The Adsorption of Non-polar Gases on Alkali Halide Crystals.
*I. The Low-temperature Adsorption of Non-polar Gases on Cubic Sodium Chloride**

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Introduction

The quantitative measurements of the low-temperature adsorption of non-polar gases (argon, oxygen, and nitrogen) on cubic potassium chloride and cesium iodide (rhombic dodecahedron) were reported by Orr1) and Tompkins and Young2) respectively. The adsorption of argon on two samples of octahedral potassium chloride (lead- and dye-modified) has recently been measured by Young3).

Though the adsorption equilibrium is

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* Part of this paper was read before the 8th Annual Meeting of the Chemical Society of Japan held in Tokyo, April, 1955. Other part of this papar was also read before the symposium on the surface heterogeneity of catalysis held in Kyoto, March, 1956.

1) W. J. C. Orr, *Proc. Roy, Soc.*, **A173**, 349 (1939).

2) F. C. Tompkins and D. M. Young, *Trans. Farad. Soc.*, **47**, 77 (1951).

3) D. M. Young, ibid., **48**, 548 (1952).

influenced both by the heats and the entropies of adsorption, the variation in the isosteric heats of adsorption with the surface coverage was discussed only in the investigations mentioned above. The variation in the entropies of argon with the coverage on cubic potassium chloride was given by Kemball[4] only from Orr's results[1]. Moreover, no reasonable explanation was given for the differences in the values of the initial heat of adsorption (the values extrapolated to zero coverage) with molecular species of adsorbates.

The present experiments were undertaken as a part of the systematic investigations to obtain the precise information on the following properties of the low-temperature adsorption.

(1) The surface heterogeneity of alkali halide crystals.

(2) The differences in the values of the initial heat of adsorption with molecular species of non-polar adsorbates.

(3) The characteristic behavior of each non-polar molecule on alkali halide crystals.

(4) The differences in these adsorptive properties with lattice parameters and crystal planes.

The choice of argon, oxygen, nitrogen and carbon dioxide as nonpolar adsorbates mainly depended on avoiding the complications which the presence of permanent dipoles would introduce and on the intention of examining the influence of permanent quadrupoles of these molecules.

Experimental

Materials.—*Sodium Chloride* was recrystallized by cooling rapidly an aqueous solution of sodium chloride (extra pure grade) 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 a vacuum dessicator over phosphorous anhydride during about two weeks. Microscopic examination of this sample of sodium chloride 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.

Helium was supplied by Teikoku Oxygen Co. as spectroscopically pure and was not further purified. *Argon* was also supplied by the Teikoku Oxygen Co. (purity was about 99.9%); this sample was purified by passing over phosphorous anhydride and then by farctionation. *Oxygen* was prepared by the thermal decomposition of silver oxide at 250°C, and was purified by passing over phosphorous anhydride and then passing through traps cooled in liquid oxygen, and finally by fractionation. *Nitrogen* was prepared by heating pure sodium azide, outgassed at 150°C for five hours, to 270°C and was purified by passing over phosphorous anhydride and then passing through traps cooled in liquid nitrogen. *Carbon dioxide* was prepared by heating magnesium carbonate (analytically pure), outgassed at 450 °C for three hours, to 650°C and was purified by passing over phosphorous anhydride, passing through traps cooled in solid carbon dioxide, and finally by several fractionations. Each sample gas was analysed using a Hitachi-RMC mass spectrometer (single focusing, 90° sector type of magnetic field, 135-mm. radius of curvature of ion path), and no impurity was detected excepting few small background peaks.

Apparatus. — The principal diagrams of the apparatus are shown in Figs. 1 and 2. The diagram of the adsorption apparatus is shown in Fig. 1. This consisted of a doser, whose volume was accurately determined with mercury, (18.06 cc. at 20°C), connected to an adsorption bulb R containing 32.3 g. of cubic sodium chloride crystals (passed through a 45-mesh sieve) and a manometer M_2 containing the oil (Apiezon B). M_1 shows a mercury manometer (inner diameter was about 12 mm.) by means of which the equilibrium pressure could be accurately determined to 0.05 mm. with a cathetometer. The lower equilibrium pressure could be accurately determined by an oil (Apiezon B) manometer M_2 to 0.05 mm. (i. e., 0.004 mmHg) with a cathetometer. T_1 and T_2 indicate traps cooled in liquid refrigerant, and the liquid level of each Dewar vessel attached to T_1 and T_2 was maintained constant throughout the measurement. In order to minimize the dead space, the adsorption system (excepting the bulb R and the doser) and

