The Adsorption of Non-Polar Gases on Alkali Halide Crystals. II[1]. *Calculations of The Adsorption Behaviour of Non-Polar Gases on Cubic Sodium Chloride**

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Introduction

The refined calculations of the adsorption energy of an isolated argon atom on cubic (100) potassium chloride crystal were carried out by Orr[2]. There is some discordance, however, between theory and experiment which may be attributed to the fact that the repulsive constant of Herzfeld for argon has been used in his theoretical calculations. The theoretical treatment of the quadrupole interaction of an isolated nitrogen molecule with cubic (100) potassium chloride crystal has recently been carried out by Drain[3]. His treatment, however, contains some incorrectness due to careless mistake. Moreover, his results on the total adsorption potential of an isolated nitrogen molecule on cubic (100) potassium chloride also contain considerable uncertainty.

The approximate calculation of the heat curve for argon on cubic (100) potassium chloride was carried out by Orr[2] and also by Young[4]. However, the discrepancy between the experimental and calculated heat curves is fairly remakable. It was, therefore, of interest in the present work to obtain the theoretical values for the heats of adsorption of non-polar gases.

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

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

2) W. J. C. Orr, *Trans. Faraday Soc.*, **35**, 1247 (1939).

3) L. E. Drain, ibid., **49**, 650 (1953).

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

(argon, nitrogen and carbon dioxide) on the (100) plane of sodium chloride crystal and to compare these values with the experimental results given in the preceding paper.

In the present work, the total repulsive potential between an isolated atom or molecule and the lattice ions was calculated using the repulsive constants of the modified Buckingham-Corner (6-exp) potential for these non-polar gases. In the case of nitrogen or carbon dioxide, the total quadrupole potential was calculated, using a method similar to that adopted by Drain and the correction due to the potential barrier hindering the turning over of the molecular axis was made.

Outline of Calculation

Theoretical Calculation of the Adsorption Potential of an Isolated Atom or Molecule on the (100) Face of an Alkali Halide Crystal.—The calculation of the adsorption potential may be divided into four sections,

(A) the Van der Waals' (dispersion) potential, (B) the electrostatic potential, (C) the repulsive potential, (D) the quadrupole potential and the correction due to the potential barrier hindering the turning over of the molecular axis.

Calculations were made of these quantities for the following representative positions on the (100) plane of an alkali halide crystal: (i) above the centre of a lattice cell (sites type A), (ii) above the mid-point of a lattice edge (sites type B), (iii) above an alkali ion (sites type C) and (iv) above a halogen ion (sites type D).

A. The Van der Waals' (Dispersion) Potential.—The total Van der Waals' potential between an adsorbate atom or molecule and a crystal is given by the Kirkwood-Müller formula[5] as

$$\left.\begin{aligned}\Phi_D = \frac{6m_e c^2}{a^6}\left[\frac{\alpha_0\alpha_+}{\alpha_0/\chi_0+\alpha_+/\chi_+}S_+(\rho)\right.\\ \left.+\frac{\alpha_0\alpha_-}{\alpha_0/\chi_0+\alpha_-/\chi_-}S_-(\rho)\right]\\ \rho=z/a\end{aligned}\right\} \quad (1)$$

where $S_+(\rho)$ and $S_-(\rho)$ are summations involving inverse sixth powers of ρ, z the perpendicular distance from the centre of gravity of the adsorbate atom or molecule to the (100) plane, a the lattice parameter of the crystal, m_e the mass of the electron, C the velocity of light, α the polarizability, χ the magnetic susceptibility. The subscripts o, $+$ and $-$ refer to the absorbate, alkali ions and halogen ions respectively. For the present systems the required values of α for the crystal ions have been derived by Mayer[6], and of χ by Brindley and Hoare[7]. The values of the ionic radii of alkali halide crystals have been given by Goldschmidt[8]. The values of α for these adsorbates* have been given by Landolt-Börnstein[9], and of χ by Mann[10], Havens[11] and Stoner[12].

