a study of the temperature dependence of the rate and the apparent energies of activation of the reactions at temperatures ranging from 0 to 50°C is described. The results and their relationship to the degree of graphitization of the carbonaceous materials are discussed.

## Experimental

In the process of determining the apparent energy of the activation of the bromine absorption by carbonaceous materials, there are several problems to be considered.

The first of them is how to estimate the relative rate of the reaction from the absorption curve at different temperatures. As has been discussed previously3), the bromine absorption is supposed to be the formation of a solid solution, and the saturation concentration of the absorbed bromine varies by changing such conditions as the temperature or the vapor pressure of bromine. In this case, the relative absorption rate could not be determined so simply. It was shown3), however, that the bromine absorption curves of almost all samples, which were drawn by plotting the measured fractional absorption against the square root of the time, fell into a single curve by merely adjusting the time scale. The adjustment was done by multipling the time scale by a suitable factor.

The inverse of the multipling factor is considered to give the relative absorption rate. In practical estimations, any of the measured points of fractional absorption may be used for the adjustment of the time scale. For the present study, the fractional absorption of 0.3 was found to be most suitable for the estimation. The reason for this choice will be discussed later.

The second problem was the variation of the saturation concentration of bromine with the reaction conditions. It was desirable to carry out the absorption experiments while the saturation concentration of bromine in carbon samples were kept constant, even at different temperatures, because a difference in the saturation concentrations might affect the rate of absorption. It was expected from a previous work by Hennig4) that this condition would be satisfied by keeping the vapor pressure of bromine saturated throughout the experiment.

In the course of experiments, however, the saturation concentration of absorbed bromine in carbonaceous materials was found to decrease with an increase in the temperature, even when the vapor pressure of bromine was kept saturated.

Thus, the Arrhenius plot might require some modification on this temperature dependence of the saturation concentration. In spite of this supposition, the Arrhenius plots obtained by the present experiments showed rather good linearities in all samples without any correction or modification of data. Therefore, the values of the apparent

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1) G. R. Hennig, "Progress in Inorganic Chemistry", Vol. I, Interscience Pub., New York (1959), p. 125.

2) W. Rüdorff, *Z. anorg. u. allgem. Chem.*, **245**, 383 (1941).

3) T. Mukaibo and Y. Takahashi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **65**, 754 (1962).

4) G. R. Hennig, "Progress in Inorganic Chemistry", Vol. I, Interscience Pub., New York (1959), p. 159.

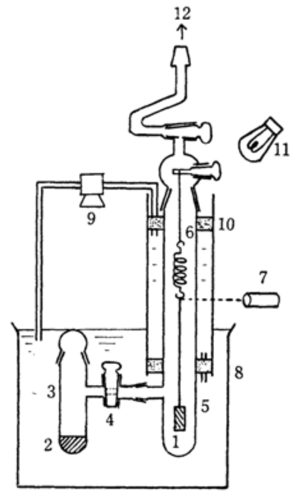

Fig. 1. Apparatus for the measurement of the rate of bromine absorption.

1. Specimen of carbonaceous materials
2. Liquid bromine
3. Bromine container
4. Stop cock
5. Reaction tube
6. Quartz spring balance
7. Running microscope
8. Water bath
9. Stroke pump
10. Cork
11. Infrared heater
12. To vacuum line

energy of activation obtained below were estimated by the conventional method mentioned above.

**Apparatus.**—The apparatus is shown in Fig. 1. The rate of absorption of bromine was measured by means of a quartz spring balance. The reaction tube and the bromine container were kept at the same temperature, thus keeping the vapor pressure of bromine saturated at the reaction temperature. To avoid the condensation of bromine on the walls of the reaction tube or on the spring balance, the upper part of the reaction tube above the surface of the water bath was kept at the same temperature as the reaction part by circulating the water of the bath. The top of the tube was warmed by an infrared lamp for the same reason.

