

INCLUSION OF VAPOURS
BY
ION-EXCHANGED FAUJASITES

by

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Abstract

An apparatus has been built to study, gravimetrically, the sorption of gases at temperatures between 100°C and 290°C and was used to study the sorption of ammonia on nine ion-exchanged forms of faujasite (LiX, NaX, KX, RbX, CsX, SrX, BaX and CoX) between these temperatures. A volumetric system was employed to study the sorption of ammonia on NaX between 0°C and 70°C.

All forms gave reproducible isotherms for ammonia sorption except CoX. From the reproducible isotherms the isosteric heats and partial molar entropies were obtained. The heat data showed that all forms, except CsX, were heterogeneous. The changes in the free energies and enthalpies of LiX, KX, and SrX, with respect to a standard state, were compared; in all cases these free energy and enthalpy changes were small.

Attempts have been made to estimate the saturation capacities of the crystals for various temperatures; the thermal expansions of the sorbed fluid were obtained from these estimates and compared with that of liquid ammonia.

Heterogeneity of the sorbents complicated the interpretation of the data, except for CsX, which was nearly homogeneous. No satisfactory isotherm

equation was found for any of the heterogeneous systems. The data for ammonia on CsX was interpreted in terms of a localised model over a wide range of θ ; the data also indicated that the rotations of the ammonia were hindered.

The dispersion and repulsion energies of ammonia with NaX were calculated using a summation over all the relevant atoms. The field at a series of points in NaX was obtained and used to determine the field-dipole energy, and the polarisation energy. The calculations showed that the field-dipole energy term was predominant but predicted unduly large polarisation energies. Some elementary calculations have been made for the interaction of two idealised ammonia molecules.

The data for CoX showed hysteresis, accompanied by colour changes. Subsequent X-ray examination showed that the lattice had collapsed.

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LIST OF THERMODYNAMIC SYMBOLS

Throughout:

Subscript ₁ refers to sorbate.

Subscript ₂ refers to sorbent.

Subscript _g refers to gas.

$\bar{X}$ = a partial derivative w.r.t. n , the number of moles of the species present.

$\tilde{X}$ = integral quantities per grm. mole.

x = ratio of concs. of sorbate to sorbent = $\frac{n_1}{n_2}$.

$\tilde{X}^0$ = integral quantity in a standard state (i.e., at standard T and P).

$\tilde{X}_{02}$ = property of pure sorbent.

In addition, various functions peculiar to Hill's and Tykodi's systems are defined in Sections 1.3.1.3 and 1.3.1.4.

ΔX^0 = difference in a property of a gas between its equilibrium state and a chosen standard state.

Φ = $\mu_2 - \mu_{02}$ = the difference in chemical potential of the sorbent in isolation and at sorption equilibrium.

φ : see Section 1.3.1.3.

SYMBOLS used in Section 1.3.2.

Q	=	partition function of system.
a	=	partition function of a single molecule.
A	=	surface area.
A_f	=	free surface area.
j	=	partition function of the internal degrees of freedom (i.e. rotational and vibrational).
U_0	=	potential energy at minimum of sorbate.
q_x	=	partition function of a molecule for motion in the x direction.
M	=	no. of sites on sorbent.
N	=	no. of gas molecules sorbed.
E_i	=	the interaction energy between sorbed molecules.
C	=	coordination no. of sites.
N_{00}	=	no. of pairs of sites unoccupied.
N_{01}	=	no. of pairs of sites with one site occupied.
N_{11}	=	no. of pairs of sites with both sites occupied.
ϵ	=	potential energy of a pair of isolated molecules r^* apart.
w	=	interaction energy between two sorbed molecules.
r^*	=	van der Waals radius of a molecule.
$\tilde{S}_c$	=	molar configurational entropy.
$\bar{S}_c$	=	partial molar configurational entropy.

SYMBOLS used in 1.4.

C_1	=	dispersion constant
C_2	=	constant
C_4	=	repulsion constant
E_x	=	ionisation potential of species x
ν_x	=	a characteristic frequency of x
c	=	velocity of light
m	=	mass of an electron
α	=	polarisability of a molecule (atom)
χ	=	magnetic susceptibility of a molecule
n	=	no. of electrons in the outer shell of a molecule
U_t	=	total interaction energy of a molecule with a sorbent
p	=	mass of lattice points / unit volume
r_0	=	equilibrium distance for a molecule sorbed to a surface

1.1.1. The Sorbents: Structure and Properties

Silicates arise from the coordination of SiO_4^{4-} groups; depending on the number of other like groups to which any one SiO_4^{4-} group is attached, the resulting structure is fibrous, lamellar or a three-dimensional network (1). Aluminium may be introduced in place of silicon in the SiO_4^{4-} groups giving rise to aluminosilicates. This produces a charge deficiency, since Al is trivalent and Si tetravalent, which is balanced by the addition of an equivalent of univalent or divalent ion (normally of a metal but organic cations can be used also). Apart from the introduction of the cations the substitution of aluminium for silicon causes little change; the two are too similar to be distinguished by X-rays, and the AlO_4^{4-} tetrahedron is only slightly larger than the SiO_4^{4-} tetrahedron. Loewenstein (2), however, has shown that two AlO_4^{4-} groups cannot share an oxygen atom and this introduces some ordering of the aluminium and silicon atoms, limiting the lowest possible silicon/aluminium ratio to 1:1, when there would be rigorous alternation of the aluminium and silicon atoms.

In this study attention is confined to the zeolites, three-dimensional aluminosilicates, in which each SiO_4^{4-} group is coordinated with four other such groups giving rise to a variety of structures. Before

proceeding to discuss the particular zeolite used, faujasite, some physical properties of the zeolites will be noted.

The zeolites have a high water content and are in general stable to high temperatures; there is very little swelling or shrinking on removal of the water molecules. However, exposure to water vapour at high temperature often will cause decomposition through hydrolytic action (3). A given type of structure can sometimes be obtained with various ratios of Al/Si and with various types of cations present. Their open structure gives rise to their sorption properties and 'molecular sieve' action (14). The channels throughout the crystal give rise to a large intracrystalline volume which is able to accommodate guest molecules. The molecular sieve action arises from the definite and periodic minimum width of the channels which can only admit molecules small enough to pass these narrow points. Barrer (4) has classified the zeolites in terms of the largest molecules which they can admit. It should be noted that the size of gaseous species able to be occluded can be modified by presorption of polar molecules, as was shown by Barrer and Rees (5) for mordenite and chabazite. In the presence of sufficient ammonia they were able to separate O_2 from N_2 and A.

Partial separation of gases may be effected where the gases have different rates of diffusion through a zeolite.

The ion present can also modify the diffusion and sorption equilibrium properties of the zeolite. One ion may sometimes block channels when another would not (e.g. NaA and CaA in which the internal volume of CaA only is available to I_2 (6)). In the same way the ion present may affect the rate of diffusion through the crystal by altering potential energy barriers in the crystal.

In some cases of sorption the guest molecule attacks and breaks down the lattice. Examples of this have been given by Barrer and Bratt (3) who studied sorption of water at high temperatures on ion exchanged faujasites. Other examples have been reported by Barrer (7) and Brook, for sorption of CHF_3 and $CClF_2H$ on chabazite, and Bratt and Reucroft (8) for sorption of perfluorocyclobutene on NaX.

In the present studies sorption of ammonia on CoX resulted in decomposition (shown by X-rays), accompanied by colour changes of the sorbent; presumably colour change and perhaps the decomposition are associated with the formation of a cobaltamine accompanied by a breakdown in the lattice.

1.1.2. Faujasite

The basic unit in faujasite is the sodalite cage (see Figure 1) (9,10). This is a cubooctahedron with eight six-membered rings of SiO_4^{-4} and AlO_4^{-4} tetrahedra and six four-membered rings of like tetrahedra. The sodalite cages can coordinate, through oxygen atoms projecting from the six membered rings, with other sodalite cages. In faujasite four tetrahedrally situated rings are used to link the sodalite cages by sharing projecting oxygen atoms of the rings (6-rings). The two 6-rings and bridge oxygen atoms form a small connecting cage. This tetrahedral stacking also introduces a new type of cage of considerable dimensions (see Figure 2). These "supercages" are linked, tetrahedrally, by twelve-membered rings to four other such cages; the free diameters of the 12-rings and the supercages are 8-9Å and 12-13Å respectively. The structure resembles the diamond structure with the sodalite cages playing the part of carbon atoms.

The formulae of the unit cell is $\text{Na}_{82}82\text{AlO}_2.110\text{Si}.240-260\text{H}_2\text{O}$ (9) for the sample used in these studies. Each unit cell contains eight sodalite cages or eight supercages; either way accounts for all the atoms. The dimensions of the unit cell obtained from X-rays and the cages (calculated values) are given in Table 1.

Figure 1 - Sodalite Cage

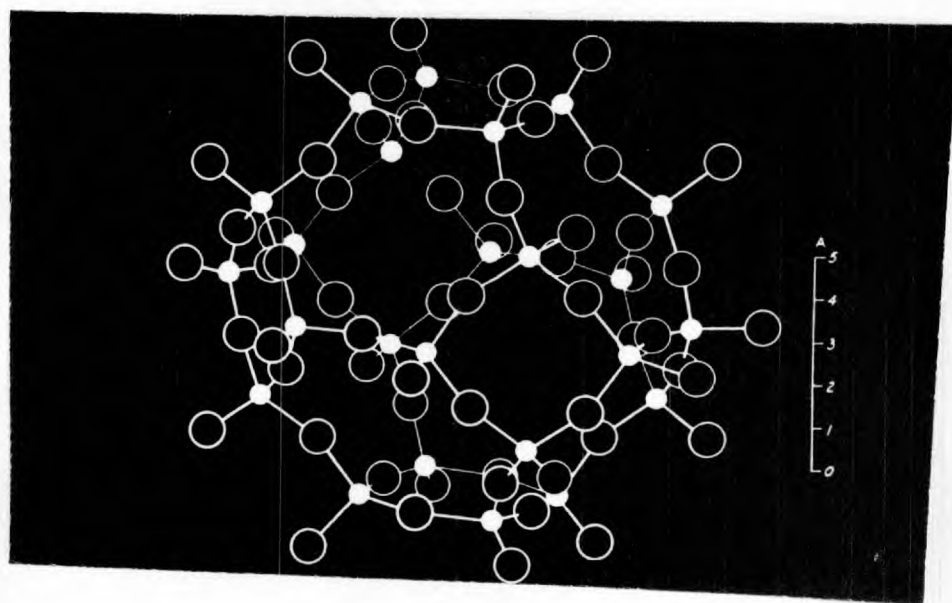
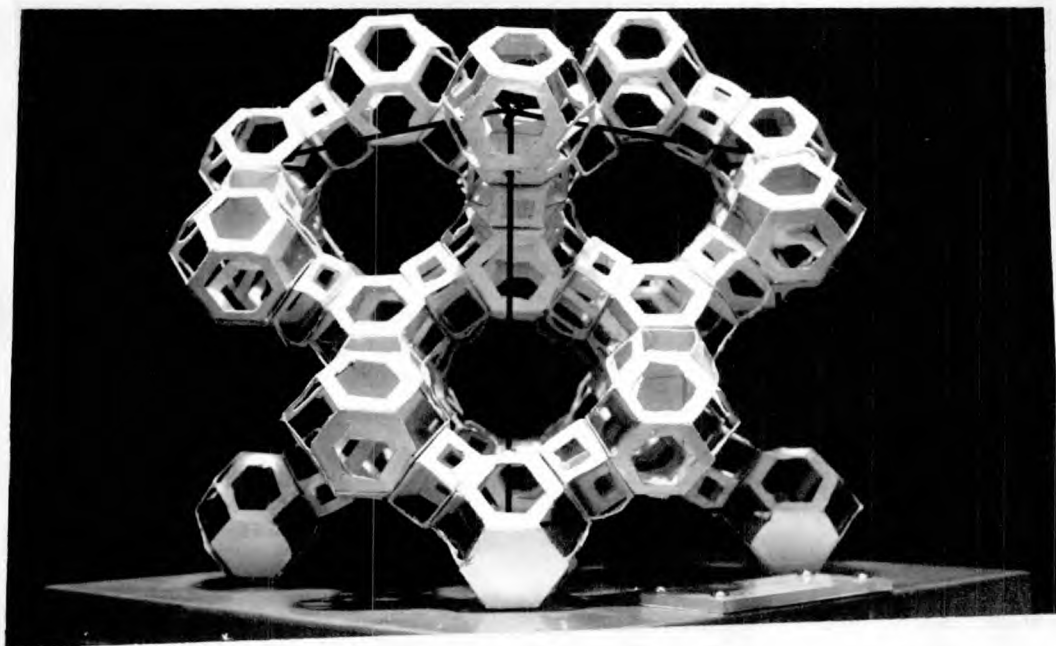


Figure 2 - Model of Faujasite



The position of the various atoms in a hydrated sample of NaX have been determined by Shoemaker and Broussard (13). Their sample had a slightly different Al/Si ratio from the sample used in these studies, containing 80 sodium atoms per unit cell against 82 in the sample used in these studies. They obtained the positions of all the silicon, aluminium and oxygen atoms but were only able to locate 48 out of 80 sodium atoms. Those located were found to be at the centres of the six-membered rings of the sodalite cages facing on to the supercages, and in the small connecting cages, giving a total of 6 cations per sodalite cage.

Exchange of the Na ions in NaX proceeds readily for all ions small enough to have access to the cationic sites. This results in a decrease in ease and extent of exchange with increase in the size of the exchanging ion. Some of the largest cations are too large to exchange at all, e.g. $\text{N}(\text{Et})_4^+$ which is unable to pass through the 12-rings. The sites need not be the same in all cases. For divalent ions the sites obviously must be different. For larger monovalent ions steric factors may cause slight shifts in position, e.g. Cs and Rb are too large to fit into the 6-ring of the sodalite cage and hence would project out from it. The unit cell size also depends slightly on the ion present and on the extent of hydration.

Breck et al (11), in a similar zeolite, the A mineral, were able to exchange, by indirect methods, hydrogen for the cation. They were able to obtain 35% exchange without collapsing the lattice; above this concentration the lattice collapsed. No direct exchange was possible as the zeolite was unstable in acid solution. Similar effects should be possible in faujasite.

1.2. Structure and Properties of Ammonia

Ammonia is a non-planar molecule with hydrogen atoms situated at three of the four corners of a tetrahedron and a lone pair of electrons on the nitrogen atom pointing towards the fourth vertex. There are two equivalent positions of the nitrogen atom on either side of the plane containing the three hydrogen atoms, and a potential energy barrier to interconversion between the two positions which gives rise to the inversion spectra; the size of the barrier has been reported by Kaplan (15) as ~6Kcal/mole. General information about ammonia may be obtained in Mellor (20).

Ammonia is a symmetrical top molecule with a symmetry number of 3. The heat capacity of the gas has been calculated by statistical mechanical methods from a knowledge of the vibration frequencies, motions of inertia, etc. by Fowler and Guggenheim (19).

Some properties of interest in this study are cited in Table 2. Spencer (21) has given a formula for calculating C_p (molar) of NH_3 in the range 291.6°K to 1000°K which is

$$C_p = 6.189 + 7.887 \cdot 10^{-5} T - 7.28 \cdot 10^{-7} T^2$$

This, in conjunction with the entropy at 25°C and 1 atm. pressure enables the entropy to be calculated at any temperature and 1 atm. pressure.

Previous Sorption Studies of Ammonia on Zeolites

Very little study has been made of systems of ammonia and zeolites. Ammonia, of course, has been studied widely as a sorbate on many other types of sorbent. Since 1943 ammonia sorption has been studied only by Barrer and co-workers briefly in the zeolites, chabazite and analcite (18), and in a synthetic species (17). Barrer and Bratt have previously studied ammonia on NaX (24).

Table 1.
Constants of Faujasite

	A° Width	$A^{\circ 3}$ Volume
Unit cell	24.8	-
Supercage	12.4 - 13	822.8 (12)
Sodalite cage	8	119 (12)
Connecting cage	-	27

Table 2.

Properties of NH_3

Tc	132.4°C.	Pc	111.5Atm. (23)
Tb	-33.1°C.	L_v at T_b . . .	5.4Kcal/mol (16)
Polarisability		$2.28 \cdot 10^{-24}$	cm. ³ /molecule
Susceptibility		$31 \cdot 10^{-30}$	c.g.s./ "
Dipole		$1.47 \cdot 10^{-18}$	e.s.u. (23)
Quadrupole		$1.5 - 0.66 \cdot 10^{-26}$	e.s.u. (22)
(Rotational state is not indicated for these values)			
Entropy/(25°C.) (1Atm.) . .		46.01 cal./mol/deg. ⁻¹	
Ionisation Potential . . .		11.2 volts. (23)	
Radius	$1.7A^{\circ}$ (24)		

1.3.1.1. THERMODYNAMICS OF SORPTION OF GASES ON SOLIDS

General:

The various approaches to the thermodynamics of sorption have been reviewed extensively in recent years by Hill (25,26,27), Everett (28,29), and Drain (30); in addition Tykodi (31) has developed an alternative and equivalent treatment. Details of the development of each approach are given in Sections 1.3.1.2-4.

The most general approach is to regard the condensed phase as a solution and treat it as an ordinary binary mixture (see ref. 25). This leads to the equations of solution thermodynamics involving partial molar quantities. Tykodi gives an equivalent treatment, based on Gibbs' approach, which gives mean molar quantities and is only slightly less exact (see Section 1.3.1.4).

All other alternative treatments assume that the sorbent is not perturbed; i.e. that only surface properties are affected, leaving the bulk of the sorbent unchanged. 'Adsorption' thermodynamics subtracts the properties of the pure sorbent from the total properties of the mixture of sorbed gas and sorbent (i.e. the condensed phase) giving expressions involving what are termed integral molar quantities for the sorbed species, which will of course contain the results of any perturbations that have occurred. An advantage in this method is that the integral quantities

obtained can be compared with those calculated by statistical mechanics for the sorbed phase. However this is not important because partial molar quantities are also obtainable using statistical mechanics.

The change in the thermodynamic functions of the sorbent can be obtained in the case of solution thermodynamics via the Gibbs Duhem relationship, as has been pointed out by Barrer (32). The corresponding changes in terms of 'adsorption' thermodynamics are given in Section 1.3.1.3.

Calorimetric Heats:

The relationships of the calorimetric heats of sorption to the isosteric heat have been discussed by Hill (25), Kington and Aston (33), Everett (28), and Drain and Morrison (34). Hill relates the isothermal cases (i.e. with and without an external work term), while Kington and Aston have related the adiabatic case, to the isosteric heat.