The quantities of $S_+(\rho)$ and $S_-(\rho)$ as a function of ρ for four representative positions mentioned above were evaluated by summation over the nearest 280 ions using expressions derived by Orr, and the remaining contributions were found by integration. The results are in good agreement with those obtained by Orr[2].

B. The Electrostatic Potential.—The resultant electrostatic potential in any given position of a non-polar molecule is given by

$$\Phi_E = -\frac{1}{2}\alpha_0 F_z^2 \quad (2)$$

where α_0 is the polarizability of a non-polar molecule, F_z the resultant electrostatic field along a line perpendicular to the surface.

The calculation of the resultant electrostatic field, F_z, as a function of ρ was carried out following closely the method used by Lennard-Jones and Dent[13] for the (100) plane of alkali halide crystals. It is easily shown that the resultant electrostatic field is zero along a line perpendicular to the centre of a lattice cell and also along lines perpendicular to the mid-point of a lattice edge. The resultant electrostatic field, as functions of ρ, above an alkali ion in the lattice plane was evaluated by summation over the nearest 40 ions. The present results are in good agreement with those obtained by Lennard-Jones and Dent[13].

C. The Repulsive Potential.—The theoretical calculations of the total repulsive

5) A. Müller, *Proc. Roy. Soc. London*, **A 154**, 624 (1936).

6) J. E. Mayer, *J. Chem. Phys.*, **1**, 270 (1933).

7) G. W. Brindley and F. E. Hoare, *Proc. Roy. Soc. London*, **A 152**, 342 (1935).

8) V. M. Goldschmidt, *Trans. Faraday Soc.*, **25**, 253 (1929).

9) Landolt-Börnstein. "Zahlenwerte und Funktionen", Band 1, Part 3, Springer (1951), p. 510.

* In the case of the nitrogen or carbon dioxide molecule, the average value of α in the three directions was adopted.

10) K. E. Mann, *Z. Physik*, **98**, 548 (1936).

11) G. G. Havens, *Phys. Rev.*, **43**, 992 (1932).

12) E. C. Stoner, "Magnetism and Matter", Methuen and Co. Ltd., London (1934), p. 460.

13) J. E. Lennard-Jones and B. M. Dent, *Trans. Faraday Soc.*, **24**, 92 (1928); **28**, 333 (1932).

potential between an isolated argon atom and the lattice ions of potassium chloride crystal were carried out by Orr[2] and Young[4]. Their results, however, seem to be insufficiently accurate because the repulsive constant of Herzfeld for argon has been used.

In the present work, therefore, the total repulsive potential was calculated using an exponential expression derived from the Born-Mayer repulsive potential formula[14] for the lattice ions and the modified Buckingham-Corner repulsive potential formula for these non-polar molecules. The modified Buckingham-Corner (6-exp) intermolecular potential[15] is given by

$$\left.\begin{aligned}\phi(r) &= \frac{\varepsilon}{1-6/\alpha}\left\{6/\alpha \exp(\alpha-\alpha r/r_m) - (r_m/r)^6\right\} = -Ar^{-6} \\ &\quad +B\exp(-\alpha r/r_m) \\ A &= \left(\frac{\varepsilon}{1-6/\alpha}\right) r_m^6, \\ B &= b_0^2 = \left(\frac{6\varepsilon}{\alpha-6}\right)\exp(\alpha)\end{aligned}\right\} \quad (3)$$

where ε is the maximum energy of attraction, r the intermolecular separation, r_m the separation at the minimum potential, α the parameter measuring the steepness of the repulsive potential, b_0 the repulsive constant of a molecule.

The values of the force constants are summarized in Table I. In this table the force constants for argon and nitrogen were evaluated by Mason and Rice[16] and those for oxygen and carbon dioxide were evaluated by the present author.

