The Adsorption of Non-polar Gases on Alkali Halide Crystals. IV[1] *Calculations of the Adsorption Behaviour of Non-polar Gases on Cubic Potassium Chloride and Cubic Potassium Bromide**

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Introduction

In the previous communication[2], the author carried out a theoretical calculations of the adsorption energy of an isolated atom or molecule (argon, nitrogen and carbon dioxide) on the (100) plane of cubic sodium chloride. In that 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. The quadrupole interaction of an isolated nitrogen or carbon dioxide molecule with the lattice ions was theoretically calculated and the correction due to the potential barrier hindering the turning over of the molecular axis was made.

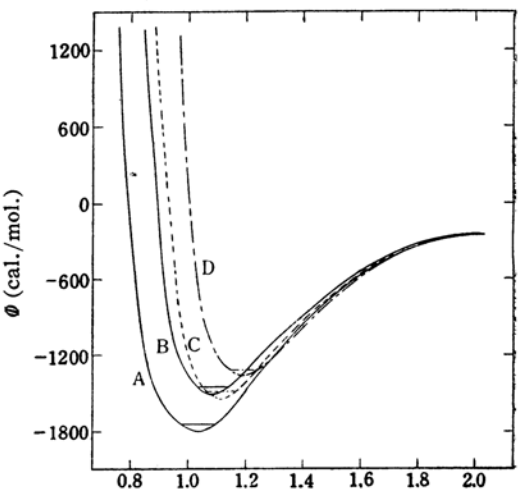
It was therefore of interest in the present work to extend a similar calculations to the (100) plane of cubic potassium chloride and cubic potassium bromide crystals and to compare the theoretical values with the experimental ones obtained by the present author.

Outline of Calculation

The calculation of the adsorption potential was divided into four sections,

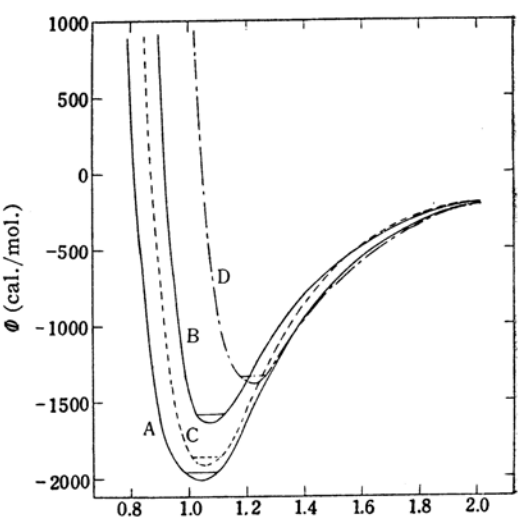
(A) the Van der Waals' (dispersion) potential, (B) the electrostatic potential, (C) the repulsive potential, (D) the quadrupole potential and the correction due to the potential barrier hindering the turning over of the molecular axis.

Calculations were made of these quantities for following four representative positions on the (100) plane of an alkali halide crystal; (i) above the center of a lattice cell (sites type A), (ii) above the



Ratio of the perpendicular distance from the surface to the lattice parameter, ρ

Fig. 1. Potential energy curves of argon on cubic (100) KCl. The symbols denote the type of sites.



Ratio of the perpendicular distance from the surface to the lattice parameter, ρ

Fig. 2. Potential energy curves of nitrogen on cubic (100) KCl. The symbols denote the type of sites.

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

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

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

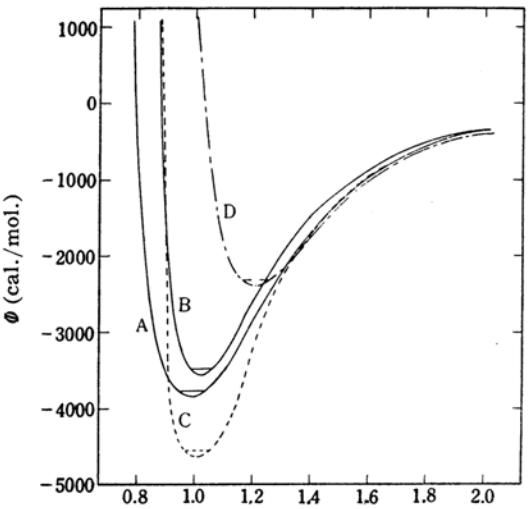


Fig. 3. Potential energy curves of carbon dioxide on cubic (100) KCl. The symbols denote the type of sites.