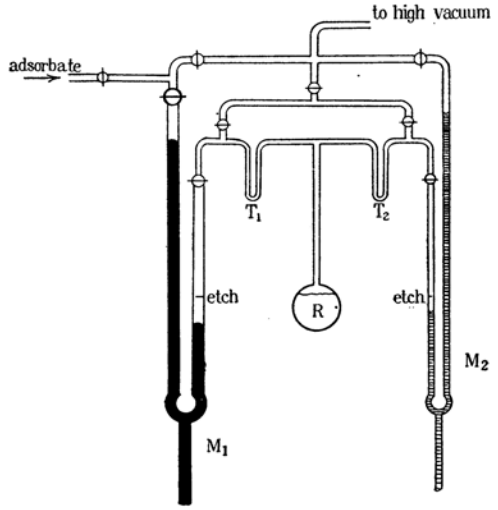

Fig. 1. Diagram of the adsorption apparatus.

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

manometer M_2 were of small bore tubing (3 mm.).

The diagram of the low-temperature thermostat regulator (similar to that used by Orr) is shown in Fig. 2. A closed Dewar vessel was filled with liquid refrigerant enclosing the small bulb (A) of a vapour pressure thermometer (M_3) containing oxygen or nitrogen, depending on the temperature to be measured. The vapour pressure thermometer acted both as a temperature resister and as a manostatic device. In one limb two Pt contacts were sealed at C, and at any desired pressure, depending on the temperature required, a relay circuit operated a filter pump through a fine capillaries (D) for controlling the rate of evacuation. Because of the low thermal conductivity of the liquid refrigerants, vigorous stirring was essential and attained by a regulated stream of oxygen or nitrogen. The position of the liquid level in the closed Dewar vessel was indicated by a float and maintained constant (2 mm.) throughout the measurements. The temperature variation recorded by the vapour pressure thermometer was never greater than 0.02°C. The vapour pressure data of Cath⁵⁾ for oxygen and of Giauque and Clayton⁶⁾ for nitrogen were used.

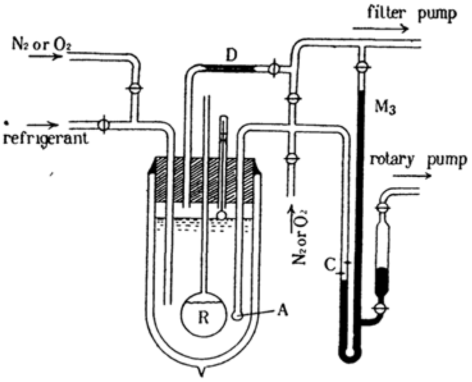

Fig. 2. Diagram of the low temperature thermostat regulator.

For the adsorption measurements of carbon dioxide, the enclosed Dewar vessel (c. f. Fig. 2) was filled with a mixture of each organic solvent (purified methanol, absolute alcohol, or dry ether) and solid carbon dioxide, depending on the temperature to be measured. In this case, the temperature was measured by a Copper-Constantan thermocouple inserted into the Dewar vessel.

Procedure.—After outgassing at 280∼300°C for six hours before commencing each experiment and cooling the adsorbent to the desired temperature of adsorption, gas was admitted to the doser and the pressure at constant volume was measured by means of a mercury manometer (M_1 in Fig. 1). Then the gas was completely transferred to the adsorption system by admitting mercury into the doser. The adsorption was practically instantaneous and the equilibrium pressure at constant volume was measured.

The amount of gas adsorbed is given by

$$\left.\begin{aligned} v&=\frac{(\sum P_D)V_D}{RT_R}-\frac{P}{R}f \\ f&=\frac{V_0}{T_R}+\frac{V-C}{T_c}+\frac{V'-C'}{T_c'} \end{aligned}\right\} \qquad (1)$$

where $\sum P_D$ is the sum of the successive doser pressures in atm., V_D the volume of the doser in litres, P the equilibrium pressure in atm., V_0 the volume in litres of the adsorption system exposed at room temperature, V the volume in litres of the adsorption bulb (excluding the adsorbent) and the connecting tube up to the level of liquid refrigerant, V' the volume in litres of traps (T_1 and T_2) up to the level of liquid refrigerant, C the volume contraction in litres of the adsorbent and bulb on cooling, C' the volume contraction in litres of traps (T_1 and T_2) on cooling, R the gas constant in l·atm./degree·mol., v the amount of gas adsorbed in moles, T_R room temperature in °K, T_c the adsorption temperature in °K, and T_c' the temperature of traps (T_1 and T_2) in °K.