TABLE I
FORCE CONSTANTS OF THE MODIFIED BUCKINGHAM-CORNER INTERMOLECULAR POTENTIAL

Molecule	α	ε/k (°K)	r_m(Å)	b_0 ($.10^{-6}$ erg$^{1/2}$)
Argon	14.0	123.2	3.86_6	123.6
Oxygen	15.2	120.1	3.79_5	207.5
Nitrogen	16.2	113.5	4.04_0	315.6
Carbon dioxide	15.1	266.1	4.11_3	287.5

In the present calculations the repulsive constants of Huggins and Mayer[17] for the crystal ions were used. For four representative positions considered, the total repulsive potential was calculated, for various values of ρ, by direct summation over the 14 to 20 nearest ions. Contributions from the remaining ions are entirely negligible.

Since these results are not of general applicability, no further details need be given.

D. The Quadrupole Potential.—Although, in general, permanent electric quadrupoles are of minor importance in the intermolecular potential between gas molecules[18], the situation is quite different when considering the adsorption potential of a molecule in the large electric fields near the surface of an ionic crystal. The permanent quadrupole moments of several molecules have been measured by Smith and Howard[19] and Hill and Smith[20] from line broadening of microwave spectra. Molecular orbital calculations of the permanent quadrupole moments of nitrogen and oxygen have been made by Greenhow and Smith[21]. Although many of these microwave values are somewhat uncertain, the order of magnitude is probably correct.

The total interaction potential of a linear quadrupole, Q, with an inhomogeneous electric field whose potential is ϕ is given by

$$\Phi_Q = \frac{1}{2} Q \cdot \partial^2\phi/\partial t^2 \quad (4)$$

where the axis t is taken along the axis of symmetry of the quadrupole. The expression for the resultant Coulomb potential at any position near the surface of an alkali halide crystal has been derived by Lennard-Jones and Dent[13]. The non-zero second derivatives of the resultant Coulomb potential for three representative positions on the (100) plane of potassium chloride were evaluated by Drain[3]. However, since his results contain some uncertainties due to a careless mistake, the evaluation of the electric field gradient near the surface was carried out by the present author.

The maximum quadrupole interaction of the nitrogen or carbon dioxide molecule for four representative positions on the (100) plane of an alkali halide crystal are obtained from the following orientations:

(i) above the centre of a lattice cell (sites type A),

$$\partial^2\phi/\partial x\partial y = e/a^3 \cdot \sigma_A;$$

14) M. Born and J. E. Mayer, *Z. Physik*, **75**, 1 (1932).
15) W. E. Rice and J. O. Hirschfelder, *J. Chem. Phys.*, **22**, 187 (1954).
16) E. A. Mason and W. E. Rice, *J. Chem. Phys.*, **22**, 522 (1954).
17) M. L. Huggins and J. E. Mayer, ibid., **1**, 643 (1933).
18) H. Margenau, *Rev. Modern Phys.*, **11**, 1 (1939).
19) W. V. Smith and R. Howard, *Phys. Rev.*, **79**, 132 (1950).
20) R. M. Hill and W. V. Smith, ibid., **82**, 451 (1951).
21) C. Greenhow and W. V. Smith, *J. Chem. Phys.*, **19**, 1298 (1951).

(ii) above the mid-point of a lattice edge (sites type B),

$$\partial^2\phi/\partial x\partial z=\partial^2\phi/\partial y\partial z=e/a^3\cdot\sigma_B;$$

(iii) above an alkali ion (sites type C),

$$\partial^2\phi/\partial z^2=-2\partial^2\phi/\partial x^2=-2\partial^2\phi/\partial y^2=e/a^3\cdot\sigma_C;$$

(iv) above a halogen ion (sites type D),

$$\partial^2\phi/\partial x^2=\partial^2\phi/\partial y^2=e/a^3\cdot\sigma_D.$$

The cartecian axes x, y, z are along the sides of a unit cell, z is normal to the surface and a is the lattice parameter and e the electronic charge. The quantities σ which represent summations over the lattice ions depend on the distance $a\rho$ of the point under consideration from the surface. The present results on the evaluations of these quantities σ are summarized in Table II.