Nevertheless, a small quantity of bromine condensation on the specimen or on the spring balance was inevitable at the last period of a run lasting for a few hours. A little experimental error was supposed to be caused by the condensed bromine in the measurement of the last stage of absorption and of the saturation concentration of the bromine. This experimental error, however, was estimated to be negligible in calculating the activation energies, as will be described later.

**Materials.** — The samples of carbonaceous materials were supplied by the Nippon Carbon K. K. The carbon source, the temperature of heat treatment, the density, and the porosity of samples are listed in Table I.

The specimen for each run was cut into a plate, $30\times10\times1$ mm. in size, and weighed.

GR grade bromine was redistilled and passed over through concentrated sulfuric acid before use.

**Procedure.**—Redistilled bromine was introduced into the evacuated bromine container in a separate vacuum line. After closing the stop cock (shown in Fig. 1) to prevent contamination by the air, the container was removed from the vacuum line and was set to the reaction tube. After keeping both of them in a water bath for a while, a specimen was suspended by a quartz spring balance in the reaction tube. Then the tube was evacuated to $10^{-3}$ mmHg by a diffusion pump.

The reaction was started by opening the stop cock. The weight gain of the specimen by the absorption of bromine was measured with a running microscope, following the elongation of the spring balance. The sensitivity of the reading was about 0.5 mg. wt. change per division.

The temperature of the water bath was kept constant within ±0.1°C of the setting temperature.

## Results

**The Saturation Concentration of Absorbed Bromine.**—It was found that the saturation concentration, $C_s$, of absorbed bromine by carbonaceous materials under the saturated vapor pressure of bromine had a tendency to decrease with an increase in the temperature. The findings are shown in Fig. 2, in which $C_s(T)$ values at different temperatures are presented as the ratio to $C_s(0)$ at 0°C. These results showed a definite tendency for $C_s$ to decrease with an increase in the temperature, although there were a few deviations from a monotonic curve. These deviations might be caused by bromine condensation on the specimen or on the spring balance, or by some inconstancy of the reaction temperature. Even a small defference in temperature between the specimen and the bromine container was found to cause rather a large deviation.

TABLE I. CHARACTERISTICS OF THE SAMPLES OF CARBONACEOUS MATERIALS

| Sample | Carbon source | Temp. of heat treatment, °C | Apparent density | True density | Porosity % |
|---|---|---|---|---|---|
| 1—4 | Oil cokes | 2000 | 1.64 | 2.109 | 22.6 |
| 1—6 | Oil cokes | 2660 | 1.67 | 2.163 | 23.8 |
| 5 | Oil cokes | 2660 | $1.56_5$ | 2.174 | 28.0 |
| 8 | Natural graphite | 2660 | 1.78 | 2.216 | 19.6 |

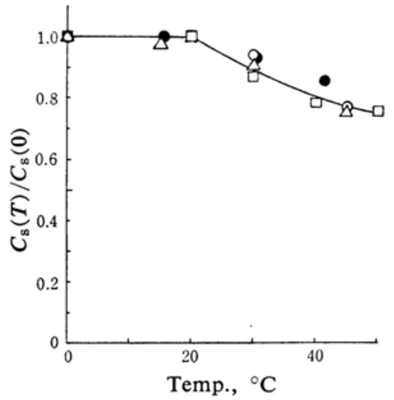

Fig. 2. Temperature dependence of bromine saturation concentration, under the saturated vapor pressure of bromine.
-○- Sample 1—4 -△- Sample 1—5
-●- Sample 5 -□- Sample 8

**The Rate of Bromine Absorption and its Temperature Dependence.** — The absorption rate curves obtained by one of the samples are shown in Fig. 3, plotting the fractional absorption against the square root of the time. In order to determine the relative absorption rate, the fractional absorption of 0.3 was chosen as a standard in finding out the multipling factor for the adjustment of the time scale. The value of 0.3 was chosen because the experimental error caused by bromine condensation, mentioned earlier, was supposed to be relatively small at the beginning of the absorption, and because the time corresponding to the standard fractional absorption was supposed to be determined most accurately in this region according to the shape of the absorption curve.

