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7/25/68

PHYSICAL ADSORPTION OF NEOPENTANE ON

AMMONIUM IODIDE IN THE REGION OF THE

 $\alpha - \beta$ PHASE TRANSITION

A THESIS

Presented to

The Faculty of the Division of Graduate

Studies and Research

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Robert Alman Magee

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Master of Science in Chemistry

Georgia Institute of Technology

June, 1972

PHYSICAL ADSORPTION OF NEOPENTANE ON

AMMONIUM IODIDE IN THE REGION OF THE

 α – $\beta\,$ PHASE TRANSITION

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To Ann

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SUMMARY

Ammonium iodide has a solid state phase transition at about 255.8 $^{\circ}$ K in which it changes from a face centered cubic crystal structure (α phase) to a simple cubic crystal structure (β phase). Adsorption isotherms have been run for neopentane on the α phase of anhydrous ammonium iodide at 260.35 $^{\circ}$ K and 257.73 $^{\circ}$ K and on the β phase at 255.16 $^{\circ}$ K and 252.66 $^{\circ}$ K. The isosteric heat of adsorption at zero coverage for each phase has been determined from these isotherms to be 4090 ± 720 cal/mole and 5710 ± 720 cal/mole respectively.

Semi-empirical calculations of the interaction energy of a neopentane molecule with the (100) plane of face centered cubic, the (100) plane of simple cubic, and the (110) plane of simple cubic ammonium iodide have been carried out utilizing a modified Buckingham (6-exp) pair potential function and summing the interactions over the nearest 20,000 ions in each crystal lattice. These calculations yielded the following values for the enthalpy of adsorption at zero coverage: the (100) plane of the face centered cubic structure, 4159 cal/mole; (100) plane of the simple cubic structure, 5940 cal/mole; and (110) plane of the simple cubic structure, 5639 cal/ mole.

CHAPTER I

INTRODUCTION

Statement of Problem

The semi-empirical calculation of the interaction energy of an adsorbate molecule with an ionic crystal surface has been carried out by a number of workers. In this calculation some potential function must be assumed for the interaction of the molecule with an ion in the crystal, and the interactions with all of the ions in the crystal are summed over the structure of the crystal.

The purpose of this work is to study the effect of crystal structure on the adsorptive interaction by investigation of the interaction on two different crystal structures composed of identical ionic species. Two phases of ammonium iodide above and below the so-called α - β transition at -17.6 °C afford just this situation plus an additional condition of having both structures available in a single sample.

Interaction Potential

In 1933 Lenel¹ presented calculations for the adsorption of argon and krypton on various ionic crystals. The dispersion forces were calculated using London's equation²

$$\Phi = -C/r^6 \tag{1}$$

where

$$C = 3/2 \alpha_1 \alpha_2 \frac{I_1 I_2}{I_1 + I_2}$$

and α_1 and α_2 are the polarizabilities and I_1 and I_2 are the ionization potentials of the interacting species. The values of these constants given by Mayer³ were used. Lenel assumed that the repulsive energy was balanced by the quadrupoledipole interaction, therefore, both were omitted from the calculation. The electrostatic interaction was estimated by integrating the variation of the field over the volume of the adsorbed molecule, and the equilibrium distance was estimated from geometrical considerations.

Orr^{4,5} made extensive calculations for the interaction of argon, oxygen, and nitrogen with the (100) face of potassium chloride and cesium iodide using the Kirkwood-Müller⁶ expression for the dispersion energy of a pair of atoms, ions, or molecules

$$\Phi_{\rm A} = \left[\frac{\alpha_1 \alpha_2}{\alpha_1 / \chi_1 + \alpha_2 / \chi_2} \right] \frac{6 {\rm mc}^2}{{\rm r}^6}$$
(2)

where m is the mass of an electron, c is the velocity of light, r the interatomic distance, and α and χ are the polarizabilities and diamagnetic susceptibilities of the two species. This term was combined with an exponential repulsive potential. The electrostatic contribution to the potential was calculated from an expression derived by Lennard-Jones and Dent⁷ for the electrostatic field

$$\Phi_{\rm E} = -\frac{1}{2} \alpha F_{\rm Z}^2 \tag{3}$$

where α is the polarizability of the adsorbed molecule and F_z is the component of the electrostatic field perpendicular to the crystal surface.

The heat of adsorption calculated by this method was in good agreement with the experimental quantities for potassium chloride but is about 600 cal/mole too high for cesium iodide.

Thompkins and Young⁸ attributed this discrepancy to the fact that cesium iodide crystallizes as rhombic dodecahedra exposing the (110) face rather than the (100) face assumed by Orr. They carried out the calculation for the (110) face assuming from geometrical considerations that the electrostatic contribution to the potential would be negligible and found that the heat of adsorption is approximately 600 cal/mole less for the (110) face than for the (100) face of cesium iodide, thus giving good agreement with the experimental value reported by Orr. This agreement points out the importance of the surface face assumed in the calculations.

Hayakawa ⁹⁻¹³ has carried out the most extensive calculations of this type to date. In a series of articles Hayakawa calculated the adsorption potential for the interaction of argon, oxygen, nitrogen, and carbon dioxide with the (100) face of cubic potassium chloride and potassium bromide, and the (111) face of octahedral potassium chloride. Calculation of the potential was divided into four parts: the Van der Waals (dispersion) potential, the repulsive potential, the electrostatic potential, and the quadrupole potential. Hayakawa used the Kirkwood-Müller formula, eq. (2), for the Van der Waals potential and eq. (3) for the electrostatic potential. The modified Buckingham-Corner repulsive potential formula for the non-polar adsorbate molecules and the Born-Mayer¹⁴ repulsive potential formula for the lattice ions were used to derive the total repulsive potential. Both of these potentials are of the form

$$\Phi = - \frac{C}{r} 6 + B e^{-\gamma r}$$

with the attractive Van der Waals term, C/r^6 , and an exponential repulsive term. The repulsive constants of Huggins and Mayer¹⁵ were used for the crystal ions. The interaction of the quadrupole moments of oxygen and nitrogen with the electrostatic field of the crystal was included in Hayakawa's calculations using the method of Drain.¹⁶ The agreement between theoretical and experimental adsorptive potentials is on the whole very good, particularly for argon. In general Hayakawa considered the discrepancy between experiment and calculation to be due to surface heterogeneity caused by distribution of sites grouped in patches.

α - β Phase Transition in Ammonium Iodide

The solid state phase transitions of ammonium iodide have been a subject of investigation since P. W. Bridgman¹⁷ discovered a second modification of ammonium iodide at low temperature (below -17.6° C) analogous to the room temperature form of the chloride and bromide. Using x-ray diffraction Bartlett and Langmuir¹⁸ investigated the crystal structures of ammonium chloride at 20°C and 250°C, ammonium bromide at 20°C and 250°C and ammonium iodide at 20°C. They found that the high temperature form of each (room temperature for the iodide) has a face-centered cubic structure like sodium chloride and the low temperature form of the chloride has a simple cubic structure like cesium chloride. An intensive x-ray diffraction study of the modifications of ammonium iodide has been carried out by Hovi and Varteva.¹⁹ The low temperature modification (β phase) was determined to have a simple cubic structure analogous to that of the chloride and bromide and having a lattice parameter of 4.335 A.

The transition temperature has been a subject of dispute since supercooling and superheating are very pronounced in these solid state transitions. Arell and Alare²⁰ observed the α - β transition of ammonium iodide by using a direct differential calorimetric method. The transition was found to fall in the temperature interval -17.4°C to -14.4°C.

CHAPTER II

EXPERIMENTAL EQUIPMENT AND PROCEDURES

Vacuum System

The main pumping system consists of a two stage mercury diffusion pump with a Model 1405 Welch roughing pump. The mercury diffusion pump is separated from the vacuum manifold by a cold trap utilizing a dry ice-acetone slush. This arrangement can reduce the pressure to about 10^{-6} or 10^{-7} torr.

An auxiliary pumping system is provided to adjust the mercury levels in the McLeod gauge, compression gauge, manometer, and mercury cut-off.

Pressure Measurement

Manifold Pressure

The measurement of manifold pressure is conveniently divided into three ranges: 0 to 10 torr, 10 to 100 torr, and 100 torr to 760 torr. Pressures in the 0 to 10 torr range are measured on a Model GM-100A McLeod gauge manufactured by Consolidated Vacuum Corporation. This gauge has three stages with workable ranges of 10^{-5} torr to 0.1 torr, 0.1 torr to 1 torr, and 1 torr to 10 torr. Each of these having an error of approximately \pm 1.0 per cent. Measurements made with this instrument are corrected for capillary depression as determined by Dr. R. A. Pierotti in an earlier calibration using a cathetometer and for nonideal compression (needed only for neopentane) utilizing the second virial coefficient (discussed later in this chapter).

Pressures in the 10 torr to 100 torr range are measured on a small compression gauge, accurate to \pm 0.4 percent, with a compression ratio of 4.6356 to 1. These measurements are also corrected for capillary depression and nonideal compression of neopentane. Higher pressures are measured on a U-tube mercury manometer accurate to \pm 0.4 percent.

Neopentane Vapor Pressure

The vapor pressure of neopentane is measured on a U-tube mercury manometer connected to a glass probe next to the sample bulb. This manometer is designed so that the vapor does not contact any stopcocks since neopentane is soluble in stopcock grease.

Constant Volume System

The adsorption line is similar to that used by Pierce and Ewing²¹ except that mercury cut-offs are utilized instead of stopcocks to prevent the neopentane from dissolving in stopcock grease. The adsorption line is shown in Figure 1.

Volume Calibration

The volume of the compression gauge was calibrated with mercury. This volume was then used to calibrate the other necessary volumes by expansion experiments with He gas (Matheson "High Purity"). In these calibrations ideal expansion was assumed, and it was further assumed that the amount of helium adsorbed on the sample was negligible. The volume of the adsorption manifold, V_m , is bounded by mark 1 and mark 2 as shown in Figure 1. Volume V_m included the volumes of



Figure 1. Schematic Diagram of Adsorption Line

the McLeod gauge, V_{G} , and the compression gauge, V_{O} .

The dead space volume, V_{D} (Fig. 1), was calibrated at room temperature, liquid nitrogen (77 O K), and dry ice temperature (195 O K). The effective dead space at other temperatures is found from equation (4) (which is obtained by making a two temperature approximation)

$$\mathbf{V}_{\mathbf{Deff}} = \mathbf{V}_{\mathbf{warm}} + \mathbf{V}_{\mathbf{cold}} \left(\mathbf{T}_{\mathbf{warm}/\mathbf{T}_{\mathbf{cold}}} \right)$$
(4)

where V_{warm} and V_{cold} are defined by

$$V_{\rm D} = V_{\rm warm} + V_{\rm cold} \tag{5}$$

Equations (4) and (5) assume also that the volume of the sample is constant over the temperature range from the calibration temperature to the experimental temperature. It can be shown that the change in sample volume due only to thermal expansion is negligible as compared with the error in the determination of the cold dead space volume. However, the volume changes involved in the β - γ and α - β phase transitions are larger and their effect should be investigated. The densities of these three phases of ammonium iodide have been reported by Stammler²² and are recorded in Table 1. If the sample is assumed to have the same density at the calibration temperatures (77 ^oK and 195 ^oK) as the γ phase density reported in Table 1 then the contribution of the volume change of the 9.3052 gram sample of ammonium iodide due to the density changes involved in the phase transitions, ΔV , to the cold dead space volume, V_{cold} , may be calculated and the calibrated value

Table	1.	Density	of	NH	I
-------	----	---------	----	----	---

Phase	Density g/cc
α ₍₂₆ ° _{C)}	2.514
³ (-17 [°] С)	2,935
(-100 ⁰ C)	2,89

of V_{cold} corrected for this change. When the sample goes over to the α phase, ΔV is -0.481cc, and when the sample goes over to the β phase, ΔV is 0.050cc. Since the ΔV value when the β phase is formed is less than the experimental error in the determination of the cold dead space volume, it may be neglected. Then V_{cold} is decreased by 0.481 cc for those isotherms for which the sample is in the α phase.

Operation

The doses are measured volumetrically in V_m . A known dose, $N_{m,i}$, is admitted to the sample by lowering the mercury cut-off. That dose is then added to the amount of adsorbate already in the dead space volume, V_D , and adsorbed on the sample from the previous doses, N_R . The total amount of adsorbate in the adsorption line is then $N_{m,i} + N_R$. When equilibrium is established the pressure is measured and from this measurement the amount of adsorbate in the dead space, N_D , and in V_m , N_m , f, are determined. Then the amount of adsorbate adsorbed on the sample for a given point, $N_{ads.}$, is

$$N_{ads} = N_{m,i} + N_R - N_{m,f} - N_D$$
(6)

The mercury cut-off is now restored to its original position and the amount of adsorbate in V_m , N_m , f' is measured. The amount of adsorbate remaining in V_D and adsorbed on the sample, N_B , to be added to the next dose is then

$$N_{R} = N_{m,i} + N_{R} - N_{M,f}$$
(7)

Each of the amounts in equations (6) and (7) can be calculated from the calibrated volumes, measured pressures, and measured temperatures. Nitrogen is assumed to be an ideal gas throughout so that n can always be replaced by PV/RT. Neopentane is assumed to be described by the pressure virial expansion equation of state terminated at the second term. We may then write

$$\frac{PV}{nRT} = 1 + B(T) \frac{P}{(RT)}$$
(8)

where B(T) is the usual second virial coefficient given by the volume expansion (discussed later in this chapter). Rearranging equation (8)

$$n = \frac{PV}{RT + B(T)P}$$
(9)

Cryostat

The Cryostat (Figure 2) is cooled by employing a thermoelectric cold plate



Figure 2. Schematic Diagram of Cold Plate Cryostat.

(Thermoelectrics Unlimited, Inc. Thermoelectric Cold Plate Model CP-2). A cold plate power supply * capable of delivering variable direct current of zero to eight amperes at zero to six volts with less than five per cent ripple may be operated in either a manual or an automatic mode. In the automatic mode power is controlled by a photoresistor mounted in an optical sensing block (Figure 4) attached to a differential manometer (Figure 3). The latter is filled with butane and connected to a glass probe located near the sample bulb. A 50 per cent solution of water and ethylene glycol cooled to approximately 0° C by an electric refrigeration unit is circulated through the cold plate heat exchanger by a small centrifugal pump at a rate of two liters per minute.

The temperature of the cryostat is adjusted by cooling to the desired temperature and closing the stopcock on the differential manometer. As the temperature rises in the cryostat, the increasing vapor pressure of the butane increases the mercury level and thereby decreases the intensity of light on the photoresistor. Its resistance is increased causing the amplifier in the cold plate power supply to become positive and thus bring about an increase in the voltage to the cold plate. A temperature decrease in the cryostat causes a reverse sequence to take place.

The cryostat is capable of regulating temperature to ± 0.005 °C over a range from 0 °C to -21 °C.

Temperature Measurement

The temperature of liquid nitrogen and dry ice are measured using a vapor

*Constructed by the Instrument Shop of the School of Chemistry.



Figure 3. Differential Manometer.



Figure 4. Schematic Diagram of Optical Sensing Block.

pressure thermometer filled either with nitrogen (Matheson "Extra Dry") or carbon dioxide (Matheson "Bone Dry"). The pressure measurements are converted to temperature by the Antoine Equation

$$\log_{10} P = A - \frac{B}{C+T}$$
(10)

where P is in torr, T in ${}^{O}C$, and A, B, and C are constants 23 for a given substance and are listed in Table 2.

	А	В	С	
N ₂	6.49457	255.680	266.550	
co_2	9.81066	1347.786	273.000	

Table 2. Constants for the Antoine Equation 23

The cryostat temperature is measured to \pm 0.002 °C using a platinum resistance thermometer calibrated by the National Bureau of Standards (Leeds and Northrup Co., serial no. 1655162) and a Leeds and Northrup Mueller bridge to measure resistance.

A mercury thermometer graduated to 0.02°C is used to determine room temperature.

Sample Bulb

Three major considerations are involved in the design of the sample bulb:

the dead space ought to be minimized; the sample must be loaded, sealed, and weighed without exposure to the atmosphere; and the sample must not be overheated when the bulb is sealed. The sample bulb shown in Figure 5 accomplishes these goals by means of a loading arm capped by a needle valve. The sample is loaded through the loading arm in a dry box and the needle valve sealed. The bulb is then pumped out through the needle valve and the loading arm sealed about one inch above the body of the bulb. The dead space created by the loading arm is partially filled by insertion of a short piece of glass rod before the needle valve is sealed in the dry box. The break seal is broken by a glass encased magnet after the bulb is attached to the system.

Sample Preparation

The ammonium iodide sample was prepared under anhydrous conditions in the system shown in Figure 6 by a gas phase reaction of ammonia and hydrogen iodide. The ammonia is Matheson "Anhydrous" which was dried further by passage through an ice temperature cold trap containing activated charcoal. The hydrogen iodide was prepared by allowing distilled water to fall dropwise on a mixture of red phosphorous (Fisher Lot No. 786748) and iodine (Fisher Lot No. 787396).²⁴ This reaction was carried out in a closed system which had been charged with the reactants¹ and evacuated before being sealed. The HI thus formed was dried by passage through two cold traps at -23°C (carbon tetrachloride slush baths) and collected in solid form at liquid nitrogen temperature. The reactions involved are given by the following stoichiometric equations.



Figure 5. Sample Bulb.



Figure 6. Schematic Diagram of Ammonium Iodide Preparation System.

$$3I_2 + 2P \rightarrow 2PI_3$$
$$PI_3 + 3H_2O \rightarrow H_3PO_3 + 3HI_{(g)}$$
$$HI_{(g)} + NH_{3(g)} \rightarrow NH_4I_{(s)}$$

The last reaction corresponds to the condensation of ammonium iodide since the vapors of ammonium salts contain the dissociation products of the salt rather than free salt molecules.²⁵ The reaction is carried out in the absence of air by allowing the vapor pressure of HI at dry ice temperature (~ 60 torr) to enter the evacuated reaction bulb. Then approximately 100 torr of ammonia was similarly allowed to expand into the reaction bulb from the ammonia storage bulb. The reaction ensued and after the fine powder had settled, the reaction bulb was again evacuated and the cycle repeated until a sufficient quantity of ammonium iodide had accumulated in the reaction bulb. The bulb was then sealed and removed from the system, and the ammonium iodide transferred to sample bulbs in a dry box.

