The Adsorption of Non-Polar Gases on Alkali Halide Crystals. III.
The Low-Temperature Adsorption of Non-Polar Gases on Cubic Potassium Chloride[*]

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Introduction

In the former papers of this series[1,2] the author studied the adsorptive properties of non-polar gases (argon, oxygen, nitrogen and carbon dioxide) on cubic

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[*] Part of this paper was read before the 6 th Annual Meeting of the Chemical Society of Japan held in Kyoto, April, 1953. 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).

sodium chloride. Considerably good agreement between the theoretical and experimental values of the initial heat of adsorption for argon, nitrogen, or carbon dioxide was obtained. The experimental results also indicated that the adsorbed molecules of argon, oxygen, or nitrogen on cubic sodium chloride have the nature of two-dimensional gas at least in the range of $\theta=0.3\sim0.9$. The measurements of the low-temperature adsorption of non-polar gases (argon, oxygen and nitrogen) on cubic potassium chloride were already reported by Orr[3]. However, since his results were limited to the variation in the isosteric heats of adsorption with coverage, no definite information on the non-uniformity of the surface and on the freedom of the adsorbed molecules was obtained. Moreover, no reasonable explanation was given for the differences in the values of the initial heat of adsorption with molecular species of adsorbates.

It was therefore of interest in the present work to re-examine the adsorptive properties of non-polar gases on cubic potassium chloride and to compare the results with those obtained for cubic sodium chloride.

Experimental

Materials.—*Potassium chloride* was recrystallized by rapidly cooling an aqueous solution of potassium chloride (Merck reagent) saturated at 100°C. The crystals were collected on a sintered glass filter funnel, washed with successive portions of 70% ethyl alcohol, absolute alcohol, and dry ether, and stored in vacuum desiccator over phosphorous anhydride during about two weeks. Microscopic examination of this sample revealed a large number of small cubes plus a few cubes in which the defects in the corners or edges were somewhat perceptible. The examination of this sample by an electron diffraction apparatus also revealed the regular pattern of (100) faces. 24.9 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 argon, oxygen, nitrogen and carbon dioxide has already been described[1].

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

Results

The isotherms obtained for the four gases on cubic potassium chloride are summarized in Fig.

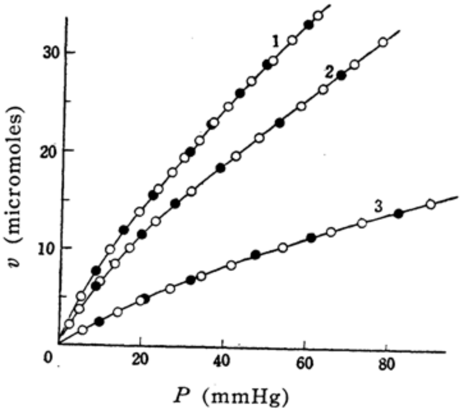

Fig. 1. Adsorption of argon on cubic potassium chloride.
curve 1⋯⋯75.29°K, curve 2⋯⋯77.32°K, curve 3⋯⋯85.42°K; ○⋯⋯adsorption, ●⋯⋯desorption.

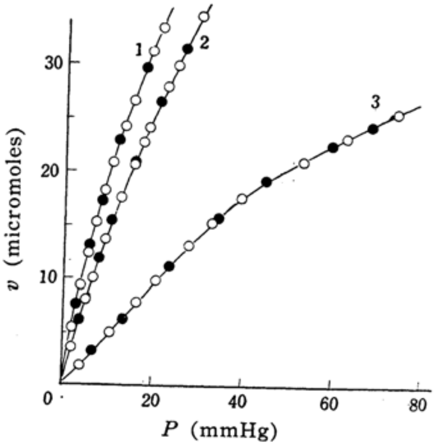

Fig. 2. Adsorption of oxygen on cubic potassium chloride.
curve 1⋯⋯75.29°K, curve 2⋯⋯77.32°K, curve 3⋯⋯85.42°K; ○⋯⋯adsorption, ●⋯⋯desorption.