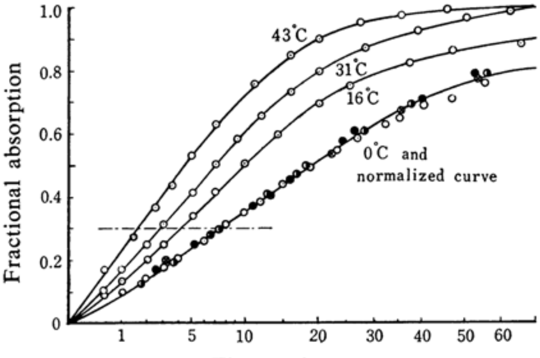

Fig. 3. The rate of bromine absorption by sample 5 and the normalized plots.
On the normalized curve: ○ 0°C, ◑ 16°C, ● 31°C, ⊗ 43°C

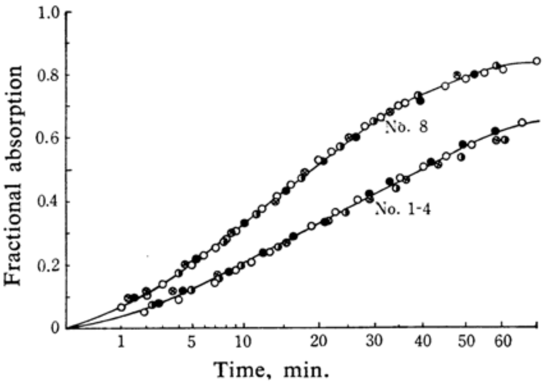

Fig. 4. The normalized rate curves of bromine absorption.
Sample 8 ; ○ 0°C ◑ 20°C
● 30°C ⊗ 40°C
Sample 1-4 ; ○ 0°C ◑ 15°C
● 30°C ⊗ 45°C

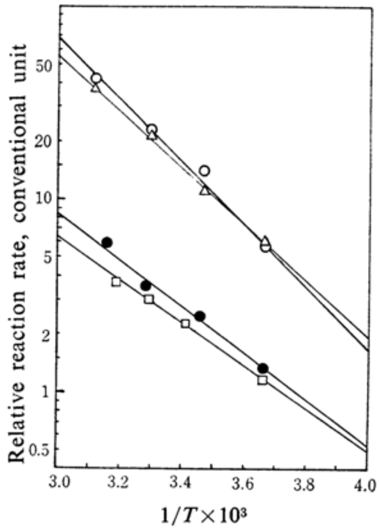

Fig. 5. Arrhenius plots of the rate of bromine absorption by carbonaceous materials.
-○- Sample 1—4
-△- Sample 1—6
-●- Sample 5
-□- Sample 8

Using the multipling factor for adjustment thus obtained, the plots normalized to the curve obtained at 0°C are shown in Fig. 3, and in Fig. 4 for other samples. These plots fell into one line, as expected, indicating that the above-mentioned procedure was acceptable.

The relative rate of bromine absorption at different temperatures was the inverse of the multipling factor of each run. From the Arrhenius plotting in Fig. 5, the apparent energies of activation were calculated; they are shown in Table II.

TABLE II. APPARENT ENERGIES OF ACTIVATION OF THE BROMINE ABSORPTION BY CARBONACEOUS MATERIALS

| Sample | Apparent energy of activation kcal./mol. |
|---|---|
| 1—4 | $7.4_5$ |
| 1—6 | 6.7 |
| 5 | $5.5_5$ |
| 8 | 5.1 |

## Discussion

**The Temperature Dependence of the Saturation Concentration of Absorbed Bromine in Carbonaceous Materials.** — The fact that the $C_s$ value of bromine in carbonaceous materials under the saturated vapor pressure of bromine decreases with an increase in the temperature has not yet hitherto been reported. Juza⁵⁾ predicted that this tendency to decrease might occur on the analogy of the decrease in the reactivity of chlorine gas to carbonaceous materials with an increase in the temperature. The saturation content of chlorine was found to decrease markedly at the temperature 100°C above the melting point of chlorine.