Electron Microscope Studies

Since ammonium iodide decomposes in the beam of the electron microscope, micrographs could only be made by replication techniques. The replicas were prepared in a dry box by spraying NH_4 powder from a nebulizer onto a glass microscope slide and coating with a two per cent solution of parlodion in amyl acetate. After drying the parlodion film is divided into small sections and mounted on microscope grids. The micrographs thus obtained were not of high quality but were adequate to indicate that the sample is in the form of nearly cubic crystals approximately 1.0 μ on an edge. One of these micrographs is shown in Fig. 7.



Figure 7. Electron Micrograph of NH₄I Replica.



Figure 8. X-ray Diffraction Pattern of NH₄I Sample.

X-ray Diffraction

X-ray diffraction patterns of the ammonium iodide sample at room temperature were made using a Debye-Scherrer camera with the film mounted in the Straumanis position. One of these patterns is shown in Fig. 8. The sample was prepared in a dry box and exposed to the x-rays for eight hours. The ammonium iodide was found to be in the face centered cubic (NaCl type) crystal structure. The lattice parameter is given in Table 2, where it is compared with various literature values. The present determination was corrected for film shrinkage and for absorption of x-rays by the sample. It agrees particularly well with the value of Havighurst, et. al. The error estimate quoted in Table 3 for the lattice parameter determined in this work is given by the standard deviation of the values found from three separate diffraction patterns and the value of the lattice parameter is the average of these individual values.

Lattice		
Parameter	Reference	
7.198	Bartlett and Langmuir	18
7.244 + .003	Havighurst, et. al.	32
7.259	Sagel	33
7.2591 + .0007	Hovi and Varteva	19
7.246 + .003	This work	

Table 3. Lattice Parameters of $NH_{A}I$

Differential Calorimetry

Differential Calorimetry studies were made of the α - β phase transition on a Perkin-Elmer Differential Scanning Calorimeter to verify the occurrence of this transition in the prepared sample. It was necessary to pre-cool the sample in liquid nitrogen in order to overcome the initial large supercooling of the α phase. Measurements were then made by allowing the sample to warm up in the calorimeter until the transition occurred. Then the sample was oscillated through the transition several times. Some characteristics of the transition were noted. The transition is broad, extending over a three degree interval when the temperature is changed at a rate of 1.25°C per minute. Although the temperature measurement of the calorimeter is approximate, it is evident that the β phase superheats by approximately five degrees centigrade and the α phase supercools by approximately five degrees centigrade. Using the heat of fusion of an ultra-pure indium metal sample as a standard for calibrating the area of the calorimeter curves, it was found that the measured heat of transition of the ammonium iodide sample increased with successive oscillations through the transition reaching a value of 790 + 30 cal/ mole after four oscillations. This value is in good agreement with the literature value of the heat of transition, 809 cal/mole.²⁰

The above evidence indicates that the sample is not totally transformed to the β phase in the initial cooling, but after three or four oscillations through the transition the sample is totally transformed on passing through the transition. This knowledge enables us to be reasonably certain that the sample used for adsorption studies has totally transformed to the β phase by a pretreatment which oscillates

it through the transition six or seven times.

Thermal Transpiration

Since the pressure measurement devices of the adsorption system are at a different temperature from the sample bulb there exists a pressure differential across the temperature boundary which, at equilibrium, is sufficient to balance the thermal diffusion of the gas across this boundary. Weber²⁶ has developed an equation for the thermal transpiration of a gas along a closed cylindrical tube

$$\frac{dP}{dT} = \frac{P}{2T} \left(\frac{1}{\alpha y^2 + \beta y + u} \right)$$

$$y = d/2$$
(11)

where P is the pressure, T the temperature, d the tubing diameter, and λ the mean free path length of the gas molecule. The constants of the equation are found by Weber to be

$$\alpha = \pi/128$$

 $\beta = \pi/12$
 $u = (1 + gy)/(1 + hy)$
 $g - h + \beta = 1 \text{ or } 3/4$
 $g/h \approx 1.25$

The derivation of Weber's equation makes the assumptions that the gas molecules are hard spheres whose size is temperature dependent and that they undergo no specular reflection off the walls of the tube.
In order to account for the effect of thermal transpiration on the adsorption pressure determinations with nitrogen at liquid nitrogen temperature, the approximate solution of Weber's equation suggested by Miller²⁷ is used, namely

$$\left(\frac{\mathrm{dP}}{\mathrm{dT}}\right)\left(\frac{2\mathrm{T}}{\mathrm{P}}\right) \simeq \frac{\Delta \mathrm{P}}{\Delta \mathrm{T}} \frac{2\mathrm{T}}{\mathrm{P}} \simeq \frac{1 - \frac{\mathrm{P}}{\mathrm{P}_{2}}}{1 - \left(\frac{\mathrm{T}}{\mathrm{T}_{2}}\right)^{\frac{1}{\mathrm{E}}}} \equiv \mathrm{X}$$
(12)

where

$$X = \frac{1}{\alpha y^2 + \beta y + u}$$
, $T_2 > T_1$ (13)

Using the kinetic theory of gases y can be found from

$$y = \frac{P_2 d\sigma^2}{2.33T} \times 10^3$$
$$T = \frac{T_1^{+}T_2}{2}$$
$$\sigma^2 = \sigma_{\infty}^2 \left(1 + \frac{C}{T}\right)$$
(14)

where C is a constant for a given gas and σ_{∞} is the limiting hard sphere molecular diameter at high temperature. Landolt-Bornstein²⁸ have listed values of C and σ_{∞} for many gases.

Using data from various sources on thermal transpiration of rare gases Miller calculated the best general values of α and β to be $\alpha = 0.0300 \ \beta = 0.245$ giving the equation

$$X = \left(0.0300y^{2} + 0.245y + \frac{1+2.5y}{1+2y}\right)^{-1}$$
(15)

Equation (15) is used to correct for the thermal transpiration of nitrogen in the adsorption experiments.

The thermal transpiration of neopentane was estimated using a somewhat different equation originally used by Liang.²⁹ The constants and relations recommended by Bennett and Tompkins³⁰ are utilized in applying this equation

$$\frac{P_1}{P_2} = R = \frac{\alpha_{\text{He}(f\phi_g X)^2 + \beta_{\text{He}(f\phi_g X) + R_m}}}{\alpha_{\text{He}(f\phi_g X)^2 + \beta_{\text{He}(f\phi_g X) + 1}}}$$
(16)

where

$$f = 1 \text{ for } d > 1 \text{ cm}$$

$$X = P_2 d$$

$$R_m = \left[\frac{T_1}{T_2}\right]^{\frac{1}{2}} T_1 < T_2$$

$$He = 3.70[1.70 - (2.6 \times 10^{-3}) \Delta T]^{-2}$$

$$T = T_2 - T_1$$

$$He = 7.88 (1 - R_m)$$

and ϕ_g is given by

$$\log r_0 = 0.43 + 0.24 \log \phi_g$$

where r_0 is the Hirshfelder³¹ value calculated from viscosity data using a Lennard-Jones 12:6 potential function.

Using equation (16) and the associated constants and relations given above, the thermal transpiration correction at the temperatures of interest was found to be less than 0.27 per cent at 0.1 torr (which is lower than the lowest experimental pressure), so it is concluded that thermal transpiration corrections in the pressure range studied may be neglected.

Gas Imperfections

The deviation of the behavior of neopentane from that of an ideal gas is taken into account in both the pressure measurements on the McLeod gauge and the isotherm calculations by use of the volume virial equation terminated after the second term

$$\frac{PV}{RT} = 1 + B/V \tag{17}$$

The second virial coefficient, B(T), of neopentane is calculated in this instance from a (28,7) interaction potential using the parameters $r_0 = 6.09 \times 10^{-8}$ cm and $\epsilon/k = 581^{\circ}K$.³⁴ This potential has been shown by Hamann and Lambert³⁴ to give better agreement with experimental values than the Lennard-Jones 12:6 potential.

Nitrogen and helium were both assumed to behave ideally.

CHAPTER III

THE ADSORPTION POTENTIAL

Interaction between a neutral molecule and an ionic crystalline substrate may be conveniently broken down into contributions due to dispersion interactions, repulsion interactions, and induction interactions. Each will be considered separately although the dispersion and repulsion parameters are actually related through use of the modified Buckingham (6 - exp) pair potential function. This potential function is of the same type as that used by Hayakawa⁹⁻¹³ in his calculations of the adsorptive potential of neutral molecules and atoms with an ionic crystal surface. The difference lies in the introduction of the modified Buckingham potential parameters for neopentane as opposed to purely theoretical parameters used by Hayakawa. The modified Buckingham (6 - exp) potential function is given by

$$\Phi(\mathbf{r}) = -\frac{C}{\mathbf{r}_6} + B \exp(-\gamma \frac{\mathbf{r}}{\mathbf{r}_m})$$
(18)

where,

$$C = \left(\frac{\epsilon}{1-\frac{6}{\gamma}}\right) r_{m}^{6}$$

$$B = \left(\frac{6\epsilon}{\gamma-6}\right) \exp \gamma$$

and ϵ is the depth of the potential well at its minimum, r_m is the equilibrium

separation, and γ is the parameter determining the steepness of the repulsive wall of the potential. These parameters are given for neopentane by Sherwood and Prausnitz⁴¹ and are quoted in Table 5.

The Dispersion Potential

The dispersion potential of the adsorbate molecule with each of the negative ions of the ionic crystal is given by

$$\Phi_{A2} = -\frac{C_{12}}{r^6}$$
(19)

where,

$$C_{12} = \left(\frac{\epsilon_{12}}{1-6/\gamma_{12}}\right) r_{m_{12}}^{6}$$

whenever the (6 - exp) potential is used. The attractive interaction with the positive ions is given by an identical expression and the reasoning which follows applies equally to the positive ions.

 C_{12} in eq. (19) is a mixed interaction parameter defining the attractive interaction between unlike species. This parameter can be calculated by several methods, two of which are described below. Various simplified theoretical approaches have been proposed for the direct calculation of C_{12} from some combination of the ionization potentials, polarizabilities, and/or diamagnetic susceptibilities. Such calculations do not give quantitative agreement with that same parameter calculated from the (6 - exp) potential. The most widely accepted of these expressions is the Kirkwood-Müller expression⁶ which was employed by Hayakawa in the calculations previously mentioned. The Kirkwood-Muller expression is given by

$$C_{12} = 6mc^{2} \left(\frac{\alpha_{1}}{\chi_{1}} + \frac{\alpha_{2}}{\chi_{2}}\right)^{-1} \alpha_{1} \alpha_{2}$$
(20)

where α_1 and α_2 are the polarizabilities and χ_1 and χ_2 are the diamagnetic susceptibilities of the molecules or ions; m is the mass of an electron; and c is the velocity of light.

A second method of calculating C_{12} is by means of various combining laws. In this method it is assumed that the self-interaction parameters for the two species are known for a given potential function. Since such parameters are difficult to determine for ionic species and are of dubious accuracy in those cases which have been determined, an alternate method is proposed here which is somewhat of a compromise between the two methods.

Eq. 20 also gives self-interaction parameters by reducing it to the case where the two interacting species are identical, namely

$$C_{11} = 6mc^2 \left(\frac{\alpha_1 \chi_2}{2}\right)$$
(21)

The values of C_{11} or C_{12} given by eq. (20) or (21) were compared with those reported by Starkschall and Gordon.⁴⁷ For the case of the rare gases, values of C_{11} or C_{12} from eq. (20) or (21) were plotted as the abscissa (units of $A^{060}K$) against comparable value from Starkschall and Gordon on the ordinate (units of $A^{060}K$). Visually the points were nearly linear and a least squares fit to a linear equation gives

$$C_{SG} = -14.1 \times 10^4 + 2.53 C_{KM}$$

with a standard error of estimate, S_y , of 8.8 x 10⁴. The small negative intercept is evidently not significant, and, therefore, it may be assumed that the two quantities are proportional to one another. The linear correlation between the two sets of values of C_{11} suggests that an acceptable approach to the determination of dispersion force coefficients may be given by

$$C_{22} = C_{11} \left(\frac{C_{22KM}}{C_{11KM}} \right)$$
(22)

An extension of this approach to the determination of mixed interaction dispersion coefficients would be

$$C_{12} = C_{11} \left(\frac{C_{12KM}}{C_{11KM}} \right)$$
 (23)

where C_{11} is a known dispersion coefficient for one of the species of interest and $C_{12\rm KM}$ and $C_{11\rm KM}$ are given by eq. (20) and (21) respectively. This expression may be compared to one given by applying the geometric mean combining law⁴⁸

$$C_{12} = (C_{11} C_{22})^{\frac{1}{2}}$$
 (24)

to the self-interaction parameters given by eq. (22). Substituting eq. (22) in eq. (24) and rearranging gives an equation similar to eq. (23) with an additional factor.

$$\mathbf{C}_{12} = \mathbf{C}_{11} \left(\frac{\mathbf{C}_{12\mathrm{KM}}}{\mathbf{C}_{11\mathrm{KM}}} \right) \frac{\boldsymbol{\alpha}_1 \boldsymbol{\chi}_2^+ \boldsymbol{\alpha}_2 \boldsymbol{\chi}_1}{2(\boldsymbol{\alpha}_1 \boldsymbol{\chi}_1 \boldsymbol{\alpha}_2 \boldsymbol{\chi}_2)^{\frac{1}{2}}}$$

The additional factor is a measure of the difference between the method of eq. (23) and the combining law of eq. (24). For the cases we are considering, the mixed interactions $C(CH_3)_4 - I^-$ and $C(CH_3)_4^-NH_4^+$, the factors are 1.005 and 1.029 respectively; therefore, it is obvious that the two methods are approximately equivalent for these cases.

Fender and Halsey⁴⁹ have suggested the harmonic mean combining law

$$C_{12} = \frac{2C_{11}C_{22}}{C_{11}+C_{22}}$$
(25)

A comparison similar to that previously made for eq. (24) may be made for eq. (25). The expression derived by the substitution of eq. (22) into eq. (25) is

$$\mathbf{C}_{12} = \mathbf{C}_{11} \left(\frac{\mathbf{C}_{12\text{KM}}}{\mathbf{C}_{11\text{KM}}} \right) \frac{\boldsymbol{\alpha}_1 \boldsymbol{\chi}_2^{+} \boldsymbol{\alpha}_2 \boldsymbol{\chi}_1}{\boldsymbol{\alpha}_1 \boldsymbol{\chi}_1^{+} \boldsymbol{\alpha}_2 \boldsymbol{\chi}_2}$$

The additional factor in this equation is equal to .956 for $C(CH_3)_4 - 1$ and .923 for $C(CH_3)_4 - NH_4^+$. Then these two methods are also approximately equivalent, with the geometric mean to be preferred. Eq. (23) will be used to determine the mixed interaction dispersion coefficients with C_{11} the dispersion coefficient of neopentane defined by eq. (18) and using the polarizabilities and diamagnetic susceptibilities of neopentane, iodide ion, and ammonium ion given in Table 4.

	$\frac{\alpha}{cm^3/mole \times 10^{25}}$	$cm^{3}/mole \ge 10^{6}$
С(СН ₃)	99.7	-63.0
ī	65.4	-50.6
NH4+	13.0	-13.3

Table 4. Polarizabilities and Diamagnetic Susceptibilities

The total dispersion potential, Φ_A , for the adsorbate molecule interacting with the ionic crystal is found by summing the dispersion potentials over all of the ions.

$$\Phi_{A} = \frac{C_{12}}{a^{6}} S_{-}(\rho) - \frac{C_{13}}{a^{6}} S_{+}(\rho)$$
(26)

where S_ and S₊ are summations for the inverse sixth power of the adsorbate molecule to ion distances. Details of carrying out these summations are described in Appendix B. a is the ion-ion distance in the crystal and ρ is a reduced distance for the molecule above the crystal surface defined by

$$\rho = \frac{z}{a}$$

where z is the distance of the molecule above the surface plane of atoms. The Repulsive Potential

The interaction of ions in a crystal has been described by Huggins and

Mayer¹⁵ using a term, $B_+B_- \exp(-\delta r)$, for the repulsive portion of the potential function. B_+ and B_- are parameters for the cation and anion respectively and δ is an empirically determined constant which has been shown to be 2.899Å⁻¹ for alkali halide crystals. An analogous term for neopentane is found in the modified Buckingham (6 - exp) potential (eq. 18). The pre-exponential parameter is then similar to B_+ and B_- if we consider

$$B_{11} = B_0^2$$
 (27)

where B_0 is now a parameter similar to B_+ and B_- .

This suggests directly the mixed interaction parameters defined by

$$B_{12} = B_0 B_-$$
(28)
 $B_{13} = B_0 B_+$

The latter definition of B_{12} is identical to the combining law of Buckingham⁴²

$$B_{12} = (B_{11}B_{22})^{\frac{1}{2}}$$
(29)

since the self-interaction parameter for the ion, $B_{22}^{}$, is simply B_{2}^{2} .

The exponential parameter for the repulsive portion of the mixed interaction may be found from the combining law of Zener.⁴³

$$\beta_{12} = \frac{1}{2} (\beta_{11} + \beta_{22}) \tag{30}$$

where β_{11} in the present calculation is simply γ/r_m from eq. (18) for neopentane,

and β_{22} is the parameter δ in the repulsive term of Huggins and Mayer already mentioned. This combining law can be shown to follow directly from the variation of the electron density of an atom with distance from the nucleus. In the outer region of an atom, the region involved in ordinary thermal collisions, the electron density is approximately proportional to $\exp(-\omega)$ where ω is a function of the distance from the atomic nucleus. The resonance energy between two atoms will then contain the factor $\exp - (\omega_1 + \omega_2)r$, r being the interatomic distance. Then the expression for the energy between two like atoms will contain a factor $\exp (2\alpha_1)r$. It follows that if we have the values of $2\alpha_1$ and $2\alpha_2$ for the self-interaction of two species, the mixed interaction parameter will be given by $\frac{1}{2}(2\omega_1 + 2\omega_2)$.