TABLE II

VALUES OF σ, ON THE (100) PLANE OF AN ALKALI HALIDE CRYSTAL

ρ	σ_A	σ_B	σ_C	σ_D
0.8	1.5310	2.1739	3.3463	1.6732
0.9	0.9942	1.4102	2.0933	1.0467
1.0	0.6424	0.9105	1.3238	0.6619
1.1	0.4142	0.5865	0.8426	0.4213
1.2	0.2662	0.3768	0.5377	0.2688
1.3	0.1711	0.2420	0.3439	0.1719
1.4	0.1098	0.1553	0.2203	0.1101
1.5	0.0704	0.0996	0.1411	0.0705
1.6	0.0452	0.0639	0.0905	0.0452
2.0	0.0076	0.0108	0.0153	0.0076

As is easily seen in these relations, at the positon of sites type A (above the centre of a lattice cell) or sites type D (above a halogen ion), the orientation for maximum quadrupole interaction is with the molecular axis parallel to the surface. Consequently, no correction due to the potential barrier hindering the turning over of the molecule is required in these positions. On the other hand, at the positions of sites type B (above the mid-point of a lattice edge) and sites type C (above an alkali ion), the maximum quadrupole energies are obtained from the orientations in which the molecular axis makes an angle of $\pi/4$ and $\pi/2$ with the surface respectively. In these positions, then the corrections due to the potential barrier hindering the rotation must be made.

In the present calculations, the approximate estimation of this potential barrier was carried out following closely the method used by Hill[22]. Although this method seems rather inadequate for the present calculations*, unfortunately, no other reliable method has been found.

The Total Adsorption Potential.—The total adsorption potential is then given by

$$\Phi=\Phi_D+\Phi_E+\Phi_Q+\Phi_R-\Phi_{H.R.} \quad (5)$$

where Φ_R is the total repulsive potential,

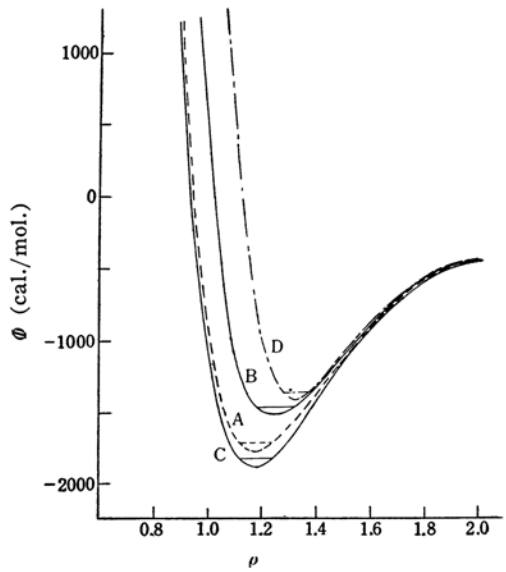

Fig. 1. Potential energy curves of argon on cubic (100) NaCl. Each symbol denotes the type of sites.

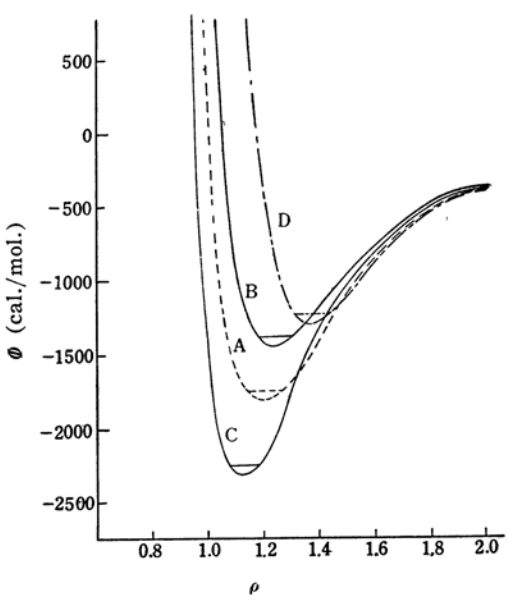

Fig. 2. Potential energy curves of nitrogen on cubic (100) NaCl. Each symbol denotes the type of sites.

