The Adsorption of Non-polar Gases on Alkali Halide Crystals. VI[1]*. The Low-temperature Adsorption of Non-polar Gases on Octahedral Potassium Chloride**

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Introduction

In recent years comparatively few experiments have been carried out to determine the influence of crystal face on low-temperature adsorption. Measurable differences between the heats of adsorption of nitrogen on the (100), (110) and (111) faces of copper were found by Rhodin[2]. The alkali halides lend themselves admirably to such a study, since they have certain habits in which the crystal is solely bound by one type of face. Moreover, the crystal habit of potassium chloride can easily be completely modified by both inorganic ions and by very small amounts of dyestuffs[3,4]. The low-temperature adsorption of argon on the lead-modified and dye-modified samples of octahedral potassium chloride has recently been measured by Young[5], who has found measurable difference in the heats of adsorption between the (111) and (100) faces of potassium chloride.

In the former papers of this series[1,6-9], the author has described the measurements and the theoretical calculations of the low-temperature adsorption of non-polar gases on cubic alkali halide crystals. It was therefore of interest in the present work to study the low-temperature adsorption on octahedral potassium chloride, since this permits a comparison of the adsorptive properties of the (100) and (111) faces of potassium chloride crystals.

Experimental

Materials. — Lead-modified octahedral potassium chloride was prepared by rapidly cooling an aqueous solution of potassium chloride (A.R., Merck) containing enough lead chloride to provide $[Pb^{++}]/[K^+]=9/1000$. 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 a vacuum desiccator over phosphorous pentoxide for about two weeks. The lead content of this sample was estimated gravimetrically as lead chromate; the analysis gave $[Pb^{++}]/[K^+]=5/100$. Microscopic examination of this sample revealed a large number of very small octahedrals plus a few large cubes in which the defects in the corners or edges were somewhat perceptible; hence it was concluded that the (111) was the predominant surface plane. 25.9 g. of this sample which passed through a 48-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[6].

Apparatus and Procedure.—The apparatus and the procedure were already described in a previous communication[6]. The lead-modified 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 lead-modified octahedral potassium chloride are summarized in Figs. 1, 2, 3 and 4. The adsorption was found to be reversible and practically instantaneous. 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 entropies of adsorption, the gas phase under the pressure of 760 mmHg and the temperature which coincides with that of each isotherm was chosen as the standard state.

1) Part V of this series, T. Hayakawa, This Bulletin, **30**, 337 (1957).

* Part of this paper was read before the 7th Annual Meeting of the Chemical Society of Japan held in Tokyo, April, 1954. Another part of this paper was also read before the symposium on the surface heterogeneity of catalysis held in Kyoto, March, 1956.

2) T. N. Rhodin, Jr., *J. Am. Chem. Soc.*, **72**, 5691 (1950).

3) C. Frondel, *Am. Mineral.*, **25**, 91 (1940).

4) H. E. Buckley, "Crystal Growth," Chapman and Hall Ltd., London (1951), p. 461.

5) D. M Young, *Trans. Faraday Soc*, **48**, 548 (1952).

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

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

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

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

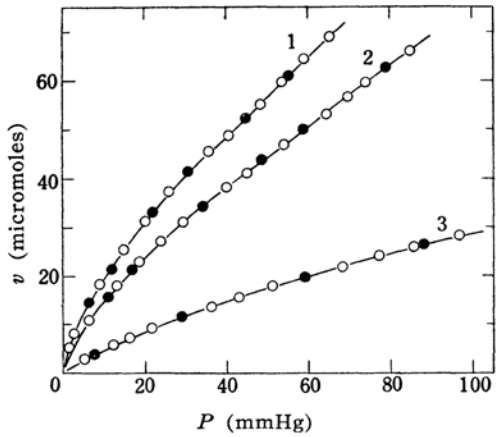

Fig. 1. Adsorption isotherms of argon on octahedral potassium chloride.
curve 1, 75.29°K; curve 2, 77.32°K;
curve 3, 85.42°K.