The repulsive potential for the adsorbate molecule interacting with the negative and positive ions of an ionic crystal is given by

$$\Phi_{R2} = B_{12} \exp(-\beta_{12} r)$$
(31)
$$\Phi_{R}^{3} = B_{13} \exp(-\beta_{13} r)$$

respectively. B_{12} and B_{13} are now defined by eq. (28), and β_{12} and β_{13} are defined by eq. (30).

The total repulsive potential, $\Phi_{\rm R}$, of the adosrbate molecule with the ammonium iodide crystal is found by summing the repulsive potentials given by eq. (31) over all of the ions.

$$\Phi_{\rm R} = B_{12}S'_{-}(\rho, \beta_{12}, a) + B_{13}S'_{+}(\rho, \beta_{13}, a)$$
(32)

where $S'_{-}(\rho, \beta_{12}, a)$ and $S'_{+}(\rho, \beta_{13}, a)$ are summations for the exponential of the molecule-ion distance and are described in Appendix C.

Using the relationships defined in eqs. (23), (28), and (30), the parameters of the modified Buckingham (6-exp) potential function for the mixed interactions of neopentane with iodide ion and with ammonium ion can be evaluated. For convenience eq. (18) is repeated here

$$\Phi(\mathbf{r}) = \frac{\mathbf{C}}{\mathbf{r}_{6}} + \mathbf{B} \exp\left(-\frac{\mathbf{r}}{\mathbf{r}_{m}}\right)$$

where,

$$C = \left(\frac{\epsilon}{1 - 6/\gamma}\right) r_{\rm m}^6 \tag{18}$$

$$B = \left(\frac{6\epsilon}{\gamma-6}\right) \exp \gamma$$

$$\beta = r_{\rm m}$$

The last expression is added to restate the meaning of β in the present calculations. The parameters for neopentane are given by Sherwood and Prausnitz.⁴¹ β for the alkali halides is assumed to be 2.899Å⁻¹ as given by Huggins and Mayer.¹⁵ B_ for iodide ion is also given by Huggins and Mayer¹⁵ to be 176.6x10¹² ergs. B₊ for ammonium ion is not given but a reasonable estimate may be obtained from the data of Huggins and Mayer for the alkali ions. It was found that a linear relationship exists between the Pauling Radii of the alkali ions (excluding Li⁺) and the logarithm of the values of B₊. If these are plotted on a graph of Pauling radii versus $\ln B^+$ then a value of B^+ for ammonium ion may be estimated by interpolation using the Pauling radius of ammonium ion.

For comparison the mixed interaction parameters and the self-interaction parameters for neopentane are reported in Table 5 in terms of the usual parameters of the modified Buckingham (6-exp) potential as well as in terms of C, B, and β .

Pair	С/к ° _К д ⁶	B/k °K	$^{\beta}_{\lambda^{-1}}$
C(CH ₃) ₄ -C(CH ₃) ₄	3.0917x10 ⁷	10.9023x10 ⁴⁴	16.7224
C(CH ₃) ₄ -I ⁻	2.2330x10 ⁷	$4.9637 \mathrm{x10}^{26}$	9.8102
$C(CH_3)_4$ -NH ₄ ⁺	4.9841x10 ⁶	$1.1553 \mathrm{x10}^{26}$	9.8102
	€/k	rm	γ
	^о к	8	
$C(CH_3)_4 - C(CH_3)_4$	635.4	5.801	100
C(CH ₃) ₄ -I	497.4	5.858	57.4
C(CH ₃) ₄ -NH ₄ ⁺	110.4	5.853	57.5

Table 5. Potential Parameters

The Electrostatic Potential

The electrostatic potential energy of a non-polar molecule, whose polarizability is , in any given position above an ionic crystal lattice is given by 4^4

$$\Phi_{\rm E} = -\frac{1}{2} \alpha F_{\rm Z}^2 \tag{33}$$

where F_z is the resultant field perpendicular to the crystal surface above the given point. F_z is given by⁷

$$F_{z} = -\frac{\delta \phi}{\delta z}$$
(34)

where ϕ is the total electrostatic potential above any given point and z is the perpendicular distance of the molecule above the surface.

The resultant field above the 100 face of a face-cented cubic lattice has been calculated by Lennard-Jones and Dent.⁷ It has been shown that the resultant field is zero above the center of a lattice square and above the mid-point of a lattice edge.

The resultant field above the 100 face of a simple cubic lattice has been calculated by Orr^4 using a direct summation over 88-96 ions.

The resultant field above the 110 face of a simple cubic lattice may be found by a modification of the derivation of Lennard-Jones and Dent⁷ giving

$$F_{2} = \frac{8\pi e}{a^{2}} \sum_{=1,3,5...} \sum_{m=1,3,5...} \left[\frac{(-1)^{\frac{1+m}{2}}}{1-\exp(-2\pi\sqrt{2+m^{2}})} \exp\left(\frac{2\pi z}{a}\sqrt{\frac{2\pi z}{1+m^{2}}}\right) \right]$$

$$\left\{\cos 2\pi \left(\frac{1x}{a} + \frac{mx}{a} - \frac{1+m}{4}\right) + \exp\left(-\pi \sqrt{1+m^2}\right) \cos 2\pi \left(\frac{1x}{a} + \frac{mx}{a}\right)\right\}$$
(35)

The derivation and explanation of equation (35) is given in Appendix D.

Equation (33) for the electrostatic potential assumes that the adsorbate molecule is adequately represented by a point. An estimate of the error introduced by this assumption may be made by calculating the electrostatic potential of one methyl group of the neopentane molecule situated directly between the central carbon atom and the surface. If the polarizability of the methyl group is assumed to be the same as that of methane and the carbon-carbon band length is 1.54 Å, this error is found to be 36.5 cal/mole. It will be seen later that this is small compared with the total potential.

The Total Potential

The total potential, Φ , is the sum of the attractive, repulsive, and electrostatic contributions.

$$\Phi = \Phi_{A} + \Phi_{E} + \Phi_{E} \tag{36}$$

It has been found in this work that the large equilibrium distance of neopentane from the surface caused the electrostatic potential to be very small compared with the attractive potential and may be omitted. The total potential curves for the interaction of neopentane with the (100) face of face centered cubic, the (100) face of simple cubic with a surface of negative ions, and the (110) face of simple cubic ammonium iodide are given in figures 7, 8, 9, and 10.

The force constant, f, for the mode of vibration of the neopentane molecule perpendicular to the crystal surface is found by fitting the region of the potential curve near the minimum to the equation for a one-dimensional anharmonic oscillator terminated at the fourth term.

$$\phi(z) = \phi(0) + b_2(z - z_m)^2 - b_3(z - z_m)^3 + b_4(z - z_m)^4$$
(37)

Now the force constant is

$$\mathbf{f} = 2\mathbf{b}_{2} \tag{38}$$

The frequency, ν , of this vibrational mode for a molecule of mass m is given by

$$\nu = \frac{1}{2\pi} \sqrt{\frac{f}{m}}$$
(39)

The energy levels of a one-dimensional harmonic oscillator are nondegenerate, and are given by

$$\epsilon_{n} = \left(n + \frac{1}{2}\right)h\nu \qquad n = 0, 1, 2, \dots$$
(40)

Then the zero point energy is given by

$$E_{o} = \epsilon^{*} + \frac{1}{2}h\nu \qquad (41)$$

where ϵ^* is the minimum of the potential curve.

The Einstein partition function, q, at the temperature T is

$$q = \frac{\exp(-h\nu/2kT)}{1-\exp(-h\nu/kT)}$$
(42)

and the average vibrational energy, E vib., is then

$$E_{vib} = kT^{2} \left(\frac{\delta_{lnq}}{\delta_{T}} \right)$$
(43)

Now the average energy of each oscillator at the temperature T is given by

$$E_{Avg.} = E_0 + E_{vib.}$$
(44)

In order to find the total average energy of interaction, $E_{Avg.}^{T}$ of the molecule over the ionic surface, it is assumed that there exists a Boltzmann distribution of the adsorbed molecule among the sites for which calculations have been made

$$\frac{N_2}{N_1} = e$$
 (45)

The distribution must also be weighted according to the relative number of each type site on a particular crystal face since there is a direct relationship between the number of sites of each type and the probability that a molecule will adsorb on that site. The probabilities introduced by this consideration will be superimposed on the Boltzmann distribution of eq. (45). Then we add the proportionality constant, p_i , and the total average energy is given by

$$E_{Avg}^{T} = P_{1} \frac{N_{1}}{N_{T}} E_{Avg}^{1} + P_{2} \frac{N_{2}}{N_{T}} E_{Avg}^{2} + \dots$$
(46)

The contribution of each site per unit surface square for the different crystal surfaces are given in Table 6.

Site	(100) FCC	(100) SC + Surface	(100) SC +Surface	(110) SC
Center of Lattice Sq.	1	1	1	1
Midpoint of Lattice Edge	2	2	2	2
Over -ion	1/2	0	1	1/2
Over +ion	1/2	1	0	1/2

Table 6. Contribution of Each Site per Unit Surface Square

The enthalpy of adsorption at zero coverage is related to E_{Avg}^{T} by

$$H^{O} = E_{Avg}^{T} + RT$$
 (47)

The results of the calculations are tabulated in the following Tables. In Table 15 the assumption has been made that for the (100) face there is an equal probability of finding surfaces composed of negative ions and of positive ions. The values of z_m are given directly by the position of the minimum of the calculated potential curves.



Figure 9. Potential Curves for Neopentane on the (100) Plane of Face-Centered Ammonium Iodide.

Z		$\Phi_{T}(z)$ for c	each type of al/mole	site
o A	А	В	С	D
2.174 2.536 2.898 3.261 3.623 3.985 4.348 4.710 5.072 5.145	$\begin{array}{r} & & & & & & & & & & & & & & & & & & &$	$\begin{array}{r} 15\\ 1.\ 069\ x\ 10 \\ 13\\ 6.\ 404\ x\ 10 \\ 12\\ 3.\ 332\ x\ 10 \\ 11\\ 1.\ 559\ x\ 10 \\ 9\\ 6.\ 716\ x\ 10 \\ 8\\ 2.\ 714\ x\ 10 \\ 7\\ 1.\ 042\ x\ 10 \\ 5\\ 3.\ 773\ x\ 10\\ 8049\\ 1635\end{array}$	$5.401 \times 10^{17} \\ 1.545 \times 10^{16} \\ 1.545 \times 10^{14} \\ 4.419 \times 10^{13} \\ 1.264 \times 10^{11} \\ 3.615 \times 10^{10} \\ 1.034 \times 10^{8} \\ 2.959 \times 10^{6} \\ 8.461 \times 10^{5} \\ 2.366 \times 10^{6} \\ $	$\begin{array}{c} 1.257 \times 10 \\ 15 \\ 3.596 \times 10 \\ 14 \\ 1.029 \times 10 \\ 12 \\ 2.942 \times 10 \\ 10 \\ 8.415 \times 10 \\ \end{array}$ $\begin{array}{c} 6.884 \times 10^{7} \\ 5.283 \times 10^{4} \end{array}$
5.253 5.326 5.436	-4380 -4668 -4575 -4338	-2422 -3429 -3921	2857	-1134
5.507 5.616 5.688	-3891	-3944 -3806	-2389 -2805	-2173 -2203
5.797 5.869 5.978	-3474	-3466 -3088	-2937 -2887 -2742	-2140 -2070 -1954
6.159 6.521 6.884	-2787 -2266 -1864	-2768 -2245 -1842	-2464 -1981	- 1765 - 1446
7.246 7.608	-1550 -1301 -1102	- 1528 - 1280 - 1082	- 1331	- 1001
1.911	- 1109	-1002	- 322	- 720

Table 7. Calculated $\Phi_{T}(z)$ for Neopentane on the (100) Plane of Face Centered Cubic Ammonium Iodide



Figure 10. Potential Curves for Neopentane on the (100) Plane of Simple Cubic Ammonium Iodide with a Surface of Positive Ions.

Z	Φ ₁ , (z)	for each type of	site
	1	cal/mole	
O A	Α	В	D
	8	10	13
3.035	$3.856 \ge 10_{7}^{\circ}$	5.943×10^{-3}	$2.706 \times 10^{-3}_{11}$
3.468	$1.667 \ge 10_{5}$	$1.730 \ge 10^{\circ}_{7}$	$3.850 \ge 10_{9}^{}$
3.902	$6.600 \ge 10_4^{\circ}$	$4.431 \times 10^{+}_{6}$	$5.476 \ge 10_7^{\circ}$
4.335	$1.721 \ge 10^{-1}$	$1.024 \ge 10^{\circ}$	$7.790 \ge 10^{\circ}$
4.552	- 343	4	6
4.769	-2980	$1.847 \ge 10^{-1}$	$1.104 \ge 10^{\circ}$
4.855	-3109		
4.985	-3066	- 30	
5.072	-2960	-1582	4
5.202	-2772	-2356	$1.290 \ge 10^4$
5.289		-2459	
5.419		-2406	
5.505		-2321	-1585
5.636	-2186	-2176	-1994
5,722			-2018
6.069	-1743	-1734	-1754
6.503	-1410	-1399	-1417
6.936	-1157	-1144	-1160
7.370	- 961	- 947	- 962
7.803	- 806	- 793	- 807
8.237	- 683	- 670	- 683
8.670	- 584	- 571	- 583
9.104	- 502	- 490	- 503
9.537	- 436	- 424	- 436

Table 8. Calculated $\Phi_T(z)$ for Neopentane on the (100) Plane
of Simple Cubic Ammonium Iodide with a Surface
of Positive Ions



Figure 11. Potential Curves for Neopentane on the (100) Plane of Simple Cubic Ammonium Iodide with a Surface of Negative Ions.

Z	$\Phi_{T}(z)$	for each type of sit	e
8	۸	D	C
A	A	D	C
3.035	1.657×10^9_7	$2.553 \times 10^{11}_{0}$	$1.163 \times 10^{14}_{12}$
3.468	$7.163 \ge 10_{6}^{\prime}$	$7.432 \ge 10^{5}_{\circ}$	$1.654 \times 10^{12}_{10}$
3.902	2.848 x 10_4°	$1.904 \ge 10^{\circ}_{c}$	2.353×10^{10}
4.335	$8.358 \ge 10^{\texttt{T}}$	4.411 x 10_{4}^{0}	$3.347 \times 10^{\circ}_{c}$
4.769	-5170	$8.689 \ge 10^{\texttt{T}}$	$4.573 \ge 10^{\circ}$
4.855	-6109		
4.985	-6350	6615	
5.072	-6187	- 341	1
5.202	-5788	-4068	$6.152 \ge 10^{\pm}$
5.289		-4762	
5.419	-5061	-4887	2776
5.505		-4741	-1538
5.636	-4410	-4424	-3593
5.722			-3894
5.852			-3840
6.069	-3385	-3398	-3437
6.503	-2644	-2641	-2673
6.936	-2099	-2089	-2112
7.370	-1690	-1677	-1696
7.803	-1379	-1365	-1381
8.237	-1139	-1125	-1140
8.670	- 951	- 937	- 951
9.104	- 801	- 787	- 801
9.537	- 681	- 668	- 680

Table 9. Calculated $\Phi_{T}(z)$ for Neopentane on the (100) Plane of Simple Cubic Ammonium Iodide with a Surface of Negative Ions



Figure 12. Potential Curves for Neopentane on the (110) Plane of Simple Cubic Ammonium Iodide.

z		$\Phi_{T}(z)$ for eac	ch type of sit	te
O 	Α	B		D
3.035	3.148×10^{11}	3.989×10^{12}	1.163 x 10 ¹⁴	2.706×10^{13}
3.468	9.162×10^9	8.528×10^{10}	$1.654 \ge 10^{12}$	3.850×10^{11}
3.902	$2.347 \ge 10^{8}$	1.682×10^9	2.353×10^{10}	$5.479 \ge 10^9$
4.335	$5.437 \ge 10^{6}$	3.124×10^{7}	$3.347 \ge 10^{8}$	$7.799 \ge 10^{7}$
4.769	$1.068 \ge 10^{5}$	5.457 x 10^{5}	$4.751 \ge 10^{6}$	$1.101 \ge 10^{6}$
5.202	-5270	1557	5.993×10^4	8301
5.289	-6118			
5.419	-6261	-4062	1378	-4634
5.505	-6074	-5612	-2864	-5353
5.636	-5674	-5505	-4828	-5445
5.722		-5285	-5062	-5274
5.852	-4985	-5891	-4924	-4931
6.069	-4371	-4321	-4393	-4332
6.503	-3421	-3366	-3436	-3410
6.936	-2719	-2668	-2727	-2714
7.370	-2195	-2145	-2200	-2192
7.803	-1795	-1747	-1799	-1794

Table 10.	Calculated $\Phi_{T}(z)$ for Neopentane on the (110) Plane
	of Simple Cubic Ammonium Iodide

Table 11. Results Obtained from the Potential Energy Curve, Neopentane on the (100) Plane of Face Centered Cubic NH₄I

$$T = 259.04^{\circ}K$$

Sites Type	Z _m	-E ⁰	f	$\nu x 10^{-12}$	-Eave.
<u></u>	(Å)	(cal/mole)	(erg/cm^2)	(sec ⁻¹)	(cal/mole)
Above an NH_4^+ ion	5.69	2204	8087	1.31	1500
Above an I ion	5.81	2941	11809	1.58	2196
Above the mid point of a lattice edge	5.49	3948	12541	1.63	3196
Above the center of a lattice cell	5.24	4661	12816	1.65	3907

Table 12. Results Obtained from the Potential Energy Curve,
Neopentane on the (100) Plane of Simple Cubic NH4I
with a Surface of Positive Ions

$$T = 253.91^{\circ} K$$

Sites Type	Zm	-E ⁰	f	$\nu \mathrm{x10}^{-12}$	-E
	(A)	(cal/mole)	(erg/cm^2)	<u>(sec</u> ⁻¹)	(cal/mole)
Above the midpoint of a lattice edge	5.32	2461	10172	1.47	1744
Above the center of a lattice cell	4.89	3113	9106	1.39	2407
Above an ion	5.71	2021	8130	1.31	1326

Table 13. Results Obtained from the Potential Energy Curve, Neopentane on the (100) Plane of Simple Cubic NH₄I with a Surface of Negative Ions

Sites Type	Zm	-E ⁰	f	$\nu x 10^{-12}$	-Eavg
	(Å)	(cal/mole)	(erg/cm^2)	(sec ⁻¹)	(cal/mole)
Above the midpoint of a lattice edge	5.39	4911	20885	2.10	4099
Above the center of a lattice cell	4.96	6360	14522	1.75	5600
Above an I ion	5.76	3909	13595	1.70	3157

Table 14. Results Obtained from the Potential Energy Curve, Neopentane on the (110) Plane of Simple Cubic $\rm NH_4I$

$T = 253.91^{\circ}H$

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Sites Type	Z om (A)	-E ⁰ (cal/mole)	f (erg/cm ²)	$\nu x 10^{-12}$ (sec ⁻¹)	-E _{avg} (cal/mole)
Above the center of a lattice cell	5.37	6295	28684	2.46	5429
Above the midpoint of a lattice edge	5.54	5627	29431	2.50	4756
Above an I ion	5.61	5448	18270	1.97	4675
Above an NH_4^+ ion	5.75	5078	24569	2.28	4239

Surface	т ^о к	$\mathbf{E}_{\mathbf{Avg}}^{\mathbf{T}}$ cal/mole	H ^O cal/mole
(100) Plane of Face Centered Cubic	259.04	3645	4160
(100) Plane of Simple Cubic	253.91	5435	5940
(110) Plane of Simple Cubic	253.91	5135	5640

Table 15.Zero Point Enthalpy from Potential Curves for the
Different Surface Planes

CHAPTER IV

EXPERIMENTAL RESULTS

Adsorption isotherms were run for the neopentane-ammonium iodide system at 260.35°K, 257.73°K, 255.16°K, and 252.66°K. The amount adsorbed, N_{ads}, versus equilibrium pressures are plotted in Figures 11-14. The experimental data is tabulated in Appendix A. The points in these isotherms are a mixture of both adsorption and desorption data.