1.3.1.2. SOLUTION THERMODYNAMICS

The starting point is the standard equation for a solution:

$$1. \quad dE = TdS - PdV + \mu_1 dn_1 + \mu_2 dn_2$$

or

$$2. \quad dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2.$$

Since μ_1 is a function of temperature, pressure and concentration for constant n_2 , then

$$3. \quad d\mu_1 = \left(\frac{\partial \mu_1}{\partial T} \right)_{P,x} dT + \left(\frac{\partial \mu_1}{\partial P} \right)_{T,x} dP + \left(\frac{\partial \mu_1}{\partial x} \right)_{T,P} dx$$

$$4. \quad \text{Also,} \quad \left(\frac{\partial \mu_1}{\partial T} \right)_{P,x} = -\bar{S}_1 \quad \left(\frac{\partial \mu_1}{\partial P} \right)_{T,x} = \bar{V}_1 \quad (\text{see 35})$$

and therefore

$$5. \quad d\mu_1 = -\bar{S}_1 dT + \bar{V}_1 dP + \left(\frac{\partial \mu_1}{\partial x} \right) dx$$

At equilibrium $\mu_1 = \mu_g$: and for constant x :

$$6. \quad -\bar{S}_1 dT + \bar{V}_1 dP = -\tilde{S}_g dT + \tilde{V}_g dP$$

$$7. \quad \tilde{S}_g - \bar{S}_1 = (\tilde{V}_g - \bar{V}_1) \frac{dP}{dT}$$

Using the usual approximations of (1) a perfect gas, (2)

$V_g \gg V_s$, the isosteric heat is obtained.

$$8. \quad \frac{q_{st}}{R} = - \frac{\Delta H}{R} = - \left[\frac{\partial (\ln p)}{\partial (1/T)} \right]_x$$

Entropy of the sorbed phase:

At equilibrium between the gas and sorbed phase
 $\Delta\mu = 0$. Therefore,

$$9. \quad \tilde{S}_g - \bar{S}_1 = \frac{\Delta H}{T}$$

or in terms of a standard entropy, $\tilde{S}_g^{\text{ot}}$

$$10. \quad \bar{S}_1 = \tilde{S}_g^{\text{ot}} - R/m \ln p/p_0 - \frac{q_{\text{st}}}{T}.$$

To obtain the integral entropy:

This can be obtained graphically from plots of $\bar{S}_1$ v x . In practise the lack of information at very low coverages makes this procedure very inaccurate. Mathematically this corresponds to the definition for S_1 for example :

$$11. \quad \tilde{S}_1 = \frac{1}{n_0} \int_0^{n_0} \bar{S}_1 dn_1, \text{ where } n_0 = \text{total amount sorbed.}$$

Similarly other integral quantities can be obtained.

Thermodynamic properties of sorbent:

These may be obtained from the isotherms. At constant T , from the Gibbs Duhem relationship:

$$12. \quad n_1 d\mu_1 + n_2 d\mu_2 = V dP.$$

$$\text{Define } N_1 = \frac{n_1}{n_1+n_2} \quad N_2 = \frac{n_2}{n_1+n_2}$$

N_x = mole fraction

$$V_M = \text{vol. of mixed mole} = \frac{V}{N_1+N_2}.$$

Substitute these quantities in equation 12 above, and one obtains:

$$N_1 d\mu_1 + (1-N_1) d\mu_2 = V_M dP$$

On rearranging

$$13. \quad d\mu_2 = \frac{V_M dP - N_1 d\mu_1}{1 - N_1}$$

14. At equilibrium $d\mu_1 = d\mu_g$. Substituting this in equation 13 leads to

$$15. \quad d\mu_2 = \frac{V_M dP - N_1 d\mu_g}{1 - N_1}$$

On integrating this and substituting for $d\mu_g$ one obtains

$$15a. \quad \Delta\mu_2 = \mu_2 - \mu_{02} = \int_0^P \frac{V_M}{1-N_1} dP - \int_0^P \frac{N_1}{1-N_1} RT \ln p \, dp.$$

The first term on the right hand side is usually negligible compared to the second term. Also:

$$16. \quad \int_0^P \left(\frac{\partial \mu_{02}}{\partial P} \right)_T = \int_0^P V_{M_2} dP$$

$$17. \quad \Delta\mu_{02} = V_{M_2} \pi_{\text{negative}}$$

where π = ^{negative} pressure of an ~~inert~~ gas necessary to produce the same change in chemical potential of the pure sorbent as is produced by the sorbed gas.

1.3.1.3. ADSORPTION THERMODYNAMICS

Adsorption thermodynamics has been given in several forms (25,27,29). The following is the most general from which more restricted forms can be obtained. The starting point is again the standard equation for a solution.

$$1. \quad dE = TdS - PdV + \mu_1 dn_1 + \mu_2 dn_2 .$$

For the pure sorbent

$$2. \quad dE_{O_2} = TdS_{O_2} - PdV_{O_2} + \mu_{O_2} dn_2 .$$

Subtract (2) from (1) and define:

$$3. \quad dE - dE_{O_2} = dE_S; \quad dS - dS_{O_2} = dS_S \quad dV_S = dV - dV_{O_2}$$

$$\bar{\phi} = \mu_2 - \mu_{O_2}. \quad \text{Then}$$

$$4. \quad dE_S = TdS_S - PdV_S + \mu_1 dn_1 + \bar{\phi} dn_2 .$$

From this equation E_S, G_S may be defined. From equation 4, by integrating w.r.t. the extensive variables with constant intensive properties, one obtains

$$5. \quad \tilde{E}_S = T\tilde{S}_S - P\tilde{V}_S + \mu_1 n_1 + \mu_2 n_2 .$$

Obtaining the total differential of this gives rise to the Gibbs Duhem relationship, on subtracting (4) from the total differential of (5)

$$6. \quad n_1 d\mu_1 + n_2 d\bar{\phi} = \tilde{V}_S dP - \tilde{S}_S dT$$

At equilibrium $d\mu_1 = d\mu_g$ and if $d\bar{\phi} = 0$, then the following equation results on substituting for $d\mu_1$ and $d\mu_g$.

$$7. \quad -\tilde{S}_g dT + \tilde{V}_g = -\tilde{S}_S dT + \tilde{V}_S dP$$

Via the usual approximations this leads to

$$8. \quad \left[\frac{dP}{dT} \right]_{\bar{\Phi}} = \frac{\tilde{S}_g - \tilde{S}_s}{\tilde{V}_g - \tilde{V}_s} \quad 9. \quad \frac{\Delta \tilde{H}}{R} = \left[\frac{\partial(\ln p)}{\partial(1/T)} \right]_{n_1, \bar{\Phi}, n_2}$$

It is possible to obtain $\bar{\Phi}$ but this is tedious and normally inaccurate owing to experimental uncertainty at low pressures. Nevertheless, equation 9 has been used by various American workers (36).

To obtain $\bar{\Phi}$:

$\bar{\Phi}$ can be obtained from equation 6; on substituting $d\mu_g$ for $d\mu_1$ and holding the temperature constant

$$9. \quad n_2 d\bar{\Phi} = n_1 (\tilde{V}_g - \tilde{V}_s) dP$$

If now $\tilde{V}_g \gg \tilde{V}_s$,

$$10. \quad n_2 d\bar{\Phi} = n_1 \tilde{V}_g dP = n_1 kT \partial(\ln p)$$

11. On integrating (10), knowing $\bar{\Phi} = 0$ at $p = 0$, one obtains

$$12. \quad \bar{\Phi} = kT \int_0^p \frac{n_1}{n_2} \partial(\ln p) \quad (T = \text{constant})$$

This is identical to Tykodi's equation for his μ_f (see Section 1.3.1.4).

Relationship of $\bar{\Phi}$ and ψ :

ψ = Two-dimensional pressure of the sorbed phase.

If there are no perturbations of the solid, there are no changes in μ_2 save for the surface properties.

Then

$$13. \quad \bar{\Phi} n_2 = \psi A, \text{ i.e. } \bar{\Phi} = \psi \frac{A}{n_2}$$

$$14. \quad \gamma - \gamma_s = \psi$$

γ = surface tension without sorbed species

γ_s = surface tension with sorbed species.

In this case the basic thermodynamic relationship for the system is

$$15. \quad dE_s = TdS_s - PdV_s + \mu_1 dn_1 + \psi dA .$$

1.3.1.4. TYKODI'S SYSTEM

Tykodi (31) has developed Gibb's approach removing the restriction of thin layers, thus making it applicable generally to sorption (37). It is considered that the total volume of the system, the gas and the sorbate are known. The properties of the pure components are taken to be well defined functions of T and P. (The pressure dependence of the properties of fine powders may be difficult to define (because there is no truly inert gas) but this dependence is slight anyway). The starting point is the usual equation for a solution, this time of the whole system.

$$1. \quad dE = TdS - PdV + \mu_g dn_g + \mu_2 dn_2.$$

Define

$$1a. \quad \Gamma = \text{surface excess} = n_g - n_g^0$$

n_g = total amount of gas in the system

n_g^0 = total amount of gas in the gas phase.

$$1b. \quad X = n_g^0 \tilde{X}_g + n_2 \tilde{X}_{O_2} + \tilde{X}_f \quad \text{where } X \text{ is any extensive quantity, e.g. } E, S.$$

$$1c. \quad \text{Also } dX = n_g^0 d\tilde{X}_g + n_2 d\tilde{X}_{O_2} + d\tilde{X}_f, \quad \text{and } V_f = 0, \quad \text{the} \\ \text{total volume being constant.}$$

Equation 1 may be integrated to give

$$2. \quad E = TS - PV + \mu_g n_g + \mu_2 n_2.$$

For the pure components

$$3. \quad \tilde{E}_g = T\tilde{S}_g - P\tilde{V}_g + \mu_g$$

$$4. \quad \tilde{E}_{O_2} = T\tilde{S}_{O_2} - P\tilde{V}_{O_2} + \mu_{O_2}.$$

Substitute for E, S, V, n_g , as defined, by equations 1a and 1b into equation 2, then

$$5. \quad n_g^0 \tilde{E}_g + n_2 \tilde{E}_{02} + E_f = T(n_g^0 \tilde{S}_g + n_2 \tilde{S}_{02} + S_f) - \\ P(n_g \tilde{V}_g + n_2 \tilde{V}_{02}) + n_g \mu_g + n_2 \mu_2.$$

Cancelling those quantities which are equal because of equations 3 and 4, one obtains

$$6. \quad E_f = TS_f + (n_g - n_g^0) \mu_g + n_2 (\mu_2 - \mu_{02})$$

which, using 1a and defining $\mu_2 - \mu_{02} = \mu_f$, yields

$$7. \quad E_f = TS_f + \Gamma \mu_g + n_2 \mu_f.$$

Similarly substituting for dS, dE , and dV in equation 1, via equation 1c and the differential forms of 3 and 4, one obtains

$$8. \quad dE_f = TdS_f + \mu_g d\Gamma + \mu_f dn_2.$$

This in conjunction with the total differential of 7 yields

$$9. \quad 0 = S_f dT + \Gamma d\mu_g + n_2 d\mu_f.$$

Defining now integral quantities $\tilde{X}$ by

$$10. \quad (a) \tilde{X} = \frac{X}{\Gamma}, \text{ and also } (b) x = \frac{\Gamma}{n_2}, \text{ on dividing}$$

across equations 9 and 7 by Γ one obtains

$$11. \quad 0 = \tilde{S}_f dT + d\mu_g + \frac{d\mu_f}{x}, \text{ and}$$

$$12. \quad \tilde{E}_f = T\tilde{S}_f + \mu_g + \frac{\mu_f}{x}.$$

Differentiating 12, in view of equation 11, gives

$$13. \quad d\tilde{E}_f = Td\tilde{S}_f - \frac{\mu_f}{x^2} dx.$$

Heats of sorption at constant μ_f :

Because there is no pressure dependence in the excess functions $\tilde{E}_f = \tilde{H}_f$, then

$$14. \Delta H = \tilde{E}_f - \tilde{H}_g$$

Substituting for $\tilde{E}_f$ from equation 12

$$15. \Delta H = T\tilde{S}_f - T\tilde{S}_g + \frac{\mu_f}{x}$$

From equation 11 with μ_f constant

$$16. -\tilde{S}_f dT = d\mu_g = -\tilde{S}_g dT + \tilde{V}_g dP$$

which on rearrangement gives

$$17. \tilde{S}_g - \tilde{S}_f = \tilde{V}_g \frac{dP}{dT}$$

Substituting equation 17 into 15 and assuming the gas is ideal,

$$\Delta H = -R \left[\frac{d(\ln p)}{d(1/T)} \right]_{\mu_f} + \frac{\mu_f}{x}$$

From equation 11, $d\mu_f$ is given by

$$18. d\mu_f = -x(d\mu_g + \tilde{S}_f dT).$$

Substituting for $d\mu_g$ and assuming a perfect gas one obtains for a constant temperature,

$$19. d\mu_f = -xRT \partial \ln p, \text{ or}$$

$$20. \mu_f = -RT \int_0^p x \partial \ln p.$$

Using equation 20 in conjunction with 17, the entropy changes can be obtained, and hence all the other functions for the system. This is open to the same

objections as adsorption thermodynamics, but it does show the effect of changes in the thermodynamic functions of the sorbent on the quantities measured.

N.B. This system is almost exact and quite general; it is not confined to thin layers as was Gibbs original system.

1.3.2.1. PHYSICAL MODELS OF THE SORBED STATE

General:

The statistical mechanics of sorption on uniform surfaces has been discussed recently by Garden, Kington and Laing (38) and Hill (39,40,41) in a series of papers. Earlier Fowler and Guggenheim (42) had derived isotherms for most of the simple cases. In the following section the partition functions for various models are given and the isotherm and configurational entropy are derived from them. Critical examination of the models is discussed in relation to experimental isotherms in a later section. The entropy, which can be obtained from the isosteric heat (see Section 1.3.1.2) in conjunction with the configurational entropy can be of great use in deciding between the various possible models.

Throughout the following description it is assumed that the sorbent is unperturbed by the sorbate. Whether this is true or not depends on the system considered. For argon in zeolites it is probably a reasonable approximation but for chemisorption it is most unreal. Sorption of substances such as water or ammonia in zeolites lie in between these two cases and this assumption may or may not be true. Also it is assumed that j , the internal partition function of the sorbed molecule, is independent of coverage.

The sorbed phase may be localised or mobile, depending on the ability of the sorbed molecules to pass freely over the surface. There are two possible causes of localisation: the first being that the sorbed molecules lack sufficient thermal energy to overcome surface energy barriers. This has been shown by Hill (40) to be possible only at very low temperatures. The second cause is the mutual caging effect of the sorbed molecules on each other. Then the situation is somewhat similar to a dense gas or a fluid, with the molecule confined to its cell by its neighbours, though occasionally able to escape from it.

In the following sections the models for homogeneous surfaces are divided into localised and mobile, each considered first as an ideal case without any interactions between the sorbed molecules, and then with various approximations to allow for the mutual interactions of the sorbed molecules. In each case the partition function is set up and from it are derived the isotherm equation, the entropies (molar and differential) and the equation of state for the sorbed phase. Heterogeneous surfaces will be discussed in a later section.

1.3.2.2.1. LOCALISED MODELS: (a) IDEAL CASE.

The following assumptions are made (42):

- (1) Sorption occurs at M independent and equivalent sites.
- (2) The sorbed molecules are localised on these sites.
- (3) There are no interactions between the sorbed molecules.

The partition function is given by

$$1. \quad Q = a^N \frac{M!}{(M-N)!N!}$$

(The combinatorial term comes from the number of distinguishable ways of arranging N molecules on M sites).

The chemical potential is given by

$$2. \quad -\frac{\mu}{kT} = \frac{\partial(\ln Q)}{\partial N}$$

Equating this with μ_g leads to the Langmuir isotherm:

$$3. \quad p = K_L \frac{\theta}{1-\theta} \quad \text{or} \quad \theta = \frac{p}{K_L + p}$$

Entropy:

The entropy is given by

$$4. \quad \tilde{S} = k \ln Q + kT \frac{\partial(\ln Q)}{\partial T}$$

Separating out the terms which depend on the configuration only leads to $\tilde{S}_c$

$$5. \quad \tilde{S}_c = R \left(\frac{1}{\theta} \ln \frac{1}{\theta} - \frac{1-\theta}{\theta} \ln \frac{1-\theta}{\theta} \right)$$

Differentiating this w.r.t. to N gives

$$6. \quad \bar{S}_c = -R \ln \frac{\theta}{1-\theta}$$

Finally the equation of state is given by

$$7. \quad \frac{\phi}{kT} = \frac{\partial(\ln Q)}{\partial M} = \ln(1-\theta)$$

1.3.2.2.2. LOCALISED MODEL WITH INTERACTIONS (b).

No exact treatment of interaction between sorbed molecules is possible at present. Restricting interactions to nearest neighbours, approximate methods are available. Two such approximations are (43):

(i) Bragg Williams: this assumes random distribution of the molecules.

(ii) Quasi Chemical: this takes account of the variation in energy of the sites due to interactions with the molecules sorbed on neighbouring sites.

In both cases it is assumed that the interaction energy is additive and constant.

(i) Bragg-Williams approximation:

The partition function is given by:

$$8. \quad Q = a^N \frac{M!}{(M-N)!N!} e^{-\frac{N_{11}w}{kT}}$$

Assuming a random distribution of N molecules on M sites,

$$9. \quad N_{11} = \frac{N}{2} \frac{CN}{M}. \quad \text{Substituting this in equation 8}$$

$$10. \quad \text{gives} \quad Q = a^N \frac{M!}{(M-N)!N!} e^{-\frac{CN^2w}{2MkT}}$$

In the usual way $-\frac{\mu}{kT} = \frac{\partial(\ln Q)}{\partial N}$, and equating this with μ_g an isotherm is obtained.

$$11. \quad p = K_{Bw} \frac{\theta}{1-\theta} e^{\frac{-\theta Cw}{kT}}$$

The entropy (38) can be obtained from equation 10, and on separating the configurational terms

$$12. \quad \tilde{S}_c = kN \left(\frac{1}{\theta} \ln \frac{1}{\theta} - \frac{1-\theta}{\theta} \ln \left(\frac{1-\theta}{\theta} \right) \right)$$

Differentiating $\tilde{S}_c$ with respect to N gives

$$13. \quad \bar{S}_c = -Nk \ln \frac{\theta}{1-\theta}$$

1.3.2.2.3. QUASI CHEMICAL APPROXIMATION (43)

The first problem is to calculate the maximum possible number of distinguishable pairs of sites formed by N molecules distributed on M sites, each of coordination number C . There are four types of distinguishable pairs of sites, each related to M , N , and N_{01} , as below.*

$$N_{11}: \quad CN = 2N_{11} + N_{01}.$$

$$N_{00}: \quad C(M-N) = 2N_{00} + N_{01}, \text{ i.e. two adjacent sites, both unoccupied.}$$

$$\frac{N_{01}}{2}: \quad \text{no. of pairs of sites which have one site occupied and one unoccupied.}$$

These give rise to two distinguishable configurations, N_{01} and N_{10} .

Then the total number of distinguishable ways of arranging these pairs of sites, assuming that they are independent, is

$$14. \quad w(M, N, N_{01}) = \frac{\left(\frac{CM}{2}\right)!}{N_{11}! N_{00}! \left[\left(\frac{N_{01}}{2}\right)!\right]^2}$$

This overestimates the actual number of configurations possible. To correct for this sum both sides over all

* N_{01} = no. of sites with one adjacent site occupied.

N_{11} = no. of pairs of sites with both sites occupied.

N_{00} = no. of pairs of sites with both sites unoccupied.