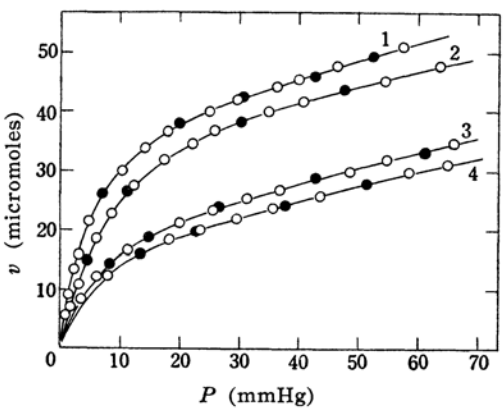

Fig. 2. Adsorption isotherms of oxygen on octahedral potassium chloride.
curve 1, 75.29°K; curve 2, 77.32°K;
curve 3, 88.41°K; curve 4, 90.20°K.

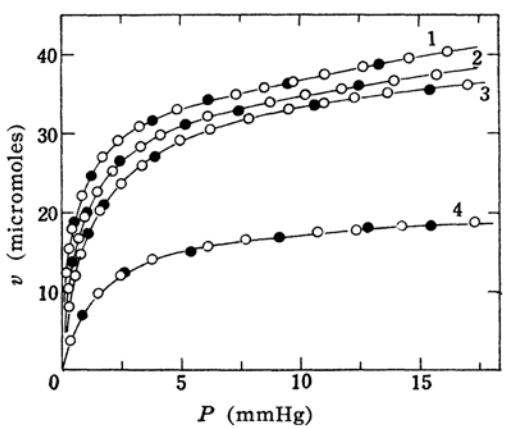

Fig. 3. Adsorption isotherms of nitrogen on octahedral potassium chloride.
curve 1, 73.69°K; curve 2, 75.79°K;
curve 3, 77.32°K; curve 4, 88.36°K.

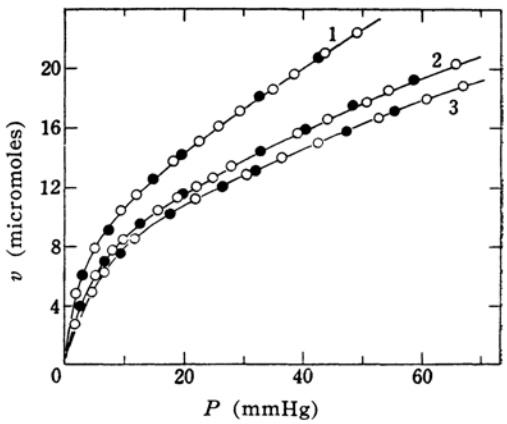

Fig. 4. Adsorption isotherms of carbon dioxide on octahedral potassium chloride.
curve 1, 187.66°K; curve 2, 192.63°K;
curve 3, 194.64°K.

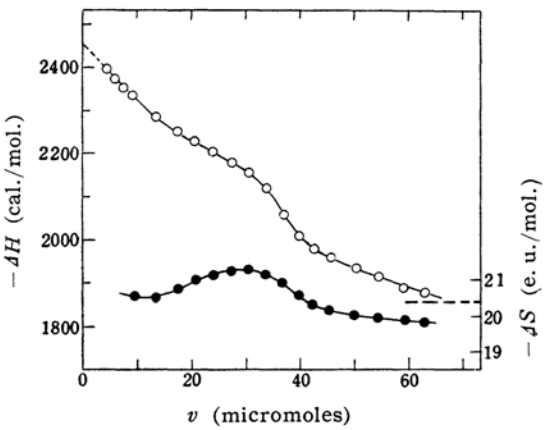

Fig. 5. Isosteric heats and entropies of adsorption of argon on octahedral potassium chloride.
-o-o-, isosteric heats of adsorption ($-\Delta H$);
-•-•-, entropies of adsorption ($-\Delta S$).

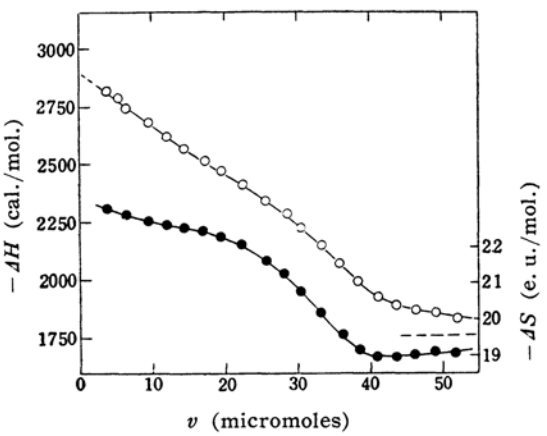

Fig. 6. Isosteric heats and entropies of adsorption of oxygen on octahedral potassium chloride.
-o-o-, isosteric heats of adsorption ($-\Delta H$);
-•-•-, entropies of adsorption ($-\Delta S$).