22) T. L. Hill, *J. Chem. Phys.*, **17**, 762 (1949).

* In the estimations made by Hill, the adsorption potential was given by the Lennard-Jones (6-12) potential formula.

and $\Phi_{H.R.}$ the potential barrier hindering the turning over of the molecular axis. In the case of argon, both values of Φ_Q and $\Phi_{H.R.}$ are surely zero.

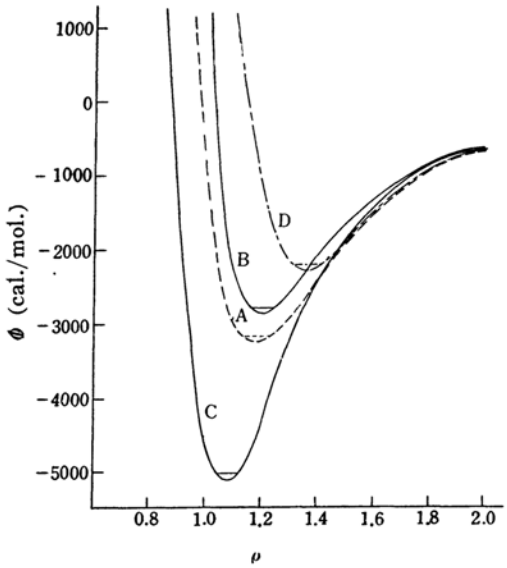

Fig. 3. Potential energy curves of carbon dioxide on cubic (100) NaCl. Each symbol denotes the type of sites.

The calculated potential energy curves for the four types of sites considered are shown in Figs. 1, 2 and 3. By plotting the region around the minimum potential on a large scale, the restoring force per unit displacement, f', of the molecule (i. e. the centre of gravity) normal to the surface in this region was calculated from the following equation**

$$(\Phi-\Phi_m)=\frac{1}{2}f'(z-z_e)^2 \tag{6}$$

where Φ_m is the minimum potential, z the perpendicular distance from the surface, z_e the equilibrium distance given by the position of the minimum potential.

The vibrational frequency normal to the surface, ν_z (sec.$^{-1}$), was then calculated from the relation

$$\nu_z=\frac{1}{2\pi}\sqrt{f'N/M} \tag{7}$$

where M is the molecular (or atomic) weight, N the Avogadro's constant.

Then, the zero-point energy, ε_0 (cal./mol.), was calculated from the relation

$$\varepsilon_0=Nh\nu_z\times10^{-7}/2\times4.186 \tag{8}$$

TABLE III

RESULTS OBTAINED FROM THE POTENTIAL ENERGY CURVE, ARGON ON CUBIC (100) NaCl

Sites type	Z_e (Å)	r_{eff} (Å)	$-\Phi_m$ (cal./mol.)	$\nu_z\times10^{-12}$ (sec.$^{-1}$.)	ε_0 (cal./mol.)	$-\Delta H_0$ at 76°K (ca./mol.)
A, above the centre of a lattice cell	3.30	2.04	1768	0.95	44.8	1875
B, above the mid-point of a lattice edge	3.47	1.94	1514	0.88	41.5	1624
C, above an Na^+	3.29	2.31	1876	1.05	49.7	1978
D, above a Cl^-	3.72	1.91	1401	0.92	43.4	1510