The value of the factor f for each successive measurement was determined by carrying out a blank run with helium, using Eq. (1) and assuming v to be zero. The experimental error in v mainly comes from the measurement of the equilibrium pressure, but the low equilibrium pressure was accurate to 0.004 mmHg as mentioned above and the consequent error in v was about ±1%. The value of f was different for two series of measurements.

Results

The isotherms obtained for the four gases on cubic sodium chloride crystals are summarized in Figs. 3, 4, 5 and 6. The adsorption was found to be reversible in this temperature range. The isosteric

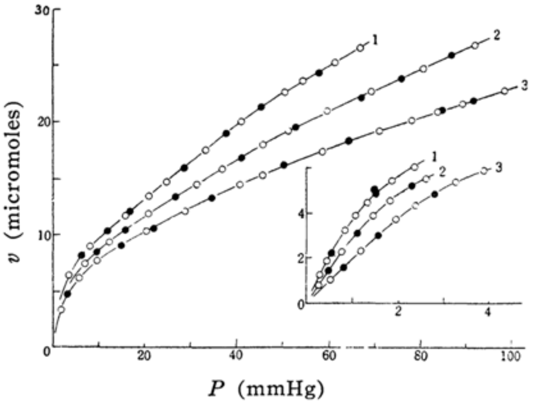

Fig. 3. Adsorption isotherms of argon on cubic sodium chloride.
1···73.69°K, 2···75.40°K, 3···77.32°K,
—○—○— adsorption, —●—●— desorption.

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5) A. Cath, Comm. Phys Lab. Univ. Leiden, No. 152d (1918).

6) W. F. Giauque and J. O. Clayton, *J. Am. Chem. Soc*, **55**, 4875 (1933).

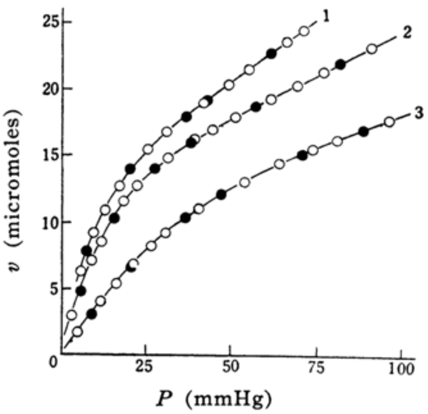

Fig. 4. Adsorption isotherms of oxygen on cubic sodium chloride.
1···75.40°K, 2···77.32°K, 3···83.08°K,
—○—○— adsorption, —●—●— desorption.

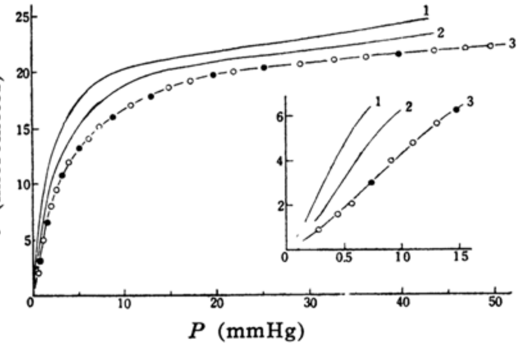

Fig. 5. Adsorption isotherms of nitrogen on cubic sodium chloride.
1···73.75°K, 2···75.41°K, 3···77.32°K,
—○—○— adsorption, —●—●— desorption.