The monolayer capacities are determined by the Point B method since the BET method did not give linear plots. It is possible to obtain reproducible values for Point B by plotting the slope of the adsorption isotherm against the amount absorbed. Since Point B is defined as the beginning of the linear portion of the isotherm, the above plot should indicate a continuously changing slope up to a point, then a region of constant slope. That point at which the slope becomes constant is Point B. This was done for each isotherm. The results are given in Table 16.

Т	$m_{\rm m}$ µmoles/g		
^о к			
260.35	11.68		
257.73	11,65		
255.16	9.98		
252.66	9.93		

Table 16. Monolayer Coverages Calculated by Point B Method



Figure 13. Adsorption of Neopentane on Ammonium Iodide at 260.35°K.



Figure 14. Adsorption of Neopentane on Ammonium Iodide at 257.73°K.



Figure 15. Adsorption of Neopentane on Ammonium Iodide at 255.16°K.

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Figure 16. Adsorption of Neopentane on Ammonium Iodide at 252.66°K.

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CHAPTER V

ISOSTERIC HEATS AND DISCUSSION

The isosteric heats of adsorption above and below the α - β phase transition of ammonium iodide are determined using the Clausius-Clapeyron equation

$$q_{st} = R\left(\frac{T_1 T_2}{[T_2 - T_1]}\right) \ln\left(\frac{P_2}{P_1}\right)$$
(48)

with R = 1.987 cal/mole ^OK and assuming that q_{st} is constant over the temperature range. The heat curves are plotted in Figs. 17 and 18 and the values are tabulated in Appendix A.

Since the error in temperature measurement is negligible, the greatest source of error is in the term $\ln(P_2/P_1)$. If a root mean square method is used to estimate the error in the isosteric heat, the percent error in $\ln(P_2/P_1)$ is

% Error =
$$\sqrt{(\% \text{ error } P_1)^2 + (\% \text{ error } P_2)^2}$$

Then the experimental isosteric heats and their uncertainties are given by

$$\mathbf{q}_{st} = \mathbf{R} \left(\mathbf{T}_{1} \mathbf{T}_{2} / [\mathbf{T}_{2} - \mathbf{T}_{1}] \right) \ln \left(\mathbf{P}_{2} / \mathbf{P}_{1} \right) \left(\mathbf{1} + \frac{\% \text{ Error}}{100} \right)$$

In general % Error is small compared to one hundred, therefore

$$\ln\left(\mathbf{P}_{2}/\mathbf{P}_{1}\right)\left(1 \pm \frac{\% \text{ Error}}{100}\right) = \ln\left(\mathbf{P}_{2}/\mathbf{P}_{1}\right) \pm \frac{\% \text{ Error}}{100}$$

The error in the isosteric heats is then estimated by

$$R\left(T_{1}T_{2}/[T_{2}-T_{1}]\right) \times \left(\frac{\% \text{ Error}}{100}\right)$$
(49)

In the low pressure region of the isotherms (<10 torr) the error in pressure measurement is approximately \pm 1 percent. Eq. (49) then estimates the error in the isosteric heat in this region to be \pm 720 cal/mole.

The error in pressure measurement in the regions of higher pressure is about ± 0.43 percent giving an error in the isosteric heat of ± 310 cal/mole.

The isosteric heats of adsorption at zero coverage are obtained by extrapolation of the heat curves to zero coverage and are listed in Table 17.

Surface	T 0 _K	-H ⁰ Calc. cal/mole	$-H^{O}_{Exp.}$ cal/mole
(100) Plane Face Centered Cubic	259.04	4159	4090 <u>+</u> 720
(100) Plane Simple Cubic	253.91	5940	
(110) Plane Simple Cubic	253.91	5639	5710 ± 720

Table 17. Experimental and Calculated Heats at Zero Coverage



Figure 17. Isosteric Heats of Adsorption for the Neopentane-Ammonium Iodide System at 259.04°K.



Figure 18. Isosteric Heats of Adsorption for the Neopentane-Ammonium Iodide System at 253.91°K.

Discussion of Results

The agreement between the calculated and experimental heats of adsorption as seen in Table 17 lends a great deal of support to the method proposed for calculations of this type. The large experimental error prevents the identification of the surface plane of the simple cubic structure on the basis of this data, but the pronounced distinction between the face-centered cubic structure and the simple cubic structure is readily apparent in both the calculated and experimental results. Hayakawa⁹⁻¹³ attributed the difference between his calculated and experimental heats of adsorption at zero coverage to the heterogeneity of the crystalline substrate. This heterogeneity is apparent in his heat curves as a rise in the isosteric heats as the coverage approaches zero. In Figs. 17 and 18 this heterogeneity is not evident and, therefore, the present data may offer a more reliable comparison between the calculated and experimental heat at zero coverage since the calculations inherently assume a homogenous substrate.

Now we may briefly consider the various alternatives to the method of calculation followed and how each of these would affect the final result of the calculations. The calculation of the dispersion coefficients using the Kirkwood-Müller equation directly is one of the most widely accepted procedures at present. The coefficients for the neopentane-iodide and neopentane-ammonium interaction from this expression are approximately a factor of 2 less than those given by eq. (23). This would reduce the depth of the potential curves and, therefore, the value of the calculated heat of adsorption would be approximately one-half that calculated using eq. (23).

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Several combining laws have been suggested for the estimation of the preexponential factor in the repulsive portion of the mixed interaction potential function. A linear combination of the self-interaction parameters

$$B_{12} = \frac{1}{2} (B_{11} + B_{22})$$

would give overwhelming weight to the neopentane parameter since it is several orders of magnitude greater than either the parameter for iodide or ammonium. When $B_{11} \gg B_{22}$,

$$B_{12} = \frac{1}{2} (B_{11}^{+} B_{22}^{-}) \approx \frac{1}{2} B_{11}^{-}$$

Then for the neopentane-iodide interaction $B_{12}^{/k}$ would be 5.9511 x 10⁴⁴ °K with the linear combining law as opposed to 4.9637 x 10²⁶ °K with the geometrical mean combining law. In terms of the parameters of the modified Buckingham (6-exp) pair potential the interaction in this case would be described by

$$\mathbf{r}_{\mathrm{m}} = 10.5 \overset{\mathrm{o}}{\mathrm{A}}$$
$$\epsilon' k = 16.4 \overset{\mathrm{o}}{\mathrm{K}}$$
$$\gamma = 103$$

This set of parameters predicts an interaction energy for neopentane-iodide which is unrealistically small. Similarly the neopentane-ammonium interaction energy would also be unrealistically small.

Another possible combining law for the estimation of the pre-exponential factor in the mixed interaction potential function would be the harmonic mean

combining law.

$$B_{12} = \frac{2B_{11}B_{22}}{B_{11}B_{22}}$$

When $B_{11} \gg B_{22}$

$$B_{12} \approx 2B_{22}$$

This gives the greatest weight to the parameter of the iodide or ammonium ion and would result in interaction energies which are unrealistically large.

Although it is obvious from these estimates that these alternatives do not give reasonable agreement with the experimental data, some combination of alternative methods for the dispersion potential and for the repulsion potential may give more acceptable agreement. No attempt is made in this work to dismiss all alternative approaches.

Examination of the calculated potential curves in Figs. 7, 8, 9, and 10 gives a great deal of insight into the characteristics of the adsorption and the differences between the surfaces considered. The most favorable position for adsorption in all cases is over the center of a lattice cell. This would be expected since the adsorbed molecule at this site is able to approach the surface closely and interact with the rest of the crystal strongly before the repulsive forces of the nearest neighbors become dominant.

One of the most noticeable differences between the face centered cubic structure and the simple cubic structure is the convergence of the curves at larger distances. The convergence is an indication of the point at which the adsorbed molecule no longer "sees" the individual ionic moieties. If we consider the (100) plane of the face centered cubic structure and the (110) plane of the simple cubic structure, which are similar surface arrays differing only in the ionic spacing, we see that this point of convergence comes at a smaller distance for the surface having the smaller ionic spacing. This may be attributed to the repulsive potential of the nearest neighbors, those ions in the surface layer closest to the point directly beneath the adsorbed molecule. In Fig. 19 the ions along the lattice edge are shown for both surfaces with the ionic spacing drawn to scale. If we have spheres of constant potential (the dotted curves) for each ion, the contours of constant repulsive potential (the solid curves) flatten out much more rapidly with distance above the (110) plane of simple cubic than for the (100) plane of face centered cubic. A similar phenomenon may be seen if the cross sections are taken through the center of the surface lattice square.

Recommendations for Further Research

The experimental error in the experimental heats of adsorption would be greatly reduced by at least one more isotherm on either side of the α - β phase transition point. These additional isotherms would be of greater interest if the supercooling and superheating of the phases were utilized to yield data on both phases at the same temperature.

Electron micrographs of the β phase could determine the actual surface plane of the crystals since those with the (100) plane of the simple cubic structure on the surface should be cubic in shape and those with the (110) plane of the simple cubic structure on all surfaces should be rhombic dodecahedra since this is the

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CROSS SECTION OF (100) PLANE OF THE FACE CENTERED CUBIC STRUCTURE ALONG THE LATTICE SQUARE EDGE.



CROSS SECTION OF (110) PLANE OF THE SIMPLE CUBIC STRUCTURE ALONG THE LATTICE SQUARE EDGE.

Figure 19. Contours of Constant Repulsive Potential.

only symmetrical solid polyhedron which can accommodate the (110) plane geometrically. This is, of course, assuming that the surface of the crystals is homogeneous. Low energy electron diffraction studies would also yield valuable information about the surface structure.

APPENDIX A

EXPERIMENTAL DATA AND ISOSTERIC HEATS

Table 18. Data for the Physical Adsorption of Neopentane on Ammonium Iodide at 260.35⁰K

o m	Po	=	313.6	torr,	N _m	=	11.	68	moles/g	ŗm
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Р	P/P	N ads
torr	Ŭ	moles/gm.
.3958	. 001263	.1882
1.335	.004253	. 4654
1.631	. 005197	. 6211
2.808	.008962	. 8673
3.484	.01111	1.201
4.398	.01402	1.320
5.588	. 01783	1.620
6.928	. 02209	1.835
8.109	. 02585	2.059
9.327	.02974	2.281
10.01	. 02194	2.387
10.94	. 03489	2.550
11.78	. 03755	2.680
12.99	.04142	2.850
14.43	.04598	3.061
16.30	.05194	3.289
18,27	.05828	3.542
20.03	.06386	3.729
22.44	.07152	4.013
25.22	.08045	4.335
27.87	. 08887	4.597
31.13	. 09935	4.955
34.56	.1102	5.291
37.40	.1193	5.686
41.05	. 1309	5.963
43.59	. 1389	6.247
47.34	.1509	6.648
51.15	. 1630	7.058
54.12	. 1726	7.535
59.85	. 1908	7.937
65.17	. 2078	8.437
72.60	. 2317	9.069

Table	18	(Continued)
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Р	P/P	$^{ m N}_{ m ads}$
torr	Ŭ	moles/gm.
76.43	.2436	9.367
81.27	.2590	9.729
86.85	. 2769	10.16
93.99	. 2998	10.69
98.75	.3147	11.02
104.3	. 3327	11.37
110.7	.3528	11.76
116.9	.3725	12.18
122.3	. 3900	12.45
127.2	.4052	12.75
135.3	. 4311	13.18
143.3	.4565	13.58
151.4	. 4833	14.05
155.0	. 4945	14.25
166.1	. 5299	14.66
179.7	. 5735	15.35
187.1	.5919	15.68
202.8	.6472	17.04
217.3	. 6933	18.39
230.7	.7362	19.81
238.4	.7608	20.84
249.4	. 7959	22.70

Table 19. Data for the Physical Adsorption of Neopentane on Ammonium Iodide at 257.73⁰K

$$P_0 = 278.9 \text{ torr}, N_m = 11.65 \text{ moles/gm}.$$

Р	P/P _o	$^{ m N}_{ m ads}$
torr		moles/gm.
. 1249	.0004464	. 0727
.7950	.002843	. 3655
1,442	.005157	.6831
2.135	.007663	.8150
2.992	.01073	1.141
3.582	.01284	1.276
4.053	.01453	1.422
5.502	.01977	1.780
6.268	.02247	1.949
7.281	. 02613	2.139
8.134	.02910	2.342
9.750	. 03503	2.628
10.13	. 03632	2.795
11.90	.04267	3.063
12,61	.04517	3.235
14.39	.05158	3.364
15.55	.05574	3.685
17.78	.06384	3,920
19.14	.06864	4.220
21.02	.07539	4.500
21.09	.07573	4.543
23.23	.08325	4.768
24.81	.08904	4.947
25.26	. 09 05 7	5.047
27.44	.09862	5.348
30.55	.1095	5.562
31.37	. 1125	5.835
33.90	. 1215	6.126
36.18	. 1296	6.417
38.71	. 1388	6.731
41.38	. 1482	7.030
44,23	. 1586	7.384
46.44	. 1665	7.687

Р	P/P o	$^{ m N}_{ m ads}$
torr		moles/gm.
50.75	. 1819	8,029
53,41	. 1914	8.299
58.77	.2106	8.762
64.25	.2303	9.240
70.92	. 2543	9.769
74.91	.2686	10.001
81.16	.2911	10.51
89.94	.3223	11.07
99.14	.3554	11.63
108.2	. 3878	12.15
114.0	.4088	12.46
122.6	.4394	12.94
131.4	.4716	13.49
136.3	.4887	13.58
145.9	. 5232	14.07
157.0	.5631	14.59
184.7	. 6625	16.03
193.7	.6942	16.72
206.2	.7390	17.63
221,3	.7911	19.76
236.8	. 8498	23.62

Table 19 (Continued)

Table 20. Data for the Physical Adsorption of Neopentane on Ammonium Iodide at 255.16⁰K

$$P_{o} = 246.3 \text{ torr, } N_{m} = 9.98 \text{ moles/gm.}$$

Р	P/P _o	N _{ads}
torr		moles/gm.
		2074
.8469	. 003442	.3374
1.549	. 006293	. 6392
1.947	.007901	.7301
2.512	.01021	.9595
3.276	.01331	1.233
3.905	. 01585	1.480
4.663	. 01895	1.791
5.444	. 02209	2.086
6.236	.02531	2.413
7.139	. 02899	2.758
8.062	.03271	3.110
8.864	. 03598	3.420
9.753	. 03959	3.711
10.76	. 04365	4.069
11.85	.04811	4.422
13.06	.05301	4.732
14.69	. 05964	5.110
16.80	.06821	5.570
19.17	.07781	6.001
21.87	.08881	6.363
24.38	. 09901	6.691
27.17	.1104	7.050
30.12	. 1223	7.362
33.59	. 1363	7.720
37.33	. 1517	8.086
42.66	. 1734	8,560
47.27	. 1921	8.940
52.92	.2149	9.374
58.22	. 2363	9.770
64.99	.2638	10.28
69.48	. 2820	10.58
75.41	. 3061	10.94
82.51	.3348	11.46

Table 20 (Continued)

Р	P/P _o	$^{ m N}_{ m ads}$
torr		moles/gm.
88 13	3576	11.91
93.71	. 3807	12.38
100.8	.4091	12.88
106.4	.4319	13.33
110.7	. 4492	13.68
117.5	.4771	14.28
122.5	.4976	14.72
129.5	.5256	15.46
137.6	.5587	16.31
144.3	.5861	16.75
148.2	.6018	17.46
156.4	.6348	18.39
167.6	.6811	19.79
176.7	.7177	21.05
182.5	.7416	22.12
188.0	.7638	23.22
192.4	.7809	24.19
194.8	.7901	24.79

Table 21. Data for the Physical Adsorption of Neopentane on Ammonium Iodide at 252.66⁰K

$$P_0 = 216.7 \text{ torr}, N_m = 9.93 \text{ moles/gm}.$$

Р	P/P _o	Nads
torr		moles/gm.
.5121	.002364	. 2257
1.186	.005474	.4723
1.689	. 007793	.7261
2.459	. 01134	1.093
3.714	. 01713	1.687
4.814	. 02219	2.125
5.362	. 02473	2.468
6.324	. 02918	2.931
7.241	.03341	3.283
8.066	. 03722	3.640
8.926	. 04121	3.950
9.812	.04532	4.217
11.20	. 05172	4,583
12.55	.05784	4.945
13.97	.06442	5.320
15.86	. 07314	5.710
18.17	. 08385	6.139
20.65	.09535	6.530
22.97	.1060	6.841
26.43	. 1219	7.260
28.25	. 1304	7.464
3.073	. 1418	7.723
36.04	. 1662	8.232
40.92	. 1888	8.669
44.78	. 2067	9.002
49.59	.2289	9.377
53.88	.2485	9.725
58.02	.2676	10.03
64.86	.2993	10.52
71.08	. 3278	11.20
76.28	.3517	11.57
82.05	. 3786	11.75
88.83	.4101	12.32

Table 21 (Continued)

P	P/P ₀	N ads moles/gra
95.11	.4391	12.75
102.8	.4747	13.48
108.2	. 4995	12.95
116.4	.5376	14.84
120.5	.5557	15.13
125.0	.5772	15.84
129.4	.5971	16.38
135.6	. 6256	17.19
140.4	.6478	17.87
144.2	.6651	18.42
148.4	.6848	19.12
153.1	.7068	19.89
158.8	.7327	20.88
164.6	.7595	22.05
169.2	.7813	23.14
173.7	.8014	24.23

N ads	$^{ m q}$ st	Nads	^q st
µmoles/gm	Kcal./mole	μ moles/gm.	Kcal./mole
. 5	5.397	13.0	3.569
1.0	6.506	13.5	3,093
1.5	7.876	14.0	2.689
2.0	9.046	14.5	2.334
2.5	10.363	15.0	2.099
3.0	11.231	15.5	1.877
3.5	11.638	16.0	1.567
4.0	11.893	16.5	1.429
4.5	11.996	17.0	1.412
5.0	12.120	17.5	1.459
5.5	12.024	18.0	1.639
6.0	11.705	18.5	1.800
6.5	11.239	19.0	1.949
7.0	10.692	19.5	2.217
7.5	10.101	20.0	2.471
8.0	9.370	20.5	2.718
8.5	8.617	21.0	2.883
9.0	7.947	21.5	3.045
9.5	7.233	22.0	3.203
10.0	6.765	22.5	3.291
10.5	5.999	23.0	3.377
11.0	5.367	23.5	3.521
11.5	4.862	24.0	3.666
12.0	4.373	24.5	3.682
12.5	3.921	25.0	3.761

Table 22. Isosteric Heats of Adsorption for the Neopentane-Ammonium Iodide System at 259.04⁰K.

