*The Adsorption of Non-polar Gases on Alkali Halide Crystals. V. The Low-temperature Adsorption of Non-polar Gases on Cubic Potassium Bromide**

By Teruo HAYAKAWA

(Received December 4, 1956)

Introduction

In the former papers of this series[1,2,3,4], the author has described the measurements and the theoretical calculations of the low-temperature adsorption of non-polar gases (argon, oxygen, nitrogen and carbon dioxide) on cubic sodium chloride and cubic potassium chloride. The high initial heat of adsorption experimentally found for nitrogen or carbon dioxide has been considered to be mainly attributed to the quadrupole interaction of each molecule with the surface. It has also been indicated from these works that the adsorbed atoms or molecules (argon, oxygen and nitrogen) have the nature of the two-dimensional gas at least in the range of $\theta=0.3\sim0.9$ and the surface is influenced by the different types of the non-uniformity due to the defects of the crystals and the distribution of sites grouped in patches.

The present paper reports similar investigations on cubic potassium bromide and discusses these problems mentioned above on the basis of the experiments and the theoretical calculations given in the preceding paper[4].

Experimental

Materials.—*Potassium bromide* was recrystallized by rapidly cooling an aqueous solution of potassium bromide (Wako Chemical Co., extra pure grade) saturated at 90°C. The crystals were collected on a sintered glass filter funnel, washed with successive portions of 70 and 99.9% ethyl alcohol, and stored in a vacuum desiccator over phosphorus pentoxide for about two weeks. Microscopic examination of this sample revealed a large number of small cubes, and in some crystals the defects in the corners or edges were somewhat perceptible. The examination of this sample by an electron diffraction apparatus also showed that the (100) was the predominant surface plane. 42.3 g. of this sample which passed through a 45-mesh sieve was used in the subsequent experiments.

Helium was supplied by the Teikoku Oxygen Co. as spectroscopically pure and was not further purified. The method of preparation of other gases has already been given[1].

Apparatus and Procedure. — The apparatus and the procedure have also been described in a previous communication[1]. The salt was outgassed by heating in vacuo at 280–300°C for a minimum period of 6 hr. prior to each experiment.

Results

The isotherms obtained for the four gases on cubic potassium bromide crystals are summarized in Figs. 1, 2, 3 and 4. The adsorption was found

---

* Part of this paper was read before the 9th Annual Meeting of the Chemical Society of Japan held in Kyoto, April, 1956. Another part of this paper was also read before the symposium on the surface heterogeneity of catalysis held in Kyoto, March, 1956.

[1] Part I of this series, T. Hayakawa, This Bulletin, **30**, 124 (1957).

[2] Part II of this series, T. Hayakawa, This Bulletin, **30**, 236 (1957).

[3] Part III of this series, T. Hayakawa, This Bulletin, **30**, 243 (1957).

[4] Part IV of this series, T. Hayakawa, This Bulletin, **30**, 332 (1957).

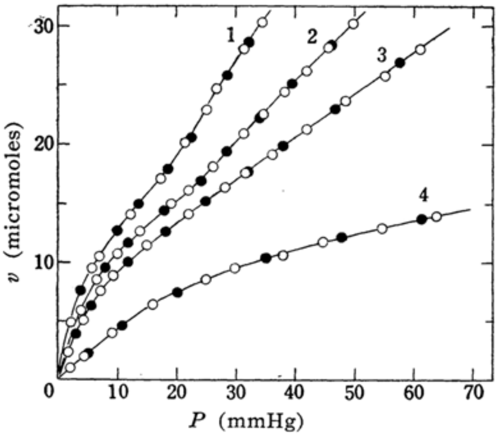

Fig. 1. Adsorption isotherms of argon on cubic potassium bromide.
curve 1……73.70°K, curve 2……75.67°K,
curve 3……77.32°K, curve 4……85.01°K.
-○-○- adsorption, -●-●- desorption.