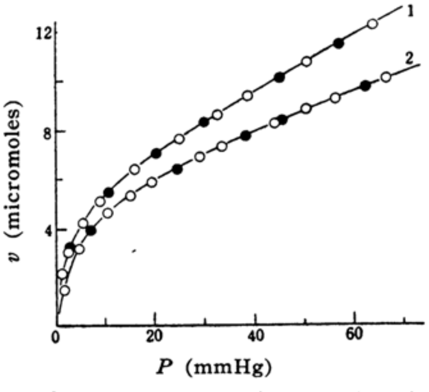

Fig. 6. Adsorption isotherms of carbon dioxide on cubic sodium chloride.
1···187.6°K, 2···194.6°K,
—○—○— adsorption, —●—●— desorption.

heats of adsorption as a function of v were calculated from these isotherms using the Clausius-Clapeyron equation in the form

$$\left(\log\frac{P_1}{P_2}\right)_v=\frac{\Delta H}{2.303\,R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \tag{2}$$

where P_1 and P_2 are the equilibrium pressures (in mmHg) at the temperatures of T_1(°K) and T_2(°K) respectively, $-\Delta H$ the isosteric heat of adsorption in cal./mol., R the gas constant (1.987 cal./degree·mol.). The isosteric heats of adsorption for argon, oxygen and nitrogen showed no definite trend with temperature within the experimental error.

The entropy decrease due to the adsorption as a function of v was then calculated from the following equation

$$\left.\begin{aligned}&4.576\,T\log(P/760)_v=\Delta H-T\cdot\Delta S\\&-\Delta S=(S_g-S_s)\end{aligned}\right\} \tag{3}$$

where T is the temperature of each isotherm in °K, P the equilibrium pressure in mmHg, $-\Delta S$ the entropy of adsorption in e.u./mol., S_g the entropy of the gas phase under the standard state in e.u./mol., S_s the entropy of the adsorbed phase in e.u./mol. The choice of the standard states of the gas was such that the pressure is 760 mmHg (independent of temperature) and the temperature coincides with that of each isotherm. Fig. 7, 8, 9 and 10 show the isosteric heats of adsorption averaged over the whole temperature range and the entropy of adsorption. The measurements were not extended to the high adsorption region for carbon dioxide, because the amount adsorbed was considerably small in this temperature range.

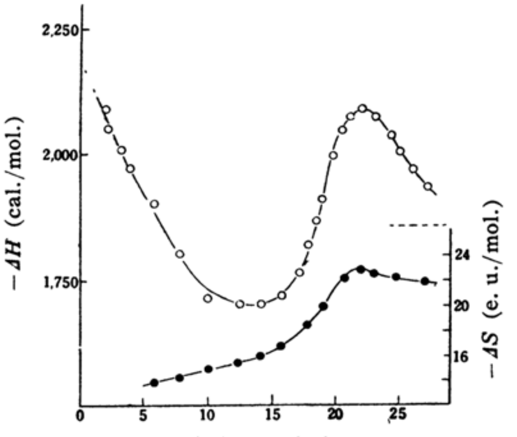

Fig. 7. Isosteric heats and entropies of adsorption for argon on cubic sodium chloride.
—○—○— isosteric heats of adsorption ($-\Delta H$),
—●—●— entropies of adsorption ($-\Delta S$),
- - - - - latent heat of sublimation.

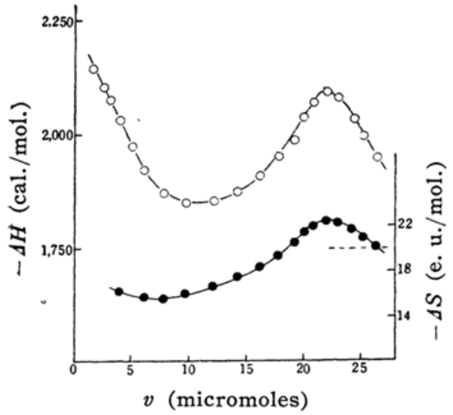

Fig. 8. Isosteric heats and entropies of adsorption for oxygen on cubic sodium chloride.
—○—○— isosteric heats of adsorption ($-\Delta H$),
—●—●— entropies of adsorption ($-\Delta S$),
- - - - - latent heat of evaporation.

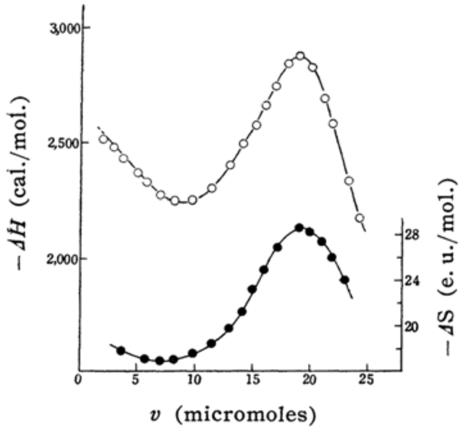

Fig. 9. Isosteric heats and entropies of adsorption for nitrogen on cubic sodium chloride.
—○—○— isosteric heats of adsorption ($-\Delta H$),
—●—●— entropies of adsorption ($-\Delta S$).