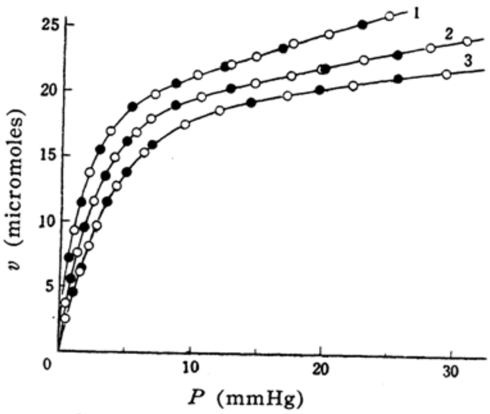

Fig. 3. Adsorption of nitrogen on cubic potassium chloride.
curve 1⋯⋯73.74°K, curve 2⋯⋯75.69°K, curve 3⋯⋯77.32°K; ○⋯⋯adsorption, ●⋯⋯desorption.

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[3] W. J. C. Orr, *Proc. Roy. Soc.*, **A173**, 349 (1939).

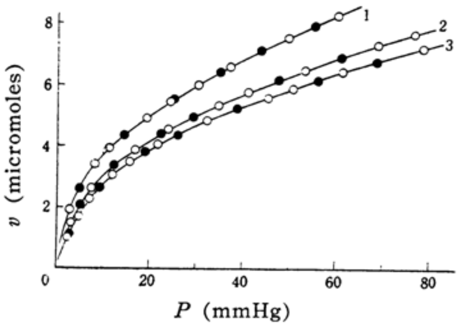

Fig. 4. Adsorption of carbon dioxide on cubic potassium chloride.
curve 1……187.66°K, curve 2……192.63°K, curve 3……194.64°K; ○……adsorption, ●……desorption.

1, 2, 3 and 4. The adsorption was found to be reversible in this temperature range. The isosteric heats of adsorption were calculated from these isotherms using the Clausius-Clapeyron equation, and these showed no definite trend with temperature within the experimental error. For the calculations of the entropy decrease due to the adsorption, the choice of the standard states of the gas phase was such that the pressure is 760 mmHg and the temperature coincides with that of each isotherm.

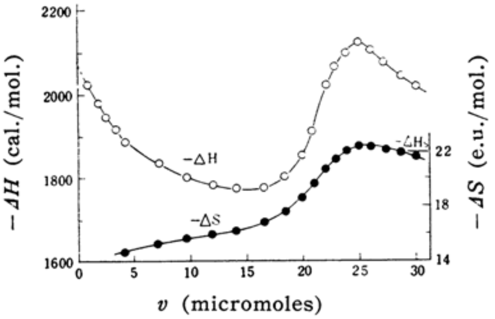

Fig. 5. Isosteric heats and entropies of adsorption for argon on cubic potassium chloride.
$-\Delta H_s$……heat of sublimation.

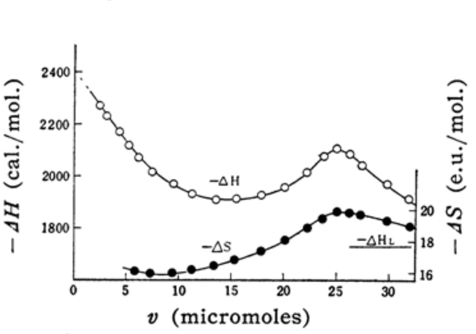

Fig. 6. Isosteric heats and entropies of adsorption for oxygen on cubic potassium chloride.
$-\Delta H_L$……heat of vaporization.

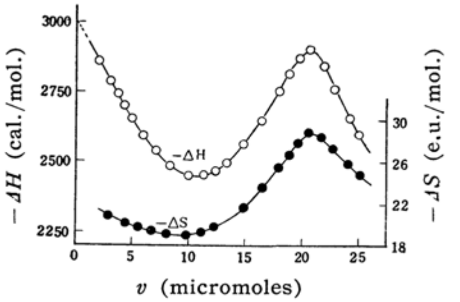

Fig. 7. Isosteric heats and entropies of adsorption for nitrogen on cubic potassium chloride.