The present results on the isosteric heats and entropies of adsorption are summarized in Figs. 5, 6, 7 and 8. In the case of carbon dioxide, the measurements were not extended to the region of high coverage, since the amount adsorbed was considerably small in this temperature range.

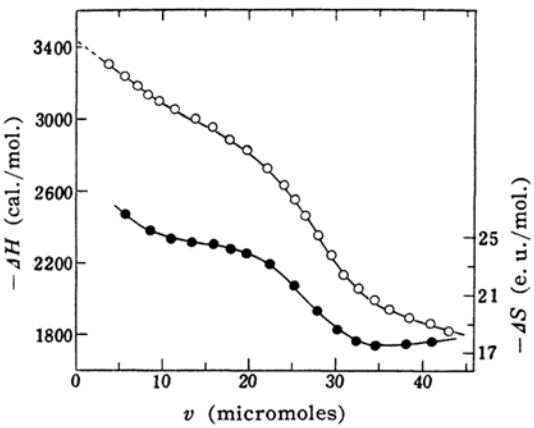

Fig. 7. Isosteric heats and entropies of adsorption of nitrogen on octahedral potassium chloride.
-o-o-, isosteric heats of adsorption ($-\Delta H$);
-•-•-, entropies of adsorption ($-\Delta S$).

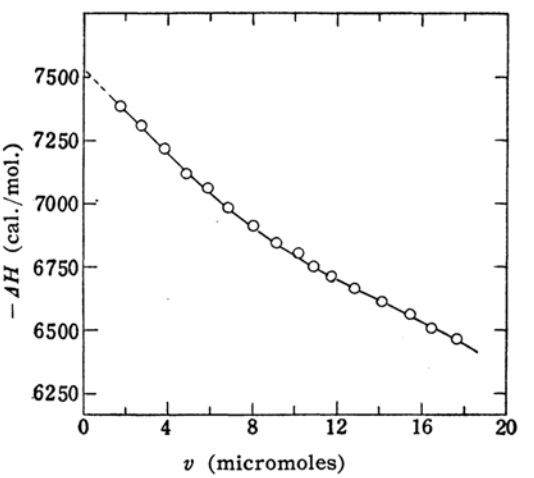

Fig. 8. Isosteric heats of adsorption of carbon dioxide on octahedral potassium chloride.

Discussion

Isosteric Heats of Adsorption.—As seen in Figs. 5, 6 and 7, the isosteric heats of adsorption obtained for the three gases (argon, oxygen and nitrogen) linearly fall at low coverage, reveal a considerably well-defined loop in the succeeding region, and then fall gradually to the value of latent heat of sublimation or evaporation at higher coverage. These results are markedly distinguishable from those already obtained for cubic potassium chloride[8].

Although the technique of habit-modification is open to the criticism that the impurities incorporated into the lattice during growth may alter the properties of the crystal surface, it has been indicated from Young's results[5] that the influence of the impurities is not clearly observable in the region where the surface is sparsely covered. The situation seems, however, somewhat different in the region of moderate coverage, since octahedral potassium chloride is bound by two types of (111) plane, one composed entirely of chlorine ions and the other of potassium ions. Now the present lead-modified adsorbent contains 5 lead ions for every 100 potassium ions, so that the heats of adsorption of these non-polar gases on the potassium faces are much more likely to be somewhat increased by the presence of this impurity. In order to obtain more informations on the isosteric heats of adsorption, the theoretical calculations of the initial heat of adsorption (i. e. the isosteric heat of adsorption at zero coverage) and the approximate calculation of the heat curve for each adsorption system were