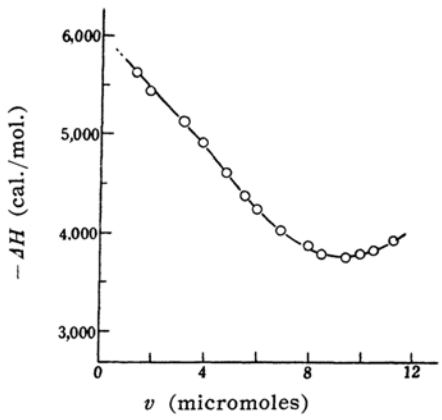

Fig. 10. Isosteric heats of adsorption for carbon dioxide on cubic sodium chloride.

Discussion

Isosteric Heats of Adsorption.—The isosteric heats of adsorption thus obtained for the three gases (argon, oxygen and nitrogen) fall initially, rise to a maximum, and then fall steadily to the value of latent heat of vaporization or sublimation with increasing amount of adsorption. These results of the present experiments for cubic sodium chloride are similar to the results obtained by Orr for cubic potassium chloride. The initial decrease in the heat of adsorption of these four non-polar gases is attributed to the non-uniformity of the surface. Since mutual interaction forces of adsorbed molecules are attractive, the isosteric heats on the uniform surface in this low coverage region must be slightly increased with the increase of the amount adsorbed. The non-uniformity of alkali halide surface in the low coverage region was attributed by Tompkins and Young[2)] to the defects in the corners and edges of the crystals. As it was generally observed, the crystal defects in the present sample were clearly visible under the microscope.

Though it seems reasonable to consider that the crystal defects or the lattice imperfections have some influence over the non-uniformity of alkali halide crystals, the magnitude of these influences in the present systems seems rather small compared with the present results. (The detailed discussion will be given in the succeeding paper.) The values of the initial heat of adsorption obtained for the four non-polar gases are summarized in Table I, together with the calculated values which will be given in the succeeding paper.

TABLE I

INITIAL HEAT OF ADSORPTION, $-\Delta H_0$, ON CUBIC (100) SODIUM CHLORIDE

Adsorbate	$(-\Delta H_0)_{\text{expt.}}$ (cal./mol.)	$(-\Delta H_0)_{\text{calc.}}$ (cal./mol.)
Argon	2190	1980
Oxygen	2240	—
Nitrogen	2670	2400
Carbon Dioxide	6070	5420

As seen in Table I, the experimental value of the initial heat of adsorption for argon comes closely near to that for oxygen. This is in good agreement with the fact that there is a very close similarity between the potential energy curves for two argon atoms and two oxygen molecules[7,8]. On the other hand, the initial heat of adsorption for nitrogen is about 450 cal./mol. greater than those of argon and oxygen. This result is, however, not peculiar to the present experiment but has been similarly observed by Orr[1] with adsorption on cubic potassium chloride. In the case of nitrogen it would be expected from the lower heat of evaporation of the liquid compared with argon or oxygen and also from the similarity of the intermolecular potential energy between nitrogen and argon, that the adsorption heat of nitrogen would be somewhat smaller than that of argon or oxygen. Though the intermolecular potential energy curve for carbon dioxide is considerably different from that of argon or oxygen, the present differences in the initial heat of adsorption for these gases are considerably greater than the results anticipated from the differences in their intermolecular potential energy curves[9].

Recently, Smith and Howard[10] and Hill and Smith[11] have been able to measure the permanent quadrupole moments from line broadening of microwave spectra. Their results show that nitrogen and carbon dioxide (especially carbon dioxide) have considerably larger permanent quadrupole moments compared with argon and oxygen. Although, in general, permanent electric dipoles and quadrupoles are of minor importance in intermolecular potentials between gas molecules[12], the situation seems quite different when considering the adsorption potential of a molecule in the large electric field near the surface of an ionic crystal. The theoretical treatment of the adsorption potential between a nitrogen or a carbon dioxide molecule and the lattice ions of cubic (100) sodium chloride has been carried out by the present author. Though the details of this theoretical treatment will be reported in the succeeding paper, it is pointed out that the order of magnitude of the experimentally obtained initial heat of adsorption for argon, nitrogen and carbon dioxide is in considerably good agreement with the results of these theoretical calculations (see Table I).