N_{01} ; this gives

$$15. \quad \sum_{N_{01}} w(M, N, N_{01}) = \frac{M!}{(M-N)!N!} = C(NM) \sum_{N_{01}} w(M, N, N_{01})$$

The sum for w is replaced by the largest term in $\ln w$ (obtained from $\frac{\partial(\ln w)}{\partial N_{01}} = 0$).

16. This gives

$$(a) \quad C(N, M) = \left(\frac{M!}{(M-N)!N!} \right)^{1-C}; \quad (b) \quad N_{01}^* = \frac{CN(M-N)}{N}$$

The partition function is now given by

$$17. \quad Q = \sum_{N_{01}} \left(\frac{M!}{(M-N)!N!} \right)^{1-C} \frac{\left(\frac{CM}{2} \right)! \left(a' e^{\frac{U_0}{kT}} \right)^N e^{\frac{N_{01} w}{2kT}}}{\left(\frac{CN}{2} - \frac{N_{01}}{2} \right)! \left(\frac{C(M-N)}{2} - \frac{N_{01}}{2} \right)! \left(\frac{N_{01}}{2}! \right)^2} e^{\frac{NCw}{kT}}$$

The sum in equation 17 is replaced by the maximum term, obtained as below.

$$18. \quad \ln Q = \left(\ln a' e^{\frac{U_0}{kT}} e^{\frac{Cw}{2kT}} \right)^N + \ln t(N_{01}, M, N, T) e^{\frac{wN_{01}}{kT}}$$

$$19. \quad \frac{\partial \ln t(N_{01}^+, M, N, T)}{\partial N_{01}} = 0 \text{ for the maximum term, } N_{01}^+.$$

This results in:

$$20. \quad \frac{(\theta - \alpha)(1 - \alpha - \theta)}{\alpha^2} = e^{-\frac{Cw}{kT}} \quad \text{where}$$

$$21. \quad \alpha = \frac{N_{01}^+}{CM} \quad \theta = \frac{N}{M}$$

On solving equation 20

$$22. \quad \frac{1}{\alpha} = \frac{2\theta(1-\theta)}{1+\beta} \quad \text{where} \quad \beta = \sqrt{1 - 4\theta(1-\theta)(1 - e^{-\frac{Cw}{kT}})}$$

The sign for β is determined from the case of $w=0$.

The chemical potential is obtained as usual.

$$23. \quad -\frac{\mu}{kT} = \frac{\partial(\ln Q)}{\partial N} = \ln a' e^{\frac{U_0}{kT} - \frac{Cw}{kT}} + (1-C) \ln \left(\frac{N}{M-N} \right) \\ - \frac{C}{2} \ln \left(\frac{CN}{2} - \frac{N_{01}^+}{2} \right) + \frac{C}{2} \ln \left(\frac{C(M-N)}{2} - \frac{N_{01}^+}{2} \right)$$

At equilibrium, $\mu = \mu_g = kT \ln \frac{p}{p_0}$.

The isotherm equation is then given, on substituting α and θ for M , N_{01} , etc., by

$$24. \quad p = \frac{p_0}{a' e^{\frac{U_0}{kT} - \frac{Cw}{kT}}} \left(\frac{\theta}{1-\theta} \right)^{1-C} \left(\frac{\theta-\alpha}{1-\theta-\alpha} \right)^{C/2} \\ = K_{QC} \left(\frac{\theta}{1-\theta} \right)^{1-C} \left(\frac{\theta-\alpha}{1-\theta-\alpha} \right)^{C/2}$$

Substituting for α from equation 22

$$26. \quad p = K_{QC} \left(\frac{\theta}{1-\theta} \right) \left(\frac{((\beta-1)+2\theta)(1-\theta)}{(\beta+1-2\theta)\theta} \right)^{C/2}$$

The entropy can be obtained from equation 17 and is given by

$$27. \quad \bar{S}_c = -R \ln \frac{\theta}{1-\theta} - CR \ln \frac{2(1-\theta)}{(\beta+1-2\theta)} + \frac{w}{T} \left(\frac{\beta-1+2\theta}{\beta} \right)$$

The difference between this entropy and the ideal case where $\bar{S}_c = -R \ln \frac{\theta}{1-\theta}$ has been considered for argon in chabazite and was found to be slight (38).

1.3.2.2.4. B.E.T. Isotherm

Brunauer, Emmett and Teller (45) developed Langmuir's approach to include multilayer formation. They assumed in addition to Langmuir's assumptions that

- (1) molecules are sorbed directly above first layer molecules;
- (2) the heat of sorption is the same in all layers other than the first and is equal to the latent heat of evaporation;
- (3) there are no lateral interactions between molecules in the same layer.

On the basis of these assumptions they derived the following isotherm by a kinetic argument:

$$1. \quad \theta = \frac{C \frac{p}{p_0}}{\left(1 - \frac{p}{p_0}\right) \left(1 - \frac{p}{p_0} + \frac{Cp}{p_0}\right)}$$

where C is the B.E.T. constant. Hill (39) later gave a statistical derivation. Halsey (106) later still developed the isotherm for multilayers differently by assuming that sorption of higher layers occurs only when there are groups of three molecules together in the first layer and that the energy of molecules in higher layers is

$$\frac{E_L}{2}.$$

The B.E.T. picture is a highly unrealistic model which cannot be expected to give a rigorous interpretation of thermodynamic properties of the sorbed phase. Aston and Kington (96) have shown that this model does not predict reasonable entropies at coverages less than a monolayer. However, it is the only approach which can, with suitable modifications, represent all five types of isotherms (as classified by Brunauer) which occur in sorption. It is therefore a useful qualitative approach.

1.3.2.3.1. MOBILE MODELS WITHOUT INTERACTIONS (38)

The following assumptions are made:

- (1) The molecules can move freely over the surface.
- (2) Each molecule excludes a fixed volume from its fellows.

The cases of one and two degrees of translational freedom are very similar, differing only in the constants involved.

Two-dimensional translational freedom:

The partition function is

$$1. \quad Q = \frac{a^N}{N!} \quad 2. \quad a = q_x q_y q_z j e^{\frac{U_0}{kT}}$$

$$3. \quad q_x q_y = \frac{(2\pi mkT)}{h^2} A_f$$

q_x and q_y are partition functions for translational motion along the surface. A_f is the free area and is given by

4. $A_f = \beta(N_s - N)$ where β is the area of cross section of a molecule and N_s the saturation value for N at a given temperature. The chemical potential is given by

$$5. \quad \frac{\mu}{kT} = \frac{\partial(\ln Q)}{\partial N} = \ln a + N \frac{\partial(\ln a)}{\partial N} - \ln N$$

By equating this with μ_g the isotherm is obtained:

$$6. \quad p = K_v \frac{\theta}{1-\theta} e^{\frac{\theta}{1-\theta}}$$

This is a Volmer type equation.

Entropy of the sorbed phase:

The entropy is given by

$$7. \quad \tilde{S} = kT \frac{\partial(\ln Q)}{\partial T} + k \ln Q$$

Separating all terms that depend on known or measured quantities

$$8. \quad {}_2\tilde{S}_T = R \left[\ln M T \beta - \ln \frac{\theta}{1-\theta} + 2 + \ln \left(\frac{2\pi k}{N_0 h^2} \right) \right]$$

Differentiating w.r.t. N gives

$$9. \quad {}_2\bar{S}_T = R \left[\ln M T \beta - \ln \frac{\theta}{1-\theta} - \frac{\theta}{1-\theta} + 1 + \ln \left(\frac{2\pi k}{N_0 h^2} \right) \right]$$

Finally the equation of state is given by

$$10. \quad \varphi = kT \frac{\partial(\ln Q)}{\partial A} = \frac{NkT}{\beta(N_s - N)}$$

$$11. \quad = \varphi(A - \beta N) = RT.$$

1.3.2.3.2. ONE-DIMENSIONAL TRANSLATIONAL FREEDOM

In this case there is translational motion in one direction only, i.e.

$$q_x = \frac{(2\pi mkT)^{\frac{1}{2}}}{h} \ell_f$$

where ℓ_f is the free length available to each molecule.

As the dependence on N and T is the same for the partition function in this case and the previous one, one obtains the same isotherm. The molar entropy is:

$$12. \quad {}_1\bar{S}_T = R \left[\ln(MT)^{\frac{1}{2}} \ell + \ln \frac{\theta}{1-\theta} + \frac{3}{2} + \ln \left(\frac{2\pi k}{N_0 h^2} \right)^{\frac{1}{2}} \right]$$

The differential entropy is given by

$$13. \quad {}_1\bar{S}_T = R \left[\ln(MT)^{\frac{1}{2}} \ell + \ln \left(\frac{2\pi k}{N_0 h^2} \right)^{\frac{1}{2}} - \ln \frac{\theta}{1-\theta} - \frac{\theta}{1-\theta} + \frac{1}{2} \right].$$

1.3.2.3.3. MOBILE MODEL WITH MOLECULAR INTERACTIONS

In deriving the isotherm below, the following assumptions are made.

- (1) The molecules are confined to a monolayer.
- (2) A hard sphere model is appropriate for the sorbed molecules.

The partition function is given by

$$14. \quad Q = \frac{a^N}{N!} \quad a = q_z \left(\frac{2\pi kT}{h^2} \right) A_f \cdot j \cdot e^{\frac{U_0}{kT}} e^{\frac{E_i}{kT}}$$

$$15. \quad A_f = A - N\beta$$

$$16. \quad E_i = a \frac{N}{A}$$

α and β are the two-dimensional van der Waals constants.

Substituting these values into 14 above leads to

$$17. \quad Q = \left[\frac{Z(A-N\beta)e^{\frac{\alpha N}{kTA}}}{N!} \right]^N$$

where Z is the remainder of a in 14 on taking out

$$\left[(A - N\beta)e^{\frac{\alpha N}{kTA}} \right].$$

The isotherm is obtained by equating μ obtained from this with μ_g , giving

$$18. \quad p = K_{vdw} \frac{\theta}{1-\theta} e^{\frac{\theta}{1-\theta} - \frac{\alpha\theta}{\beta kT}}$$

Entropy:

The entropy is identical with that of the mobile two dimensional case in Section 1.3.2.3.1, the temperature coefficient being eliminated.

Equation of State:

This is obtained by differentiating $\ln Q$ w.r.t. A giving

$$19. \quad \frac{p}{kT} = \frac{\partial \ln Q}{\partial A} = \frac{N}{(A - N\alpha)} - \frac{\alpha N^2}{kTA^2}$$

On rearrangement this gives

$$20. \quad \left[p + \frac{\alpha N^2}{A^2} \right] (A - N\beta) = NkT,$$

the van der Waals equation for the monolayer.

Relationship of a and β to the three-dimensional van der Waals constants, a and b .

In the case of a mobile monolayer and a hard sphere model

$$21. (a) \beta = \pi \frac{r^{*2}}{2} \quad \text{while} \quad (b) \quad b = \frac{2}{3} \pi r^{*3}$$

If in addition it is assumed that the interaction is between non polar molecules and is additive

$$22. (a) a = \frac{\pi \epsilon r^{*2}}{4} \quad \text{while} \quad (b) \quad a = \frac{2\pi \epsilon r^{*3}}{3}$$

Combining equations

$$23. \quad \frac{a}{b} = \frac{a}{2\beta} \quad .$$

1.3.2.4. Changes of Phase

All the models so far considered which take interactions in account predict first order phase changes in monolayer sorption. The critical amount sorbed corresponds to $\theta = \frac{1}{2}$; the critical temperature is obtained from

$$1. \quad \partial \left(\frac{\bar{\Phi}}{kT} \right) / \partial T = 0$$

T_c depends, inter alia, on c the co-ordination number for a particular model. In the past there has been little evidence to show that changes of phase occur in gases sorbed on solids, though it is well established for sorption on liquids. Previous to 1950 Harkins and Jura were the only experimenters who reported evidence on this point. Since then changes of phase have been found for sorption on several solids. For the change to be observable the sorbent must be energetically homogeneous; the lack of truly homogeneous sorbents has been the main reason why this phenomenon had not been confirmed earlier. Recently Graham (74) obtained definite evidence of two dimensional condensation in a monolayer for sorption of C_2H_6 and CCl_4 on P.33, a homogeneous carbon. Very accurate studies have been made by Fisher and MacMillan (72,73) for Kr and N_2 on NaBr

crystals, which were examined repeatedly after successive heat treatments of the crystals. The heat treatment eliminated any heterogeneity in the crystals. Very well defined phase changes were observable once the sorbents were truly homogeneous for A and Kr; N₂ showed no phase change and no doubt the presence of a quadrupole in N₂ and the field near the crystal are partly responsible for this.

The values of T_c predicted by the Bragg Williams and Quasi Chemical equations are in varying degrees in error. The transition condition for a monolayer on a square lattice has been obtained exactly and is given by $\frac{cW}{kT_c} = -7.05$ (43); the values predicted by the Bragg Williams and Quasi Chemical equations for a square lattice (with $c=4$) are -4 and -5.5 respectively. In view of the simplicity of the equations the agreement is surprisingly good.

1.3.2.5. Heterogeneous Surfaces

The theory of sorption on heterogeneous surfaces is very much less advanced than that for homogeneous surfaces. Tompkins (75,76) has discussed various limiting cases which lead to approximate isotherms. Halsey and Taylor (99) applied Langmuir's model to sorption on a series of sites of equal energy of sorption and obtained the following equation:

$$1. \quad \theta = \int \frac{N_E d_E}{1 + \frac{K_E}{p}} \quad \text{where } K_E = e^{\frac{T\Delta S_E - E}{kT}}$$

To take the argument any further assumptions must be made concerning (i) the limits of the integration, (ii) the form of N_E , the site distribution, and (iii) the dependence of K_E on E . Originally Halsey and Taylor assumed ΔS_E independent of E but later Halsey (100) modified the approach to allow an empirical linear variation of ΔS_E with E : $\Delta S_E = \Delta S_0 + rE$. The limits of the integration were chosen as $+\infty$ and $-\infty$ for mathematical convenience. This has been criticised by Hill who maintained it implied sorption on sites with a repulsive energy; however, Hepler (101) showed, mathematically, that the negative region contributes a negligible amount to the total integral.

The distribution function chosen was:

$$2. \quad N_E = e^{-\frac{E}{E_m}}$$

On carrying out the integration the Freundlich isotherm results:

$$3. \quad \theta = \left(\frac{p}{p_0}\right)^{\frac{E_m}{kT} (1-rT)} c E_m .$$

Sips (102) and Honig (52) have given methods of inverting equation 1 to obtain the energy site distribution, assuming localised sorption; an interpolation formula which can represent the isotherm data accurately is required before this approach may be applied.

1.3.3.1.1. Alternative Approaches: Equations of State

There are two types of "equations of state" used in sorption studies. The first is a relationship of the form $f(\Phi, x, T)$ for the sorbed phase. (Alternatively ψ may replace Φ in $f(\Phi, x, T)$). This type of equation arises from the Gibbs Duhem relationship, and has been discussed in Sections 1.3.1.3 and 1.3.2.2-3. The second approach is to assume an equation of state for the gas and the sorbed phase and assume that the change in free energy of the gas on sorption is given by the work done in compressing the gas plus the decrease in the potential energy of the gas (the sorbent being assumed inert).

$$1. \quad \text{i.e.} \quad \Delta G = U + \int_{P_g}^{P_s} V dP$$

P_s = pressure developed in the intracrystalline
volume

P_g = equilibrium gas pressure.

At equilibrium $\Delta G = 0$, so

$$2. \quad U = - \int_{P_g}^{P_s} V dP$$

where U is the decrease in potential energy of the sorbate on sorption.

An equation of state is now introduced relating P to V and the integration carried out. This has been

done for several equations of state (44,48,49). In the following section the approach using a modified van der Waals equation is developed. However, none of these treatments can be expected to give better results in the sorbed phase than they do in the gas phase at comparable concentrations. Van der Waals type equation is chosen because it is accurate up to the critical region and hence is the most promising (50), and has virial coefficients which have a physical meaning.

1.3.3.1.2. Modified van der Waals Equation (44)

This equation of state is

$$3. \quad \left(P + \frac{a}{V^2} + \frac{a'}{V^3}\right)(V - b - \frac{b'}{V}) = RT$$

The constant a' is introduced to allow the internal energy to vary linearly with the temperature and quadratically with the density as is the actual experimental case. The term $\frac{b'}{V}$ is introduced to allow the virial form of van der Waals equation (with $a = 0$) to follow closely the rigorously established virial equation for gases.

dP is obtained from equation 3

$$4. \quad dP = RT \left[- \frac{V^2 + b'}{(V^2 - bV + b')^2} - \frac{2a}{V^3} - \frac{3a'}{V^4} \right]$$

Substitution of this into equation 1, and changing the

limits of integration to V_s and V_g gives, on taking logs on both sides

$$5. \quad V_g = (V_s^2 - V_s b + b')^{\frac{1}{2}} \exp \left[\frac{2a}{RTV_s} + \frac{3a'}{2RTV_s} - \frac{\emptyset}{RT} - \frac{bV_s - b'}{V_s^2 - bV_s + b'} \right. \\ \left. - \left[\frac{1}{2V_s - b} - \frac{1}{3} \frac{4b' - b^2}{2V_s - b} + \frac{1}{5} \frac{(4b' - b^2)^2}{2V_s - b} \right] \right]$$

At sufficiently low pressures this reduces to

$$6. \quad V_g = V_s e^{-\frac{\emptyset}{RT}}$$

where V_g is related to P_g by $P_g V_g = RT$.^(6a) On taking logs on both sides of 6, and substituting from 6a, on differentiating w.r.t. T one obtains

$$7. \quad - \frac{\partial(\ln P_g)}{\partial T} = - \frac{\partial \ln RT}{\partial T} + \frac{\emptyset}{RT^2} = - \frac{\Delta H^\ell}{RT^2} \quad \text{or}$$

$$8. \quad RT + \Delta H^\ell = \emptyset \quad (\text{see Section 1.3.1}),$$

where ΔH^ℓ is the limiting value of ΔH at low coverage.

Using equation 5 for various values of V_s , $\emptyset$ may be calculated and compared to the value obtained from 8.

There is a difference, which is attributed to there being an entropy change on sorption greater than that predicted by equation 5. This is attributed to a loss of thermal entropy of the sorbate in the restricted intracrystalline environment. This is corrected by introducing a term ΔS_e , calculated from the difference between the two values,

calculated from eqs. 8 and 5, for a particular temperature and pressure. Equation 6 now reads

$$V_g = V_s \exp \left(\frac{\Delta S_e}{R} - \frac{\phi}{RT} \right)$$

In addition it was found necessary to introduce a correction for the smaller coordination number possible for a sorbed molecule with its next neighbours in the restricted intracrystalline environment. This introduces a modification in the interaction energy terms so that eq. 3 is modified to

$$9. \quad \left[P + \frac{n}{12} \left(\frac{a}{V_s^2} + \frac{a'}{V_s^3} \right) \right] \left(V - b + \frac{b'}{V} \right) = RT$$

where n is the coordination number of the sorbed molecule in the crystal, twelve being the coordination number of a molecule in the gas phase (approx.). This correction alters the predicted entropy change by a negligible amount. Equation 5 now reads

$$10. \quad V_g = (V_s^2 - V_s b + b')^{\frac{1}{2}} \exp \left(\frac{2a}{RTV_s} + \frac{3a'}{2RTV_s} \right) \frac{n}{12} - \frac{\phi}{RT} - \frac{bV_s - b'}{V_s^2 - bV_s + b'} + \frac{\Delta S_e}{R} - \left[\frac{1}{2V_s - b} - \frac{1}{3} \frac{4b' - b^2}{2V_s - b} \dots \dots \dots \right]$$

This equation may now be used to calculate the isotherm, P_g being obtained from V_g assuming the gas to be ideal. It gave good agreement with the experimental isotherms in the cases considered for densities up to the critical

density (A in Na and Ba-near faujasite and N₂ in K-near faujasite).