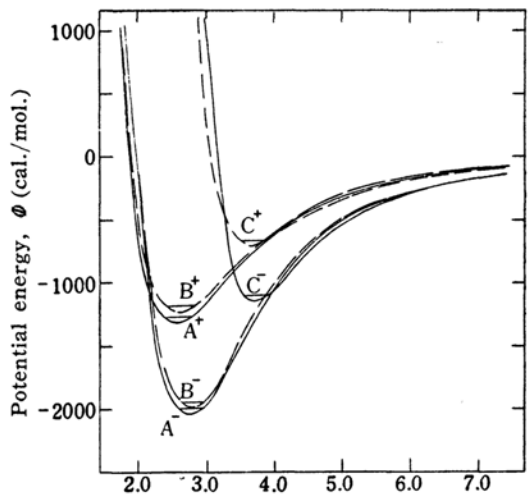

Fig. 9. Potential energy curves of argon on the (111) plane of potassium chloride. The symbols denote the type of sites and the surface layer.
A, above the center of a lattice triangle (directly above an underlying ion); B, above the centre of a lattice triangle (directly above the centre of an underlying lattice triangle); C, above a lattice point.

undertaken. In the case of nitrogen or carbon dioxide, however, owing to the low symmetry of the (111) plane and the poor covergence of the values of the quadrupole interaction potential, no satisfactory results have yet been obtained. The theoretical calculation of the adsorption potential of an isolated argon atom on the (111) plane of potassium chloride was carried out similarly following the method used by Young[10] except that the repulsive constant[7] of the modified Buckingham-Corner repulsive potential for argon was used. The calculated potential energy curves of argon for the six types of sites considered are shown in Fig. 9. From these curves the values of the equilibrium distance from the surface (Z_e), the minimum potential ($-\Phi_m$), the vibrational frequency normal to the surface (ν_z), the zero-point energy (ε_0) and the initial heat of adsorption ($-\Delta H_0$) were calculated. The results are summarized in Table I, together with the theoretical values of the initial heat of adsorption by Young.

As seen in Table I, the initial heat of adsorption of argon has been evaluated theoretically as 2140 cal./mol. for the Cl^- faces (sites type A) and 1420 cal./mol. for the K^+ faces (sites type A). Thus it may be anticipated that adsorption at low coverage proceeds exclusively on the Cl^- faces and when these faces become almost covered ($\theta > 0.5$) the proportion of argon atoms being adsorbed on the K^+ faces greatly increases. Similar tendencies may be expected for the adsorption of other non-polar gases on octahedral potassium chloride. Since the K^+ faces, on which adsorption takes place predominantly between $\theta = 0.5$ and 1.0, are somewhat activated by the presence of lead ions, the loop in each experimental heat curve (see Figs. 5, 6 and 7) may be mainly attributed to this activation by lead ions. Table I also indicates that the non-localized mobile adsorption is improbable* on account of the low adsorption heat of an argon atom adsorbed above a lattice point (sites type C). The approximate calculation of the heat curve of argon was also carried out similarly following the method used by Young[10], in which a localized hexagonal arrangement and an uniform surface were assumed. In the present calculation of the heat curve in a primary monolayer, the energy of a pair of argon atoms (distance 4.44 Å) was calculated using the modified Buckingham-Corner (6-exp) intermolecular potential[11]. The calculated heat curve for argon is shown in Fig. 10, together with the corresponding experimental values. For the sake of comparison, the

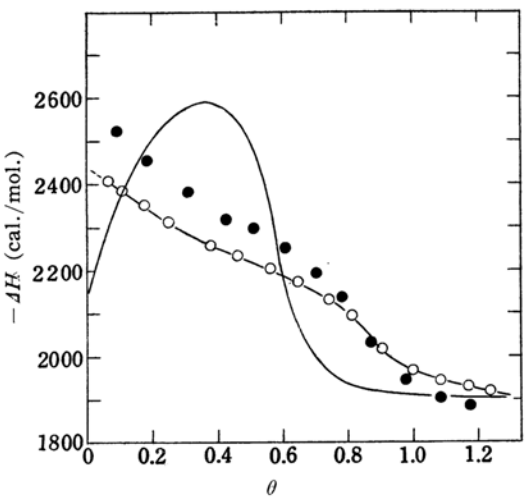

Fig. 10. Heat curves of argon on octahedral potassium chloride.
——, calculated heat curve; -o-o-, present experimental curve; •, values obtained by Young.

experimental curve obtained by Young is also shown in this figure. The values of coverage θ correlated to the present experimental values were derived from the monolayer capacity given in the subsequent discussion.