TABLE IV

RESULTS OBTAINED FROM THE POTENTIAL ENERGY CURVE, NITROGEN ON CUBIC (100) NaCl

Sites type	Z_e (Å)	$-\Phi_m$ (cal./mol.)	$-\Phi_Q$ at Z_e (cal./mol.)	$\nu_z\times10^{-12}$ (sec.$^{-1}$)	ε_0 (cal./mol.)	$-\Delta H_0$ at 76°K (cal./mol.)
A, above the centre of a lattice cell	3.38	1807	550	1.23	58.1	1901
B, above the mid-point of a lattice edge	3.42	1432	774	1.10	51.9	1532
C, above an Na^+	3.12	2308	1738	1.32	62.3	2398
D, above a Cl^-	3.84	1277	232	1.12	52.9	1376

TABLE V

RESULTS OBTAINED FROM THE POTENTIAL ENERGY CURVE, CARBON DIOXIDE ON CUBIC (100) NaCl

Sites type	Z_e (Å)	$-\Phi_m$ (cal./mol.)	$-\Phi_Q$ at Z_e (cal./mol.)	$\nu_z\times10^{-12}$ (sec.$^{-1}$)	ε_0 (cal./mol.)	$-\Delta H_0$ at 190°K (cal./mol.)
A, above the centre of a lattice cell	3.28	3245	1328	1.12	52.9	3572
B, above the mid-point of an lattice edge	3.36	2852	1869	1.07	50.6	3181
C, above an Na^+	3.03	5102	4184	1.33	62.7	5419
D, above a Cl^-	3.77	2237	554	1.06	50.2	2567

** In Equ. (6), Φ and Φ_m must be expressed in erg/molecule.

where h is the Planck's constant.

Consequently, the initial heat of adsorption (i. e. the isosteric heat of adsorption at zero coverage), $-\Delta H_0$ (cal./mol.), is given by the expression

$$-\Delta H_0 = (-\Phi_m - \varepsilon_0) + RT = -U_0 + RT \quad (9)$$

where U_0 is the potential energy of the lowest vibrational state of the molecule on the bare surface.

The calculated values of these quantities for these non-polar gases are summarized in Table III, IV and V. The values of the effective radius of argon, $r_{eff.}$, were calculated from the equilibrium distances, and the results are given in column 3 of Table III.

Approximate Calculation of the Heat Curve for Argon on the (100) Plane of Cubic Sodium Chloride.—The approximate calculation of the heat curve for argon was carried out following similar method used by Young[4] for the (100) plane of cubic potassium chloride. In the present calculations, as well as in those made by Young, the following assumptions were made:

(1) In the formation of a primary monolayer, argon atoms are exclusively adsorbed from $\theta=0$ to about 0.4* above sodium ions (c.f. Table III), but as θ tends to unity there will be a phase transition from localized square arrays to a hexagonally closed-packed layer.
(2) The non-uniformity of the surface is negligible.
(3) The heat of adsorption of the second-layer atoms is close to the heat of sublimation of argon (i. e. 1860 cal./mol. at 76°K).
(4) In the range restricted to θ values near unity, the adsorption in the third and higher layers is negligible.

The variation of the heats of adsorption in the primary monolayer with coverage, due to Van der Waals' mutual interaction between the adsorbed atoms, was calculated using the equation statistically derived by Wang[23]. The intermolecular potential energy of a pair of argon atoms was calculated using the modified Buckingham-Corner (6-exp) potential formula, and the effect of the electrostatic repulsion between the adsorbed atoms was taken into consideration.

The effect of the second-layer formation was evaluated using the equations developed by Tompkins and Young[24].

The calculated heat curve is shown in Fig. 4, together with the experimental values reported in the preceding paper.