Entropies of Adsorption.—As indicated in Figs. 7, 8 and 9, the variation of the entropies of adsorption with the amount adsorbed in the comparatively high coverage region is in the similar tendency with the variation of the isosteric heats of adsorption.

The present results on the entropy of adsorption for three non-polar gases are listed in Table II. For the reasons discussed below, the amount adsorbed corresponding to the maximum value of the heats or the entropies of adsorption was preferred as the monolayer capacity.

TABLE II

ENTROPIES OF ADSORPTION, $-\Delta S$, ON CUBIC SODIUM CHLORIDE AT 76.3°K

Adsorbate	$-\Delta S$ (e. u./mol.)	
	$\theta=0.5$	$\theta=1.0$
Argon	15.2	22.8
Oxygen	16.4	22.5
Nitrogen	18.0	28.7

As seen in Table II, Figs. 7, 8 and 9, the magnitudes of the entropies of adsorption and the variation of these with coverage for argon and oxygen resemble each other, while nitrogen shows considerably different features from those in the region of $\theta=0.5\sim1$. In order to obtain more information about the freedom of the adsorbed molecules, the entropy curves obtained in the present experiments were compared with the calculated values for these three gases. The entropy (the practical entropy) of each gas under the standard state (760 mmHg) was statistically calculated in the following manner.

The translational entropy of a perfect three-dimensional gas was calculated from the Sackur-Tetrode equation. No correction depending on deviation from ideal behavior was made, because each correction calculated from the Berthelot equation resulted in a small value and, furthermore, no correction of the same kind was made for the translational entropy (two-dimensional) of each adsorbed molecule.

The rotational entropy was calculated from an expression given by Halford[13], and the vibrational entropy was calculated from the usual statistical expression given below, which was shown to be nearly zero. Further, oxygen has an electronic entropy amounting to 2.17 e. u./mole., while the

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[7] J. E. Lennard-Jones, *Proc. Phys. Soc.*, **43**, 461 (1931).

[8] R. H. Fowler, *Physica*, **5**, 44 (1938).

[9] J. O. Hirschfelder, R. B. Bird and E. D. Spoz, *J. Chem. Phys.*, **16**, 968 (1948).

[10] W. V Smith and R. Howard, *Phys. Rev.*, **79**, 132 (1950).

[11] R. M. Hill and W. V. Smith, ibid, **82**, 451 (1951).

[12] H. Margenau, *Rev. Mod. Phys.*, **11**, 1 (1939).

[13] J. O. Halford, *J. Chem. Phys.*, **2**, 694 (1934).

nuclear spin contribution of nitrogen was omitted in the present calculations according to the common practice.

The statistical calculation of the entropy of the adsorbed material was as follows.

For non-localized adsorption the translational entropy of a perfect two-dimensional gas was calculated according to the equation derived by Kemball[14]

$$S'_T\,(\text{e. u./mol.}) = 4.576 \log MTa_0\left(\frac{1-\theta}{\theta}\right) \tag{4}$$

where M is the molecular weight and a_0 the cross-sectional area of the adsorbed molecule.

The entropy associated with the vibration normal to the surface, replacing the translational motion, was calculated from an expression

$$S_v\,(\text{e. u./mol.}) = 1.987\left\{\frac{h\nu}{KT}\left(e^{h\nu/KT}-1\right)^{-1} - 2.303 \log\left(1-e^{-h\nu/KT}\right)\right\} \tag{5}$$

where ν is the frequency of the vibration normal to the surface*, h the Planck's constant and K the Boltzmann's constant.

Since the surfce essentially introduces a high potential barrier restricting the turning over of the molecule, the two rotational degrees of freedom of oxygen or nitrogen will become effectively one degree of freedom of planar rotation in the plane parallel to the surface and one degree of freedom of rocking vibration as discussed by Hill[15]. In the present calculations the entropy associated with this rocking vibration was assumed to be negligible and the entropy associated with one degree of planar rotation was calculated from the above-mentioned expression given by Halford. The entropy associated with the intramolecular vibration of the adsorbed molecule was also calculated from Eq. (5), but these calculations resulted in the values of nearly zero.