The agreement between the present experimental and calculated heat curves for argon is considerably satisfied at higher coverage, and this is probably attributed to the fact that the localized configuration has been adopted. While the discrepancy between the experimental and calculated heat curves at low coverage indicates that the surface heterogeneity is considerably predominant. Since it is of interest to compare the values of the initial heat of adsorption for the two crystal planes of potassium chloride, the experimental and theoretical values obtained in the present and preceding works[7,8] are given in Tables II and III. Since 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 imperfection of the crystal,

10) D. M. Young, *Trans. Faraday Soc.*, **47**, 1228 (1951).
* A partially localized arrangement seems, however, somewhat feasible on account of the similar properties of sites type A and B.
11) E. A. Mason and W. E. Rice, *J. Chem. Phys.*, **22**, 522 (1954).

TABLE I

RESULTS OBTAINED FROM THE POTENTIAL ENERGY CURVE, ARGON ON OCTAHEDRAL (111) KCl

Sites type	Surface layer	Z_e (Å)	$-\Phi_m$ (cal./mol.)	$\nu_z \times 10^{-12}$ (sec.$^{-1}$)	ε_0 (cal./mol.)	$-\Delta H_0$ (at 76°K) (cal./mol.)
Above the center of a lattice triangle (type A)	K^+	2.65	1307	0.86	40.7	1420(1610*)
	Cl^-	2.86	2030	0.94	44.6	2140(2220*)
Above the center of a lattice triangle (type B)	K^+	2.69	1232	0.82	38:9	1350(1500*)
	Cl^-	2.90	1988	0.96	45.5	2100(2370*)
Above a lattice ion (type C)	K^+	3.72	698	0.90	42.5	810(840*)
	Cl^-	3.74	1145	0.90	42.5	1250(1210*)

* values obtained by Young[10].

TABLE II

INITIAL HEAT OF ADSORPTION, $(-\Delta H_0)$, OF ARGON ON CUBIC (100) AND OCTAHEDRAL (111) KCl (in cal./mol.)

	(111) plane	(100) plane	$(-\Delta H_0)_{(111)} - (-\Delta H_0)_{(100)}$
$(-\Delta H_0)_{\text{expt.}}$	2460	2080	380
$(-\Delta H_0)_{\text{calcd.}}$	2140	1900	240
$(-\Delta H_0)_{\text{expt.}} - (-\Delta H_0)_{\text{calc.}}$	320	180	

TABLE III

INITIAL HEAT OF ADSORPTION, $(-\Delta H_0)_{\text{expt}}$, OF NON-POLAR GASES ON CUBIC (100) AND OCTAHEDRAL (111) KCl (in cal./mol.)

Adsorbate	$(-\Delta H_0)_{(111)}$	$(-\Delta H_0)_{(100)}$	$(-\Delta H_0)_{(111)} - (-\Delta H_0)_{(100)}$
Oxygen	2870	2410	460
Nitrogen	3440	3010	430
Carbon dioxide	7540	6400	1140

TABLE IV

MONOLAYER CAPACITIES (V_m) AND SURFACE AREAS (A), OCTAHEDRAL POTASSIUM CHLORIDE (25.9 g.)

Adsorbate	Cross-sectional area, a (Å^2)	V_m (micromoles) from $(-\Delta S)$	V_m (micromoles) (B. E. T.)	A (m^2) from $(-\Delta S)$	A (m^2) (B. E. T.)
Argon	14.4	41.4	(40.9)	3.59	(3.55)
Oxygen	14.1	40.2	(36.6)	3.41	(3.11)
Nitrogen	17.0	34.4	(37.2)	3.52	(3.81)

TABLE V

NON-CONFIGURATIONAL ENTROPIES (S_{NC}) ON OCTAHEDRAL POTASSIUM CHLORIDE AT $\theta = 0.4$

Adsorbate	$(S_{NC})_{\text{calcd.}}$, (e. u./mol.)	$(S_{NC})_{\text{expt.}}$, (e. u./mol.) $(S_s - S_c)$	$(S_s - S_c)$
Argon	9.6(a)	5.7	6.7
Oxygen	13.9(b)	12.9	13.4
Nitrogen	10.9(c)	7.8	8.9

(a) $\nu_x = \nu_y = 8.2 \times 10^{11}$ sec.,$^{-1}$ ν_z (mean value) $= 0.93 \times 10^{12}$ sec.$^{-1}$

(b) Following values were assumed: $\nu_x = \nu_y = 8 \times 10^{11}$ sec.,$^{-1}$ $\nu_z = 1.0 \times 10^{12}$ sec.$^{-1}$