1.3.3.2.1. Polanyi Potential Theory

The Polanyi potential (45) theory equates the adsorption potential with the work done in compressing the gas from its state in the gas phase to its state in the sorbed phase,

$$1. \quad \text{i.e.} \quad \epsilon_i = - \int_{P_0}^{P_g} V dP$$

where P_g and P_0 are the pressure at equilibrium and the saturated vapour pressure of the liquid at the temperature of the experiment. Each potential value encloses between its boundary and the sor bent a volume V_i ; if now it is assumed that ϵ_i is independent of temperature, then so is V_i and the variation of ϵ_i throughout the adsorption space is also temperature independent.

Assuming also that the gas is below its critical temperature, that the vapour behaves as a perfect gas, and the liquid in the sorbed phase is incompressible, then ϵ_i is given by

$$2. \quad \epsilon_i = \int_{P_g}^{P_0} \frac{RT}{P} dP = RT \ln \frac{P_0}{P_g}$$

neglecting the work done in creating a liquid surface.

The volume V_i is given by

$$3. \quad V_i \delta_T = x_i$$

where δ_T is the density of the liquid at the experimental temperature. A plot of V_i against $\mathcal{C}_i$ may then be made, called a characteristic curve, which should be temperature independent. This enables the temperature dependence of sorption to be predicted from one isotherm and a knowledge of the liquid density in the temperature range considered. Its application and accuracy has been discussed extensively by Brunauer (45). It has also been applied to sorption of several alkyl halides on zeolites, by Barrer and Brook (7) who found that the more polar the sorbate the greater the deviation from the values predicted by the theory, as would be expected when polar forces, which are temperature dependent, are involved.

Corrections for non-ideality of the gas and compressibility of the liquid can be made but they do not alter the results very much.

In passing it should be noted that the Polanyi potential is approximately equal to the difference in free energy of the sorbate in the liquid phase and in the sorbed phase. Constant $\mathcal{C}_i$ may be thought of as a constant free energy difference. In the following section the variation of the amount sorbed with temperature at constant

free energy difference, or ϵ_i , is obtained in terms of the coefficient of expansion of the intracrystalline fluid.

1.3.3.2.2. Thermal Expansion of the Sorbed Phase

The thermal expansion of the sorbed phase at constant ϵ_i is obtained as follows for intracrystalline sorbed phase (46). The amount sorbed, x_i , is related to the density δ by

$$3. \quad x_i = V_i \delta$$

For intracrystalline fluids, near saturation V_i is the total intracrystalline volume. Differentiating eq. 3 w.r.t. T only gives

$$4. \quad \left(\frac{\partial x_i}{\partial T} \right)_{\epsilon_i} = +V_i \left(\frac{\partial \delta}{\partial T} \right)_{\epsilon_i} + \delta \left(\frac{\partial V_i}{\partial T} \right)_{\epsilon_i}$$

Dividing across equation 4 by $V_i \delta$ one obtains

$$5. \quad \frac{1}{x} \left(\frac{\partial x_i}{\partial T} \right)_{\epsilon_i} = \frac{1}{\delta} \left(\frac{\partial \delta}{\partial T} \right)_{\epsilon_i} + \frac{1}{V_i} \left(\frac{\partial V_i}{\partial T} \right)_{\epsilon_i}$$

The expansivities, α and α_i , of the intracrystalline fluid and the interstitial volume are defined by

$$6. \quad (a) \quad \alpha = - \frac{1}{\delta} \left(\frac{\partial \delta}{\partial T} \right)_{\epsilon_i} ; \quad (b) \quad \alpha_i = \frac{1}{V_i} \left(\frac{\partial V_i}{\partial T} \right)_{\epsilon_i}$$

δ , being assumed incompressible, is dependent only on the

temperature, and one can write

$$7. \quad \left(\frac{\partial \epsilon}{\partial T} \right)_{\epsilon_i} = \left(\frac{d\epsilon}{dT} \right)_{\epsilon_i}$$

x_i also depends solely on the temperature at constant ϵ_i ,
so

$$8. \quad \left(\frac{\partial x_i}{\partial T} \right)_{\epsilon_i} = \left(\frac{dx_i}{dT} \right)_{\epsilon_i}.$$

However, V_i is $f(x, T, \epsilon_i)$.

$$9. \quad \text{so} \quad \left(\frac{\partial V_i}{\partial T} \right)_{\epsilon_i} \neq \left(\frac{dV_i}{dT} \right)_{\epsilon_i}.$$

Accordingly equation 5 becomes

$$10. \quad -\frac{1}{x} \left(\frac{dx}{dT} \right)_{\epsilon_i} = \alpha - \frac{1}{V_i} \left(\frac{\partial V_i}{\partial T} \right)_{\epsilon_i}.$$

In general the coefficient of expansion is close to but below the value for that of the liquid as would be expected from equation 10.

1.3.3.3. Everett's Isotherm

Everett (29) has proposed a general isotherm, based on the difference of free energy of the sorbate in the crystal and in a standard state in the gas phase. At equilibrium

$$1. \quad \Delta\mu^0 = \Delta H^0 - T\Delta S^0.$$

Assuming a perfect gas, as usual

$$2. \quad \Delta\mu^0 = RT \ln \frac{p}{p_0}, \quad \Delta H^0 = \Delta H.$$

Substituting these values into equation 1, and taking antilogs on both sides

$$3. \quad p = p_0 e^{\frac{\Delta H}{RT} - \frac{\Delta S^0}{R}}$$

If now it is assumed that ΔS^0 contains a $-R \ln \frac{\theta}{1-\theta}$ term, ΔS^0 may be written as

$$4. \quad \Delta S^0 = -R \ln \frac{\theta}{1-\theta} + \Delta S^{0*}$$

where ΔS^{0*} is the remainder of the entropy which may also be a function of θ .

Equation 3 becomes, on substituting for ΔS^0 from 4,

$$5. \quad p = p_0 e^{\frac{\Delta H}{RT} - \frac{\Delta S^{0*}}{R}} \frac{\theta}{1-\theta}$$

If now ΔH and ΔS^{0*} are independent of θ , or vary with θ in opposite senses so that their difference

remains constant, then (5) reduces to the Langmuir isotherm.

For localised models on homogeneous surfaces (4) corresponds to separating the entropy into configurational and thermal entropy terms. (With or without molecular interactions $-R\ln \frac{\theta}{1-\theta}$ is a good approximation to the configurational entropy (see Section 1.3.2) in this case). In addition Everett proposes that any sorption data may be conveniently examined in terms of the ideal localised model and excess functions. In the case of heterogeneous surfaces the difficulty of obtaining, theoretically, a separable $-R\ln \frac{\theta}{1-\theta}$ term is noted; in this case it is interesting to note that heterogeneous systems have been quite successfully analysed in terms of equation 5 (e.g. iodine on NaX (47)).

1.4.1. Intermolecular Forces.

General

Intermolecular forces between molecules arise from the motion and alignment of electrons. However, because the forces are so complex, it is convenient to divide them up into dispersion, repulsion and electrostatic forces (the latter includes polarisation effects as well as electrical multipole interactions). The same forces which occur between sorbate molecules are responsible for the attraction between the sorbate molecules and the sorbent. In the following sections the causes of, and formulae to represent, the interactions between molecules are indicated; the limitations of the formulae are discussed. These are then applied to obtain the total interaction of a probe molecule with a massive sorbent.

Dispersion forces

These arise from the motion of electrons in the molecules which give rise to fluctuating multipoles. The coupling of these multipoles in adjacent molecules produces an attraction between them, the energy of which is given by an expression of the form (52):

$$1. \quad U(r) = - \frac{C_1}{r^6} - \frac{C_2}{r^8} - \frac{C_3}{r^{10}}$$

(i) (ii) (iii)

(the terms are in order of decreasing magnitude)

- (i) arises from fluctuating dipole/dipole coupling
- (ii) arises from fluctuating dipole/quadrupole coupling
- (iii) arises from fluctuating quadrupole/quadrupole coupling.

The first term is usually the only one considered in calculating the dispersion energy, and the other two being ignored. However the second term has been estimated to be, at the equilibrium distance, as much as 15-30% of the first term (de Boer (51)); Kiselev (56) estimates it at 10% of the first term. In all that follows C_2 and C_3 are assumed to be zero.

Repulsion forces

From wave mechanics these should vary exponentially with a high power of the distance. It is more convenient, and hardly less accurate, except for very short distances, to use a high inverse power of r , usually r^{-12} :

$$2. \quad U_r = + \frac{C_4}{r^{12}}$$

Combining this with the dispersion energy expression, $\frac{C_1}{r^6}$, and using the fact that at the equilibrium distance $\frac{dU}{dr} = 0$, the following relationship is obtained:

$$3. \quad 2C_4 = C_1 r_e^6 .$$

The dispersion and repulsion energy expressions may be

combined to give a modified Lennard Jones 6-12 potential for the total interaction of the two types of forces.

$$4. \quad U(r) = C_1 \left[\frac{1}{r^6} - \frac{r_e^6}{2r^{12}} \right]$$

Two important properties of the dispersion and repulsion forces are that they are nearly additive and temperature independent.

Approximate forms of C_1

London (55) derived a formula for C_1 from considering the interaction of two electrons, oscillating quantally with different frequencies. The formulae are

$$5. \quad C_1 = \frac{3}{2} \alpha_1 \alpha_2 \frac{h\nu_1 h\nu_2}{h\nu_1 + h\nu_2}$$

or

$$6. \quad C_1 = \frac{3}{2} \alpha_1 \alpha_2 \frac{E_1 E_2}{E_1 + E_2}$$

where in the second formula the ionisation energy replaces the characteristic frequency in equation 5. This assumes that the attraction between molecules arises from the optical electron only; as other electrons are present, and do contribute, the values obtained using this formula give energies which are too small generally.

Kirkwood and Muller (58) have derived a formula for C_1 which is

$$7. \quad C_1 = 6mc^2 \frac{a_1 a_2}{\frac{a_1}{\chi_1} + \frac{a_2}{\chi_2}}$$

This in general gives values for the energy which are too large and has been shown by Salem (54) to be an upper limit for the dispersion energy; this is because it ignores electron correlation which arises from the repulsion between electrons.

The third approximate form for C_1 , obtained by Slater and Kirkwood (57) is

$$8. \quad C_1 = \frac{3}{4\pi} \frac{eh}{m^{\frac{1}{2}}} \frac{a_1 a_2}{\left(\frac{a_1}{n_1}\right)^{\frac{1}{2}} + \left(\frac{a_2}{n_2}\right)^{\frac{1}{2}}}$$

In using this formula n_1 and n_2 , which are the number of electrons in the outermost shells, are often uncertain for molecules.

1.4.2. Electrostatic Forces

A neutral distribution of positive and negative charges gives rise to an electrostatic potential which at any point is given by

$$1. \quad \phi = \sum_i \frac{e_i}{r_i} \quad (59)$$

where r_i is the distance of the i^{th} charge from the point considered. This expression is not convenient to use as it requires a knowledge of r_i (for all i) for each position chosen. It is usual to expand $\frac{1}{r_i}$ in terms of $\frac{1}{r}$, where r is the distance of the point considered from an arbitrary origin and s_i^* the distance of the i^{th} charge from this origin.

Expanding $\frac{1}{r_i}$ in terms of r and s_i in a Taylor series (59a)

$$2. \quad \frac{1}{r_i} = \frac{1}{r} + x_i \frac{\partial}{\partial x} \left(\frac{1}{r} \right) + y_i \frac{\partial}{\partial y} \left(\frac{1}{r} \right) + z_i \frac{\partial}{\partial z} \left(\frac{1}{r} \right) \\ + x_i^2 \frac{\partial^2}{\partial x^2} \left(\frac{1}{r} \right) + y_i x_i \frac{\partial^2}{\partial x \partial y} \left(\frac{1}{r} \right) + \dots$$

On substituting this into equation 1

$$3. \quad \phi = \sum_i \frac{e_i}{r} + \sum_i x_i e_i \frac{\partial}{\partial x} \left(\frac{1}{r} \right) + \dots + \\ \sum_i e_i x_i^2 \frac{\partial^2}{\partial x^2} \left(\frac{1}{r} \right) + \sum_i x_i y_i e_i \frac{\partial^2}{\partial x \partial y} \left(\frac{1}{r} \right) + \dots$$

The coefficients of the differentials are the electrical

$$* \quad s_i^2 = x_i^2 + y_i^2 + z_i^2$$

moments of the system. Considering second order terms, in cases where there is axial symmetry all the second order cross terms are eliminated and the remaining second order terms (for symmetry about the z axis say) are related by

$$4. \quad \sum_i e_i z_i^2 = -\frac{1}{2} \sum_i e_i (x_i^2 + y_i^2)$$

In general these moments are not independent of the choice of origin; this is true only of the first non zero moment.

The interaction of a system of charges with an external field is given by $E_{\text{inter}} = - \sum_i e_i \phi_i$ where ϕ_i is the potential at the i^{th} charge. Choosing an arbitrary origin and expanding ϕ_i about the origin in a like manner to $\frac{1}{r_i}$ in the previous paragraph the interaction can be represented as that between a series of point multipoles at the origin and the potential gradient (dipole), field gradient (quadrupole) and so on for higher order multipoles.

In this section the dipole and quadrupole of axially symmetric molecules will be the only multipoles to be discussed. In molecules both these may be calculated from quantum mechanics; for the dipoles good agreement between experimental results and theoretical calculations has been obtained. For the quadrupole

unambiguous measurements have yet to be made and the various theoretical estimates for any one molecule vary widely. The dipole and quadrupole will now be discussed in more detail, ignoring for the moment the polarisability.

Dipole Interactions

The dipoles of molecules are not the point dipoles considered in the previous section, and to obtain their interaction with a field accurately the dipole should be replaced by an expansion similar to that in the previous section; however, this refinement will not be made here as other approximations would make it a futile labour. An ideal dipole may be defined by

$$m = \sum_i (ne_i \frac{\vec{s}_i}{n}) \lim_{n \rightarrow \infty}$$

i.e. an ideal dipole is obtained by increasing the charges (ne_i) and decreasing the distance ($\frac{s_i}{n}$) between the charges keeping their product constant. The limit as the charges coincide is an ideal dipole.

The dipoles in the previous section were assumed to be static; any molecule will possess thermal motion and in evaluating the interaction of a dipole with a field it is necessary to obtain the weighted average of the

interaction over all the possible orientations of the molecule w.r.t. the field. If the z axis is chosen to lie in the direction of the field the interaction of a dipole is given by equation 3 as

$$\begin{aligned}
 5. \quad E_{\text{inter}} &= - \sum_i \frac{e_i z_i}{r^2} \left(\frac{\partial \phi}{\partial z} \right) = - \sum_i \frac{e_i r_i}{r^2} \cos \theta \cdot \frac{\partial \phi}{\partial z} \\
 &= - \frac{m}{r^2} F \cos \theta
 \end{aligned}$$

where m is the dipole moment. Keesom (59) averaged this interaction over all orientations introducing a Boltzmann factor to allow for the greater probability of the favourable orientations and obtained

$$5a. \quad \bar{E}_{\text{inter}} = L\left(\frac{\mu F}{kT}\right)$$

where L is a Langevin function, which has been tabulated for various values of the exponent. Note that this average is temperature dependent.

Interaction of two dipoles

This interaction depends markedly on the orientations of the dipoles. The field due to a dipole at any point, P, is given by (59a):

$$6. \quad \vec{F} = \text{grad} \frac{\vec{m}_1 \cdot \vec{r}}{r^3} = \frac{3\vec{m}_1 \cdot \vec{r}}{r^5} \vec{r} - \frac{\vec{m}_1}{r^3}$$

The work done in bringing a second dipole to P is

$$7. \quad W = -\vec{F} \cdot \vec{m}_2 = - \frac{3(\vec{m}_1 \cdot \vec{r})(\vec{m}_2 \cdot \vec{r})}{r^5} + \frac{\vec{m}_1 \cdot \vec{m}_2}{r^3}$$

When $\vec{m}_1$, $\vec{m}_2$ and $\vec{r}$ are in the same direction this becomes

$$8. \quad W = - \frac{2m_1 m_2}{r^3} ;$$

if $\vec{m}_2$ is parallel and opposed to $\vec{r}$ this becomes

$$9. \quad W = + \frac{2m_1 m_2}{r^3}$$

Keesom averages may be obtained for the average interaction of two dipoles when $E_{\text{inter}} - \bar{E}_{\text{inter}} \ll kT$.

1.4.3. Quadrupoles

Quadrupole moments have recently been discussed by Buckingham (22). There are various definitions of the quadrupole in use. The definition arising from equation 3, for axially symmetric charges, i.e.

$$Q_{zz} = \sum_i e_i z_i^2$$

will normally be dependent on the choice of origin, if there is a dipole present also, and so it is more general to define it as a traceless tensor, thus making it independent of the choice of origin as is done by Hirschfelder et al (60),

who define a quadrupole as

$$10. \quad Q = \sum_i e_i (3\vec{s}_i \vec{s}_i - s_i^2 U)$$

where U is a unit tensor. In cases of axial symmetry this reduces to three axial quadrupoles which for symmetry about the z axis are related by

$$11. \quad Q_{xx} = Q_{yy} = -\frac{1}{2}Q_{zz}$$

The quadrupole is then represented by the scalar Q_{zz} . For an axially symmetric molecule equation 10 becomes

$$12. \quad Q_{zz} = \sum_i e_i s_i^2 (3\cos^2\theta - 1)$$

An alternative definition introduces a factor of a $\frac{1}{2}$ in (12) (61). If the molecule is rotating the quadrupole is effectively reduced to about a half its value for the non-rotating state (60a). A Keesom temperature average may be obtained, as in the case of a dipole, for its interaction with a field.

The role of the quadrupole in sorption has received much attention of late. Drain (62) has calculated the interaction of a quadrupole at planes of ions in KCl where he was able to obtain an analytic expression for the field gradient. Barrer and Stuart (63) explained the preferred sorption of N_2 to A in faujasite in terms of a quadrupole interaction, while Kingston and McLeod (64) have

demonstrated the influence of the quadrupole on the heat of sorption for a series of small molecules in chabazite.