N ads μ moles/gm	^q st Kcal./mole	μ moles/gm.	^q st Kcal./mole
.0	6 952	13.5	2.300 2.415
1.0	7 350	14.0	2.410
2.0	7.550	14.5	2.000
2.0	7 817	15.0	2.105
2,9	7 625	15.5	2.304
3.5	7 167	16.0	3 322
4 0	6 813	16.5	3 444
4.5	6 495	17.0	3 718
5.0	6 179	17.5	3 863
5.5	5 865	18.0	4 021
6.0	5.507	18.5	4 281
6.5	5 231	10.0	4 565
7.0	4 902	19.0	4 662
7.5	4 594	20.0	4.002
8.0	4 296	20.5	4 974
8.5	4 013	20.0 21.0	5.052
9.0	3.678	21.5	5,160
9.5	3 370	22.0	5,169
10.0	3, 045	22.5	5,303
10.5	2.741	23.0	5,326
11.0	2.458	23.5	5.314
11.5	2.251	24.0	5,263
12.0	2.184	24.5	5.214
12.5	2.247	25.0	5.171

Table 23. Isosteric Heats of Adsorption for the Neopentane-Ammonium Iodide System at 253.91[°]K.

APPENDIX B

INVERSE POWER SUMMATIONS OF MOLECULE-ION DISTANCES FOR A MOLECULE ABOVE AN IONIC LATTICE

APPENDIX B

INVERSE POWER SUMMATIONS OF MOLECULE-ION DISTANCES FOR A MOLECULE ABOVE AN IONIC LATTICE

The inverse power distance summations to the positive ions, $S_{+}(\rho)$, and to the negative ions, $S_{-}(\rho)$, in equation (25) of Chapter III are expressed in terms of three summations of the inverse power of the distances to all of the lattice points. This method was presented by Orr.⁴ The three summations are:

- $\sum_{n=1}^{\infty} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{i=1}^{n} \sum_{i=1}^{n} \sum_{i=1}^{n} \sum_{i=1}^{n} \sum_{i=1}^{n} \sum_{i=1}^{n} \sum_{i$
- Σ, where the point is situated above the mid-point of a lattice edge;
 Σ, where the point is situated above a lattice point.

In these summations the Cartesian coordinate system is used and

$$1 = \frac{z}{a}$$
$$m = \frac{y}{a}$$
$$n = \frac{x}{a}$$

where 1, m, n are unit distances, a is the ion-ion distance in the crystal, and

 ρ is in the z direction.

For \sum_{1} the solid is divided into four equivalent sections by the planes m = 0and n = o. In each of these sections there are two types of lattice points: those on the symmetry plane m = 2, and those not on this plane, which are duplicated in each section. The distance, R_1 , to each lattice point on the symmetry plane is given by

$$\mathbf{R}_{1} = \left[\left(\rho + 1 \right)^{2} + \frac{n^{2}}{2} \right]^{\frac{1}{2}}$$

then,

$$\sum_{n=1}^{\infty} \frac{1}{R_{1}^{n}} = \sum_{l=0,1,2...}^{\infty} \sum_{n=1,3,5...}^{\infty} \left[(\rho+1)^{2} + \frac{n^{2}}{2} \right]^{-\frac{1}{2}}$$
(50)

The distance, R_2 , to each lattice point not on the symmetry plane is given by

$$R_{2} = \left[(o+1)^{2} + m(m+n) + \frac{n^{2}}{2} \right]^{\frac{1}{2}}$$

then,
$$\sum_{r} \frac{1}{R_{2}^{r}} = \sum_{l=0, 1, 2...}^{\infty} \sum_{m=1, 2, 3...}^{\infty} \sum_{n=1, 3, 5...}^{\infty} \left[(\rho+1)^{2} + m(m+n) + \frac{n^{2}}{2} \right]^{\frac{-r}{2}}$$
(51)

For Σ the solid is divided into two equivalent sections by the plane n = o. 2 The distance, R_3 , to each lattice point in one of these sections is given by

$$\mathbf{R}_{3} = \left[\left(\boldsymbol{\rho} + 1 \right)^{2} + \mathbf{m}^{2} + \left(\frac{\mathbf{n}}{2} \right)^{2} \right]^{\frac{1}{2}}$$

then,

$$\sum_{\substack{n=0,1,2 \\ n}}^{\infty} \frac{\alpha}{1} \sum_{\substack{n=0,1,2 \\ n}}^{\infty} \frac{\alpha}{1} \sum_{\substack{n=0,1,2 \\ n}}^{\infty} \frac{\alpha}{1} \sum_{\substack{n=1,3,5 \\ n=1,3,5}}^{\infty} \left[\left(\rho+1\right)^2 + m^2 + \left(\frac{n}{2}\right)^2 \right]^{-\frac{r}{2}}$$

$$(53)$$

 Σ is then given by 2

$$\sum_{2} = 2 \sum_{l=0, 1, 2} \sum_{m=0, \pm 1, \pm 2} \sum_{n=1, 3, 5} \left[(\rho + 1)^{2} + m^{2} + \left(\frac{n}{2}\right)^{2} \right]^{-\frac{r}{2}}$$
(54)

For Σ there are two types of lattice points: those on the axis of lattice $\frac{3}{3}$ points directly below the point, and those not on this axis. The points not on the axis are divided into four equivalent sections by the planes m = 0 and n = 0. The distance, R_4 , to each lattice point on the axis is given by

$$R_{4} = \rho + 1$$

then,

$$\sum_{n=0,1,2}^{\infty} \frac{1}{\mathbf{R}_{3}^{\mathbf{r}}} = \sum_{l=0,1,2}^{\infty} (\rho+1)^{-\mathbf{r}}$$
(55)

The distance, R₅, to each of the lattice points in one of the sections not on the axis is given by

$$R_5 = [(\rho+1)^2 + m^2 + n^2]^{\frac{1}{2}}$$

Then for all lattice points in one section

$$\sum_{n=0}^{\infty} \frac{1}{R_{5}^{\mathbf{r}}} = \sum_{l=0,1,2}^{\infty} \sum_{m=0,1,2}^{\infty} \sum_{n=1,2,3}^{\infty} \left[(\rho+l)^{2} + m^{2} + n^{2} \right]^{-\frac{\mathbf{r}}{2}}$$
(56)

and for all four sections

$$\sum_{R_{5}}^{\infty} \frac{1}{r} = 4 \sum_{l=0,1,2}^{\infty} \sum_{m=0,1,2}^{\infty} \sum_{n=1,2,3}^{\infty} \left[(\rho + l)^{2} + m^{2} + n^{2} \right]^{-\frac{r}{2}}$$
(57)

For all lattice points in the solid, Σ is given by the sum of equations (55) and (57) $_3$

$$\sum_{n=0,1,2}^{\infty} \sum_{n=0,1,2}^{\infty} (\rho+1)^{-r} + 4 \sum_{n=0,1,2}^{\infty} \sum_{m=0,1,2}^{\infty} \sum_{n=1,2,3}^{\infty} [(\rho+1)^{2} + m^{2} + n^{2}]^{-\frac{r}{2}}$$
(58)

These equations are derived for a crystal with a cubic lattice structure and, therefore, apply to the (100) face of the simple cubic and the face centered cubic structures. For the (110) face of the simple cubic structure a square surface lattice has been defined (fig. 20) which extends into the crystal to form rectangular volume elements. Now the expressions for Σ , Σ , and Σ must be modified since $1 \ 2 \ 3$ these volume elements



Figure 20. Lattice Structure as Defined for the Simple Cubic Lattice with the (110) Plane on the Surface.

$$\sqrt{2} 1 = \frac{z}{a}$$

$$\sqrt{\frac{1}{2}} m = \frac{y}{a}$$

$$\sqrt{\frac{1}{2}} n = \frac{x}{a}$$
(59)

where a is still the lattice parameter for the simple cubic crystal. Substituting equation (59) into equations (52), (54), and (57) gives for the (110) face of the simple cubic crystal structure

$$\sum_{n=0}^{\infty} = 4 \left\{ \sum_{n=0,1,2}^{\infty} \sum_{n=1,3,5}^{\infty} \left[(\rho + \sqrt{2} 1)^2 + \frac{n^2}{4} \right]^{-\frac{r}{2}} + \sum_{n=1,3,5}^{\infty} \sum_{n=1,3,5}^{\infty} \left[(\rho + \sqrt{2} 1)^2 + \frac{m}{2} (m + n) + \frac{n^2}{4} \right]^{-\frac{r}{2}} \right\}$$
(60)
$$\sum_{n=0,1,2}^{\infty} = 2 \sum_{n=1,2,3}^{\infty} \sum_{n=1,3,5}^{\infty} \sum_{n=1,3,5}^{\infty} \left[(\rho + \sqrt{2} 1)^2 + \frac{m^2}{2} + \frac{1}{2} \left(\frac{n}{2} \right)^2 \right]^{-\frac{r}{2}}$$
(61)

$$\sum_{3}^{\infty} \sum_{l=0,1,2}^{(\rho+\sqrt{2}l)^{-r}+4} \sum_{l=0,1,2}^{(\rho+\sqrt{2}l)^{-r}+4} \sum_{m=0,1,2}^{(\rho+\sqrt{2}l)^{2}+\frac{m^{2}}{2}+\frac{n^{2}}{2}} \int_{-\frac{1}{2}}^{-\frac{1}{2}} (62)$$

Both sets of Σ , Σ , and Σ have been evaluated for values of ρ by summing over 1 2 3 20,000 lattice points on a Burroughs 5500 computer. These are given in Tables 24 and 25.

Now $S_{+}(\rho)$ and $S_{-}(\rho)$ may be expressed as functions of \sum_{1}, \sum_{2} , and \sum_{2} for 1, 2

r

each of the three crystal faces. There are four positions of interest for the adsorbed molecule: over the center of a lattice square, over the mid-point of a lattice edge, over a positive ion, and over a negative ion.

For the (100) face of the simple cubic lattice these expressions are given by Orr.⁴ This face has two additional possibilities since the crystal surface may consist of either all positive ions or all negative ions. Using equations (52), (54), and (57) for Σ , Σ , and Σ , $S_{+}(\rho)$ and $S_{-}(\rho)$ are given by $1 \quad 2 \qquad 3$

1. Above the center of a lattice square with a surface of positive ions

$$S_{+}(\rho) = \sum_{n=1}^{\infty} \rho$$
(63)

$$S_{(\rho)} = \sum_{\beta \in \Theta} (\rho + \frac{1}{2})$$
(64)

2. Above the center of a lattice square with a surface of negative ions

$$S_{+}(\rho) = \sum_{3} (\rho + \frac{1}{2})$$
 (65)

$$S_{(\rho)} = \sum_{i} \rho$$
(66)

3. Above the mid-point of a lattice edge with surface of positive ions

$$S_{+}(\rho) = \sum_{2} \rho$$
(67)

$$S_{\underline{\rho}} (\rho) = \sum_{\underline{\rho}} (\rho + \frac{1}{\underline{z}})$$
(68)

The notation $(\rho + \frac{1}{2})$ indicates that $(\rho + \frac{1}{2})$ is substituted for ρ in the expression.

4. Above the mid-point of a lattice edge with surface of negative ions

$$S_{+}(\rho) = \sum_{2} (\rho + \frac{1}{2})$$
 (69)

$$\mathbf{S}_{(\rho)} = \sum_{2} \rho \tag{70}$$

5. Above an ion in the surface face with surface of positive ions

$$S_{+}(\rho) = \sum_{3} \rho \tag{71}$$

$$S_{-}(\rho) = \sum_{1} (\rho + \frac{1}{2})$$
(72)

6. Above an ion in the surface face with surface negative ions

$$S_{+}(\rho) = \sum (\rho + \frac{1}{2})$$
(73)

$$S_{(\rho)} = \sum_{\beta} \rho$$
(74)

For the (100) face of the face-centered cubic lattice these expressions have also been given by Orr.⁴ Using equations (52), 54), and (57), for \sum_{1} , \sum_{2} , and \sum_{1} $S_{+}(\rho)$ and $S_{-}(\rho)$ are given by

1. Above the center of a lattice square

$$S_{+}(\rho) = \frac{1}{2} \sum_{i} \rho$$
(75)

$$S_{(\rho)} = \frac{1}{2} \sum_{\rho} \rho$$
(76)

2. Above the mid-point of a lattice edge

$$S_{+}(\rho) = \frac{1}{2} \sum_{n} \rho$$
(77)

$$\mathbf{S}_{(\boldsymbol{\rho})} = \frac{1}{2} \sum_{\boldsymbol{\rho}} \boldsymbol{\rho}$$
(78)

3. Above a positive ion in the lattice plane

$$S_{+}(\rho) = \left(\frac{1}{2}\right)^{r} \left[\sum_{1} \frac{\rho}{2} + 2\sum_{2} \frac{\rho+1}{2} + \sum_{3} \frac{\rho}{2}\right]$$
(79)

$$S_{-}(\rho) = \left(\frac{1}{2}\right)^{r} \left[\sum_{1} \frac{\rho+1}{2} + 2\sum_{2} \frac{\rho}{2} + \sum_{3} \frac{\rho+1}{2}\right]$$
(80)

4. Above a negative ion in the lattice plane

$$S_{+}(\rho) = \left(\frac{1}{2}\right)^{T} \left[\sum_{1} \frac{\rho+1}{2} + 2\sum_{2} \frac{\rho}{2} + \sum_{3} \frac{\rho+1}{2} \right]$$
(81)

$$\mathbf{S}_{-}(\boldsymbol{\rho}) = \left(\frac{1}{2}\right)^{\mathbf{r}} \left[\sum_{1} \frac{\boldsymbol{\rho}}{2} + 2\sum_{2} \frac{\boldsymbol{\rho}+1}{2} + \sum_{3} \frac{\boldsymbol{\rho}}{2}\right]$$
(82)

The expressions for the (110) face of the simple cubic structure have not been given and must be derived. The lattice cells as defined (fig. 20) are of two types, those with a positive ion at the body-centered position and those with a negative ion at the body-centered position. The lattice may be thought of as two identical intertwined lattices, one composed of the ions at the lattice points (Lattice 1) and the other composed of the ions at the body-centered positions (Lattice 2). The two lattices are displaced from one another by one half unit in each direction. Equations (60), (61), and (62) are used for Σ , Σ , and Σ for this case. 1 2 3

1. Above the center of a lattice square with a positive ion in the body-centered position

$$S_{+}(\rho) \text{ for Lattice 1}$$

$$S_{+}(\rho)^{(1)} = \frac{1}{2} \sum \rho$$

$$1$$

$$S_{+}(\rho) \text{ for Lattice 2.}$$
(83)

For Lattice 2 the point is above an ion. There will be two sets of ions if we now consider a lattice cell for which the sides are double those of the previously defined cell (fig. 20). (This approach is similar to that used by Orr^4 for the point above an ion in the (100) face of the face-centered cubic lattice). The first set of ions (set A) are those for which the point is over a lattice point of the double cell. There are two sets of these ions, one displaced one unit in the 1 direction from the other. The summation over these ions is given by

$$\mathbf{S}_{+}^{2\mathbf{A}}(\rho) = \left(\frac{1}{2}\right)^{\mathbf{r}} \left[\sum_{3} \left(\frac{\rho + \frac{\sqrt{2}}{2}}{2} \right) + \sum_{3} \left(\frac{\rho + \frac{\sqrt{2}}{2} + \sqrt{2}}{2} \right) \right]$$
(84)

The second set of ions (set B) are those for which the point is over the center of the double lattice cell. There are again two sets of these ions, one displaced one unit in the 1 direction from the other. The summation of these ions is given by

$$S_{+}^{2B}(\rho) = \left(\frac{1}{2}\right)^{r} \left[\sum_{1} \left(\frac{\rho + \frac{\sqrt{2}}{2}}{2}\right) + \sum_{1} \left(\frac{\rho + \frac{\sqrt{2}}{2} + \sqrt{2}}{2}\right)\right]$$
(85)

The summation over all positive ions in Lattice 2 is given by the sum of equations (84) and (85)

$$S_{+}^{2}(\rho) = \left(\frac{1}{2}\right)^{r} \left[\sum_{1} \left(\frac{\rho}{2} + \frac{\sqrt{2}}{4}\right) + \sum_{1} \left(\frac{\rho}{2} + \frac{3\sqrt{2}}{4}\right) + \sum_{3} \left(\frac{\rho}{2} + \frac{\sqrt{2}}{4}\right) + \sum_{3} \left(\frac{\rho}{2} + \frac{3\sqrt{2}}{4}\right) \right]$$
(86)

Then the summation over all positive ions in the solid is given by the sum of equations (83) and (86)

$$S_{+}(\rho) = \frac{1}{2} \sum_{1} \rho + \left(\frac{1}{2}\right)^{r} \left[\sum_{1} \left(\frac{\rho}{2} + \frac{\sqrt{2}}{4}\right) + \sum_{1} \left(\frac{\rho}{2} + \frac{3\sqrt{2}}{4}\right) + \sum_{3} \left(\frac{\rho}{2} + \frac{\sqrt{2}}{4}\right) + \sum_{3} \left(\frac{\rho}{2} + \frac{3\sqrt{2}}{4}\right) \right]$$
(87)
$$S_{-}(\rho) \text{ for Lattice 1.}$$
$$S_{-}(\rho)^{1} = \frac{1}{2} \sum_{1} \rho$$
(88)

 S_{ρ} (ρ) for Lattice 2.