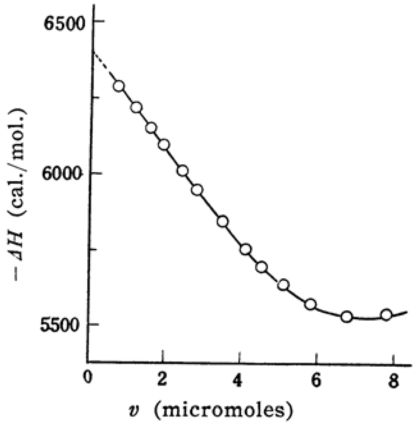

Fig. 8. Isosteric heats of adsorption for carbon dioxide on cubic potassium chloride.

The present results on the isosteric heats of adsorption and the entropy decrease due to the adsorption are shown in Fig. 5, 6, 7 and 8. The measurements were not extended to the high coverage region for carbon dioxide, since the amount adsorbed was fairly small in this temperature range.

Discussion

The Isosteric Heats of Adsorption.—The magnitudes of the isosteric heats of adsorption and the variation of these with coverage for the three gases (argon, oxygen and nitrogen) are in fairly good agreement with the experimental values of Orr(3). The experimental 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 experimental values of Orr(3) and Lenel(4) and the theoretical values of the present author.

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4) F. V. Lenel, *Z. physik. Chem.*, **B23**, 379 (1933).

TABLE I

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

Adsorbate	$(-H_0)_{\text{expt.}}$ (cal./mol.)		$(-\Delta H_0)_{\text{calc.}}$ (cal./mol.)
	Present author	(Literature)	
Argon	2080	(2140*)	1900
Oxygen	2410	(2350*)	—
Nitrogen	3010	(3200*)	2120
Carbon dioxide	6400	(6500**)	4970

* Obtained by Orr.

** Obtained by Lenel.

In the theoretical calculations, as will be reported in the succeeding paper, the crystal lattice was assumed to be an ideal (i. e. the surface heterogeneity due to the defects or the lattice imperfecticn was ignored) and the quadrupole interaction of the molecule (nitrogen or carbon dioxide) with the surface was taken into consideration. Table I indicates that the present experimental values of the initial heat of adsorption are in good agreement with those of other investigators. Although the discrepancies between the experimental and theoretical values for nitrogen and carbon dioxide are quite remarkable, as seen in Table I, the order of magnitude of the experimental values for these non-polar gases is similar to that of the theoretical values. Considering the matter from this fact, it seems reasonable to consider that the high initial heats of adsorption experimentally found for nitrogen and carbon dioxide are mainly attributed to the quadrupole interactions of these molecules with the surface of cubic potassium chloride.

The initial decrease in each heat curve is attributed to the non-uniformity of the surface, since mutual interaction forces of adsorbed molecules, being attactive, would result in an increase in the heat. The difference between the experimental and theoretical values of the initial heat of adsorption shown in Table I gives a crude measure of the surface heterogeneity due to the lattice imperfection or the defects of the crystals. Then, the value of 180 cal./mol. for argon (i. e. the difference between the experimental and theoretical values of the initial heat of adsorption) may be attributed to the surface hetrogeneity of this type, while Fig. 5 indicates that the initial decrease in the heat curve for argon roughly amounts to about 300 cal./mol.* Consequently, it is reasonable to consider that the surface may be influenced by the non-uniformity of the other type.

In the case of nitrogen or carbon dioxide, however, the situation seems quite different, since the difference between the experimental and theoretical values of the initial heat of adsorption is considerably greater than the initial decrease in the heat curve shown in Figs. 7 or Fig. 8. Although these results obtained for nitrogen and carbon dioxide are inconsistent with those for argon, it may be pointed out that the theoretical calculations of the initial heat of adsorption for nitrogen and carbon dioxide are less correct than those for argon. This incorrectness in the theoretical calculations is mainly attributed to the fact that the values of the quadrupole moment of these molecules (nitrogen and carbon dioxide) cannot yet be considered as definitely proved.

The Monolayer Capacities and the Surface Areas.—Since the heat curves (Figs. 5, 6 and 7) indicate that the non-uniformity of the surface considerably predominates in the low coverage region and that the mutual interaction between the adsorbed molecules in the succeeding region is sharply increased with the increase of the amount adsorbed, 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 the entropy decrease curves for all these gases. The gradual decrease in each heat or entropy decrease curve beyond the maximum may be attributed to the formation of multilayers. Considering these facts, it seems reasonable to assign the value corresponding to the maximum in the heat or entropy decrease curve as the monolayer capacity.