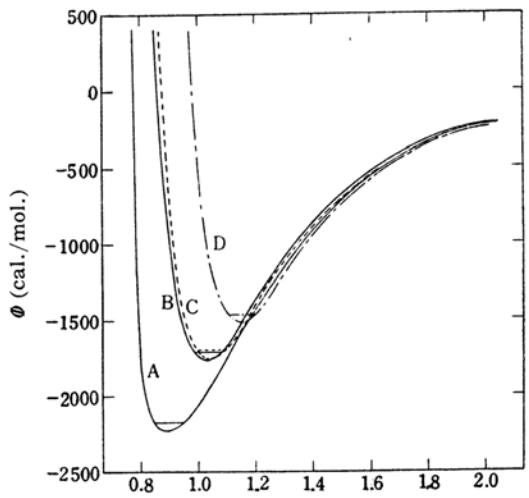


Fig. 4. Potential energy curves of argon on cubic (100) KBr. The symbols denote the type of sites.

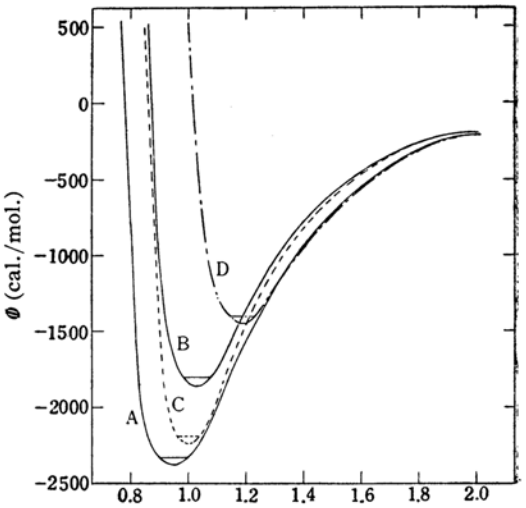


Fig. 5. Potential energy curves of nitrogen on cubic (100) KBr. The symbols denote the type of sites.

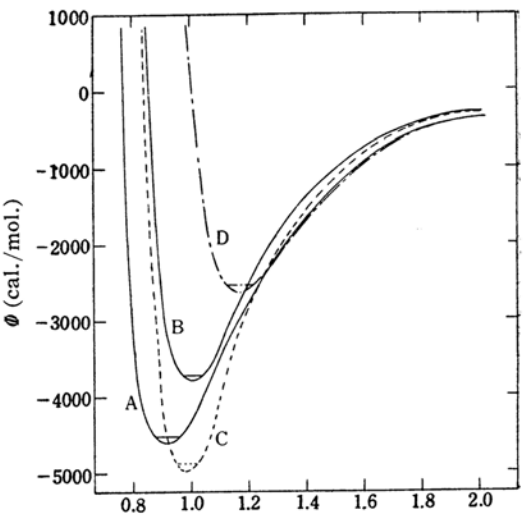


Fig. 6. Potential energy curves of carbon dioxide on cubic (100) KBr. The symbols denote the type of sites.

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).

The method of calculation of each interaction potential was already described in a previous communication[2]. The calculated potential energy curves for the four types of sites considered are shown in Figs. 1, 2, 3, 4, 5 and 6. From these curves the values collected in the following tables were calculated. The position of the minimum gives the equilibrium distance Z_e from the surface; the depth of the trough at Z_e is $-\Phi_m$. For each curve, the region around the minimum was fitted to a parabola and the vibrational frequency normal to the surface ν_z and the zero-point energy ε_0 were calculated. The values of the quadrupole potential Φ_Q are also listed in these tables, from which the considerably large contribution of the quadrupole inter-

TABLE I

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

Sites type	Z_e (Å)	$r_{eff.}$ (Å)	$-\Phi_m$ (cal./mol.)	$\nu_z \times 10^{-12}$ (sec.$^{-1}$)	ε_0 (cal./mol.)	$-\Delta H_0$ (at 76°K) (cal./mol.)
A, Above the center of a lattice cell	3.22	2.10	1792	0.98	46.3	1898
B, Above the mid-point of a lattice edge	3.44	1.98	1506	0.90	42.7	1615
C, Above a K^+	3.52	2.19	1532	0.99	46.7	1637
D, Above a Cl^-	3.75	1.94	1365	0.94	44.2	1473

TABLE II

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

Sites type	Z_e (Å)	$-\Phi_m$ (cal./mol.)	$-\Phi_Q$ at Z_e (cal./mol.)	$\nu_z \times 10^{-12}$ (sec.$^{-1}$)	ε_0 (cal./mol.)	$-\Delta H_0$ (at 76°K) (cal./mol.)
A, Above the center of a lattice cell	3.25	2021	815	1.19	56.0	2117
B, Above the mid-point of a lattice edge	3.34	1635	1016	1.06	50.1	1737
C, Above a K^+	3.31	1915	1522	1.20	56.7	2010
D, Above a Cl^-	3.85	1384	352	1.12	53.1	1483