1.4.4. Polarisation

When a polarisable molecule is placed in an electric field dipoles are induced, which for small fields are given by: $m_{\text{ind}} = \alpha F$ (the substance is assumed to be isotropic). The nett interaction of m_{ind} with the field, after allowing for the work done in its creation, is

$$E_{\text{ind}} = -\frac{1}{2}\alpha F^2$$

This linear relationship of m_{ind} with the field may not persist to high strengths of the field. Barrer and Bratt (24) have suggested that there may be a limiting value for m_{ind} at high fields.

The polarisability of molecules affects the interaction between molecules markedly at small distances. For the interaction of two polarisable dipoles the resulting dipoles are

$$\vec{m}_1^* = \vec{m}_1 + \alpha_1 \left(\frac{3\vec{m}_2^* \cdot \vec{r}}{r^5} \vec{r} - \frac{\vec{m}_2^*}{r^3} \right)$$

Similarly for $\vec{m}_2^*$.

Two limiting cases will be considered.

(i) $\vec{m}_1 = \vec{m}_2$, $a_1 = a_2$; $\vec{m}_1, \vec{m}_2, \vec{r}$ in the same direction

$$m^* = \frac{m}{1 - \frac{2a}{r^3}}$$

The energy of interaction is given by

$$E_{\text{inter}} = - \frac{2(m^*)^2}{r^3} + \frac{(m^* - m)^2}{a}$$

(ii) As in (i) with $\vec{m}_1, \vec{m}_2$ parallel and perpendicular to $\vec{r}$

$$m^* = \frac{m}{1 + \frac{a}{r^3}}$$

The energy of interaction is given by

$$E_{\text{inter}} = + \frac{(m^*)^2}{r^3} + \frac{(m^* - m)^2}{a}$$

1.4.5. Relationship of Intermolecular Forces to the Isosteric Heat

The isosteric heat, q_{st} , is related to the energy of the sorbed phase by

$$1. \quad q_{st} = \tilde{E}_g - \tilde{E}_1 - n_1 \bar{E}_1 + RT .$$

At 0°K where $\tilde{E}_1 = \phi - \phi_0$ where ϕ is the interaction of the sorbed molecule with the sorbent and ϕ_0 is the zero point energy (normally about $\sim .1$ Kcal/mole). The isosteric heat at 0°K, q_{st}^0 , is given by

$$2. \quad q_{st}^0 = \phi - \phi_0 - n_1 \frac{d}{dn_1}(\phi - \phi_0) .$$

At any temperature

$$3. \quad q_{st} = q_{st}^0 - \int (\tilde{C}_p - \bar{C}_x) dT$$

To relate q_{st} rigorously to the intermolecular forces requires a knowledge of $\bar{C}_x$ and $\tilde{C}_p$.

Orr (65), using an empirical formula to represent the heat capacity of the sorbate, was able to show that between 0°K and 80°K there would be a negligible change in the heat of sorption (.04 Kcal/gm mole). In view of this any change in q_{st} with temperature, even at these high temperatures, should be within the experimental error. If the second term in

equation 2 is small, the calculated intermolecular energies may be equated directly with the heat.

1.4.5.1. Calculation of Intermolecular Forces in Sorption.

The total interaction of a polarisable molecule possessing a dipole, and quadrupole with a sorbent which has an electrostatic field and field gradient is given by

$$1. \quad U_T = U_D + U_R + U_{PF} + U_Q + U_I$$

(i) (ii) (iii) (iv) (v)

In order to calculate these energies it is necessary to know r_o , the equilibrium distance of the molecule from the surface; this must be obtained indirectly as it cannot be measured. For hard sphere models r_o is taken as either the sum of the radii of a probe molecule and a sorbent atom or from the radius of the guest molecule and the dimensions of the lattice spacing of the sorbent atoms. Using a Lennard Jones potential function, having assumed an r_e for the probe molecule and a sorbent atom it is probably best, where polar forces are involved, to obtain r graphically from a plot of U_T v r_o , the distance from the surface. It should be noted, as has been pointed out by de Boer (51), that good agreement for experimental and theoretical

results can be obtained by small adjustments in r_0 , the equilibrium distance from the sorbent; agreement between observed and calculated results must therefore be treated with some reserve.

In the calculation of (i) and (ii) in equation 1 a sum of the form

$$2. \quad U_D + U_R = C_1 \sum_i \left(\frac{1}{r_i^6} - \frac{re^6}{2r_i^{12}} \right)$$

must be carried out. This assumes that the dispersion and repulsion terms are pairwise and additive. The constant C_1 , -approximately obtained from equations in Section 1.4.1, can be made further indefinite by a lack of knowledge of the state of the atoms of the sorbent. For the alkali halides, ions seem a reasonable supposition; the real state of oxygen atoms in the zeolites is far less certain.

The summation in equation 2 is very laborious, and it is often replaced by an integration over the solid. This assumes that the sorbent can be treated as a continuum; the result will not show any periodic variation of the interaction energy with position of the probe molecule. The integration is of the form

$$3. \quad U_D + U_R = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} C_1 \left(\frac{1}{r_i^6} - \frac{re^6}{2r_i^{12}} \right) p dx dy dz .$$

This integration has been carried out for plane surfaces (e.g. London) (52) and for cavities in faujasite (63). The magnitude of the total interaction depends on the number density of the sorbent atoms, as has been pointed out by Barrer (68), not on whether the molecule is sorbed in an intracrystalline space or at a surface.

The most extensive summations have been carried out for alkali halides by Orr (65) and have been extended by Young (66) to include the (111) plane. These covered virtually all the atoms which contribute to the dispersion energy for a representative range of positions of the probe molecule.

Extensive calculations have also been carried out for sorption on carbon; Barrer (69) has made calculations for the interaction energy of the permanent gases using several forms for C_1 ; the Kirkwood Muller formula gave the best agreement with the heat data. Recently Kiselev (70) has made calculations for a wide variety of sorbates on carbon using the Kirkwood Muller expression for C_1 ; his repulsion constants were calculated from the compressibility of the solid.

Barrer and Wasilewski (71) have carried out a summation for the oxygen atoms of a supercage of faujasite for a series of positions on a line approaching the centre of a 6 ring. Using these summations and the Slater

Kirkwood expression for C_{ij} , they obtained the interaction energy of iodine and the lattice oxygen atoms which gave quite good agreement with the residual heat of sorption, ie. after initial heterogeneity had died away.

1.4.5.2. Electrostatic Forces in Sorption

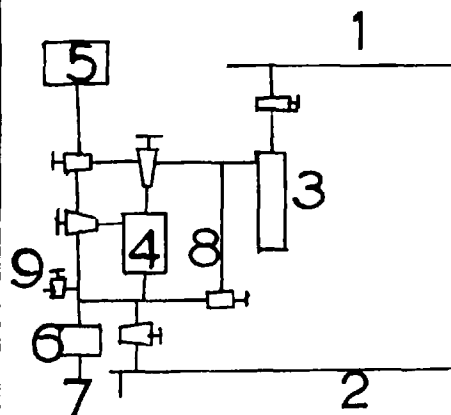
The main difficulty in obtaining the electrostatic interaction is in obtaining an accurate value for the field and field gradient. Lennard Jones and Dent (67) calculated the field for a simple cubic system for various positions on the lattice cell edge; Orr (65) applied this to the (100) plane of potassium chloride and also obtained the field at some other positions by a direct summation over the nearest 90 atoms or so, combined with an integration over the rest of the crystal. Orr also showed that for the rare gases the electrostatic energy was negligible. Crawford and Tompkins (98) used Orr's calculations to obtain the dispersion and electrostatic interaction energies for CO_2 , NH_3 , and SO_2 , sorbed on BaF_2 , and obtained reasonable agreement with the heat data. Drain (62) extended Orr's calculations to include the field gradient and was able to explain the high q_{st} for N_2 in terms of the quadrupole interaction with the field gradient.

Section 2.1 Experimental Apparatus

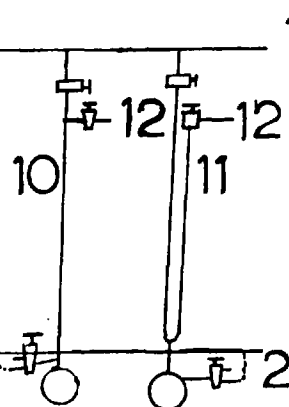
In this study of sorption the sorption equilibria were measured in the range 100°C to 290°C using a modified McBain sorption balance (78) which was a simpler version of the apparatus designed by Dr. Wasilewski (77). A standard volumetric system was employed in the region 0° to 70° although most measurements were made with the McBain balance. In sections 2.2 and 4 the apparatus used to obtain a good vacuum and high purity of the sorbate will be described.

In the range 100° to 290°C a furnace was used as a high temperature thermostat (sections 2.5 and 7), the temperature being measured by a platinum resistance thermometer, made and calibrated for that purpose (section 2.6). The mode of thermostating is discussed in a later section (section 2.7). In addition to temperature control at sorption equilibria, the amount sorbed and the pressure have to be measured. The instruments used for this and their calibration are discussed in section 2.2. and 8. Finally the purity and the composition of the solid must be determined and this is discussed in section 2.9.

The standard volumetric system and its temperature control is described in section 2.12. We now turn to a detailed description of each section of the apparatus.

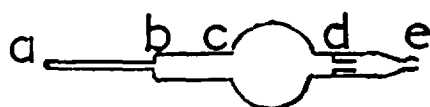
Figure 3
(a)

(b)



- | | |
|----------------------|---------------------|
| 1: high vac line | 10 McLeod gauge |
| 2: low " | 11 manometer |
| 3: cold trap | 12 to sorption bal- |
| 4: hg diffusion pump | ance |
| 5: buffer volume | |
| 6: oil trap | |
| 7: to oil pump | |
| 8 by pass | |
| 9 air inlet | |

Figure 4



2.2.1. Pumping System

The pumping system is shown schematically in figure 3. The vacuum is obtained using an oil rotary pump backed by a mercury diffusion pump (4). The essential features of the pumping system are:-

1. The oil trap (6) which prevents the oil from sucking into the system in the event of a mishap to the pump.

2. The reservoir (5) (approx. 5-litre capacity) which permits the mercury pump to run unbacked for up to about 12 hours.

3. The cold trap (3) which is cooled with liquid oxygen prevents any condensable substance from contaminating the mercury pump.

4. The bypass (8) which enables the initial evacuation to be carried out without using the mercury pump.

5. The taps as shown to permit isolation of any desired part.

All taps in the pumping system were large (8mm. bore) to ensure a good pumping rate. The vacuum lines were also made of 2cm. diameter tubing to facilitate this end. With this system vacua of better than 10^{-6} cm. Hg can be produced.

The pressure was measured using a mercury manometer and a cathetometer for pressures down to .3cm.; below

this a McLeod gauge was used. The calibration of the McLeod gauge is described below. The manometer and gauge were connected as shown to the low and high vacuum lines and to the sorption balance. The manometer was made of 1 cm. wide tubing to render negligible any thermomolecular effects at low pressures and to reduce meniscus depression effects. The pressure was read using a cathetometer.

2.2.2. Calibration of the McLeod gauge

The gauge was calibrated, before it was attached to its reservoir, in the form shown in the diagram 4. Six marks were etched on the tube ABC, three on AB and three on BC. This was done by coating the tube ABC with paraffin wax, cutting the coat with a razor blade, and then allowing the tube to stand in conc. HF for $\sim \frac{1}{2}$ hour in a fumecupboard.

The volume between each mark and A is found by filling the tube with mercury up to each mark. To fill sections of the capillary tube AB the whole system must be evacuated; this is done by attaching pressure tubing at E and pumping the air out. Mercury is placed in the large bulb before evacuating and is tapped down to fill the capillary to the required mark. It is then removed and weighed. Finally the large bulb is filled to D and the mercury weighed.

A correction is required to allow for the

curvature of the meniscus when calibrating the volumes; this is because the meniscus in calibration is facing the opposite way to the meniscus in an actual reading. The correction, which is small, was made using the formulae derived by Jnanananda (79) which are:

$$y = .023a \text{ where } a \text{ is the radius of the tube, and } y \text{ the volume correction}$$

or

$$y = .057m \text{ where } m \text{ is the height of the meniscus, assuming a contact angle for Hg/glass is } 135^\circ.$$

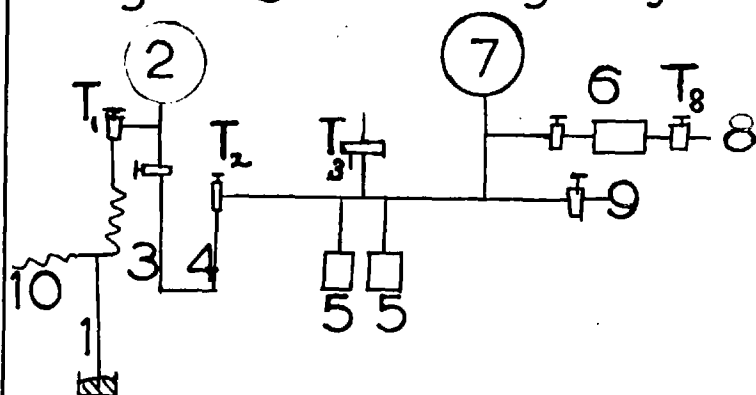
In using the McLeod gauge the gas is assumed to be ideal. It gives measurements accurate to 1% down to pressures of $.10^{-4}$ cm. provided no condensable gases are present.

2.3. Purification and Storage System for Ammonia

The system is shown schematically in figure 5. The ammonia is stored in cold traps cooled with liquid oxygen to prevent any possible decomposition of the ammonia. The taps of the cold traps are left open so that the bulb (7 in figure 5) is accessible to the ammonia. This prevents any blow outs.

Purification of ammonia

The apparatus is connected by (10) figure 5) to the ammonia cylinder and evacuated as much as possible; the vacuum is determined by the air tightness of the poly-

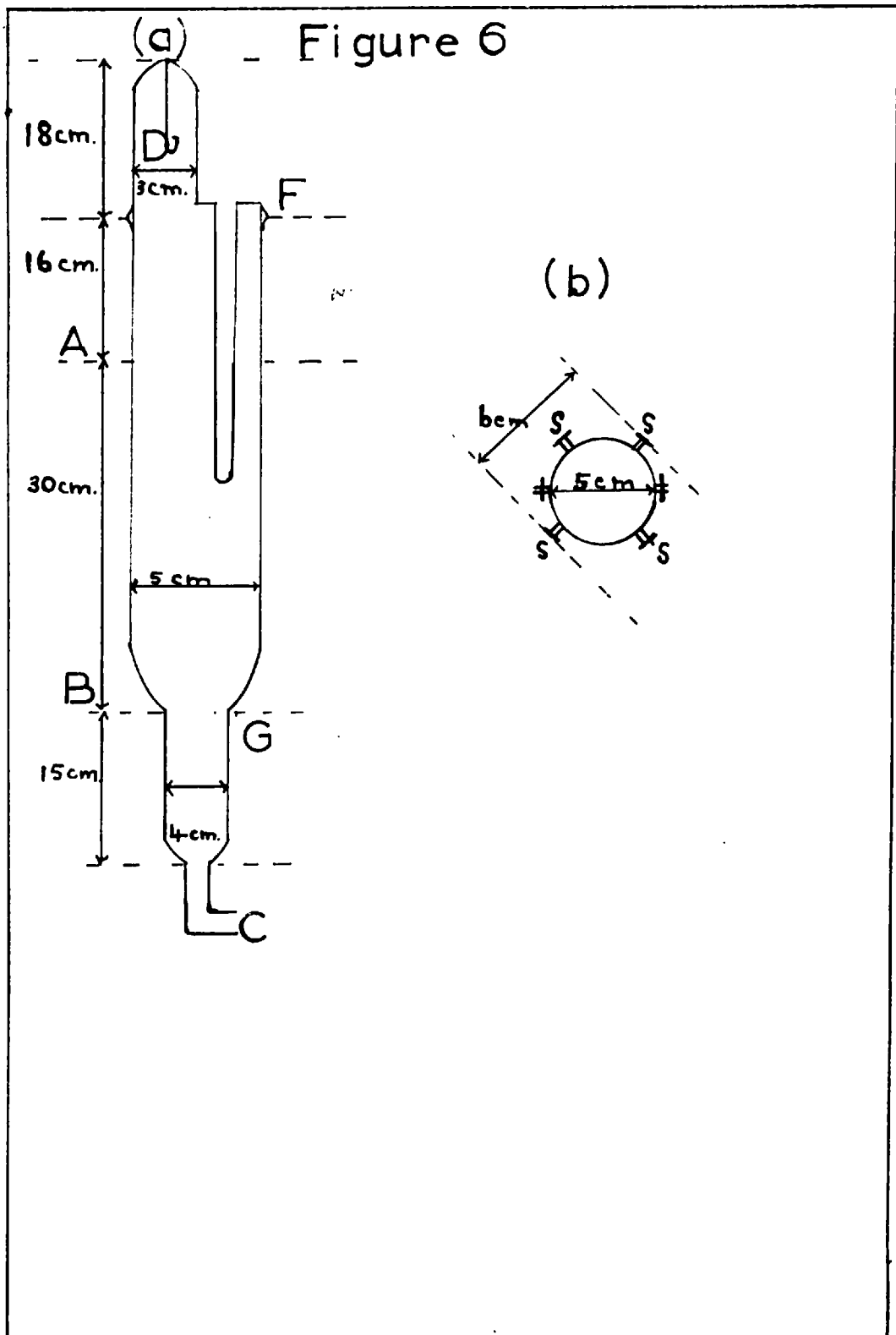
Figure 5 Storage system for NH_3 

- 1 manometer
- 2 buffer volume
- 3 tube of ignited CaO
- 4 " " NaOH pellets
- 5 cold traps
- 6 " "
- 7 buffer volume (5L)
- 8 to high vac line
- 9 to sorption balance
- 10 tubing to NH_3 cylinder

-these joints which are sealed with picene. The system in figure 5 is then isolated from the rest of the vacuum system by closing tap T8. Ammonia is now admitted from the cylinder, the flow being controlled by a brass pin needle valve and the pressure change being followed on the manometer ((1) in figure 5). The main impurity being water, the ammonia is passed through columns of ignited calcium oxide and sodium hydroxide pellets. When enough ammonia has been admitted tap T1 is closed, and the gas condensed in a cold trap, T2 is now closed and on opening T8 the system is pumped down to a hard vacuum.

The purification is completed by three bulb to bulb distillations retaining the middle fraction each time (80). The two-way tap T3 which has a B10 socket attached is used to attach the gas cell employed in the infra red analysis of the gas. This checks the purity of the gas, detecting any water present but not showing the absence of permanent gas. These should be removed by pumping.

In order to minimise the effect of any water that might still be present excess ammonia is put in so that some liquid ammonia is always in the cold trap; then any water present will be frozen in too.