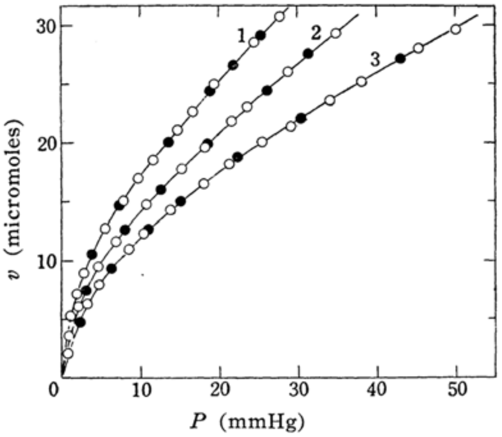

Fig. 2. Adsorption isotherms of oxygen on cubic potassium bromide.
curve 1……73.70°K, curve 2……75.44°K,
curve 3……77.32°K.
-○-○- adsorption, -●-●- desorption.

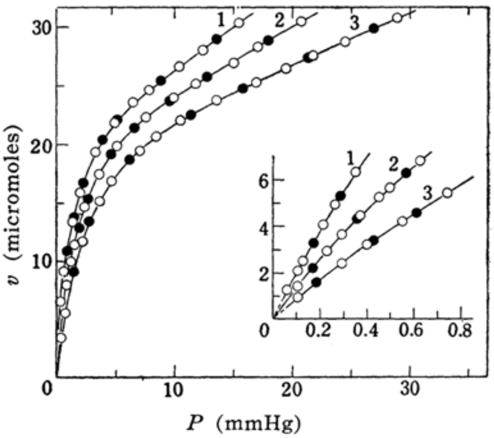

Fig. 3. Adsorption isotherms of nitrogen on cubic potassium bromide.
curve 1……73.75°K, curve 2……75.44°K,
curve 3……77.32°K.
-○-○- adsorption, -●-●- desorption.

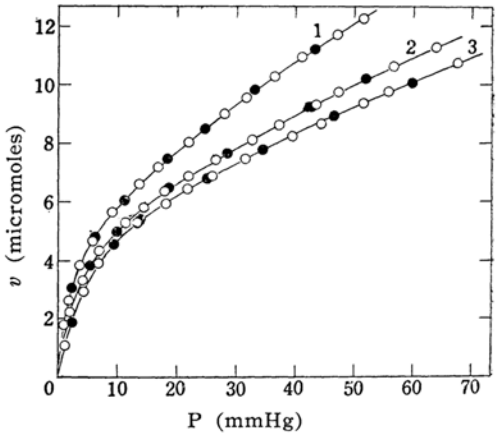

Fig. 4. Adsorption isotherms of carbon dioxide on cubic potassium bromide.
curve 1……187.66°K, curve 2……192.63°K,
curve 3……194.64°K.
-○-○- adsorption, -●-●- desorption.

to be reversible in this temperature range. The isosteric heats of adsorption were calculated from these isotherms using the Clausius-Clapeyron equation and showed no definite trend with temperature within the experimental error. In the calculations of the entropy decreases due to the adsorption, the gas phase under the pressure of 760 mmHg and the temperature which coincided with that of each isotherm was chosen as the standard state.

The present results on the isosteric heats of adsorption and the entropy decreases caused by the adsorption are shown in Figs. 5, 6, 7 and 8. Since the adsorbed amount of carbon dioxide was considerably small in this temperature range, the measurements were not extended to the region of high coverage.

Discussion

Isosteric Heats of Adsorption. — The heat curves shown in Figs. 5, 6 and 7 indicate that the initial decrease due to the nonuniformity of the surface and the increase in the succeeding region for these three non-polar gases are considerably predominant. The present results on cubic potassium bromide indicate, however, that the increase in the heats of adsorption for each adsorbate, which gives a measure of the mutual interaction between the adsorbed atoms or molecules, is somewhat less than that obtained for cubic sodium chloride and cubic potassium chloride[1,3].

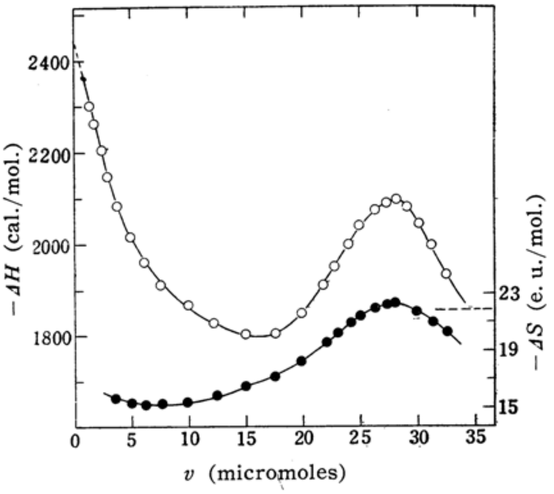

Fig. 5. Isosteric heats and entropies of adsorption for argon on cubic potassium bromide.
-○-○-, isosteric heats of adsorption $(-\Delta H)$;
-●-●-, entropies of adsorption $(-\Delta S)$;
-----, heat of sublimation.