For the localized adsorption there will be a configurational term associated with the number of ways of distributing the molecules over the surface. The configurational entropy on the Langmuir model, where the surface heterogeneity and the mutual interaction between the adsorbed molecules are both ignored, is given by

$$S'_c\,(\text{e. u./mol.}) = 4.576\left\{\frac{1}{\theta}\log\frac{1}{\theta} - \left(\frac{1-\theta}{\theta}\right)\log\left(\frac{1-\theta}{\theta}\right)\right\} \tag{6}$$

This equation (6) could not be used for the present calculations, because the heat curves indicate that the non-uniformity of the surface and the mutual interaction between the adsorbed molecules are both predominant.

Drain and Morrison[16] have recently experimentally determined the configurational entropy for the system in which the non-uniformity of the surface was taken into consideration and the mutual interaction between the adsorbed molecules was ignored. From this, we obtain approximately for the present systems

$$S_c\,(\text{e. u./mol.}) = 1.987 \times \frac{\pi^2}{3} \times \frac{d\ln v}{d\ln P} \tag{7}$$

where v is the amount adsorbed and P the equilibrium pressure.

The entropy curves determined from the present experimental results and the entropy curves calculated from the above-mentioned methods are summarized in Figs. 11, 12 and 13. The experimentally determined values in these figures are the partial molar total entropies and hence

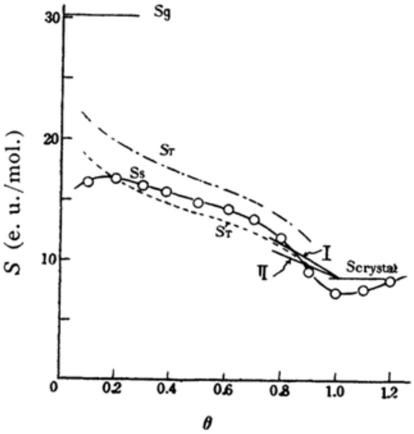

Fig. 11. Entropies of argon adsorbed on cubic sodium chloride at 76.4°K.

S_S···experimental values, S_T···calculated values (two-dimensional gas), Curve I···(Scrystal+S_c) Curve II···(Scrystal+$\overline{S}_c$). (The entropy of the solid was calculated from the heat of sublimation and the value of the saturation pressure at 76.4 °K.)

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14) C. Kemball, *Proc. Roy. Soc.*, A **190**, 117 (1947).

* Since each adsorption site gives a slightly different value, as will be shown in the succeeding paper, the average value was used for the present calculations.

15) T. L. Hill, *J. Chem. Phys.*, **16**, 181 (1948).

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

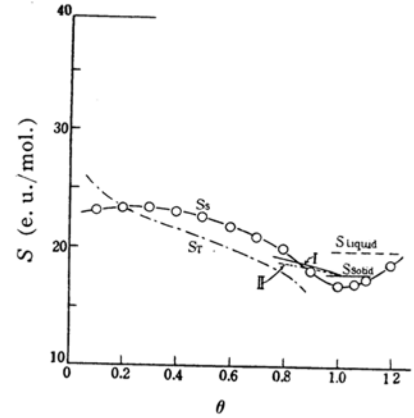

Fig. 12. Entropies of oxygen adsorbed on cubic sodium chloride at 76.4°K.

S_S···experimental values, S_T···calculated values (two-dimension gas). Curve I··· ($S_{\mathrm{solid}}+S_c$), Curve II··· ($S_{\mathrm{solid}}+\bar{S}_c$).
(The entropies of solid and liquid oxygen were calculated from the data obtained by Giauque and Johnston[17].)

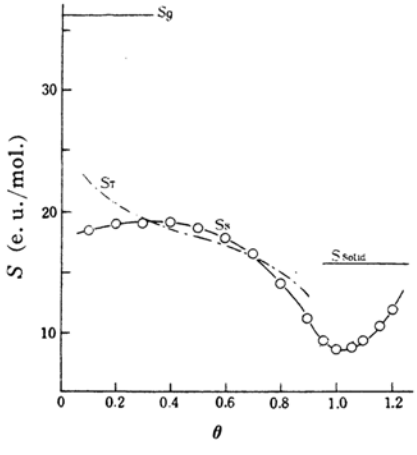

Fig. 13. Entropies of nitrogen adsorbed on cubic sodium chloride at 76.4°K.