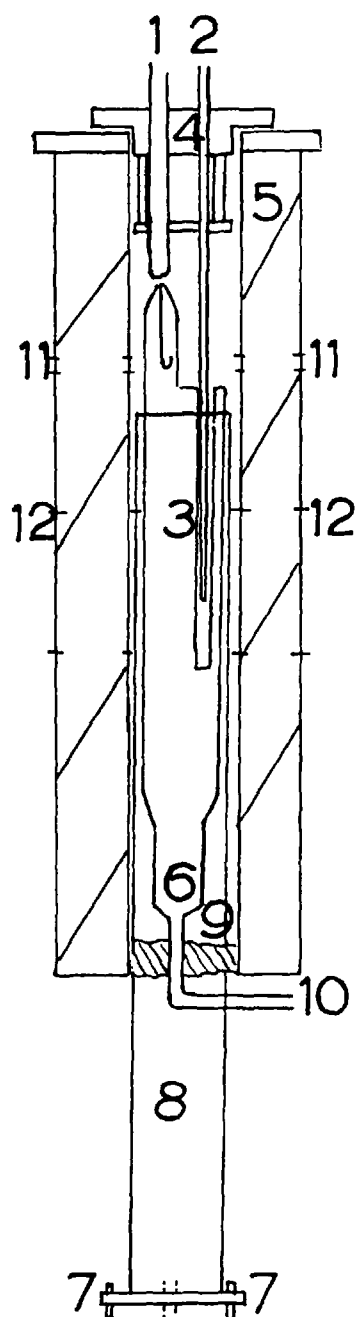
2.4 Sorption Balance

The balance is shown diagrammatically in figure 6a, with its dimensions indicated. The only modification in this balance is the insealing of a platinum resistance thermometer into the balance case near the bucket so that the temperature may be read as close to the bucket as possible; this is essential because of the thermal gradients in the furnace. The other point is that there are strong thermal gradients in the exit tube at C (in figure 6a) where it leaves the furnace to go to the manometer. In order to eliminate thermomolecular effects at low pressures it is necessary to have the exit tube 1 cm. in diameter (82).

The other points are of a practical nature:

- (1) The hooks of the spring must be viewed clearly, so it is essential to have (a) hook D (in 6a) clear of the junction to the wide part of the tube, (b) a length of ~ 30 cm. from A to B free of joints.
- (2) The spring must be kept in the centre of the tube to ensure the bucket is free from the walls.
- (3) The tube C (figure 6a) is connected to the rest of the vacuum line through a glass spiral to mitigate the effects of any vibrations on moving the furnace.
- (4) The balance case is held in the support tube by a ring of stainless steel (see figure 6b) at F in figure 6a.

Figure 7



1: hole for regulating thermometer.

2: hole for leads of measuring therm. at 3.

4: lid of furnace

5: large furnace

6: sorption balance

7: support tube leveling screws

8: support tube

9: asbestos wool

10: to vac line

11: window to view top hook of spring

12: ditto bottom hook

A strip of silica cloth is held between it and the glass tube. The screws (S), which project, slip into slots at the top of the support tube. A similar ring, without screws, is placed at G to act as a centring device; this fits inside the support tube.

2.5.1 Furnace

The measurements of the central steel tube and the outer asbestos case are given in figure 8.

The heating elements are wound around the central steel tube. First of all silica glass windows are cemented into the slots in the steel tube with pyruma cement and left for the cement to dry overnight. Two turns of asbestos paper are then wound on to the cylinder and openings are cut out for the windows. Then one turn of silica cloth is wound around, and holes are cut for the windows. (It is necessary to sew the cloth temporarily).

The nickel alloy wire ($R = 7.16 \Omega / \text{yd}$) is wound around to give a total resistance of 300Ω . The spacing is varied so that at the ends the spacings are $\frac{1}{3} < \text{average}$ and $\frac{1}{3} > \text{average}$ in the middle of the tube. Then the whole is covered with alumina cement and allowed to dry overnight. The windows are then cut out.

When the cement is dry another turn of silica cloth is put on, sewn to keep in place, and the windows

cut out. The heavy current wire is now wound on ($R = 1.15 \Omega/\text{yd}$), sufficient to give a total resistance of $\sim 60 \Omega$, with spacing adjusted as with the other winding. It is then covered with alumina cement and, when dry, with silica cloth. The windows are then cut out.

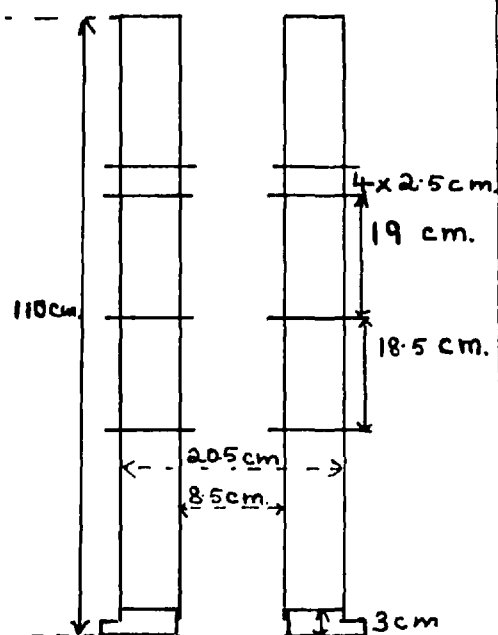
The ends of both windings are placed ~ 3 cm. from the ends of the tube. The nickel alloy wire is held by doubling and twisting a stretch of wire and then looping a loop round the tube and twisting the ends of the loop till it grips the tube tightly. Then one end is connected to the terminal in the asbestos case, the other end is wound around the tube. The heavy current wire is clamped by stainless steel rings; these are then connected to the terminals in the outer tube.

The lagging consisted of asbestos wool which is pushed between the outer asbestos case and the central steel tube. The windows are kept free by metal frames which run from the central tube to the outer case. Pyrex windows are put in the openings of the asbestos case.

The ends of the furnace were asbestos plates which were held in place by stainless steel rods running the length of the furnace and were bolted to the end plates. This is to allow for the expansion of the stainless steel tube with heating.

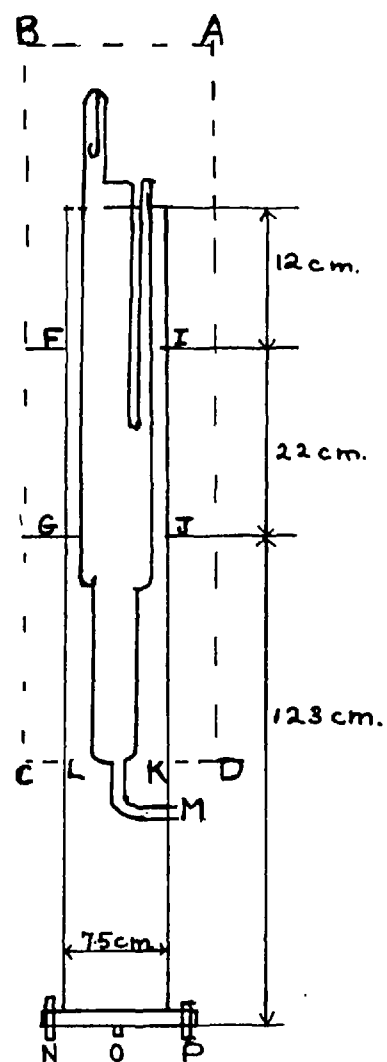
The furnace is held in a vertical position by

Figure 8



FURNACE

Figure 9



SUPPORT TUBE

two brackets which are able to move on sliders up and down greased rods. To facilitate movement a counter-weight is attached by wires passed over a pulley to one of the brackets holding the furnace. Clamps are provided on the sliders to prevent any undesired movement of the furnace.

2.5.2. The Support Tube

The support is shown in the diagram 9 with the sorption balance inside it. The dotted lines ADCB indicate the position of the furnace when in use. The dimensions are indicated. Though shown as a complete cylinder, in fact large windows (dimensions 30x4 cm.) were cut at GF and JI in order that the spring may be seen. Also below KL large sections were cut out. This is necessary at M where glassblowing has to be done; this is where the exit tube is joined to the vac. line.

The support tube is attached to a plate which is levelled by three screws (N.O.P). The tube must be adjusted so that the furnace can move up and down without touching the support tube. This is done by adjusting N, O and P. When the furnace is in position it may be necessary to alter the position of the support tube so that the hooks may be seen clearly;--this is done by re-adjusting the screws N, O and P. The furnace, support tube and balance are shown assembled in figure 7.

Figure 10 Thermometer

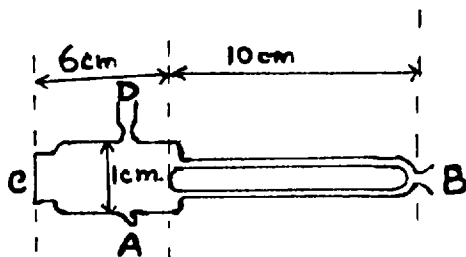


Figure 11

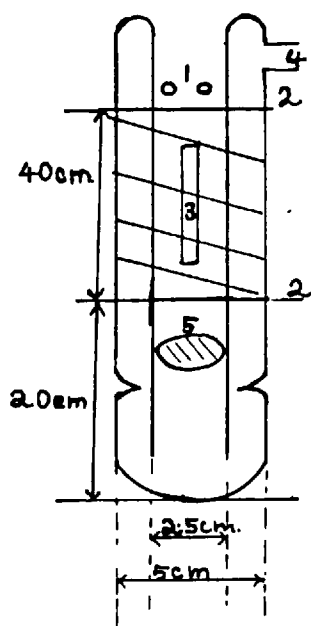
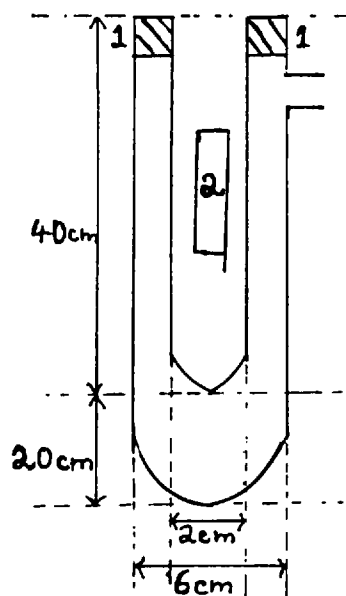


Figure 12



2.6.1. Thermometers

Platinum resistance thermometers were made, calibrated and used for all temperature measurements. The platinum was supplied thermally pure by Johnson Matthey and Co. .02" diameter wire was used for the resistance, the leads being made from wire .1" in diameter.

First some resistance wire was wound on a steel spoke (diameter $\sim .05$ ") as uniformly as possible, sufficient to give a resistance of $\sim 11\Omega$ at room temperature. This was then spot welded on to two 2' lengths of the lead wire. The dummy leads were made from two other 2' foots of lead wire spot welded on to a very short piece of resistance wire.

These were then placed in the glass case (see figure 10), from an opening in the glass case of the resistance (B in figure 10). The dummy leads were put in through C and sealed to the glass at A. The opening at B is then sealed as is the pinch seal at C. The whole thermometer is then evacuated and a third of an atmosphere of helium admitted. The evacuation is effected through the side arm DE and the sealing off is done at a constriction at D.

The thermometer is then annealed at 450°C for several days.

2.6.2. Calibration

The thermometers were calibrated at the ice, steam and sulphur points. The resistance was measured using a Callendar Griffiths bridge accurate to $.0005\Omega$. The calibration of the platinum resistance thermometer (81) at the boiling points of sulphur and water was carried out using the apparatus shown in figure 11. It consisted of two concentric tubes of the dimensions shown. The inner tube does not extend down the entire length of the outer tube and has a pad of glass wool at 5 in figure 11 to prevent splashing. Holes are made through it at the top (see 1 in figure 11). The resistance winding (2 in figure 11) around the outer tube is used as a heating jacket.

The procedure is to put some of the substance (water or sulphur) in the outer tube and place the platinum resistance thermometer in the inner tube to the position shown (3 in figure 11); the opening at the top of the inner tube is then packed with glass wool. The whole of the resistance element of the thermometer must be well inside the inner tube in the length wound round by the resistance wire. The thermometer is then connected to a Callendar-Griffiths bridge.

A bunsen or, in the case of sulphur, a meker burner is used to vaporise the liquid. The voltage through the windings is now adjusted till the level of the vapour

is just below the exit (4 in figure 11). Sulphur vapour tends to oxidise in air; to reduce this to a minimum the exit is blocked with glass wool. After some fluctuation the resistance reaches a steady value which was recorded as the equilibrium value. Each reading was repeated and the two readings found to be in very good agreement.

Calibration at the Ice Point

The calibration was carried out using the apparatus in figure 12. It consisted of two concentric tubes, the inside tube being held in a cork at the top (1 in diagram 12). The bottom of this tube is sealed. The thermometer is introduced to the position shown as 2 in figure 12, i.e. with the resistance element entirely below the water level. The top of the inner tube is now stuffed with cotton wool to reduce any convection currents.

The outer tube is now filled, with a mixture of distilled water and ice made from distilled water, to the level shown. The system is then surrounded by a crude ice bath made up in a large Dewar to prevent the ice in the outer tube from melting too quickly.

The system is then allowed to come to equilibrium and the resistance of the thermometer measured using a Callendar Griffiths bridge. This was repeated; the two readings gave very good agreement.

2.6.3. Corrections

The boiling point varies with the atmospheric pressure; the variation is given by the following formulae (taken from Johnson and Matthey's Handbook of Platinum Resistance Thermometry) (81).

For water:

$$1. \quad t = 100 + .0367 (p-760) + .000023 (p-760)^2$$

For sulphur:

$$2. \quad t = 444.6 + .0909 (p-760) - .00048 (p-760)^2$$

(p in mm. of mercury).

The pressure was measured on a Fortin barometer in the same building, accurate to .001 cm.

Formula for using resistance thermometer

The formula used in the International Temperature Scale for Platinum resistance thermometers is

$$3. \quad R_t = R_0 (1 + At + Bt^2).$$

To avoid the arithmetical labour involved in using this, the following adaptation by Callendar is used:

$$4. \quad t = \frac{R_t - R_0}{R_{100} - R_0} 100 + \delta (t - 100)t .$$

δ may be obtained from the resistance readings at the three calibration points. Tables are available for various values of δ ; ^{once} /this is known the temperature can be obtained from these tables and t_{Pt} , which is just the

first term in equation 4.

The International Temperature Scale requires the following conditions to be satisfied:

$$(i) \frac{R_{100}}{R_0} \geq 1.3910$$

$$(ii) 4.216 < \frac{R_s - R_0}{R_{100} - R_0} < 4.218 .$$

The thermometers made conformed very closely to these values.

A large scale graph was made of temperature versus resistance to enable temperatures measured during the calibration of the spring to be read off. For temperatures of actual sorption experiments, the appropriate resistance was calculated using equation 4.

2.7.1. Temperature Control: Electrical Circuit

Of the two windings of the furnace one carries a large current and provides most of the heating effect, the other a much smaller current and acts as a fine control governed by a platinum thermometer placed in the top of the furnace. The winding carrying the large current is run off a Variac which must be set appropriately to obtain any temperature required.

Fine control

The circuit for this is shown in figure 13. The

modified Roberts control is such that when the decade box has a resistance less than the platinum resistance thermometer, current flows and there is a heating effect and vice versa. In practice a shunt resistance is put in so that the current is altered less and thus the control is finer (see dotted part of figure 13). (N.B. The controlling thermometer is placed in the top of the furnace near the wall, see figure 14).

2.7.2. Temperature Control: Convection Current Control

Convection currents inside the furnace affect the temperature. To minimise these the bottom opening is packed with asbestos wool and the top is covered by the apparatus shown in diagram 14. This consists of two asbestos plates held together by steel rods with a gap of $\sim 10-15$ cm. between them. Holes are left in the plates for the regulating thermometer and for the leads of the measuring thermometer (not shown). The space between the two plates is filled with asbestos wool which cuts down the convection currents. This then fits into the top of the furnace, resting on the end plate.

Figure 13

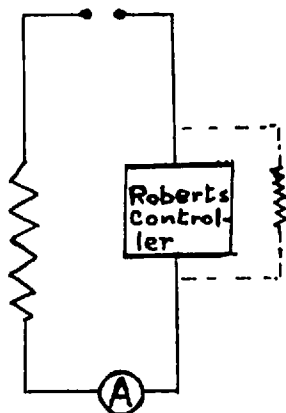


Figure 14

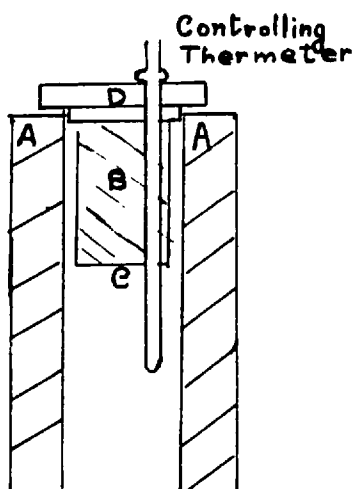
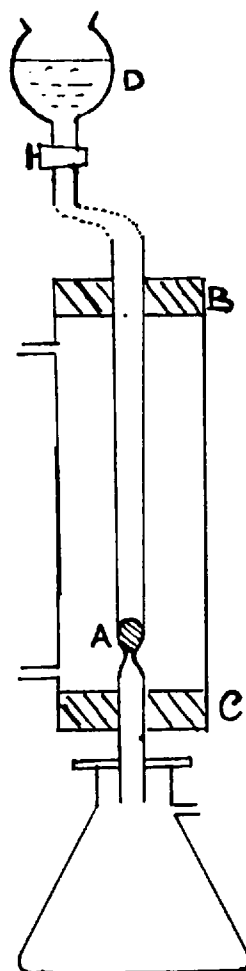


Figure 15



2.8. Springs

Springs were supplied by Thermal Syndicate Ltd. They had sensitivities of ~ 35 -40 cm/gm. and maximum load of 1 gm. They showed hysteresis above 350°C and sometimes above 300°C .

The springs were first annealed by being taken on several cycles up to 350°C and back to room temperature with a median weight ($\sim .7$ gm.) attached. Readings were then taken every 30°C up to $\sim 320^{\circ}\text{C}$ and every 30°C from ~ 305 to room temperature. This gives readings every 15°C for each weight. The process is repeated for four weights in all. Graphs of length v. temperature were plotted for each weight. From these graphs, using the method of least squares, the weight for any length of spring at any temperature in the range can be obtained. The constants a and b (see equation below) were worked out for the temperatures at which the isotherms were to be taken, from the formulae in reference. (83)

$$l = a + bm \quad \text{for a given temperature.}$$

Accuracy of calibration

The maximum deviation increased with temperature. Below 230° the maximum deviation is $\leq .2$ mgm, the average $< .1$ mgm. Above 230°C the maximum deviation is $\leq .4$ mgm, the average $\leq .2$ mgm.

This is the biggest single error in the whole of the experiment and means that for amounts sorbed of < 50 mgm. there is an error between 4 and 8% depending on the temperature.

2.9. Preparation of Materials

Sorbents

The sorbents used were all ion-exchanged faujasites, all prepared from the same batch provided by the Linde Air Products Co. Before use, all forms were washed thoroughly with distilled water at $\sim 95^{\circ}\text{C}$, to remove any excess alkali present, and sieved through a 200-mesh sieve. To make the ion-exchanged forms two methods were used.

The first method (84) consisted of allowing ~ 5 gm. of the sodium faujasite supplied to equilibrate with a 20% solution of the exchanging ion, using an automatic shaker. This is repeated three times using about 50 c.c. of solution each time. About three days are allowed for equilibration.