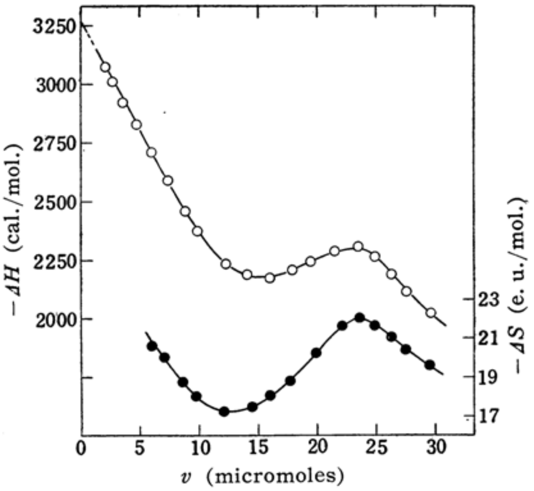

Fig. 7. Isosteric heats and entropies of adsorption for nitrogen on cubic potassium bromide.
-○-○-, isosteric heats of adsorption $(-\Delta H)$;
-●-●-, entropies of adsorption.

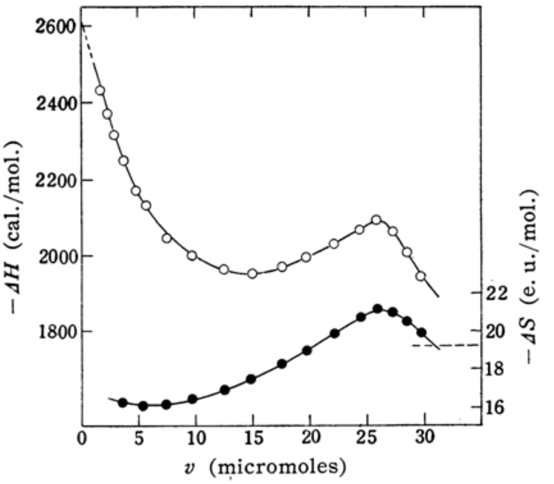

Fig. 6. Isosteric heats and entropies of adsorption for oxygen on cubic potassium bromide.
-○-○-, isosteric heats of adsorption $(-\Delta H)$;
-●-●-, entropies of adsorption $(-\Delta S)$;
-----, heat of evaporation.

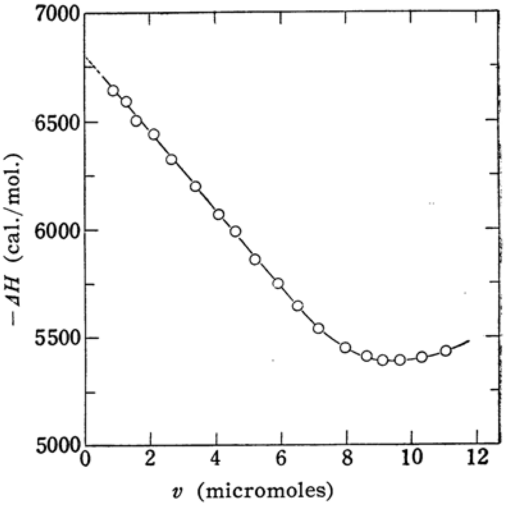

Fig. 8. Isosteric heats of adsorption for carbon dioxide on cubic potassium bromide.