TABLE III

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

Sites type	Z_e (Å)	$-\Phi_m$ (cal./mol.)	$-\Phi_Q$ at Z_e (cal./mol.)	$\nu_z \times 10^{-12}$ (sec.$^{-1}$)	ε_0 (cal./mol.)	$-\Delta H_0$ (at 190°K) (cal./mol.)
A, Above the center of a lattice cell	3.09	3826	2432	1.22	57.6	4148
B, Above the mid-point of a lattice edge	3.22	3548	2887	1.21	57.1	3871
C, Above a K^+	3.18	4656	4390	1.40	66.0	4970
D, Above a Cl^-	3.75	2483	968	1.21	57.1	2806

TABLE IV

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

Sites type	Z_e (Å)	$r_{eff.}$ (Å)	$-\Phi_m$ (cal./mol.)	$\nu_z \times 10^{-12}$ (sec.$^{-1}$)	ε_0 (cal./mol.)	$-\Delta H_0$ (at 76°K) (cal./mol.)
A, Above the center of a lattice cell	2.95	1.79	2228	1.17	55.2	2325
B, Above the mid-point of a lattice edge	3.39	1.81	1762	0.99	46.7	1867
C, Above a K^+	3.42	2.09	1750	1.02	48.1	1854
D, Above a Br^-	3.77	1.81	1507	0.95	44.8	1614

TABLE V

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

Sites type	Z_e (Å)	$-\Phi_m$ (cal./mol.)	$-\Phi_Q$ at Z_e (cal./mol.)	$\nu_z \times 10^{-12}$ (sec.$^{-1}$)	ε_0 (cal./mol.)	$-\Delta H_0$ (at 76°K) (cal./mol.)
A, Above the center of a lattice cell	3.05	2389	1130	1.25	59.0	2482
B, Above the mid-point of a lattice edge	3.35	1855	1071	1.12	52.9	1954
C, Above a K^+	3.29	2256	1664	1.26	59.5	2348
D, Above a Br^-	3.92	1458	358	1.17	55.2	1555

TABLE VI

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

Sites type	Z_e (Å)	$-\Phi_m$ (cal./mol.)	$-\Phi_Q$ at Z_e (cal./mol.)	$\nu_z \times 10^{-12}$ (sec.$^{-1}$)	ε_0 (cal./mol.)	$-\Delta H_0$ (at 190°K) (cal./mol.)
A, Above the center of a lattice cell	2.99	4610	2915	1.33	62.8	4927
B, Above the mid-point of a lattice edge	3.32	3810	2667	1.25	59.0	4131
C, Above a K^+	3.27	4982	3924	1.35	63.7	5298
D, Above a Br^-	3.85	2601	952	1.23	58.1	2923

TABLE VII

INITIAL HEATS OF ADSORPTION ON CUBIC (100) KCl

Adsorbate	$(-\Delta H_0)_{\text{expt.}}$ (cal./mol.)	$(-\Delta H_0)_{\text{calc.}}$ (cal./mol.)	$(\Delta H_0)_{\text{expt.}} - (-\Delta H_0)_{\text{calc.}}$ (cal./mol.)
Argon	2080 (2140[9])	1900 (1780[10])	180 (360[9,10])
Nitrogen	3010 (3200[9])	2120	890
Carbon dioxide	6400	4970	1430

TABLE VIII

INITIAL HEATS OF ADSORPTION ON CUBIC (100) KBr

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

action energy will be at once apparent*. The initial heat of adsorption (i. e. the isosteric heat of adsorption at zero coverage) in these tables was calculated from the relation

$$-\Delta H_0 = (-\Phi_m - \varepsilon_0) + RT.$$

The values of the effective radius of argon $r_{eff.}$ were calculated from the equilibrium distances, assuming Goldschmidt's values[3] for the radii of the ions. The results are given in column 3 of Tables I and IV.

Discussion

The Initial Heat of Adsorption.—As seen in Tables I, II, IV and V, the most energetic positions for argon and nitrogen on the (100) plane of cubic potassium chloride and cubic potassium bromide are sites type A (i. e. above the center of a lattice cell), and these results are dissimilar from those obtained for the (100) plane of cubic sodium chloride. On the other hand, Tables III and VI indicate that the most energetic positions for carbon dioxide on the (100) plane of cubic potassium chloride and cubic potassium bromide are sites type C (i. e. above a K^+ in the lattice plane). These results may be attributed to the following causes:

(1) Although, in general, sites type C gives the greatest value of the quadrupole interaction potential for the same value of the equilibrium distance (Z_e) from the surface, the value of the quadrupole interaction potential at each sites type is inversely proportional to the third powers of the lattice parameter of the crystal[4].

(2) The repulsive constant of a K^+ is considerably greater than that of an Na^+ [5].