The present results show, however, that the decrease in the saturation concentration of bromine occurs gradually, even at temperatures as low as 30°C, which is only 37.3°C higher than the melting point of bromine.

At the present stage, the data are not numerous enough to enable us to discuss further the significance of the tendency to decrease. A more precise investigation of this problem is now being carried out, however, and will be reported on later.

**The Activation Energies and their Relation to the Degree of Graphitization of Carbonaceous Materials.**—The Arrhenius plots of the rate of bromine absorption gave good linearities for all samples, indicating that the rate of absorption was not very much affected by a small difference in the saturation concentration of bromine in the lamellar compounds. This fact may support the view that the bromine absorption is a kind of formation of a solid solution.

From the results presented in Table II, the apparent energies of activation are supposed to be dependent upon the degree of graphitization of the carbonaceous materials. To make this clear, the values of the true density of the samples were taken as the measure of the degree of graphitization. The results of X-ray diffraction measurement were not used for this purpose, because the samples were mixed with some binding materials in the course of production. The relation between the activation energies and the values of the true density of the samples is shown in Fig. 6. The plots show clearly that the apparent energies of activation decrease with an increase in the degree of graphitization.

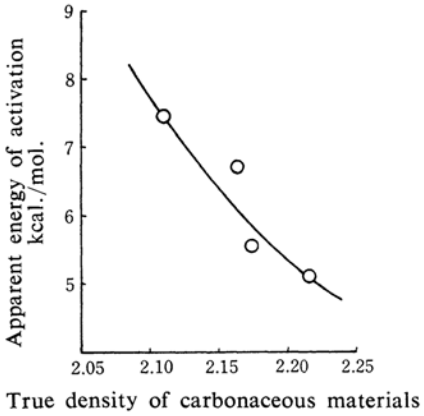

Fig. 6. Relation between the apparent energy of activation and the true density of carbonaceous materials.

The results indicate that the bromine absorption, followed by the diffusion or migration of absorbed bromine into the interior of graphite crystals, proceeds more easily with an increase in the degree of graphitization of the samples. This means that, with the growth of the net plane of graphite crystals, the movements of the molecules intercalated between the net planes of graphite crystals became easier.

Iwata et al.⁶⁾, in calculating the activation energy for the migration of Xe in the interlamellar positions of graphite crystal, have obtained the value of 0.69 kcal./mol. It should be noted that the self-energy of Xe interstitial atoms in graphite was also calculated to be 347 kcal./mol., in contrast to the small value of the migration energy. In the case of the bromine absorption, as bromine molecules have some interactions and are stabilized energetically in the lamellar compounds, the uptake of bromine molecules proceeds very easily. On the other hand, the activation energy for the migration of bromine molecules seems to be rather higher in comparison with that of inert Xe molecules. The present finding, the activation energy of 5∼7 kcal./mol. for bromine absorption, revealed, however, that the migration of bromine molecules also proceeds very easily, even at room temperatures.

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5) R. Juza and A. Schmeckenbecher, *Z. anorg. u. allgem. Chem.*, **292**, 16 (1957).

6) T. Iwata, F. E. Fujita and H. Suzuki, *J. Phys. Soc. Japan*, **16**, 197 (1961).

## Summary

In the present paper, the temperature dependence of the rate of bromine absorption by the carbonaceous materials has been studied. The apparent energies of activation of the reaction have been found to be 5∼7 kcal./mol. and had a dependence upon the degree of graphitization of carbonaceous materials. The value of the activation energy became smaller with an increase in the degree of graphitization. The results indicate that the mobilities of reactant molecules of the interlamellar compounds increase with the growth of the net plane of graphite crystals.

The saturation concentration of bromine in carbonaceous materials, under a saturated vapor pressure of bromine, was found to decrease with an increase in the temperature at temperatures above 30°C.

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