TABLE I

INITIAL HEAT OF ADSORPTION, $-\Delta H_0$, ON CUBIC POTASSIUM BROMIDE

Adsorbate	$(-\Delta H_0)_{\text{expt.}}$ (cal./mol.)	$(-\Delta H_0)_{\text{calcd.}}$ (cal./mol.)	$(-\Delta H_0)_{\text{expt.}}-(-\Delta H_0)_{\text{calcd.}}$ (cal./mol.)
Argon	2440	2330	110
Oxygen	2610	—	—
Nitrogen	3280	2480	800
Carbon dioxide	6780	5300	1480

TABLE II

MONOLAYER CAPACITIES (V_m) AND SURFACE AREAS (A), CUBIC POTASSIUM BROMIDE (42.3 g.)

Adsorbate	Cross-sectional area, (Å^2)	V_m (micromoles) from heat curve	(B. E. T.)	A (m^2) from heat curve	(B. E. T.)
Argon	12.8	27.8	(25.7)	2.14	(1.98)
Oxygen	14.1	26.2	(24.1)	2.22	(2.05)
Nitrogen	13.8	24.1	(28.3)	2.00	(2.35)

The values of the initial heat of adsorption (i. e. the isosteric heat of adsorption extrapolated to zero coverage) obtained for the four gases are summarized in Table I, together with the theoretical values obtained by the present author$^{4)}$.

As already reported in the previous paper$^{4)}$, the high initial heat of adsorption theoretically obtained for nitrogen or carbon dioxide is mainly attributed to the quadrupole interaction of each molecule with the surface. Although the discordance between the experimental and theoretical values for nitrogen or carbon dioxide is somewhat remarkable (see Table I), the order of magnitude of the experimental values is similar to that of the theoretical values. Moreover, the experimental values of the initial heat of adsorption inevitably contain some uncertainty due to the extrapolation, and the theoretical values for nitrogen and carbon dioxide also contain some incorrectness due to the uncertainty of the observed values of the permanent quadrupole moment. Considering the question from these facts, it seems reasonable to consider that the high initial heat of adsorption experimentally found for nitrogen or carbon dioxide is mainly attributed to the quadrupole interaction of each molecule with the surface of cubic potassium bromide.

Since the theoretical calculations were carried out on the assumption of an ideal lattice, the difference between the experimental and theoretical values of the initial heat of adsorption gives a crude measure of the surface heterogeneity due to the lattice imperfection and the defects of the crystals. As seen in Table I, the values of this difference for argon, nitrogen and carbon dioxide amount to 110, 800 and 1480 cal./mol. respectively. On the other hand, the heat curves shown in Figs. 5, 7 and 8 indicate that the initial decreases due to the non-uniformity of the surface for argon, nitrogen and carbon dioxide roughly amount to 640, 1100 and 1400 cal./mol. respectively. Since the mutual interaction between the adsorbed atoms or molecules is included in these values of the initial decreases and the theoretical values for nitrogen and carbon dioxide are also somewhat uncertain, it is reasonable to consider that the surface is influenced not only by the non-uniformity due to the lattice imperfection and the defects of the crystals but by another type of the non-uniformity. As already discussed in the preceding paper$^{4)}$, this latter type of the surface heterogeneity may be attributed to the distribution of sites on the surface.

Monolayer Capacities.—Since the heat curves indicate that the surface heterogeneity in the low coverage region and the mutual interaction in the succeeding region are both predominant, it is quite unreasonable to apply the B. E. T. theory to the present systems. As seen in Figs. 5, 6 and 7, there are fairly sharp maxima in the isosteric heat and entropy decrease curves for all three non-polar gases, and the gradual decrease beyond each maximum may be attributed to the formation of multilayers. Considering this fact, it is reasonable to assign the amount adsorbed corresponding to this maximum in the heat or entropy decrease curve as a monolayer capacity.

The present results on the monolayer capacities and on the surface areas which are thus obtained are summarized in Table II. The values of the cross-sectional area in this table were calculated from the results on the entropies of the adsorbed atoms and molecules using the assumption of a hexagonally close-packed layer.