(3) The permanent quadrupole moment of the carbon dioxide molecule is considerably greater than that of the nitrogen molecule[6,7].

The values of the initial heats of adsorption obtained from the present theoretical calculations are listed in Tables VII and VIII, together with the experimental values by the present author[1,8]. For the sake of comparison, Orr's results[9,10] are also listed in Table VII.

* In the case of argon, the quadrupole potential is surely zero.

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

4) L. E. Drain, *Trans. Faraday Soc.*, **49**, 650 (1953).

5) M. L. Huggins and J. E Mayer. *J. Chem. Phys.*, **1**, 643 (1933).

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

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

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

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

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

As seen in Tables VII and VIII, the present theoretical values of the initial heat of adsorption for argon on the (100) plane of cubic potassium chloride and cubic potassium bromide are in considerably good agreement with the experimental values, while the discordance between the experimental and theoretical values for nitrogen or carbon dioxide is somewhat remarkable. However, since the order of magnitude of the theoretical values for these gases agrees with that of the experimental values, it seems reasonable to consider that the high initial heat of adsorption experimentally found for nitrogen or carbon dioxide is mainly attributed to the quadrupole interaction of each molecule with the surface of the crystal.

The Non-Uniformity of the Surface.—Tables I, II and III indicate that the differences between the highest and the weighted mean values of the initial heats of adsorption for argon, nitrogen and carbon dioxide on the (100) plane of cubic potassium chloride amount to about 230, 280 and 1030 cal./mol. respectively. In the case of cubic (100) potassium bromide, as seen in Tables IV, V and VI, the corresponding values for argon, nitrogen and carbon dioxide amount to about 380, 400 and 970 cal./mol. respectively. Since the mutual interaction between the adsorbed atoms or molecules in the low coverage region gives no marked influence upon the heats of adsorption, the surface heterogeneity of this type may be maintained especially in the non-localized adsorption.

On the other hand, the difference between the experimental and theoretical values of the initial heat of adsorption gives a crude measure of the surface heterogeneity of the other type due to the lattice imperfection or the defects of the crystals. As seen in Tables VII and VIII, the differences between the experimental and theoretical values for nitrogen or carbon dioxide are considerably greater than the values anticipated from the results for argon. Although these results are not satisfactorily explained from the difference in the intermolecular potential energy between these non-polar molecules, it may be pointed out that the accuracy of the theoretical calculations for nitrogen or carbon dioxide is somewhat inferior to that for argon. This incorrectness is mainly attributed to the facts that the values of the permanent quadrupole moment of nitrogen and carbon dioxide are somewhat uncertain and that the estimation of the potential energy barrier hindering the turning over of the molecular axis is insufficiently accurate.

Surface Migration of the Adsorbed Atoms and Molecules.—As already discussed in a previous communication[2], the height of the potential energy barrier separating two sites which belonged to the same type in the low coverage region is roughly equal to the difference in the initial heat of adsorption between one of them and the adjacent site separating them. In the case of the (100) plane of cubic potassium chloride, as seen in Tables I, II and III, the values of these potential energy barriers for argon, nitrogen (excepting the difference between the sites type A and D) and carbon dioxide amount to about 0.9–3.0 RT, 0.7–2.5 RT and 0.7–3.5 RT respectively. Tables IV, V and VI also indicate that the values of the potential energy barriers (excepting the difference between the sites type A and D) for argon, nitrogen and carbon dioxide on the (100) plane of cubic potassium bromide amount to about 1.5–3.0 RT, 0.9–3.5 RT and 1.0–3.0RT, respectively. Since the mean kinetic energy of thermal movement of the adsorbed atoms or molecules is RT per mole, it seems reasonable to consider that the adsorbed atoms or molecules easily pick up the energy corresponding to each potential energy barrier from the thermal energy fluctutaions. The present results on the surface migration of the adsorbed atoms or molecules in the low coverage region are qualitatively in good agreement with the nature of the experimental entropy curves for these non-polar gases[1,8].

Summary

The potential energy of each isolated atom or molecule (argon, nitrogen, or carbon dioxide) adsorbed on the (100) plane of cubic potassium chloride and cubic potassium bromide has been theoretically calculated at four representative positions on the surface.

According to the present theoretical calculations, it seems reasonable to consider that the high initial heat of adsorption experimentally found for nitrogen or carbon dioxide is mainly attributed to the quadrupole interaction of each molecule with the surface of the crystals. The present results suggest that the surface may be influenced by the different types of the surface heterogeneity due to the

defects of the crystals and the distribution of sites grouped in patches. The present theoretical calculations also suggest that the adsorbed atoms or molecules of these non-polar gases easily migrate two-dimensionally along the surface in the low coverage region. These results on the surface migration are qualitatively in good agreement with the experimental entropy curves.

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