Again we consider the double lattice cells. There are again two sets of ions: those for which the point is over an edge of the lattice square in the plane m = 0, and those for which the point is over an edge of the lattice square in the plane n = 0. Since these two sets are equivalent all ions will be included if the sums for one set are multiplied by two. Each of the above sets of ions are composed of two sub sets each of which is displaced one unit in the 1 direction from the other. The summation over the negative ions in Lattice 2 is given by

$$S_{-}^{2}(\rho) = \left(\frac{1}{2}\right)^{r} \left[2\sum_{2} \left(\frac{\rho}{2} + \frac{\sqrt{2}}{4}\right) + 2\sum_{2} \left(\frac{\rho}{2} + \frac{3\sqrt{2}}{4}\right) \right]$$
(89)

The summation over all of the negative ions is given by the sum of equations (88) and (89).

$$S_{(\rho)} = \frac{1}{2} \sum_{n} \rho + \left(\frac{1}{2}\right)^{n} \left[2 \sum_{n} \left(\frac{\rho}{2} + \frac{\sqrt{2}}{4}\right) + 2 \sum_{n} \left(\frac{\rho}{2} + \frac{3\sqrt{2}}{4}\right) \right]$$
(90)

2. Above the center of a lattice square with a negative ion in the body-centered position. These expressions are the same as equations (87) and (90) but the positive and negative ions are reversed.

$$S_{+}(\rho) = \frac{1}{2}\Sigma\rho + \left(\frac{1}{2}\right)^{r} \left[2\sum_{2}\left(\frac{\rho}{2} + \frac{\sqrt{2}}{4}\right) + 2\sum_{2}\left(\frac{\rho}{2} + \frac{3\sqrt{2}}{4}\right)\right]$$
(91)

$$S_{-}(\rho) = \frac{1}{2}\sum_{1}\rho + \left(\frac{1}{2}\right)^{r} \left[\sum_{1}\left(\frac{\rho}{2} + \frac{\sqrt{2}}{4}\right) + \sum_{1}\left(\frac{\rho}{2} + \frac{3\sqrt{2}}{4}\right) + \sum_{3}\left(\frac{\rho}{2} + \frac{\sqrt{2}}{4}\right) + \sum_{3}\left(\frac{\rho}{2} + \frac{3\sqrt{2}}{4}\right)\right]$$
(92)

3. Over the mid-point of a lattice edge

Lattice 1

$$S_{+}^{1}(\rho) = \frac{1}{2}\sum_{2}\rho \qquad (93)$$

$$S_{-}^{1}(\rho) = \frac{1}{2}\sum_{2}\rho$$
(94)

Lattice 2

$$S_{+}^{2}(\rho) = \frac{\frac{1}{2}}{2} \sum_{n} \left(\rho + \frac{\sqrt{2}}{2}\right)$$
(95)

$$S_{\perp}^{2}(\rho) = \frac{1}{2} \sum_{2} \left(\rho + \frac{\sqrt{2}}{2}\right)$$
(96)

The summation of all ions is then given by

$$\mathbf{S}_{+}(\boldsymbol{\rho}) = \frac{1}{2} \begin{bmatrix} \sum \boldsymbol{\rho} + \sum \left(\boldsymbol{\rho} + \frac{\sqrt{2}}{2} \right) \end{bmatrix}$$
(97)

$$\mathbf{S}_{(\rho)} = \frac{1}{\Xi} \left[\sum_{2} \rho + \sum_{2} \left(\rho + \frac{\sqrt{2}}{2} \right) \right]$$
(98)

4. Above a positive ion

These summations are similar to equations (87) and (90) except than in this case Lattice 1 and Lattice 2 are interchanged.

$$\mathbf{S}_{+}(\boldsymbol{\rho}) = \frac{1}{2} \sum_{1} \left(\boldsymbol{\rho} + \frac{\sqrt{2}}{2} \right) + \left(\frac{1}{2} \right)^{\mathbf{r}} \left[\sum_{1} \frac{\boldsymbol{\rho}}{2} + \sum_{1} \left(\frac{\boldsymbol{\rho}}{2} + \frac{\sqrt{2}}{2} \right) + \sum_{3} \frac{\boldsymbol{\rho}}{2} + \sum_{3} \left(\frac{\boldsymbol{\rho}}{2} + \frac{\sqrt{2}}{2} \right) \right]$$
(99)

$$\mathbf{S}_{(\boldsymbol{\rho})} = \frac{1}{2} \sum_{1} \left(\boldsymbol{\rho} + \frac{\sqrt{2}}{2} \right) + \left(\frac{1}{2} \right)^{\mathbf{r}} \left[2 \sum_{2} \frac{\boldsymbol{\rho}}{2} + 2 \sum_{2} \left(\frac{\boldsymbol{\rho}}{2} + 2 \sum_{2} \left(\frac{\boldsymbol{\rho}}{2} + \frac{\sqrt{2}}{2} \right) \right]$$
(100)

5. Above a negative ion

These expressions are the same as equations (99) and (100) except the positive and negative ions are reversed

$$\mathbf{S}_{+}(\boldsymbol{\rho}) = \frac{1}{2} \sum_{1} \left(\boldsymbol{\rho} + \frac{\sqrt{2}}{2} \right) + \left(\frac{1}{2} \right)^{\mathbf{r}} \left[2 \sum_{2} \frac{\boldsymbol{\rho}}{2} + 2 \sum_{2} \left(\frac{\boldsymbol{\rho}}{2} + \frac{\sqrt{2}}{2} \right) \right]$$
(101)

$$\mathbf{S}_{(\rho)} = \frac{1}{2} \sum_{1} \left(\rho + \frac{\sqrt{2}}{2} \right) + \left(\frac{1}{2} \right)^{\mathbf{r}} \left[\sum_{1} \frac{\rho}{2} + \sum_{1} \left(\frac{\rho}{2} + \frac{\sqrt{2}}{2} \right) + \sum_{3} \frac{\rho}{2} + \sum_{3} \left(\frac{\rho}{2} + \frac{\sqrt{2}}{2} \right) \right]$$
(102)

ρ	Σ 1	Σ 2	Σ
			3
.30	20.6504	53.5406	1376.0600
.35	17.6588	41.1409	547.9388
.40	14.9028	31,2635	247.7265
.45	12.4490	23.6379	123.6649
.50	10.3218	17.8686	66.9078
.55	8.5153	13.5547	38.7261
.60	7.0050	10.3464	23.7492
.65	5.7568	7.9618	15.3158
.70	4.7338	6.1843	10.3222
.75	3.8997	4.8522	7.2311
.80	3.2218	3.8467	5.2400
.85	2.6715	3.0813	3.9110
.90	2.2247	2.4934	2.9948
1.00	1.5652	1.6806	1.8713
1.10	1.1243	1.1735	1.2498
1.20	. 8249	.8453	.8776
1.30	.6177	.6256	.6404
1.40	. 4717	.4740	.4815
1.50	. 3667	.3666	.3710
1.60	.2897	.2886	.2916
1.70	. 2323	.2308	.2332
1.80	. 1888	.1871	. 1892
1.90	. 1553	.1535	.1554
2.00	. 1292	.1274	.1292
2.10	.1085	.1067	.1084
2.20	.09189	.09020	.09186
2.30	.07849	. 07685	.07844
2.40	.06754	. 06595	.06749
2.50	.05851	. 05697	. 05845
2.60	.05100	.04951	.05094
2.70	.04471	.04327	.04465

Table 24.Calculated Values for the Summations of the Reciprocal
Sixth Power of Distance from Equations (52), (54),
and (57) for the (100) Plane
~	7	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	2
ρ	2/ 1	2	2
	L		
.7	12.0949	13,1079	14.7767
$.7 + \sqrt{2}/2$.8660	.8578	.8665
$.7/2 + \sqrt{2}/4$	11.8818	12.8529	14.4439
$.7/2 + 3\sqrt{2}/4$.8576	.8495	.8581
$.7/2 + \sqrt{2}/2$	2,6031	2.6103	2.6394
.7/2	81.5637	144.4007	564.8721
.8	7.4777	7.7854	8.2407
$.8 + \sqrt{2}/2$.6661	.6580	.6661
$.8/2 + \sqrt{2}/4$	9.3018	9,3018	10.6607
$.8/2 + 3\sqrt{2}/4$.7507	.7425	.7508
$.8/2 + \sqrt{2}/2$	2.1787	2.1788	2.1992
.8/2	61.9103	97.3727	262.0059
.9	4.8146	4.9049	5.0421
$.9 + \sqrt{2}/2$.5217	.5139	.5215
$.9/2 + \sqrt{2}/4$	7.3566	7.6514	8.0869
$.9/2 + 3\sqrt{2}/4$.6602	.6521	.6601
$.9/2 + \sqrt{2}/2$	1.8376	1,8337	1.8491
.9/2	46.7436	66.5063	135.5752
. 0	3,2222	3.2445	3.2924
$.0 + \sqrt{2}/2$.4151	.4076	.4149
$0/2 + \sqrt{2}/4$	5.8777	6.0386	6.2748
$0/2 + 3\sqrt{2}/4$.5832	.5752	.5831
$1.0/2 + \sqrt{2}/2$	1.5611	1,5550	1.5676
0/2	35.2754	46.2132	76.7616
.1	2,2335	2,2343	2.2556
$1.1 + \sqrt{2}/2$.3350	.3278	.3347
$1.1/2 + \sqrt{2}/4$	4.7434	4,8296	4.9614
$1.1/2 + 3\sqrt{2}/4$.5173	.5096	.5172
$1/2 + \sqrt{2}/2$	1.3352	1.3279	1.3388
1.1/2	26.7068	32.7416	46.8328

Table 25. Calculated Values for the Summations of the Reciprocal Sixth Power of Distance from Equations (60), (61), and (62) for the (110) Plane

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Table 25 (Continued)

ρ	Σ	Σ	Σ
	<u>I</u>	2	<u>3</u>
1.2	1,5970	1,5912	1.6041
$1.2 + \sqrt{2}/2$.2737	.2669	.2735
$1.2/2 + \sqrt{2}/4$	3.8651	3.9095	3.9858
$1.2/2 + 3\sqrt{2}/4$.5607	.4531	.4605
$1.2/2 + \sqrt{2}/2$	1.1491	1.1428	1.1511
1.2/2	20.3402	23.6673	30.3978
1.3	1.1735	1.1657	1.1756
$1.3 + \sqrt{2}/2$.2262	.2197	.2259
$1.3/2 + \sqrt{2}/4$	3.1786	3.1997	3.2460
$1.3/2 + 3\sqrt{2}/4$.4119	.4044	.4116
$1.3/2 + \sqrt{2}/2$.9948	.9867	.9958
1.3/2	15.6135	17.4487	20.7570
1.4	.8829	.8747	.8835
$1.4 + \sqrt{2}/2$.1888	.1826	.1886
1.5	.6782	.6701	.6782
$1.5 + \sqrt{2}/2$.1591	.1531	.1588
$1.5/2 + \sqrt{2}/4$	2,2059	2.2064	2.2272
$1.5/2 + \sqrt{2}/2$.7577	.7495	.7579
1.5/2	9.4619	10.0209	10.8827
1.6	.5305	.5227	.5304
$1.6 + \sqrt{2}/2$.1351	. 1295	.1349
1.7	.4217	.4142	.4215
$1.7 + \sqrt{2}/2$.1157	.1103	.1154
$1.7/2 + \sqrt{2}/4$	1.5789	1.5730	1.5857
$1.7/2 + 3\sqrt{2}/4$.2718	.2650	.2716
$1.7/2 + \sqrt{2}/2$.5883	.5803	.5881
1.7/2	5.9702	6.1383	6.3848
1.8	.3400	.3328	.3397
$1.8 + \sqrt{2}/2$. 0997	. 0946	. 0994

APPENDIX C

12

EXPONENTIAL SUMMATIONS OF MOLECULE-ION DISTANCES

FOR MOLECULE ABOVE AN IONIC LATTICE

APPENDIX C

EXPONENTIAL SUMMATIONS OF MOLECULE-ION DISTANCES FOR MOLECULE ABOVE AN IONIC LATTICE

The exponential distance summations to the positive ions, $S'_{+}(\rho, \beta, a)$, and to the negative ions, $S'_{-}(\rho, \beta, a)$, in equation (32) of Chapter III are expressed in terms of three summations of the exponential of the distances to all of the lattice points analogous to those summations derived in Appendix B for the inverse power of the distance and the form of these summations are quite similar. $\Sigma'(\rho, \beta, a)$ is analogous to Σ ; $\Sigma'(\rho, \beta, a)$ is analogous to Σ ; and $\Sigma'(\rho, \beta, a)$ is analogous to Σ . $1 \ 2 \ 3 \ 3$ l, m, and n are as defined in Appendix B; β is the exponential constant for the potential function, and a is the ion-ion distance in the crystal. The derivations are similar to those in Appendix B and, therefore, will not be repeated here. The summations are given by

$$\sum_{i=0,1,2}^{\prime} \begin{pmatrix} \infty & \infty \\ \beta,a \end{pmatrix} = 4 \sum_{i=0,1,2}^{\prime} \sum_{n=1,3,5}^{\prime} \left\{ \exp\left[-\left\{\left(\rho+1\right)^{2}+\frac{n^{2}}{2}\right\}^{\frac{1}{2}}\beta a\right] \right\}$$
(103)

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$$\sum_{n=0}^{\prime} \sum_{n=0}^{\infty} \left\{ \exp\left[-(\rho+1)\beta a\right] \right\}$$

$$= 0,1,2 \left\{ \exp\left[-(\rho+1)\beta a\right] \right\}$$

$$= 0,1,2 \quad m=0,1,2 \quad m=1,2,3 \quad \left\{ \exp\left[-\left\{(\rho+1)^{2}+m^{2}+n^{2}\right\}^{\frac{1}{2}}\beta a\right] \right\}$$

$$= 0,1,2 \quad m=0,1,2 \quad m=1,2,3 \quad \left\{ \exp\left[-\left\{(\rho+1)^{2}+m^{2}+n^{2}\right\}^{\frac{1}{2}}\beta a\right] \right\}$$

$$= 0,1,2 \quad m=0,1,2 \quad m=1,2,3 \quad \left\{ \exp\left[-\left\{(\rho+1)^{2}+m^{2}+n^{2}\right\}^{\frac{1}{2}}\beta a\right] \right\}$$

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Values of $\Sigma'(\rho, \beta, a)$, $\Sigma'(\rho, \beta, a)$, and $\Sigma'(\rho, \beta, a)$ have been evaluated for various 1 2 3 values of ρ with β having the appropriate value for the neopentane-ammonium iodide interaction given in Table 5, and with a having the appropriate value for the crystal structure. The calculations were made by summing over 54 lattice points. The results are given in Tables 26, 27, and 28.

Now $S'_{+}(\rho, \beta, a)$ and $S'_{-}(\rho, \beta, a)$ may be expressed as functions of $\Sigma'(\rho, \beta, a)$, and $\Sigma'_{-}(\rho, \beta, a)$, $\Sigma'_{-}(\rho, \beta, a)$ for each of the three crystal faces, and for the four 2 3 positions of interest above the crystal face.