The present results on the monolayer capacities and the surface areas are summarized in Table II. Each value of the cross-sectional area in this table was determined from the results on the entropies of the adsorbed molecules.

TABLE II

MONOLAYER CAPACITIES (v_m) AND SURFACE AREAS (A), CUBIC POTASSIUM CHLORIDE (24.9 g.)

Adsorbate	Cross-sectional area a_0(Å^2)	v_m (micromoles)		A (m^2)	
		from $(-\Delta H)$	(B.E.T.)	from $(-\Delta H)$	(B.E.T.)
Argon	12.8	25.1	(24.0)	1.93	(1.85)
Oxygen	14.1	25.0	(23.6)	2.12	(2.00)
Nitrogen	13.8	20.7	(23.2)	1.73	(1.93)

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* Since the value of 300 cal./mol. includes the effect of the intermolecular attraction between adsorbed atoms, the true effect of the surface heterogeneity may amount to a considerably greater value than 300 cal./mol.

The Entropies of Adsorption.—As seen in Figs. 5, 6 and 7, the entropy decrease curve for each non-polar gas in the comparatively high coverage region has a tendency similar to the respective heat curve. The present results on the entropy of adsorption for the three gases are listed in Table III.

TABLE III
ENTROPY OF ADSORPTION, $-\Delta S$, ON CUBIC POTASSIUM CHLORIDE

Adsorbate	Temperature (°K)	$-\Delta S$ (e. u./mol.)	
		$\theta=0.5$	$\theta=1.0$
Argon	76.3	15.9	22.2
Oxygen	76.3	16.9	19.8
Nitrogen	76.5	19.0	28.7

As seen in Table III, Figs. 5, 6 and 7, the magnitudes of the entropies of adsorption and the variation of these with coverage for argon and oxygen resemble each other, while nitrogen shows a considerably different feature from other gases in the region of $\theta=0.5\sim1$. In order to obtain more information about the freedom of the adsorbed molecules, the entropies of the adsorbed molecules obtained from the present experiments were compared with those statistically calculated. The methods of the statistical calculations of the entropy for each gas under the standard states and of the entropy of each adsorbed phase were already given in the preceding paper$^{1)}$.

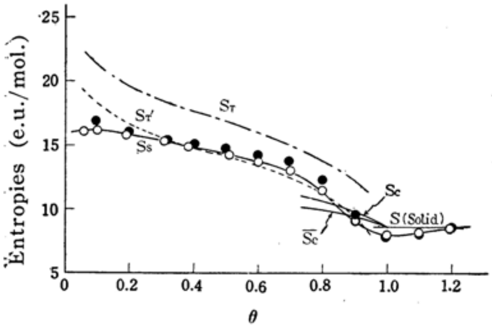

Fig. 9. Entropies of adsorbed argon on cubic potassium chloride at 76.3°K.
S_S……Experimental values;
○……Present values,
●……Kemball's values (79°K).
S_T……Entropies of the two-dimensional gas.
$S_{T'}$……Translational entropies of the two-dimensional gas.
S_C……Configurational entropies.
$\overline{S_C}$……Differential configurational entropies.

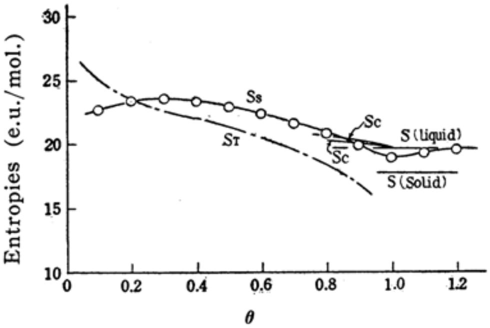

Fig. 10. Entropies of adsorbed oxygen on cubic potassium chloride at 76.3°K.
S_S……Experimental values.
S_T……Entropies of the two-dimensional gas.
S_C……Configurational entropies.
$\overline{S_C}$……Differential configurational entropies.