S_S···experimental values, S_T···calculated values (two-dimensional gas).
(The entropy of solid nitrogen at 76.4°K was calculated from the data obtained by Giauque and Clayton[6].)

contain the entropy changes of the adsorbent caused by the adsorption[18]. On the other hand, the calculated values are all the integral entropies and are usually somewhat greater than the values of the partial molar total entropies. Considering the problem from this fact, the experimental entropies (S_S) for adsorbed argon and nitrogen are in considerably good agreement with the calculated entropies of the two-dimensional gas (S_T) in the region of $\theta=0.3\sim0.9$. Since the entropy for oxygen associated with the vibrational motion normal to the surface was calculated from assuming that the frequency of oxygen is identical with that of argon, the calculated entropies of the two-dimensional gas for oxygen (S_T) probably resulted in smaller values. Therefore, the agreement of the experimental curve for oxygen in the region of $\theta=0.2\sim0.9$ with the calculated curve of the two-dimensional gas is rather good. The discrepancy between the experimental and calculated values in the low coverage region ($\theta<0.2$) must be mainly attributed to the entropy changes of the adsorbent.

The suggestion of the phase change of argon adsorbed on cubic potassium chloride from a gaseous film to a condensed film was made by Kemball[4]. According to this, the phase change of argon on cubic potassium chloride occurred at about $\theta=0.8$, because the experimental values shifted from the curve of the two-dimensional gas to the curve of the localized adsorption obtained by adding the configurational entropy (Eq. (6)) to the entropy of the solid argon. This explanation involves considerable uncertainties, because it seems unreasonable to use Eq. (6) for the calculations of the configurational entropy on the adsorption system in which the non-uniformity of the surface and the mutual interaction between the adsorbed molecules are both predominant.

In the present work, the configurational entropy for the localized adsorption was calculated from Eq. (7) given by Drain and Morrison. From the results shown in these figures it will be seen that the phase changes of argon and oxygen occur at about $\theta=0.9$. But the mutual interaction between the adsorbed molecules was ignored in Eq. (7) ; therefore, the present results on the phase change of the adsorbed molecules from a gaseous film to a condensed film also contain considerable uncertainties as those obtained by Kemball do.

Monolayer Capacities. — Since the present results (Figs. 7, 8 and 9) indicate that the non-uniformity of the surface considerably predominate in the low coverage region and the mutual interaction (including the mutual interaction caused by the induced dipoles) in the succeeding region is sharply increased with the increase of

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[17] W. F. Giauque and H. J. Johnston, *J. Am. Chem. Soc.*, **51**, 2300 (1929).

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

the amount adsorbed, it is unreasonable to apply the B. E. T. theory to the present adsorption systems. In these figures the isosteric heats and also the entropies of adsorption in the region of the comparatively high coverage are sharply increased and there is a fairly sharp maximum for all three gases on cubic sodium chloride. Here, the values of the amount adsorbed for the maximum heat and entropy change of adsorption coincide well with each other.

The gradual decrease in each heat curve (and also in each entropy change curve) beyond the maximum may be attributed to the formation of multilayers. Thus it seems reasonable to assign this value corresponding to the maximum in the heat curve or in the entropy change curve as the monolayer capacity as Orr adopted[1].

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

TABLE III

MONOLAYER CAPACITIES (v_m) AND SURFACE AREAS (A), CUBIC SODIUM CHLORIDE (32.3 g.)

Adsorbate	Cross-sectional Area, a_0 (Å^2)	v_m (Micromoles) From ($-\Delta H$)	v_m (Micromoles) (B.E.T.)	A (m^2) From ($-\Delta H$)	A (m^2) (B.E.T.)
Argon	12.8	22.1	(19.1)	1.70	(1.47)
Oxygen	12.1	21.9	(20.4)	1.60	(1.49)
Nitrogen	13.8	19.0	(22.0)	1.58	(1.83)

Summary

The low-temperature adsorption of non-polar gases (argon, oxygen, nitrogen and carbon dioxide) on cubic sodium 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 predominate in the low coverage region and the mutual interaction between the adsorbed molecules is also distinguished in the region of the comparatively high coverage.

The entropies of the adsorbed materials (argon, oxygen and nitrogen) were experimentally determined and compared with the calculated values of the two-dimensional gas. These results show that the adsorbed molecules have the nature of the two-dimensional gas at least in the region of $\theta = 0.3 \sim 0.9$.

The present results indicate that the phase change (a gaseous film→a condensed film) of argon or oxygen may occur at about $\theta = 0.9$, but this fact is somewhat uncertain.

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