(c) Following values were assumed: $\nu_x = \nu_y = 8.5 \times 10^{11}$ sec.,$^{-1}$ $\nu_z = 1.1 \times 10^{12}$ sec.$^{-1}$

Table II indicates that the surface heterogeneity of this type for octahedral potassium chloride is more predominant than that for cubic crystals. As seen in Tables II and III, the experimental values of the initial heat of adsorption for these non-polar gases on the (111) plane of potassium chloride are all considerably greater than the corresponding values on the (100) plane. As it has already been pointed out by Young[5], this is mainly attributed to the facts that the (111) plane contains fewer ions per unit area than the (100) plane and that initial adsorption on the (111) plane occurs predominantly on the Cl^- faces.

Monolayer Capacities. — As discussed above, it is reasonable to consider that adsorption in the range between $\theta=0.5$ and 1.0 takes place predominantly on the K^+ faces. In this range, since the increase in the heats due to the mutual interaction may be overcome by the decrease in the heats due to the increased proportion of adsorption on the K^+ faces, the isosteric heats steadily decrease with the increased amounts adsorbed. At higher coverage ($\theta>1$), since the formation of multilayers proceeds on a large scale, the isosteric heats of adsorption in this range slowly decrease and approach the latent heat of sublimation or evaporation. Consequently, in the region where θ approaches unity, there will be a bend point in each heat or entropy curve (see Figs. 5, 6 and 7). Considering this fact, it seems reasonable to assign this value of the amount adsorbed as a monolayer capacity.

The present results on the monolayer capacities and thus calculated surface areas are summarized in Table IV. Each value of the cross-sectional area in this table was determined from referring to the results on the entropies of the adsorbed phase.

Entropies of the Adsorbed Phase. — The present results on the entropies of adsorption shown in Figs. 5, 6 and 7 are obviously distinguishable from those already obtained for cubic potassium chloride[8]. In order to obtain more information about the freedom of the adsorbed atoms or molecules, the entropies of the adsorbed phase were calculated from the experimental data and compared with those already obtained for cubic potassium chloride. The method of the statistical calculations of the entropies of the gas phase under the standard states was already given in a previous communication[6]. The integral (S_c) and differential ($\bar{S}_c$) configurational entropies were calculated from the present experimental data using the expressions derived by Drain and Morrison[12]. The experimental entropy curves of the adsorbed phase on octahedral potassium chloride are summarized in Figs. 11, 12 and 13, together with the experimental curves on cubic potassium chloride. As seen in these

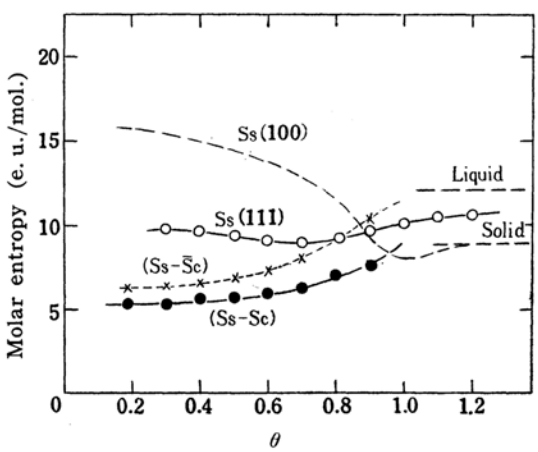

Fig. 11. Molar entropies of adsorbed argon on potassium chloride.
-o-o-, entropies on the (111) plane;
-----, entropies on the (100) plane.

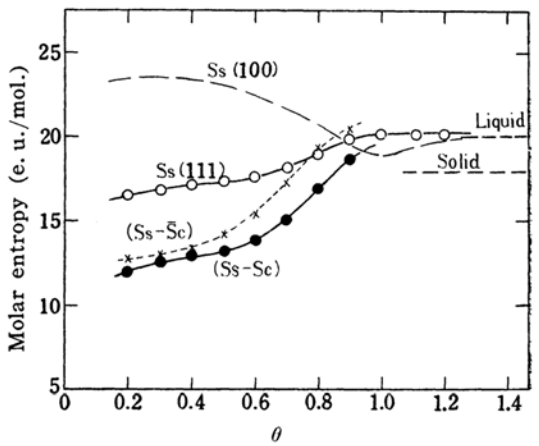

Fig. 12. Molar entropies of adsorbed oxygen on potassium chloride.
-o-o-, entropies on the (111) plane;
-----, entropies on the (100) plane.