The (100) face of the simple cubic lattice:

1. Above the center of a lattice square with a surface of positive ions

$$S'_{+}(\rho,\beta,a) = \sum_{1} (\rho,\beta,a)$$
(106)

$$S'_{(\rho,\beta,a)} = \sum_{\beta \in \mathcal{I}} (\rho + \frac{1}{2}, \beta, a)$$
(107)

2. Above the center of a lattice square with a surface of negative ions

 $S'_{+}(\rho,\beta,a) = \sum_{3} (\rho + \frac{1}{2},\beta,a)$ (108)

$$S'(\rho,\beta,a) = \sum_{1} (\rho,\beta,a)$$
(109)

3. Above the midpoint of a lattice edge with a surface of positive ions

$$S'_{+}(\rho,\beta,a) = \sum_{2} (\rho,\beta,a)$$
(110)

$$S'_{2}(\rho,\beta,a) = \sum_{\alpha} (\rho + \frac{1}{2}, \beta, a)$$
(111)

4. Above the midpoint of a lattice edge with a surface of negative ions

$$S'_{+}(\rho, \beta, a) = \sum_{2} (\rho + \frac{1}{2}, \beta, a)$$
(112)

$$S'_{-}(\rho,\beta,a) = \sum_{2} (\rho,\beta,a)$$
(113)

5. Above an ion in the surface plane with a surface of positive ions

$$S'_{+}(\rho, \beta, a) = \sum_{3} (\rho, \beta, a)$$
(114)

$$S'_{-}(\rho, \beta, a) = \sum_{n=1}^{\infty} (\rho + \frac{1}{2}, \beta, a)$$
(115)

6. Above an ion in the surface plane with a surface of negative ions

$$S'_{+}(\rho, \beta, a) = \sum_{1} (\rho + \frac{1}{2}, \beta, a)$$
(116)

$$S'_{-}(\rho, \beta, a) = \sum_{3} (\rho, \beta, a)$$
(117)

The (100) face of the face centered cubic lattice:

1. Above the center of lattice square

$$S'_{+}(\rho,\beta,a) = \frac{1}{2} \sum_{i} (\rho,\beta,a)$$
(118)

$$S'_{-}(\rho,\beta,a) = \frac{1}{2} \sum_{n} (\rho,\beta,a)$$
(119)

2. Above the midpoint of lattice edge

$$S'_{+}(\rho,\beta,a) = \frac{1}{2} \sum_{2} (\rho,\beta,a)$$
(120)

$$S'(\rho,\beta,a) = \frac{1}{2} \Sigma(\rho,\beta,a)$$
(121)

3. Above a positive ion in the surface plane

$$\mathbf{S}_{+}^{\prime}(\boldsymbol{\rho}, \boldsymbol{\beta}, \mathbf{a}) = \sum_{1}^{\prime} \left(\frac{\boldsymbol{\rho}}{2}, \boldsymbol{\beta}, 2\mathbf{a} \right) + 2 \sum_{2}^{\prime} \left(\frac{\boldsymbol{\rho}+1}{2}, \boldsymbol{\beta}, 2\mathbf{a} \right) + \sum_{3}^{\prime} \left(\frac{\boldsymbol{\rho}}{2}, \boldsymbol{\beta}, 2\mathbf{a} \right)$$
(122)

$$\mathbf{S}'(\rho, \beta, 2\mathbf{a}) = \sum_{1}' \left(\frac{\rho+1}{2}, \beta, 2\mathbf{a} \right) + 2\sum_{2}' \left(\frac{\rho}{2}, \beta, 2\mathbf{a} \right) + \sum_{3}' \left(\frac{\rho+1}{2}, \beta, 2\mathbf{a} \right)$$
(123)

4. Above a negative ion in the lattice plane

$$S'_{+}(\boldsymbol{\rho},\boldsymbol{\beta},\mathbf{a}) = \sum_{1} \left(\frac{\boldsymbol{\rho}+1}{2}, \boldsymbol{\beta},\mathbf{a} \right) + 2\sum_{2} \left(\frac{\boldsymbol{\rho}}{2}, \boldsymbol{\beta}, 2\mathbf{a} \right) + \sum_{3} \left(\frac{\boldsymbol{\rho}+1}{2}, \boldsymbol{\beta}, 2\mathbf{a} \right)$$
(124)

$$\mathbf{S}'(\mathbf{o},\boldsymbol{\beta},\mathbf{a}) = \sum_{1}' \left(\frac{\boldsymbol{\rho}}{2},\boldsymbol{\beta},2\mathbf{a}\right) + 2\sum_{2}' \left(\frac{\boldsymbol{\rho}+1}{2},\boldsymbol{\beta},2\mathbf{a}\right) + \sum_{3}' \left(\frac{\boldsymbol{\rho}}{2},\boldsymbol{\beta},2\mathbf{a}\right)$$
(125)

For the (110) face of the simple cubic lattice equations (103), (104), and (105) must be changed by substituting for 1, m, and $n\sqrt{2}$ 1, $\sqrt{\frac{m}{\sqrt{2}}}$, and $\sqrt{\frac{n}{\sqrt{2}}}$ as was done in equations (60), (61), and (62) of Appendix B.

This gives

$$\sum_{1}^{\prime} (\rho, \beta, a) = 4 \sum_{1=0, 1, 2}^{\infty} \sum_{n=1, 3, 5}^{\infty} \exp \left[-\left\{ (\rho + \sqrt{2}i)^{2} + \frac{n}{4}^{2} \right\}^{\frac{1}{2}} \beta a \right]$$

$$+ 8 \sum_{l=0,1,2}^{\infty} \sum_{m=0,\pm1,\pm2}^{\infty} \sum_{n=1,3,5}^{\infty} \exp\left[-\left\{(\rho + \sqrt{2} 1)^{2} + \frac{m}{2}(m+n) + \frac{n^{2}}{4}\right\}^{\frac{1}{2}} \beta \alpha\right]$$
(126)

$$\sum_{l=0,1,2}^{\prime} (\rho,\beta,a) = 2 \sum_{l=0,1,2}^{\infty} \sum_{m=0,\pm1,\pm2}^{\infty} \sum_{n=1,3,5}^{\infty} \exp\left[-\left\{(\rho + \sqrt{2} 1)^{2} + \frac{m}{2} + \frac{1}{2}(\frac{n}{2})^{2}\right\}^{\frac{1}{2}} \beta a\right]$$
(127)

$$\sum_{l=0,1,2}^{\prime} (\rho,\beta,a) = \sum_{l=0,1,2}^{\infty} \exp\left[-(\rho + \sqrt{2} 1)\beta a\right]$$

$$+ 4 \sum_{l=0,1,2}^{\infty} \sum_{n=0,1,2}^{\infty} \exp\left[-\left\{(\rho + \sqrt{2} 1)^{2} + \frac{m^{2}}{2} + \frac{n^{2}}{2}\right\}^{\frac{1}{2}} \beta a\right]$$
(128)

$$l=0, 1, 2 m-0, 1, 2 n=1, 2, 3$$

The (110) face of the simple cubic lattice:

1. Above the center of a lattice square with a positive ion in the body-centered position

$$S'_{+}(\rho,\beta,a) = \frac{1}{2} \sum_{1}'(\rho,\beta,a) + \sum_{1}' \left(\frac{\rho}{2} + \frac{\sqrt{2}}{4},\beta,2a\right) + \sum_{1}' \left(\frac{\rho}{2} + \frac{3\sqrt{2}}{4},\beta,2a\right) \sum_{3}' \left(\frac{\rho}{2} + \frac{\sqrt{2}}{4},\beta,2a\right) + \sum_{3}' \left(\frac{\rho}{2} + \frac{3\sqrt{2}}{4},\beta,2a\right) + \sum_{3}' \left(\frac{\rho}{2} + \frac{3\sqrt{2}}{4},\beta,2a\right)$$
(129)
$$S'_{-}(\rho,\beta,a) = \frac{1}{2} \sum_{1}' (\rho,\beta,a) + 2 \sum_{2}' \left(\frac{\rho}{2} + \frac{\sqrt{2}}{4},\beta,2a\right) + 2 \sum_{2}' \left(\frac{\rho}{2} + \frac{3\sqrt{2}}{4},\beta,2a\right)$$
(130)

2. Above the center of a lattice square with a negative ion in the body-centered

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(128

position

$$\mathbf{S}_{+}^{\prime}\left(\boldsymbol{\rho},\boldsymbol{\beta},\mathbf{a}\right) = \frac{1}{2}\sum_{1}^{\prime}\left(\boldsymbol{\rho},\boldsymbol{\beta},\mathbf{a}\right) + \sum_{2}^{\prime}\left(\frac{\boldsymbol{\rho}}{2} + \frac{\sqrt{2}}{4}, \boldsymbol{\beta}, 2\mathbf{a}\right) + \sum_{2}^{\prime}\left(\frac{\boldsymbol{\rho}}{2} + \frac{3\sqrt{2}}{4}, \boldsymbol{\beta}, 2\mathbf{a}\right)$$
(131)

$$\underline{S}'(\rho,\beta,\mathbf{a}) = \frac{1}{2} \sum_{1}'(\rho,\beta,\mathbf{a}) + \sum_{1}' \binom{\rho}{2} + \frac{\sqrt{2}}{4}, \beta, 2\mathbf{a} + \sum_{1}' \binom{\rho}{2} + \frac{3\sqrt{2}}{4}, \beta, 2\mathbf{a}$$

+
$$\sum_{3}' \left(\frac{\rho}{2} + \frac{\sqrt{2}}{4}, \beta, 2a \right) + \sum_{3}' \left(\frac{\rho}{2} + \frac{3\sqrt{2}}{4}, \beta, 2a \right)$$
 (132)

3. Above the midpoint of a lattice edge

$$\mathbf{S}_{+}^{\prime}(\boldsymbol{\rho},\boldsymbol{\beta},\mathbf{a}) = \frac{1}{2} \left[\sum_{2}^{\prime} (\boldsymbol{\rho},\boldsymbol{\beta},\mathbf{a}) + \sum_{2}^{\prime} \left(\boldsymbol{\rho} + \frac{\sqrt{2}}{2},\boldsymbol{\beta},\mathbf{a} \right) \right]$$
(133)

$$\mathbf{S}'(\boldsymbol{\rho},\boldsymbol{\beta},\mathbf{a}) = \frac{1}{2} \sum_{2} \boldsymbol{\rho}'(\boldsymbol{\rho},\boldsymbol{\beta},\mathbf{a}) + \sum_{2} \left(\boldsymbol{\rho} + \frac{\sqrt{2}}{2},\boldsymbol{\beta},\mathbf{a}\right)$$
(134)

4. Above a positive ion in the surface plane

$$S'_{+}(\rho, \beta, a) = \frac{1}{2} \sum_{1}' \left(\rho + \frac{\sqrt{2}}{2}, \beta, a \right) + \sum_{1}' \left(\frac{\rho}{2}, \beta, 2a \right) + \sum_{1}' \left(\frac{\rho}{2} + \frac{\sqrt{2}}{2}, \beta, 2a \right) + \sum_{3}' \left(\frac{\rho}{2}, \beta, 2a \right) + \sum_{3}' \left(\frac{\rho}{2}, \beta, 2a \right) + \sum_{3}' \left(\frac{\rho}{2}, \beta, 2a \right)$$
(135)

$$\mathbf{S}'_{2}(\boldsymbol{\rho}, \boldsymbol{\beta}, \mathbf{a}) = \frac{1}{2} \sum_{n=1}^{\infty} \left(\boldsymbol{\rho} + \frac{\sqrt{2}}{2}, \boldsymbol{\beta}, \mathbf{a} \right) + 2 \sum_{n=1}^{\infty} \left(\frac{\boldsymbol{\rho}}{2}, \boldsymbol{\beta}, 2\mathbf{a} \right) + 2 \sum_{n=1}^{\infty} \left(\frac{\boldsymbol{\rho}}{2}, \boldsymbol{\beta}, 2\mathbf{a} \right)$$
(136)

5. Above a negative ion in the lattice plane

$$\mathbf{S}_{+}'(\boldsymbol{\rho},\boldsymbol{\beta},\mathbf{a}) = \frac{1}{2}\sum_{n}'\left(\boldsymbol{\rho} + \frac{\sqrt{2}}{2}, \boldsymbol{\beta}, \mathbf{a}\right) + 2\sum_{n}'\left(\frac{\boldsymbol{\rho}}{2}, \boldsymbol{\beta}, 2\mathbf{a}\right) + 2\sum_{n}'\left(\frac{\boldsymbol{\rho}}{2} + \frac{\sqrt{2}}{2}, \boldsymbol{\beta}, 2\mathbf{a}\right)$$
(137)

$$\mathbf{S}_{-}^{\prime}(\boldsymbol{\rho},\boldsymbol{\beta},\mathbf{a}) = \frac{1}{2} \sum_{1}^{\prime} \left(\boldsymbol{\rho} + \frac{\sqrt{2}}{2}, \ \boldsymbol{\beta}, \ \mathbf{a} \right) + \sum_{1}^{\prime} \left(\frac{\boldsymbol{\rho}}{2}, \ \boldsymbol{\beta}, \ 2\mathbf{a} \right) + \sum_{1}^{\prime} \left(\frac{\boldsymbol{\rho}}{2} + \frac{\sqrt{2}}{2}, \ \boldsymbol{\beta}, \ 2\mathbf{a} \right) + \sum_{1}^{\prime} \left(\frac{\boldsymbol{\rho}}{2}, \ \boldsymbol{\beta}, \ 2\mathbf{a} \right)$$

$$+ \sum_{3}^{\prime} \left(\frac{\boldsymbol{\rho}}{2}, \ \boldsymbol{\beta}, \ 2\mathbf{a} \right) + \sum_{3}^{\prime} \left(\frac{\boldsymbol{\rho}}{2} + \frac{\sqrt{2}}{2}, \ \boldsymbol{\beta}, \ 2\mathbf{a} \right)$$
(138)

Table 26. Calculated Values for the Summations of the Exponential of Distance from Equations (103), (104), and (105) for the (100) Plane of the Face Centered Cubic Crystal Structure

 β = 9.81018 Å a = 3.623 Å

ρ	Σ 1	Σ 2	Σ 3
. 6	$1.9385 \ge 10^{-14}$	$1.7590 \ge 10^{-12}$	5.4766×10^{-10}
.7	$1.7523 \ge 10^{-15}$	1.0535×10^{-13}	$1.5665 \ge 10^{-11}$
.8	1.3217×10^{-16}	5.4816×10^{-15}	$4.4807 \ge 10^{-13}$
.9	8.6091×10^{-18}	2.5638×10^{-16}	1.2816×10^{-14}
1.0	$4.9788 \ge 10^{-19}$	1.1047×10^{-17}	3.6659×10^{-16}
1.1	$2.6128 \ge 10^{-20}$	4.4654×10^{-19}	1.0486×10^{-17}
1.2	$1.2661 \ge 10^{-21}$	$1.7158 \ge 10^{-20}$	$2.9993 \ge 10^{-19}$
1.3	$5.7430 \ge 10^{-23}$	6.3304×10^{-22}	$8.5792 \ge 10^{-21}$
1.4	2.4656×10^{-24}	$2.2597 \ge 10^{-23}$	$2.4540 \ge 10^{-22}$
1.5	$1.0108 \ge 10^{-25}$	7.8504×10^{-25}	7.0196 x 10^{-24}
1.6	$3.9848 \ge 10^{-27}$	2.6665×10^{-26}	2.0080×10^{-25}
1.7	$1.5195 \ge 10^{-28}$	$8.8873 \ge 10^{-28}$	$5.7441 \ge 10^{-27}$
1.8	$5.6313 \ge 10^{-30}$	2.9151×10^{-29}	$1.6432 \ge 10^{-28}$
1.9	2.0362×10^{-31}	9.4327×10^{-31}	$4.7013 \ge 10^{-30}$
2.0	7.2069×10^{-33}	3.0167×10^{-32}	$1.3451 \ge 10^{-31}$
2.1	2.5037×10^{-34}	$9.5505 \ge 10^{-34}$	$3.8490 \ge 10^{-33}$
2.2	$8.5565 \ge 10^{-36}$	$2.9972 \ge 10^{-35}$	1.1015×10^{-34}
2.3	2.8824×10^{-37}	$9.3338 \ge 10^{-37}$	$3,1528 \ge 10^{-36}$
2.4	$9.5865 \ge 10^{-39}$	2.8872×10^{-38}	9.0253 x 10^{-38}
2.5	3.1523×10^{-40}	$8.8779 \ge 10^{-40}$	$2.5841 \ge 10^{-39}$

Table 27.Calculated Values for the Summations of the Exponential
of Distance from Equations (103), (104), and (105) for the
(100) Plane of the Simple Cubic Crystal Structure.

Q	$\frac{\Sigma}{1}$	$\frac{\Sigma}{2}$	Σ 3
.7	1.6801×10^{-18}	2.5890×10^{-16}	1.1789×10^{-13}
.8	7.6511 x 10^{-20}	$7.5358 \ge 10^{-18}$	$1.6771 \ge 10^{-15}$
.9	2.9039×10^{-19}	$1.9307 \ge 10^{-19}$	2.3858×10^{-17}
1.0	$9.5914 \ge 10^{-23}$	$4.4846 \ge 10^{-21}$	3.3939×10^{-19}
1.1	2.8205×10^{-24}	$9.6492 \ge 10^{-23}$	$4.8281 \ge 10^{-21}$
1.2	$7.5388 \ge 10^{-26}$	$1.9541 \ge 10^{-24}$	$6.8682 \ge 10^{-23}$
1.3	$1.8621 \ge 10^{-27}$	$3.7694 \ge 10^{-26}$	$9.7704 \ge 10^{-25}$
1.4	$4.3062 \ge 10^{-29}$	$6.9865 \ge 10^{-28}$	$1.3899 \ge 10^{-26}$
1.5	$9.4231 \ge 10^{-31}$	$1.2546 \ge 10^{-29}$	$1.9772 \ge 10^{-28}$
1.6	$1.9678 \ge 10^{-32}$	2.1921×10^{-31}	$2.8128 \ge 10^{-30}$
1.7	$3.9489 \ge 10^{-34}$	$3.7442 \ge 10^{-33}$	4.0014×10^{-32}
1.8	7.6584×10^{-36}	$6.2741 \ge 10^{-35}$	5.6924×10^{-34}
1.9	$1.4421 \ge 10^{-37}$	$1.0343 \ge 10^{-36}$	$8.0981 \ge 10^{-36}$
2.0	$2.6471 \ge 10^{-39}$	1.6813×10^{-38}	$1.1521 \ge 10^{-37}$
2.1	$4.7515 \ge 10^{-41}$	2.7000×10^{-40}	$1.6390 \ge 10^{-39}$
2.2	$8.3636 \ge 10^{-43}$	4.2904×10^{-42}	2.3319×10^{-41}
2.3	$1.4470 \ge 10^{-44}$	$6.7525 \ge 10^{-44}$	3.3160×10^{-43}

		0-1		0
$\beta =$	9.81018	A	a = 4.335	Α

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Table 28. Calculated Values for the Summations of the Exponential of Distance from Equations (126), (127), and (128) for the (110) Plane of the Simple Cubic Crystal Structure