The faujasite is then transferred to A in diagram 15, where it rests on a cotton wool pad above a constriction. The large tube BC acts as a steam jacket, supplied with steam from a steam generator (not shown).

One litre of 10% solution of the exchanging ion is placed in the reservoir D and is drawn through the zeolite by the water pump. in ~ 36 hours. The exchange of the last traces occurs more readily at the temperature of steam. The sorbent is then prepared for use, as described above.

The second method is to put the zeolite (~ 5 gm.) in a glass tube with $\sim 10-20$ cc. of 20% solution of the exchanging ion. The tube is then sealed and placed in a thermostatted oven on a rotator. The temperature is set at $\sim 95^{\circ}\text{C}$ and the system left to equilibrate for 2 days. This is repeated six times after which the zeolite is prepared for use, as described above.

X-ray photographs were taken of each sample before use and of the outgassed forms.

N.B. The materials used were of the highest possible purity; whenever possible AnalaR reagents were used.

2.10.1. Analysis of the Silicates

The Li, K, Rb, Cs, Ca, Sr, Ba and Co faujasite forms have been prepared. A gravimetric analysis was necessary to establish the extent of ion-exchange which had occurred. The procedure followed was taken from Meier's thesis for the silicate analysis (84). Two or three analyses were necessary to establish the extent of exchange reliably.

A sample was weighed in a platinum crucible (with lid); it was then ignited to constant weight. This gave the water content.

The $\text{SiO}_2\%$ was obtained by filling the platinum crucible with conc. HCl and leaving for 12 hr. The HCl was then evaporated off on a water bath. This process was repeated. After evaporating HCl off a second time conc. HCl was added and, after 5 minutes, dissolved as much as possible in cold water. SiO_2 was precipitated and filtered off. The filtrate was evaporated to dryness and dissolved in HCl; this then dissolved in cold water giving a little more SiO_2 . The precipitate was washed with hot water, ignited in a silica crucible and weighed.

The filtrate was treated as below:

- (1) Conc. HCl was added to filtrate.
- (2) 1:1 NH_3 soln was added to the boiling soln until it was just alkaline to methyl red.

(3) The precipitate was filtered and washed with hot 2% NH_4Cl soln and ignited in a platinum crucible and weighed. This gave the $\text{Al}_2\text{O}_3\%$.

For alkali metals the percentage of each was obtained from the weight of the residue of the filtrates from the previous steps after igniting the filtrate.

CaX was analysed in the same way as the alkali metals for the percentages of Al_2O_3 and SiO_2 . The amount of Ca^{++} present was determined by ppt. from the residue as calcium oxalate. It was then dried at 110°C and weighed as the monohydrate.

Radioactive Tracer Method:

Solutions were made up of known concentrations of SrCl_2 , BaCl_2 , and CsCl which were rendered radioactive by the addition of negligible weights of radioactive isotopes (Sr^{85} , Sr^{89} , Ba^{140} , Cs^{137}) which gave the solution a count of $\sim 20,000$ per kilosecond. 15 ml. of solution were then equilibrated with a known quantity of zeolite, placed in a sealed tube on a rotator and allowed to come

to equilibrium for three days; the amount of zeolite was that calculated to reduce the count by approximately half. The zeolite was then removed from the equilibrated solution by centrifuging and then extent of exchange established as below.

2.10.2. Calculation of Percent Exchange

The water content of each form is first of all determined by igniting some of the sample. The amount of anhydrous material equilibrating with the solution is then established from a knowledge of the weight of hydrated sample. The amount of ^{cation}~~zeolite~~ present in the crystal is obtained from the following formula:

$$\frac{m}{c} = \frac{\text{decrease activity (count/sec)}}{\text{equilibrium activity (count/sec)}}$$

where m is the amount of the ion in the crystal, and c is the total amount of the ion in the solution, which stays constant and is equal to the concentration of the solution as made up. A correction was applied to this to allow for the dead time of the instrument using the standard formula

$$N_T = \frac{N}{1 - N_T \tau}$$

where τ is the dead time of the instrument in micro-

minutes and N_T and N are the true and observed number of counts per minute. The correction introduces very little change in the calculated percentage of ion exchange. Knowing the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio the percentage of exchange is easily obtained from successive approximations.

2.11. Experimental Procedure

Isotherms were obtained at temperatures between 290° and 100°C , starting at the highest temperature in each case. Pressure control is obtained easily; the ammonia is stored as a solid, frozen in cold traps cooled with liquid oxygen. To increase the pressure this is allowed to melt and a slow pressure increase results. To decrease the pressure the ammonia is frozen out, the rate being controlled by taps. In between isotherms, the sorption balance was left open to the cold trap, which resulted in a negligible gas pressure, indicating that no permanent gases had formed.

Accuracy of isotherms:

For each point on the isotherm there are three measurements to be made:

1. temperature - this is accurate to $\pm 0.2^{\circ}\text{C} \sim .025\%$
2. weight sorbed - this is accurate to ± 0.2 to $.4$ g.
according to temperature
3. pressure - this is accurate to ± 0.005 cm.

1. The temperature was set for each isotherm by setting the Variac controlling the main heating current so that a temperature $\sim 20^{\circ}\text{C}$ below the desired temperature was obtained from this alone. The auxiliary heating current, controlled by the Roberts controller, supplied the rest of the heating. A plot of Variac voltage v. temperature was obtained and used to predict settings of the Variac thereafter. It was found that the temperature drifts with the room temperature; this is corrected by altering the decade box on the Roberts controller to maintain the temperature steady. (The drift was not serious - $\sim 1.2^{\circ}\text{C}$ over a day). The temperature was found to be reproducible and could be measured accurately.

Errors in the temperature measurement could also be caused by strong temperature gradients in the furnace; the temperature would then be quite reproducible but would not be accurately measurable. A separate experiment was carried out to determine the importance of possible temperature gradients, using a chrome/alumel thermocouple to measure the temperature at a series of points throughout the furnace. These measurements showed

a maximum variation of 30-35°C over the length, 90 cm., of the furnace. The temperature reading obtained was an average over the length of the thermometer and is probably within 1°C of the temperature of the bucket; the constancy of the temperature would be much better, constant to $\sim .2^\circ\text{C}$.

2. Weight sorbed:

This was measured by the extension of the calibrated spring. Corrections for the buoyancy of the spring and bucket were found to be negligible and accordingly were not made.

3. The pressure measurement has three possible corrections:

- (a) change of density of mercury with temperature;
- (b) expansion of cathetometer scale with temperature;
- (c) meniscus depression.

The first two are very slight and the corrections were not made. The third is also very small and was made using the tables of Gould and Vickers (104) for tubes 1 cm. in diameter. The maximum correction was $\sim .02$ cm, and this at high pressure (~ 50 cm.). In addition this assumes:

- (a) clean contact between the glass and mercury;
- (b) the surface tension is the same on both sides of the manometer.

The variation of these factors introduce error into the pressure measurement only, as the associated error in the amount sorbed is always very much less than the error due to the spring reading.

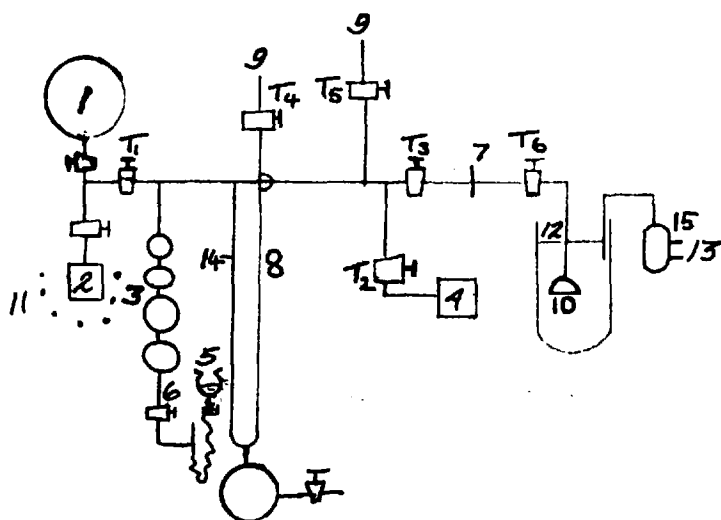
In conclusion the main error is in the calibration of the spring and ~~that~~ the results depend on the accuracy of this calibration, and on the accuracy of the temperature measurement.

2.12. Volumetric Apparatus

2.12.1.

The system was as shown in figure 16. It consisted essentially of a sorption bulb (10) with some sorbent in it, attached to calibrated volumes (specified below). These, in conjunction with the pressure, read on the manometer (8) using a cathetometer, enable the mass of the gas in the gas phase to be determined if the ideal gas laws are assumed. The amount sorbed can be determined as the difference between the total amount admitted (measured in a volume from which the sorbent is isolated) and the amount of gas in the gas phase when in equilibrium with the sorbent. The temperature of the sorbent must be known; its measurement and control are discussed in a later section.

Figure 16 Volumetric System



- | | | | |
|---|-------------------------|----|-------------------|
| 1 | bulb (1L) | 8 | Hg. manometer |
| 2 | NH ₃ storage | 9 | to high vac. line |
| 3 | gas burette | 10 | sorbent bulb |
| 4 | He. bulb | 11 | cold trap |
| 5 | Hg. reservoir | 12 | mark on tube |
| 6 | Hg. level device | 13 | water inlet |
| 7 | B ₇ joint | 14 | mark on manometer |
| | | 15 | water level |

2.12.2. Calibration of Volumes

There were four volumes to be determined:

- (1) The volumes between the marks on the capillaries of the gas burette,
- (2) The doser volume, delimited by T, T_2, T_3, T_5 and 14,
- (3) The doser volume plus the volume of the sorbent attachment, delimited by $T, T_2, T_5, 14$ and 10,
- (4) The volume between 10 and 12, a mark on the sorbent vessel. Volumes (1) and (4) were obtained by filling them with mercury before attaching them to their respective systems, and then weighing the mercury; an average of three readings was taken for each volume. A correction was made for the temperature of the gas in volume (4), in actual experiments.

The other two volumes were obtained using helium, assuming the ideal gas laws, by measuring the pressures with the various bulbs of the burette accessible to helium. In fact the volumes were not measured to the mark 14 on the manometer. The cross-sectional area of the manometer tube was found by weighing the mercury required to fill a known length of the tube, cut off before joining the manometer to the rest of the system. This was then used to calculate the volume occupied by the gas at the equilibrium pressure between the meniscus and the mark. It is probably more accurate to obtain all

the volumes by weighing the mercury required to fill them; however, the helium calibration was found to be accurate to .5%. Details of the calibration^{and use} may be found in (85)

Temperature control and measurement:

Temperature control was obtained using a 5-litre Dewar vessel as a water thermostat. The temperature control was obtained using a Sunvic T.S.7 binetallic strip in conjunction with a 500-watt Robertson heating lamp, Temperature control was better than $.1^{\circ}\text{C}$. The water was stirred vigorously to eliminate temperature gradients, and a constant level head device kept the water level constant (see 15 in figure 16) in the thermostat. Temperature measurement was made with a mercury in glass thermometer which was calibrated against a platinum resistance thermometer in the actual water thermostat.

2.12.3. Accuracy of the Volumetric Isotherms

The quantities to be determined in order to establish the isotherms accurately in the volumetric system are:

- (1) The volumes of the burette bulbs, the doser volume and the sorbent bulb attachment and the diameter of the manometer tube.
- (2) The pressure, initial and equilibrium.
- (3) The temperature.

The volumes were determined with the following inaccuracies:

- (1) Gas burette: negligible.
- (2) Doser Volume to the mark on the manometer ± 5 c.c.
 $\pm .8\%$ of the doser volume.
- (3) Doser Volume plus volume of sorbent bulb attachment
 ± 5 c.c. $\pm .6\%$.

In practice gas was admitted and removed with the gas burette available to the gas, the error thus being reduced to $.2\%$. The pressures were read on a cathetometer and were accurate to $.005$ cm.; corrections were applied for the unequal menisci depressions, where necessary, using the tables of Vickers and Gould.

Finally it should be noted that the errors made in this system are cumulative, thus the later readings may be in substantial error; it is in order to minimise this that the maximum volume possible is made available to the gas on admission. The ideal gas laws are assumed throughout, which a brief experiment showed to be a good approximation, accurate to 1% .

The sizes of ^{the} /volumes are shown in table 3.

TABLE 3.

Volume	Doser	Bulb 1	Bulb 2	Bulb 3	Bulb 4
Volume in c.c.	58.4	15.4	18.6	25.3	52.2

3.1 RESULTS

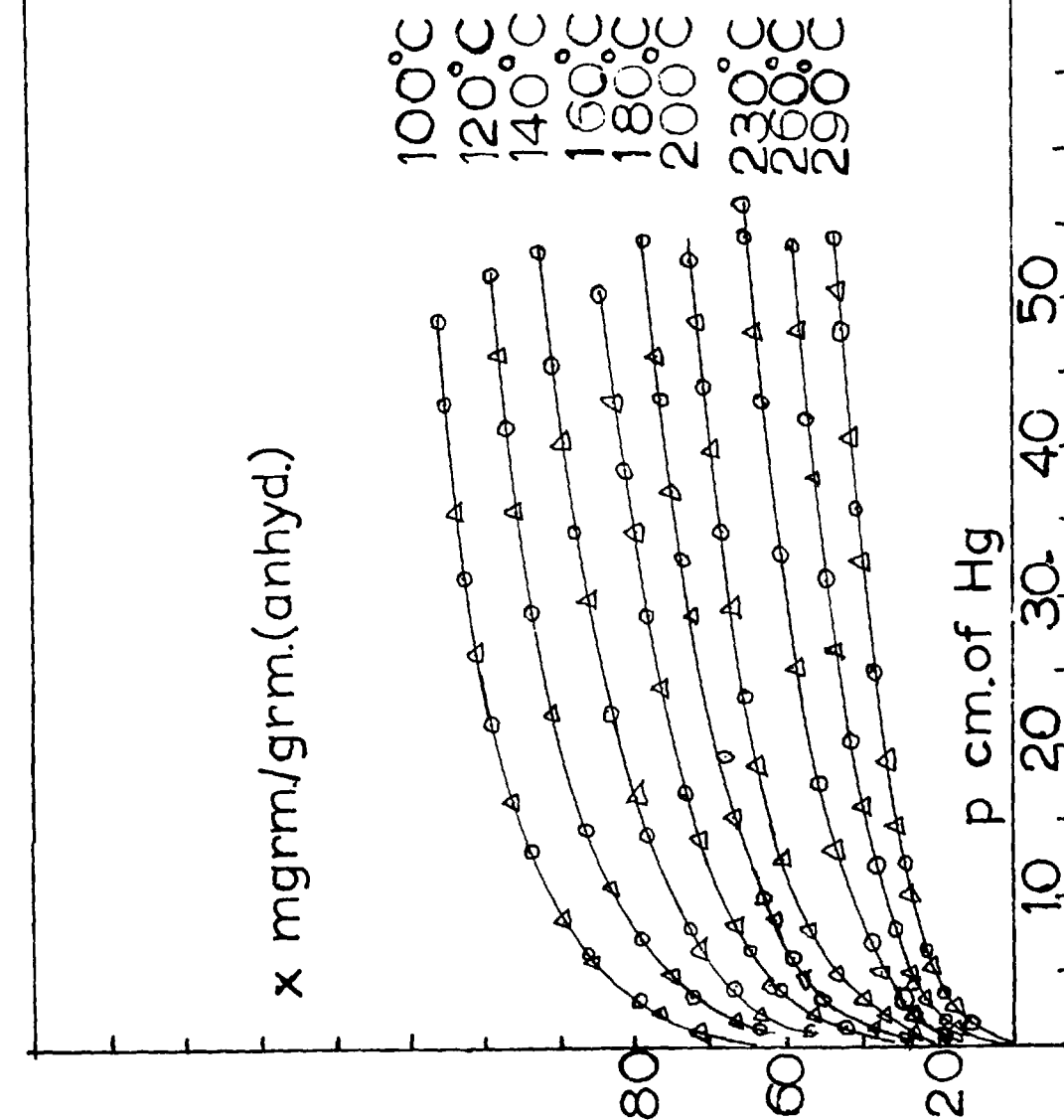
Isotherms were obtained at intervals of 20°C or 30°C between 100°C and 290°C for ammonia sorbed on each of the nine forms examined (LiX, NaX, KX, RbX, CsX, CaX, SrX, BaX, CoX) using the McBain balance; in addition isotherms were obtained for ammonia on NaX between 0°C and 70°C using the volumetric apparatus. There was a small difference in the isotherms obtained for NaX from the two experimental systems; this difference will be discussed in a later section. Accurate, reversible isotherms were obtained in all cases except for sorption on CoX which showed hysteresis; hence the CoX data are excluded from comparison and will be discussed separately in a later section. Equilibrium was established quickly and readily, most of the ammonia being sorbed within minutes of exposing it to the crystal, followed by a slow process accounting for ~5% of the sorption; equilibrium was fully established within an hour. Between an hour and an half and two hours was allowed between readings. The accuracy of the isotherms has been discussed previously. Examples of the families of isotherms obtained for NaX, CsX and SrX are shown in graphs 1, 2 and 3; these and all the others are all type 1 (of Brunauer's classification) which thus excludes multilayer formation. Layers have no obvious meaning in

such intracrystalline sorption.