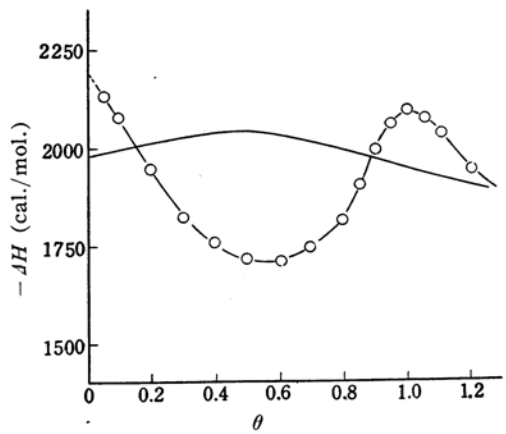

Fig. 4. Heats of adsorption of argon on cubic (100) NaCl.
·····, approximately calculated curve;
-○-○-, observed curve.

Discussion

The Initial Heat of Adsorption.—As seen in Table III, IV and V, the most energetic positions for these non-polar gases (argon, nitrogen and carbon dioxide) on the (100) plane of cubic sodium chloride are all sites type C (above an Na^+ in the lattice plane). These results are peculiar to the (100) plane of cubic sodium chloride. As will be shown in the succeeding paper, the most energetic positions for argon and nitrogen on cubic (100) KCl and cubic (100) KBr are sites type A* (above the centre of a lattice cell). This particular nature of the (100) plane of sodium chloride crystal may be attributed to the fact that the ionic radius and the repulsive constant of Na^+ are both considerably smaller than those of K^+.

The values of the initial heats of adsorption obtained from the present theoretical calculations are listed in Table VI, together with the experimental values reported in the preceding paper.

As seen in Table VI, the calculated values for these non-polar gases are in rather good agreement with the experimental values. It is quite reasonable,

* The diameter of an argon atom derived from the liquid density was taken at 4.05 Å.

23) J. S. Wang, *Proc. Roy. Soc. London*, **A 161**, 127 (1937).

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

* According to the theoretical calculations made by Orr[2], the most energetic position for argon on cubic (100) KCl is also sites type A.

TABLE VI

INITIAL HEATS OF ADSORPTION ON CUBIC (100) NaCl

Adsorbate	$(-\Delta H_0)_{expt.}$ (cal./mol.)	$(-\Delta H_0)_{calc.}$ (cal./mol.)	$(-\Delta H_0)_{expt.} - (-\Delta H_0)_{calc.}$ (cal./mol.)
Argon	2190	1980	210
Nitrogen	2670	2400	270
Carbon dioxide	6070	5420	650

therefore, 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 sodium chloride.

The Non-Uniformity of the Adsorbent Surface.—Table III indicates that the maximum difference of the initial heat of adsorption for argon between these sites grouped in patches amounts to about 500 cal./mol. The corresponding values for nitrogen and carbon dioxide amount, as seen in Table IV and V, to about 1000 cal./mol. and about 2850 cal./mol. respectively. Since the mutual interaction between the adsorbed atoms or molecules in the low coverage region is slightly attractive and gives no marked influence upon the heats of adsorption, the surface heterogeneity of this type may be maintained, especially in the non-localized adsorption, in this low coverage region.

The difference between the experimental and theoretical values of the initial heat of adsorption shown in Table VI gives a crude measure of the surface heterogeneity of the other type due to the lattice imperfection or the defects of the crystals. An argon atom has no permanent quadrupole moment; then the value of 210 cal./mol. shown in Table VI may be attributed to the surface heterogeneity of this type. On the other hand, the theoretical values of the initial heats of adsorption for nitrogen and carbon dioxide are somewhat inaccurate, and this uncertainty is attributed to two causes:

(a) The values of the quadrupole moment of these molecules cannot yet be considered as definitely proved.

(b) The estimation of the potential barrier hindering the turning over of the molecule was carried out following the method used by Hill, but this method is rather inadequate for the present calculations.

Nevertheless, Table VI shows that the difference between the experimental and theoretical values of the initial heat of adsorption for each adsorbate is of the right magnitude to explain the difference of the intermolecular potential energy betwen these non-polar gases.