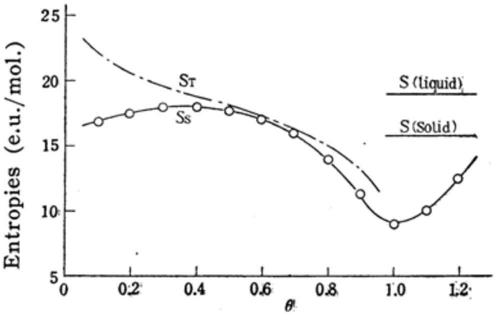

Fig. 11. Entropies of adsorbed nitrogen on cubic potassium chloride at 76.5°K.
S_S……Experimental values.
S_T……Entropies of the two-dimentional gas.

The entropy curves of the adsorbed molecules obtained from the present experiments are summarized in Figs. 9, 10 and 11, together with the calculated curves. For the sake of comparison, Kemball's values$^{5)}$ obtained from Orr's results$^{3)}$ are also shown in Fig. 9. The experimentally determined values in these figures are the partial molar total entropies and hence contain the entropy changes of the adsorbent$^{6)}$, while the calculated values are all the integral entropies and are usually somewhat greater than the values of the partial molar total entropies. Considering this fact, the experimental values (S_S) for adsorbed argon and nitrogen are in fairly good agreement with the calculated values of the two-dimensional gas (S_T) in the range of $\theta=0.3\sim0.9$. Since the entropy for oxygen associated with the vibrational

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5) C. Kemball, "Advances in Catalysis", Vol. II, Academic Press Inc., New York (1950), p. 233.
6) T. L. Hill, *J. Chem. Phys.*, **17**, 520 (1949).

motion normal to the surface was calculated from assuming that the vibrational frequency of oxygen is identical with that of argon, the present calculations of the two-dimensional gas for oxygen (S_T in Fig. 10) probably resulted in smaller values. Therefore, the agreement of the experimental curve (S_S) for oxygen with the calculated curve (S_T) of the two-dimensional gas in the region of $\theta=0.2\sim0.9$ is satisfied to a great extent.

The discrepancy between the experimental and calculated values at lower coverage ($\theta<0.2$) in each entropy curve would imply the entropy changes of the adsorbent. When θ approaches to unity, as seen in these figures, the restriction on the freedom of the adsorbed molecules is further increased and each entropy curve (S_S) falls below the calculated curve of the two-dimensional gas (S_T). In the range of $\theta>1$, the entropy of adsorbed argon remains close to the entropy of solid argon*, while the entropy of adsorbed oxygen closely approaches to the entropy of liquid oxygen**. This is in accord with the fact that the heat of sublimation of argon is similar to that of vaporization of oxygen. On the other hand, the entropy of adsorbed nitrogen in this same range is considerably smaller than that of solid nitrogen***.

According to the suggestion given by Kemball[5], 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, however, contains considerable uncertainties, since it is unreasonable to adopt the Langmuir model for the systems in which the non-uniformity of the surface in the low coverage region and the mutual interaction in the succeeding region are both predominant. In the present work, the configurational entropy for the localized adsorption was calculated from the expression given by Drain and Morrison[7]. The results shown in Fig. 9 or Fig. 10 indicate that the phase change of argon or oxygen from a gaseous film to a condensed film occurs at about $\theta=0.9$. However, since the mutual interaction between the adsorbed molecules was ignored in the present calculations of the configurational entropy, the present results on the phase change are also somewhat inaccurate.

Summary

The low-temperature adsorption of non-polar gases (argon, oxygen, nitrogen and carbon dioxide) on cubic potassium chloride was investigated. The present results on the isosteric heats of adsorption for these four gases indicate that the non-uniformity of the surface considerably predominates in the low coverage region and this is partly attributed to the lattice imperfection or the defects of the crystals.

The entropies of the adsorbed molecules were experimentally determined and compared with the calculated values of the perfect two-dimensional gas. These results show that the adsorbed molecules of argon, oxygen and nitrogen have the nature of the two-dimensional gas at least in the range of $\theta=0.3\sim0.9$. The present results also suggest that the phase change of adsorbed argon or oxygen from a gaseous film to a condensed film may occur at about $\theta=0.9$. These results on the freedom of the adsorbed molecules are similar with those on cubic sodium chloride previously reported.

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

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* The entropy of solid argon was calculated from the heat of sublimation and the value of the saturation pressure at 76.3° K.

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

*** The entropy of solid nitrogen was calculated from the work of Kingston, et al (*J. Am. Chem. Soc.*, **72**, 1780 (1950)).

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