Entropies of the Adsorbed Phase.—As seen in Figs. 5, 6 and 7, the magnitudes of the entropies of adsorption and the variation of these with the amount adsorbed for argon and oxygen are similar to each other, while nitrogen shows somewhat different features from other gases. In order to obtain more information about the freedom of the adsorbed atoms or molecules, the entropies of the adsorbed phase derived from the present results were compared with those statistically calculated. The methods of the statistical calculations of the entropies of the gas phase under the standard states and of

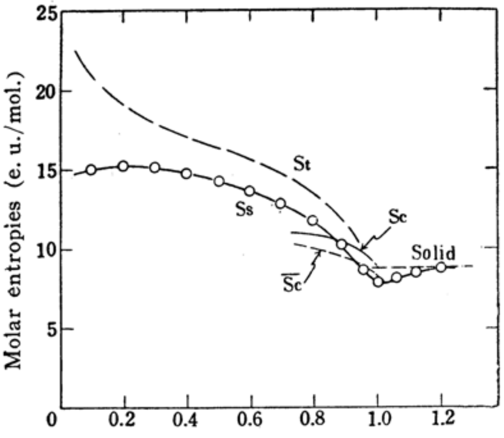

Fig. 9. Molar entropies of argon adsorbed on cubic potassium bromide at 76.5°K.
S_s, experimental values; S_t, calculated values of the two-dimensional gas; S_c, integral configurational entropies; $\bar{S}_c$, differential configurational entropies.

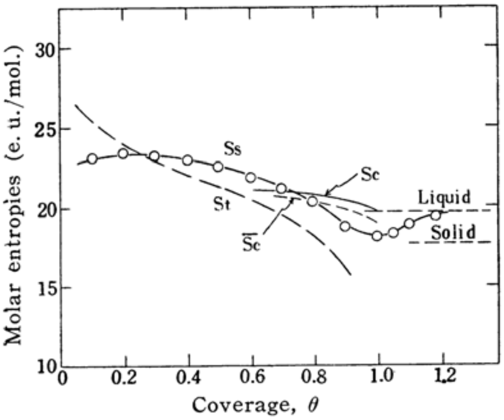

Fig. 10. Molar entropies of oxygen adsorbed on cubic potassium bromide at 76.4°K.
S_s, experimental values; S_t, calculated values of the two-dimensional gas; S_c, integral configurational entropies; $\bar{S}_c$, differential configurational entropies.

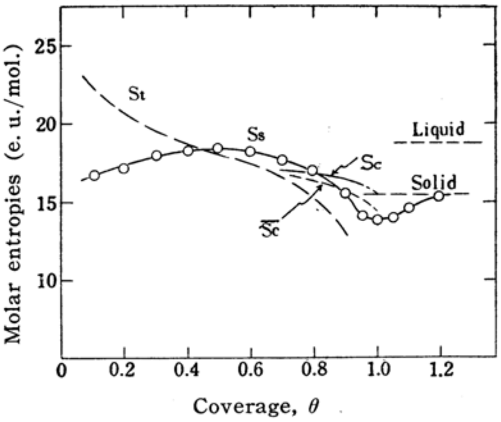

Fig. 11. Molar entropies of nitrogen adsorbed on cubic potassium bromide at 76.4°K.
S_s, experimental values; S_t, calculated values of the two-dimensional gas; S_c, integral configurational entropies; $\bar{S}_c$, differential configurational entropies.

the entropies of the adsorbed phase were already given in a previous communication[1].

The entropy curves of the adsorbed phase obtained from the present experiments are summarized in Figs. 9, 10 and 11, together with the calculated curves. The experimental values in these figures are the partial molar total entropies and hence contain the entropy changes of the adsorbent[5], while the calculated values are all the integral entropies and are usually somewhat greater than those of the partial molar total entropies. Considering this fact, the experimental curves (S_s) for adsorbed argon and nitrogen are comparatively in good agreement with the calculated curves (S_t) of the two-dimensional gas in the ranges of $\theta=0.3$–0.9 and $\theta=0.3$–0.8 respectively. In the case of oxygen, since the entropy associated with the vibrational motion normal to the surface was calculated on assuming that the vibrational frequency of the adsorbed oxygen molecule was identical with that of the adsorbed argon atom, the present calculations of the two-dimensional gas for oxygen (S_t in Fig. 10) probably resulted in somewhat smaller values. Consequently, it seems reasonable to consider that the agreement of the experimental curve for oxygen with the calculated curve of the two-dimensional gas is considerably satisfied in the range of $\theta=0.2$–0.8.