ρ	Σ 1	Σ 2	Σ 3
.7 .7 + $\sqrt{2}/2$	$5.1781 \times 10^{-16} \\ 1.0516 \times 10^{-27}$	$6.5623 \times 10^{-15} \\ 3.2048 \times 10^{-27}$	$\begin{array}{r} -13\\1.1790 \times 10 \\1.0307 \times 10 \end{array}$
.8 .8 + $\sqrt{2}/2$	1.5072×10^{-17} 1.8836 x 10 ⁻²⁹	$1.4029 \times 10^{-16}_{-29}$ 5.1453 x 10	1.6772×10^{-15} 1.4687×10^{-28}
.9 .9 + $\sqrt{2}/2$	3.8615×10^{-19} 3.2853×10^{-31}	$2.7677 \times 10^{-18} \\ 8.1452 \times 10^{-31}$	$2.3861 \times 10^{-17} \\ 2.0940 \times 10^{-30} \\ 10^{-30}$
1.0 1.0 + $\sqrt{2}/2$	8.9893×10^{-21} 5.6034 x 10 ⁻³³	$5.1461 \times 10^{-20} \\ 1.2745 \times 10^{-32} \\ 0.000 \\ 0.00$	$3.3949 \times 10^{-19}_{-32}$ 2.9876 x 10
1.1 1.1 + $\sqrt{2}/2$	1.9298×10^{-22} 1.8071×10^{-35}	9.1491 x 10^{-22} 1.9749 x 10	$4.8309 \times 10^{-21}_{-34} \\ 4.2654 \times 10^{-22}_{-22}$
1.2 1.2 + $\sqrt{2}/2$	3.9082×10^{-24} 1.5443×10^{-36}	$\begin{array}{r}1.5713 \times 10^{-23}\\3.0355 \times 10^{-36}\end{array}$	$\begin{array}{r} 6.8757 \times 10^{-2.5} \\ 6.0945 \times 10^{-36} \\ \end{array}$
1.3 1.3 + $\sqrt{2}/2$	$7.5389 \times 10^{-26} \\ 2.5080 \times 10^{-38} \\ 2.5080 \times 10^{-38} \\ 37$	$2.6264 \times 10^{-23} \\ 4.6334 \times 10^{-38} \\ 27$	9.7890×10^{-23} 8.7149 x 10 -26
$1.4 \\ 1.4 + \sqrt{2}/2$	1.3979×10^{-27} 4.0244 x 10	$\begin{array}{r} 4.2959 \times 10^{-27} \\ 7.0311 \times 10 \\ \end{array}$	$\begin{array}{r} 1.3942 \times 10^{-20} \\ 1.2472 \times 10^{-39} \\ -28 \end{array}$
1.5 1.5 + $\sqrt{2}/2$	$\begin{array}{r} 2.5092 \times 10^{-23} \\ 6.3904 \times 10^{-42} \\ -31 \end{array}$	$\begin{array}{r} 6.9048 \times 10 \\ -41 \\ 1.0616 \times 10 \\ -30 \end{array}$	$\begin{array}{r} 1.9867 \ge 10 \\ -41 \\ 1.7864 \ge 10 \\ -30 \end{array}$
1.6 1.6 + $\sqrt{2}/2$	$\begin{array}{r} 4.3841 \times 10 \\ 1.0051 \times 10 \\ -33 \end{array}$	$\begin{array}{c} 1.\ 0940 \ge 10 \\ -43 \\ 1.5956 \ge 10 \\ -32 \end{array}$	$2.8324 \times 10 - 43 \\ 2.5595 \times 10 - 32$
1.7 1.7 + $\sqrt{2}/2$	7.4885×10^{-45} 1.5686×10^{-45}	$\begin{array}{c} 1.7132 \times 10 \\ 2.3252 \times 10 \end{array} \begin{array}{c} -45 \\ \end{array}$	$\begin{array}{c} 4.0487 \times 10 \\ 3.4868 \times 10 \end{array}$

 $\beta = 9.81018 \stackrel{\rm O-1}{\rm A} \qquad a = 4.335 \stackrel{\rm O}{\rm A}$

APPENDIX D

THE ELECTROSTATIC FIELD AND POTENTIAL

APPENDIX D

THE ELECTROSTATIC FIELD AND POTENTIAL

The Electrostatic Field Above the (110)

Face of a Simple Cubic Lattice

The expression for the electrostatic potential due to the surface layer of the (110) face of a simple cubic lattice is identical to the expression given by Lennard-Jones and Dent⁷ for the potential due to the surface layer of the (100) face of a face-centered cubic lattice since the structure of the surface layers are identical.

$$\phi_{1}'(\mathbf{x},\mathbf{y},\mathbf{z}) = \frac{4e}{a} \sum_{\substack{l=\pm 1,\pm 3,\pm 5 \\ l=\pm 1,\pm 3,\pm 5 \\ m=\pm 1$$

(The point x=0, y=0 is above a positive ion).

The potential due to the next layer is given by substituting (a + z) for z in equation (137). Then the potential of successive lower layers is obtained by adding successive increments of a to z. By summing in this manner we are considering only the ions at the lattice points and excluding the ions in the identical lattice at the body-centered positions. The summation gives a geometrical

progression of the form

$$\sum_{n=1}^{n} A \mathbf{r}^{n} = \frac{A}{1-\mathbf{r}}$$
(140)

where,

A =
$$\frac{4e}{a} \sum_{\substack{1=\pm1,\pm3,\\ 1=\pm1,\pm3}}^{\infty} \sum_{\substack{m=\pm1,\pm3\\ m=\pm1,\pm3}}^{\infty} (1)^{\frac{1+m}{2}} \frac{\exp\left(-\frac{2\pi^2}{a}\sqrt{1^2+m^2}\right)}{\sqrt{1^2+m^2}}$$

$$\cos 2\pi \left(\frac{\ln x}{a} + \frac{\ln x}{a} - \frac{1+m}{4}\right)$$
$$\mathbf{r} = \exp\left(-2\pi \sqrt{1^2 + m^2}\right)$$

 $n = 0, 1, 2, 3, \ldots$

Then the potential of the whole crystal bounded by the (110) face, excluding the lattice of ions at the body-centered positions, is given by

$$\phi_{1}(\mathbf{x},\mathbf{y},\mathbf{z}) = \frac{4e}{a} \sum_{\substack{l=\pm,1,\pm3 \\ l=\pm,1,\pm3}}^{\infty} \sum_{\substack{m=\pm,1,\pm3 \\ m=\pm,1,\pm3}}^{\infty} \left[\frac{\frac{1-m}{2}}{\sqrt{1-\frac{2}{2}}} \cos 2\pi \left(\frac{1x}{a} + \frac{mx}{a} - \frac{1+m}{a} \right) - \frac{\exp\left(-\frac{2\pi z}{a} \sqrt{1-\frac{2}{2}}\right)}{\sqrt{1-\frac{2}{2}}} - \frac{\exp\left(-\frac{2\pi z}{a} \sqrt{1-\frac{2}{2}}\right)}{1 - \exp\left(-2\pi \sqrt{1-\frac{2}{2}}\right)} \right]$$
(141)

The lattice formed by the body centered ions is identical to that formed by the ions at the lattice points, but is shifted with respect to the coordinate origin defined for equation (139) by (a/4) in the x and y directions and (a/2) in the z direction.

The electrostatic potential due to this lattice is then

$$\phi_{2}(\mathbf{x},\mathbf{y},\mathbf{z}) = \frac{4e}{a} \sum_{\substack{1=\pm 1,\pm 3 \ m=\pm 1,\pm 3}} \sum_{\substack{m=\pm 1,\pm 3 \ \sqrt{1^{2}+m^{2}}}} \cos 2\pi$$

$$\left(\frac{1x}{a} + \frac{mx}{a}\right) \frac{\exp\left(-\frac{2\pi\left(2+\frac{a}{2}\right)}{a}\sqrt{1^{2}+m^{2}}\right)}{1-\exp\left(-2\pi\sqrt{1^{2}+m^{2}}\right)}$$

The total electrostatic potential is then the sum of equations (139) and

$$\phi(\mathbf{x}, \mathbf{y}, \mathbf{z}) = \phi_1(\mathbf{x}, \mathbf{y}, \mathbf{z}) + \phi_2(\mathbf{x}, \mathbf{y}, \mathbf{z})$$
(143)

and,

(140)

$$\phi(\mathbf{x},\mathbf{y},\mathbf{z}) = \frac{4\mathbf{e}}{\mathbf{a}} \sum_{\substack{1=\pm 1,\pm 3 \\ m=\pm 1,\pm 3}}^{\infty} \sum_{\substack{(-1) \\ m=\pm 1,\pm 3}}^{\infty} \frac{\left(\frac{1+m}{2}\right)}{\sqrt{1^2+m^2}} \frac{\exp\left(\frac{2\pi z}{a}\sqrt{1^2+m^2}\right)}{1-\exp\left(-2\pi\sqrt{1^2+m^2}\right)} \left\{\cos 2\pi \sqrt{1^2+m^2}\right\}$$

$$\left(\frac{4x}{a} + \frac{mx}{a} - \frac{1+m}{4}\right) + \exp\left(-\pi\sqrt{\frac{2+2}{1+m^2}}\right)\cos 2\pi\left(\frac{4x}{a} + \frac{mx}{a}\right)\right\}$$
(144)

The field strength at any point is given by $-\text{grad} \phi$, but we are only interested in the resultant field normal to the surface, which is given by

$$\mathbf{F}_{\mathbf{Z}} = -\frac{\partial \mathbf{\phi}}{\partial \mathbf{Z}} \tag{145}$$

Therefore,

(142)

$$F_{z}(x, y, z) = \frac{8 \pi e}{a^{2}} \sum_{\substack{l=\pm 1, \pm 3 \\ l=\pm 1, \pm 3 \\ m=\pm 1, \pm 3 \\ m=\pm$$

In evaluating ${\rm F}_{\rm Z}$ we want to define

$$\rho = \frac{z}{a^*} \tag{147}$$

where a* is the lattice parameter of the simple cubic lattice

$$a^* = \sqrt{2} a \tag{148}$$
$$\frac{z}{a} = \sqrt{2} \rho$$

Substituting equation (148) in equation (146) puts F_z in terms of ρ , the same reduced distance parameter used for the (100) face by Orr⁴ and for the lattice sums in Appendix C.

$$\mathbf{F}_{\mathbf{z}} = \frac{4\pi e}{a^{*2}} \sum_{\substack{l=\pm 1, \pm 3 \\ l=\pm 1, \pm 3}}^{\infty} \sum_{\substack{m=\pm 1, \pm 3 \\ m=\pm 1, \pm 3}}^{\infty} \left[\frac{\frac{1+m}{2}}{\frac{(-1)}{1-\exp(-2\pi\sqrt{1+m^{2}})}} \exp(-2\sqrt{2}\pi\rho\sqrt{1+m^{2}}) \left\{ \cos 2\pi + \frac{1+m}{2} \right\} \right] \left\{ \cos 2\pi + \frac{1+m}{2} \right\}$$

$$\left(\frac{\mathbf{lx}}{\mathbf{a}} + \frac{\mathbf{mx}}{\mathbf{a}} - \frac{\mathbf{l}+\mathbf{m}}{4}\right) + \exp\left(\pi\sqrt{\mathbf{l}^2 + \mathbf{m}^2}\right) \cos 2\pi \left(\frac{\mathbf{lx}}{\mathbf{a}} + \frac{\mathbf{my}}{\mathbf{a}}\right) \right\}$$
(149)

The resultant electrostatic energy of a non-polar molecule, whose polarisability is α , is given by

$$\Phi_{\rm E} = -\frac{1}{2} \alpha F_{\rm Z}^2 \tag{150}$$

(110) Face of Simple Cubic

Table 29. Electrostatic Field Over the Center of a Lattice SquareOver a Negative Ion in Lattice 2.

(Over Positive Ion Lattice 2, ${\rm F}_{_{\rm Z}}$ has Opposite Sign)

q	$\mathbf{F}_{\mathbf{Z}}$	$\Phi_{\rm E}$ cal./mole
0.25	-4.068×10^{-4}	-2.962
0.5	-1.757×10^{-4}	-5.529×10^{-3}
0.6	-5.002×10^{-5}	-4.479×10^{-4}
0.7	$-1.424 \ge 10^{-5}$	-3.628×10^{-5}
0.8	-4.052×10^{-6}	-2.938×10^{-6}
0.9	-1.153×10^{-6}	-2.382×10^{-7}
1.0	-3.282×10^{-7}	$-1.928 \text{ x} 10^{-8}$
1.5	-6.330×10^{-10}	-7.174×10^{-14}

 F_z in Units of $\frac{2\pi e}{a^2}$

(110) Face of Simple Cubic

Table 30. Electrostatic Field Over a Positive Ion

(Over Negative Ion, $\mathbf{F}_{\mathbf{Z}}$ has Opposite Sign)

ρ	$\mathbf{F}_{\mathbf{Z}}$	$\Phi_{ m E}$ cal./mole
0.25	36.086×10^{-2}	-23314.6
0.5	14.954×10^{-2}	-40.04
0.6	4.254×10^{-2}	- 3.24
0.7	$1.210 \ge 10^{-3}$	- 0.262
0.8	3.444×10^{-3}	-2.12×10^{-2}
0.9	9.804×10^{-4}	- 1.72×10^{-3}
1.0	2.790×10^{-4}	-1.39×10^{-4}
1.5	5.190×10^{-8}	-4.824×10^{-10}

$$F_z$$
 in Unit of $\frac{2 \pi e}{a^2}$

.

(100) Face of Simple Cubic

Table 31. Electrostatic Field Over the Center of a Lattice Square Surface of Negative Ions (Surface of Positive Ions has F_z of Opposite Sign)

ρ	$\mathbf{F}_{\mathbf{Z}}$	$\Phi_{ m E}$ cal./mole
0.2	64.410×10^{-2}	74274.67
0.3	35.806×10^{-2}	22952.77
0.4	24.904×10^{-2}	11103.70
0.5	15.502×10^{-2}	4302.61
0.6	7.701×10^{-2}	1061.82
0.7	4.801×10^{-2}	412.62
0.8	2.700×10^{-2}	130.56
1.0	6.001×10^{-3}	6.447

 F_{Z} in units of $\frac{2\pi e}{a}$

(100) Face of Simple Cubic

Table 32. Electrostatic Field Over a Negative Ion in the Surface (Surface of Positive Ions has F_z with Opposite Sign)

	ů	
ρ	F z	$\Phi_{\rm E}$ cal./mole
0.5	-25.904×10^{-2}	-12013.47
0.6	-11.802×10^{-2}	- 2493.64
0.7	-6.401×10^{-2}	- 733.55
0.8	-3.200×10^{-2}	- 183.39
1.0	-1.100×10^{-2}	- 21.67

г	in	Unita	of	$2\pi e$
٢z	m	Umis	OL	$\frac{1}{2}$
				a

(100) Face of Face-Centered Cubic

Table 33. Electrostatic Field Over a Negative Ion (Over a Positive Ion Has Opposite Sign for F_z)

ρ	$\mathbf{F}_{\mathbf{Z}}$	Φ _E cal./mole
0.25	-197.304×10^{-2}	-92536.77
0.5	-18.760×10^{-2}	- 836.58
0.6	-7.672×10^{-2}	- 139.913
0.7	-3.148×10^{-2}	- 23.562
0.8	-1.294×10^{-2}	- 3.980
0.9	-5.320×10^{-3}	- 0.673
1.0	-2.188×10^{-3}	- 0.114
1.5	-1.029×10^{-4}	-2.515×10^{-4}

 F_{z} in Units of $\frac{2\pi e}{a^2}$

INDEX OF SYMBOLS

,

Φ, φ	Potential of interaction
Φ_{A}	Dispersion potential
$\Phi_{\rm R}$	Repulsion potential
$\Phi_{\rm E}$	Electrostatic potential
₫ _T	Total potential
С	Dispersion potential constant
C _{ii}	Self- interaction dispersion potential constant
C _{ij}	mixed interaction dispersion potential constant
В	Repulsion potential pre-exponential constant
B _{ii}	Self-interaction repulsion potential pre-exponential constant
B _{ij}	Mixed interaction repulsion potential pre-exponential constant
β	Repulsion potential exponential constant
β_{ii}	Self-interaction repulsion potential exponential constant
β_{ij}	Mixed interaction repulsion potential exponential constant
E	Minimum of potential curve
r	Intermolecular distance
r _m	Equilibrium intermolecular distance
γ	Exponential parameter of modified Buckingham potential
α	Polarizability
x	Diamagnetic susceptibility

m	Rest mass of an electron
с	Velocity of light
$\mathbf{F}_{\mathbf{Z}}$	Component of the electrostatic field perpendicular to the crystal surface
V _m	Adsorption manifold volume
V _G	McLeod gauge volume
v_{c}	Compression gauge volume
V _D	Dead Space volume
$v_{ m Deff}$	Effective dead space volume
V _{warm}	Warm dead space volume
V _{cold}	Cold dead space volume
N ads	Amount of adsorbate adsorbed
^N m,i	Initial amount of adsorbate in manifold
N _{m,f}	Final amount of adsorbate in manifold
$^{N}\mathbf{D}$	Amount of adsorbate in dead space
$^{N}_{R}$	Amount of adsorbate remaining in dead space at end of run
Р	Pressure
n	Moles
R	Gas constant
Т	Temperature
V	Volume
B(T)	Second virial coefficient in volume expansion
C _{SG}	Dispersion potential constant from Starkschall and Gordon (ref. 47)

$c_{\rm KM}$	Dispersion potential constant from Kirkwood-Muller expression
s_	Summation of inverse sixth powers of molecule-negative ion distances
s_+	Summation of inverse sixth powers of molecule-positive ion distances
s_′	Summation of exponential of molecule-negative ion distances
s' +	Summation of exponential of molecule-positive ion distances
p	Reduced distance of adsorbate molecule above crystal surface
Z	Distance of adsorbate molecule above crystal surface
a	Ion-ion distance in crystal
ω	Exponential function describing electron density with distance from atomic nucleus
k	Boltzmann constant
ν	Frequency of vibration
f	Force constant of vibration
b_2	Coefficient of square term in anharmonic oscillator equation
€ _n	n th energy level of harmonic oscillator
Eo	Zero point energy
E vib	Average vibrational contribution to the energy
Eavg	Average energy of oscillation
${}^{\mathrm{E}}_{\mathrm{Avg}}^{\mathrm{T}}$	Total average energy
N _i	Number of adsorbate molecules on site i assuming a Boltzmann distribution
P.	Proportionality constant

Enthalpy at zero coverage

- Σ Summation of inverse rth power of distances from a point above the 2 midpoint of a lattice edge to all lattice points
- Σ Summation of inverse rth power of distances from a point above an 3 ion to all lattice points
- Σ' Summation of exponential of distances from a point above the center of a lattice square to all lattice points
- Σ' Summation of exponential of distances from a point above the midpoint 2 of a lattice edge to all lattice points
- Σ' Summation of exponential of distances from a point above an ion to all 3 lattice points
- 1 Unit distance parameter in the z direction
- m Unit distance parameter in the y direction
- n Unit distance parameter in the x direction
- e Charge on an electron

 H^{0}

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