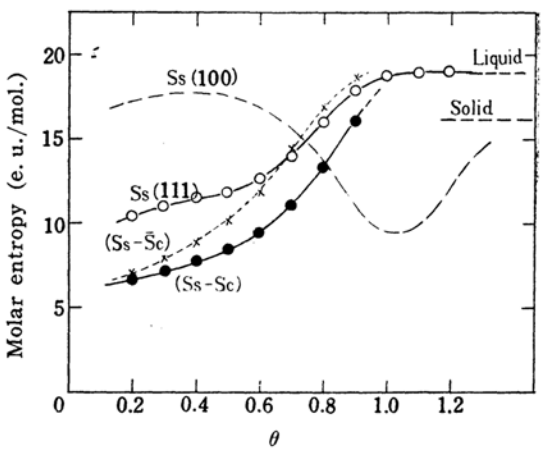

Fig. 13. Molar entropies of adsorbed nitrogen on potassium chloride.
-o-o-, entropies on the (111) plane;
-----, entropies on the (100) plane.

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

figures, the experimental curves (S_s) of these non-polar gases on octahedral potassium chloride show quite different features from those on cubic potassium chloride. Since the experimental curves for the (100) plane of potassium chloride well agree with the calculated curves of the two-dimensional gas at least in the range of $\theta<0.8$[8], it is reasonable to consider that the low-temperature adsorption of these non-polar gases on the (111) plane of potassium chloride is localized (or at least partially localized) in this same range. These figures also indicate that at higher coverage ($\theta>1$) the entropies of each adsorbed phase all remain close to the entropies of the liquid state.

Since the experimentally determined values (S_s) in these figures are the partial molar total entropies[13], the non-configurational entropies of the adsorbed phase on octahedral potassium chloride may be indicated approximately by ($S_s-\bar{S}_c$) or (S_s-S_c) curves shown in these figures. Now the non-configurational entropies of the adsorbed atoms or molecules are approximately calculated and compared with the experimental values at $\theta=0.4$. The reason of choosing the experimental values at $\theta=0.4$ is mainly that at this coverage adsorption proceeds exclusively on the Cl^- faces and these surfaces are almost covered by the adsorbed atoms or molecules.

In the present work, the entropy associated with the vibrational motion parallel to the surface (two degree of freedom, x and y directions) was approximately calculated following the method used by Hill[14], in which the vibrational motion was assumed to be isotropic. In the case of oxygen or nitrogen, the entropy associated with the planar rotation in the plane parallel to the surface was calculated using an expression derived by Halford[15]. Since the surface essentially introduces a high potential barrier restricting the turning over of the molecular axis, another rotational motion may be replaced by the rocking vibration of the molecular axis[14]. In the present calculations, however, the entropy associated with this rocking vibration was assumed to be negligible. The calculations of the entropy associated with the intramolecular vibration resulted in the values of nearly zero. Further, the electronic entropy of the oxygen molecule was taken into consideration. The calculated results are summarized in Table V, together with the experimental values.

As seen in Table V, the agreement between the experimental and approximately calculated values of the non-configurational entropy for oxygen is considerably satisfied, while the experimental values of argon and nitrogen are somewhat smaller than the calculated values. However, in view of the facts that the present calculations contain considerable approximations and that the experimentally determined values (S_s) are all the partial molar total entropies, the agreement may be regarded as rather satisfactory.

Summary

1. The low-temperature adsorption of non-polar gases on octahedral potassium chloride was studied. The present results were compared with those already obtained for cubic potassium chloride.

2. The initial heats of adsorption of non-polar gases on the (111) plane of potassium chloride are all considerably greater than the corresponding values on the (100) plane.

3. The surface heterogeneity due to the imperfection of the crystal for octahedral potassium chloride is more predominant than that for cubic crystals.

4. The present results on the isosteric heat of adsorption and the entropies of the adsorbed phase indicate that the low-temperature adsorption of non-polar gases on the (111) plane of potassium chloride is practically localized.

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13) T. L. Hill, *J. Chem. Phys.*, **17**, 520 (1949).
14) T. L. Hill, ibid., **16**, 181 (1948).
15) J. O. Halford, ibid., **2**, 694 (1934).