For the reasons discussed above, it is reasonable to consider that the surface heterogeneity due to the distribution of sites grouped in patches is more distinguished than that due to the lattice imperfection or crystal defects. Both types of the surface heterogeneity discussed above give rise to the decrease of the heat of adsorption as more molecules are adsorbed in the low coverage region. This is qualitatively in good agreement with the experimental heat curves.

Surface Migration of the Adsorbed Atoms or Molecules.—In order to enable the adsorbed atom or molecule to move along the surface from one site to the next site, where it is bounded in exactly the same manner as in the first one, this atom or molecule must pick up such an amount of energy that it may overcome the potential energy barrier separating the atoms and molecules. Owing to the high symmetry of the (100) plane of an alkali halide crystal and the small distance from one site to the adjacent site of another type, it is not unreasonable to consider that the height of this potential energy barrier is roughly equal to the difference of the heat of adsorption between them[25]. Since the mutual interaction between the adsorbed atoms or molecules in the low coverage region gives no marked influence, the heat of adsorption at each site in the low coverage region may be replaced by the initial heat of adsorption in the present discussion.

As seen in Table III, the difference of the initial heat of adsorption between two adjacent sites (i.e. the height of the potential energy barrier mentioned above) for argon amounts to about $0.7 \sim 2RT$. In the case of nitrogen, as seen in Table IV, the height of this potential energy barrier roughly amounts to about $1 \sim 3\ RT$ (excepting the value corresponding to the difference between site B and C). Since the mean kinetic energy of thermal movement of the adsorbed atom or molecule is RT per mole, it is reasonable to consider that the adsorbed argon atom or nitrogen molecule easily picks up the energy corresponding to each potential energy barrier from the thermal energy fluctuations. The present results on the surface migration of the adsorbed argon atom or nitrogen molecule

25) J. H. de Boer, "The Dynamical Character of Adsorption", Clarendon Press, Oxford (1953), p. 96.

in the low coverage region are qualitatively in good agreement with the nature of the experimental entropy curves for argon and nitrogen already reported in the preceding paper.

The Heat Curve for Argon.—As seen in Fig. 4, the discrepancy between the experimental and approximately calculated heat curves in the region of $\theta=0.2\sim0.8$ is considerably remakable. This is mainly attributed to the fact that in the present approximate calculations, as well as in those made by Orr and Young, the uniform surface and the localized model have been assumed. These two assumptions are inconsistent not only with the results of the present theoretical calculations but with the experimental results reported in the preceding paper.

Summary

The potential energy of each isolated atom or non-polar molecule (argon, nitrogen, or carbon dioxide) adsorbed on the (100) plane of cubic sodium chloride has been theoretically calculated at four different positions on the crystal surface. In the present calculations, the repulsive constants of the modified Buckingham-Corner (6-exp) intermolecular potential for these non-polar gases have been used. The quadrupole interaction of the nitrogen or carbon dioxide molecule with a crystal has been taken into consideration. The good agreement between the theoretical and experimental values of the initial heat of adsorption for each adsorbate has been obtained.

The present theoretical calculations suggest that the surface heterogeneity caused by the lattice imperfection or crystal defects is of minor importance compared with other types of surface heterogeneity due to the distribution of sites grouped in patches. The present results also suggest that the adsorbed argon atoms or nitrogen molecules easily migrate two-dimensionally along the surface in the low coverage region. These results on the surface migration are in good agreement with the entropy curves of adsorbed argon and nitrogen experimentally determined.

The approximate calculation of the heat curve for argon on the (100) plane of cubic sodium chloride has been carried out following a similar method used by Young. The discordance between the experimental and approximately calculated heat curves is considerable, and this is attributed to the fact that the unreliable model (i. e. the uniform surface and the localized adsorption) has been assumed in these approximate calculations.

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