The discrepancy between the experimental and calculated curves at lower coverage ($\theta<0.2$) in these figures would imply the entropy changes of the adsorbent. When θ approaches to unity, as seen in Fig. 9, the restriction on the freedom of adsorbed argon is further increased and the experimental curve (S_s) falls below the calculated curve (S_t) of the two-dimensional gas. At higher coverage ($\theta>1$), the entropy of adsorbed argon remains close to the entropy of solid argon*, while the entropy of adsorbed oxygen approaches

---

[5] T. L. Hill, *J. Chem. Phys.*, **17**, 520 (1949).

* The entropy of solid argon was calculated from the heat of sublimation and the value of the saturation pressure at 76.5°K.

to the entropy of liquid oxygen**. These results obtained for cubic potassium bromide are similar to those obtained for cubic potassium chloride[3]. In the case of nitrogen, the entropy of the adsorbed phase at higher coverage approaches to the entropy of solid nitrogen***.

Kemball[6] suggested that the phase change of argon on cubic potassium chloride occurred at about $\theta=0.8$, since the experimental values shifted from the entropy curve of the two-dimensional gas to the entropy curve of the localized adsorption obtained by adding the configurational entropy on the Langmuir model to the entropy of solid argon. This explanation involves, however, considerable uncertainty, since it is quite unreasonable to apply the Langmuir model to the adsorption system in which the surface heterogeneity at lower coverage and the mutual interaction in the succeeding region are both predominant. In the present work, therefore, the configurational entropy (S_c) and the differential configurational entropy ($\overline{S}_c$) for the localized adsorption were calculated from the experimental results using the expressions derived by Drain and Morrison[7]. In these expressions, however, the non-uniformity of the surface was taken into consideration, while the mutual interaction between the adsorbed atoms or molecules was almost entirely ignored.

The present results on the configurational and differential configurational entropies for these three gases (argon, oxygen and nitrogen) are also summarized in Figs. 9, 10 and 11. As seen in Fig. 9, the present results suggest that the phase change of argon from a gaseous film to a condensed film has occurred at about $\theta=0.9$. On the other hand, Figs. 10 and 11 suggest that the phase changes of oxygen and nitrogen on cubic potassium bromide have occurred at about $\theta=0.8$. However, since the mutual interaction between the adsorbed atoms or molecules was almost entirely ignored in these calculations of the configurational and differential configurational entropies, the present results on the phase change of the adsorbed phase inevitably contain some uncertainty.

Summary

The low-temperature adsorption of non-polar gases (argon, oxygen, nitrogen and carbon dioxide) on cubic potassium bromide was investigated. According to the results of the present experiments and the theoretical calculations given in the preceding paper, the high initial heat of adsorption experimentally found for nitrogen or carbon dioxide is mainly attributed to the quadrupole interaction of each molecule with the surface of the crystal. The present results also indicate that the non-uniformity of the surface is considerably predominant at lower coverage and this is partly attributed to the lattice imperfection and the defects of the crystals.

According to the present results on the entropies of the adsorbed atoms or molecules, the adsorbed phase of argon has the nature of the two-dimensional gas at least in the range of $\theta=0.3$–0.9, while the adsorbed phase of oxygen or nitrogen shows a similar nature in the range of $\theta=0.3$–0.8. The present results suggest that the phase change of argon from a gaseous film to a condensed film has occurred at about $\theta=0.9$. In the case of oxygen or nitrogen, it is also suggested that the phase change of each adsorbed phase from a gaseous film to a condensed film has occurred at about $\theta=0.8$.

The author wishes to express his grateful thanks to Dr. S. Horiba and Professor O. Toyama of Osaka Prefectural University for their kind encouragement and discussions. The author's sincere thanks are also due to Professor R. Kiyama of Kyoto University for his kind discussions.

Department of Chemistry
Faculty of Education
Osaka Prefectural University, Sakai

** The entropies of solid and liquid oxygen were calculated from the work of Giauque and Johnston (*J. Am. Chem. Soc.*, **51**, 2300 (1929)).

*** The entropies of solid and liquid nitrogen were calculated from the work of Kingston et al. (*J. Am. Chem. Soc.*, **72**, 1780 (1950)).

[6] C. Kemball, "Advances in Catalysis," Vol. II, Academic Press Inc., New York (1950), p. 233.

[7] J. M. Drain and J. O. Morrison, *Trans. Faraday Soc.*, **48**, 316 (1952).