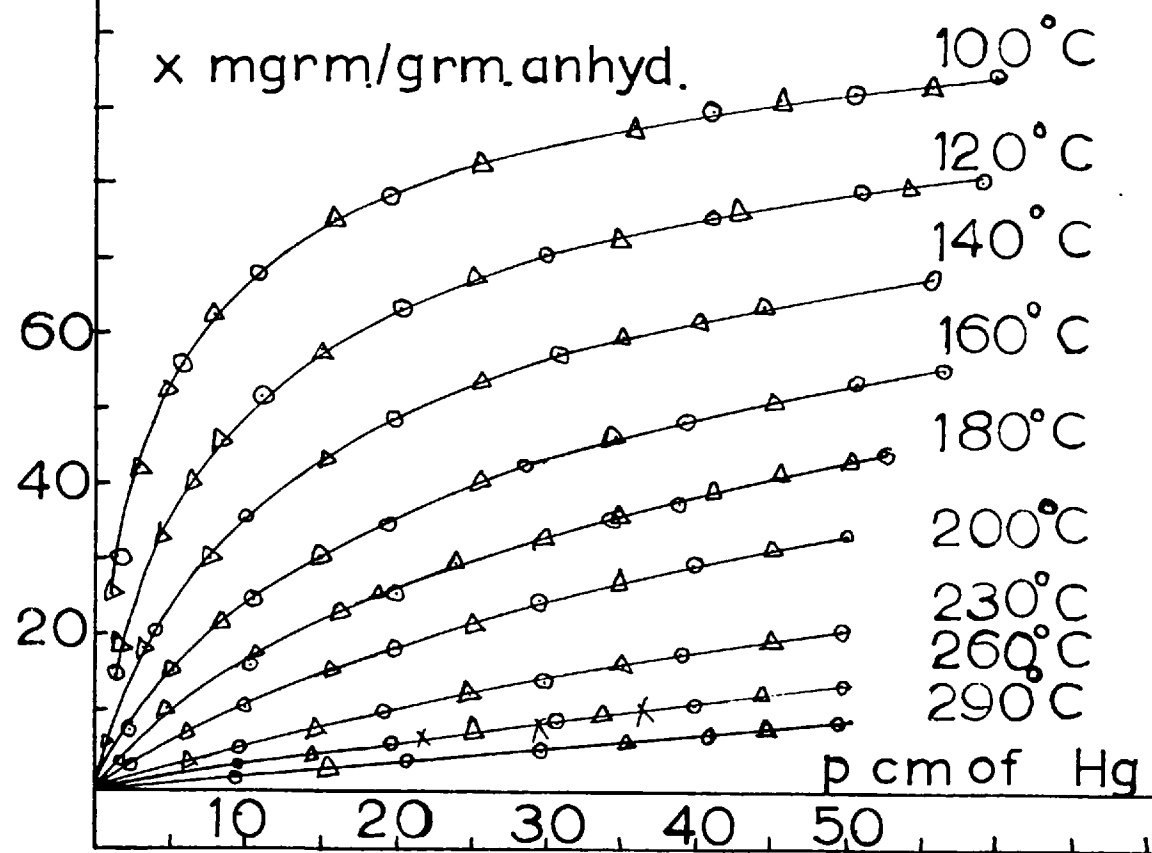
In section 3.1 - 3.3 quantities which can be obtained without reference to any reasoning other than general thermodynamic arguments will be the only ones to be discussed; in section 3.4.1 an attempt is made to interpret changes in the properties of the sorbent in terms of a statistical model. In section 4.1 methods of obtaining values for the saturation capacities and thermal expansion of ammonia sorbed in the various crystals will be discussed. An attempt to interpret the data in terms of statistical mechanical models for the sorbate will be made in section 5.1-3; this involves specific assumptions concerning the sorbent as well as sorbate. Though partial molar quantities are used in the discussion they do not arise from solution thermodynamics as such because in assuming that the sorbent is unperturbed the so-called 'solution' thermodynamics is now reduced to 'adsorption' thermodynamics.

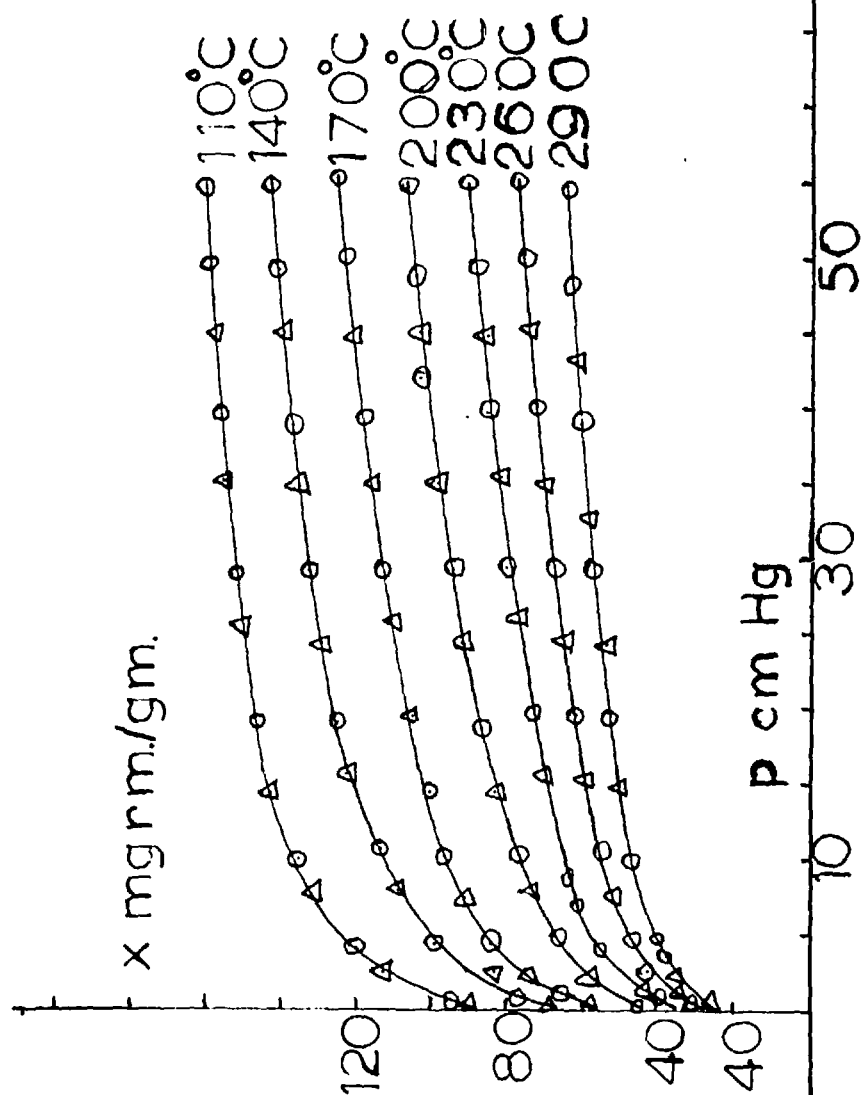
3.1.2. Percent Ion Exchange

The percentage of ion exchange was determined by gravimetric analysis in the cases of NaX, LiX, KX, RbX and CaX; in the cases of CsX, SrX and BaX it was determined using a radioactive tracer technique. The

GRAPH 1 NH_3/NaX Isotherms

GRAPH 2 NH_3/CSX Isotherms



GRAPH 3 SrX/NH₃ Isotherms

extent of exchange in each case is shown in Table 4 in which the accuracy of the determinations is also indicated.

TABLE 4

	% Cation	% Na	Estimated error	Method of analysis	% H ₂ O hydrated sample
LiX	100%	-	$\bar{+}$ 2%	grav.	28.4
NaX	100%	-		"	26.4
KX	100%	-	2%	"	23.4
RbX	60%	40%	3%	"	20.6
CsX	57%	43%	$\bar{+}$ 3%	radio-active	18.1
CaX	98%	2%	$\bar{+}$ 2%	grav.	28.6
SrX	96%	4%	$\bar{+}$ 3%	radio-active	26.1
BaX	66%	34%	$\bar{+}$ 3%	radio-active	22.8

The forms containing Rb and Cs and Ba might more accurately be referred to as RbNaX etc.; for convenience they will be referred to as RbX etc. but this should not be understood to imply complete exchange.

All the data are expressed in terms of amount sorbed per N unit cells unless otherwise stated (N unit cells is the number of unit cells per gram of anhydrous

NaX). In order to express readings on other zeolites in these terms it is necessary to know the extent of ion exchange and the percentage of Al and Si in the faujasite. Once these are known conversion factors are easily obtained, which are listed in Appendix 2.

3.2. Thermodynamic Properties of Sorbate

3.2.1. Isosteric Heats

Isosteric heats were determined for NH_3 on all forms of faujasite which were examined, except for CoX where there was irreversible sorption. The heats were obtained from plots of the experimental data in the form $\ln p$ versus x at each temperature, using the integrated Clausius Clapeyron equation:

$$1. \quad \ln p_1/p_2 = \frac{q_{st}}{4.60} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

This was used to obtain the isosteric heat from pairs of isotherms, the result being averaged over all combinations of pairs for a given amount sorbed. This method is thought to be more accurate than plots of $\ln p$ v $\frac{1}{T}$ at constant amount sorbed, and also indicates the average deviation in the heats. There appeared, in most cases, to be some evidence of a temperature coefficient but as it was within the experimental error nothing can be said

of it. The average deviation in each case was $\leq 3\%$, the maximum error being $\leq 5\%$, i.e. $\sim .5$ Kcal/g.mole.

The results are shown in graph 4 for forms of faujasite containing monovalent ions and in graph 5 for faujasites containing divalent ions. In each case the isosteric heat is plotted in Kcal/g.mole as functions of amount sorbed, measured in mg/N no. of unit cells. Alternative plots in terms of θ at 100°C or 110°C are shown in graphs 6 and 7. The heats obtained from the volumetric data are not as accurate as those obtained from the gravimetric system as in most cases they were evaluated from only three isotherms.

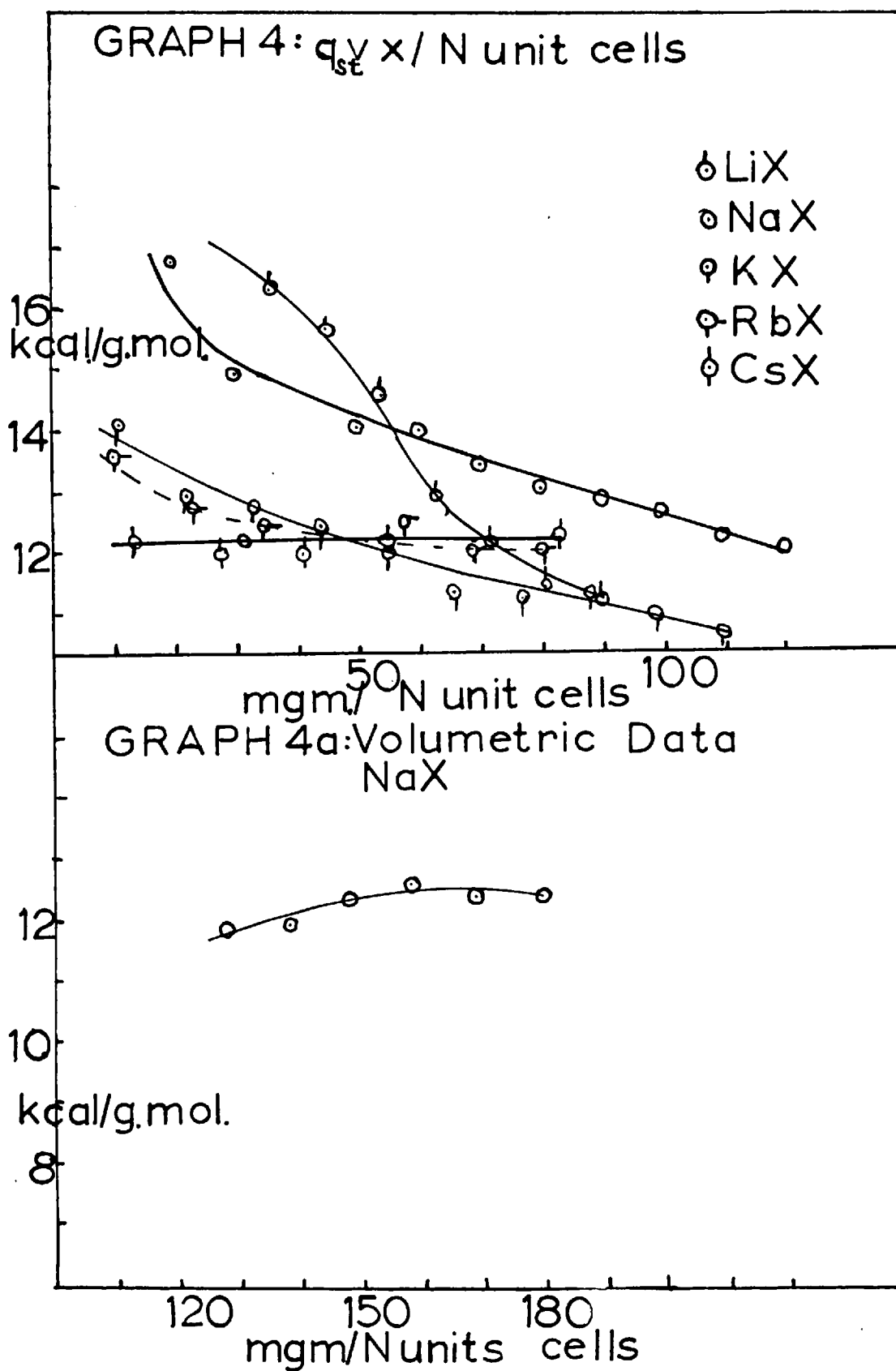
The integral as distinct from the differential heat of sorption may be compared to the latent heat of evaporation. The integral heat may be obtained by graphical integration of curves of the isosteric heat vs. amount sorbed from zero to the total coverage measured; an extrapolation of the isosteric heats to zero coverage is required for this integration to be carried out. Alternatively the integral heat may be derived at constant ψ (or ϕ). Other things being equal, the integral heat should be between one and two times the latent heat of vaporization, because a liquid regains about half the heat required to remove one molecule by the collapse of the hole made by the removal of

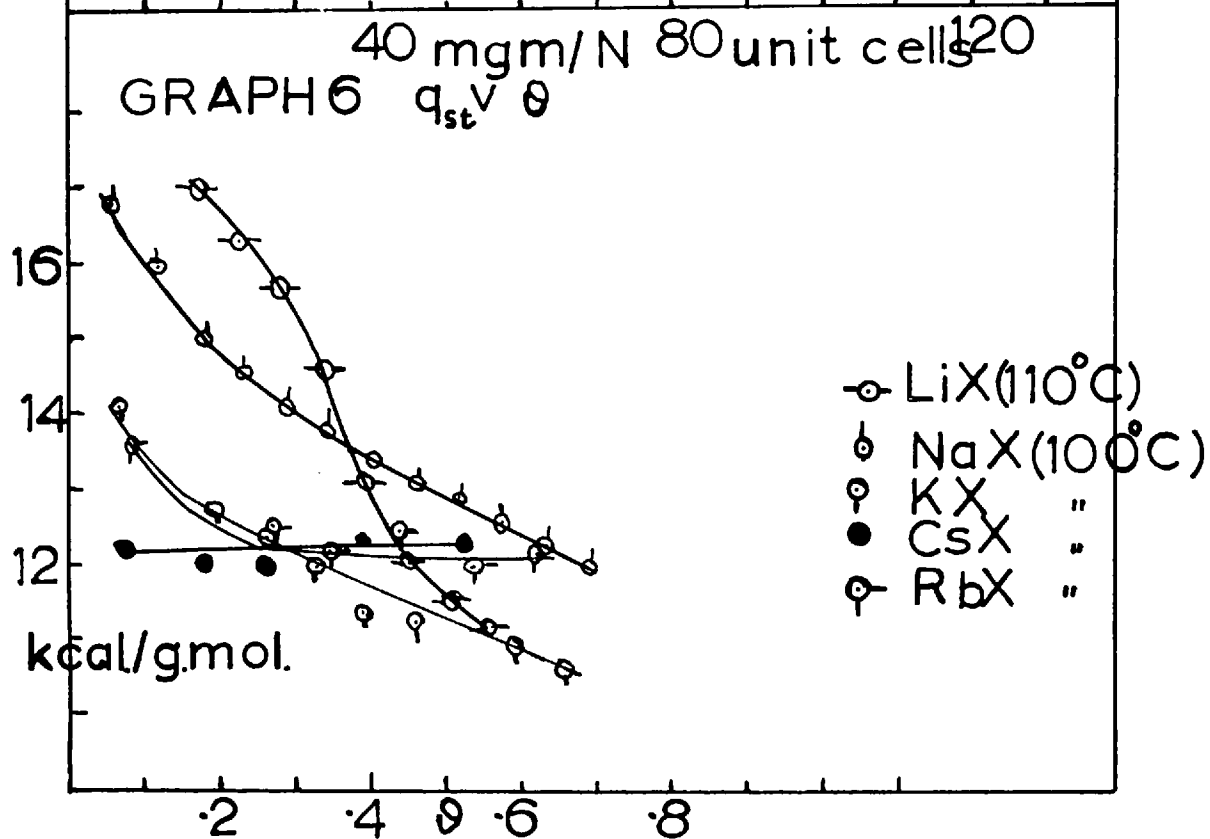
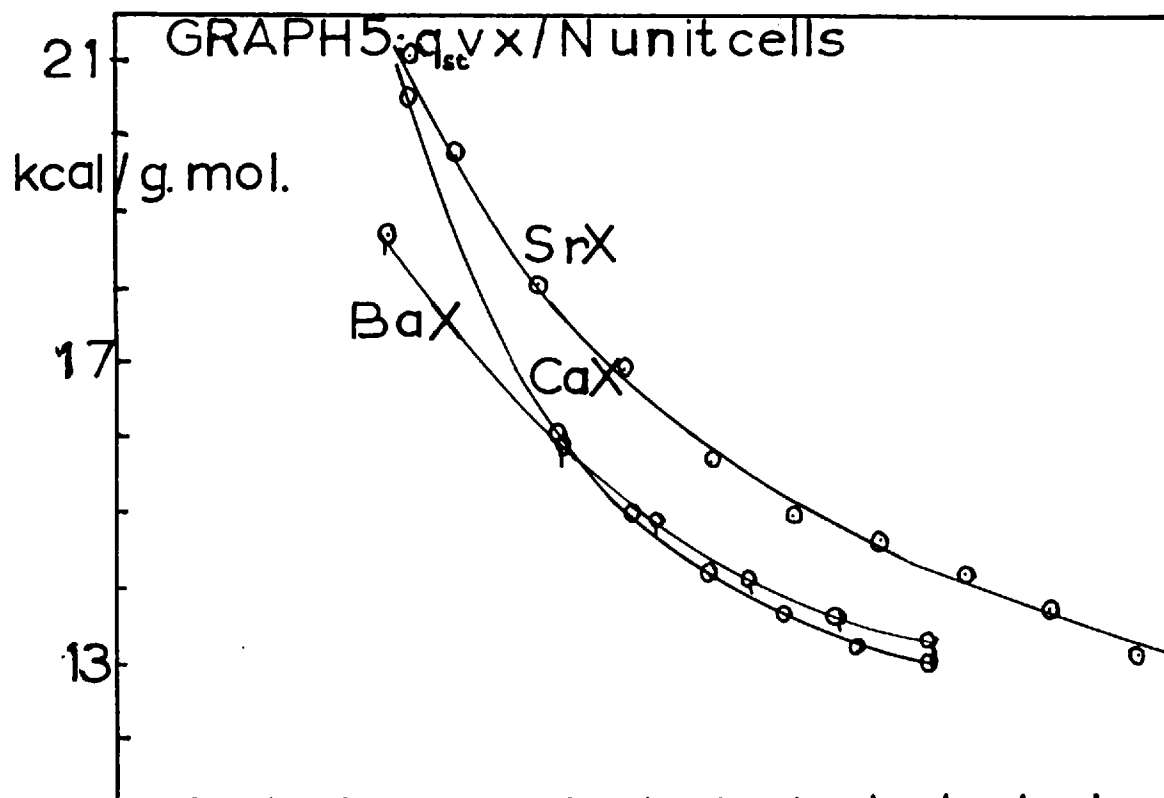
one molecule. This assumes that the type of forces responsible for the interaction energy in the sorbed and liquid states are the same. The integral heat of sorption corresponds to taking all the clusters of molecules from the sorbate into the gas phase and dispersing them therein. The values of the integral heats for NaX and SrX are shown in graph 8 for various coverages. In each case the values for two estimates of the initial heats are shown; the final value of the integral heat is not very dependent on this choice. These then are lower limits to the integral heats as the initial heats probably rise above the values chosen.

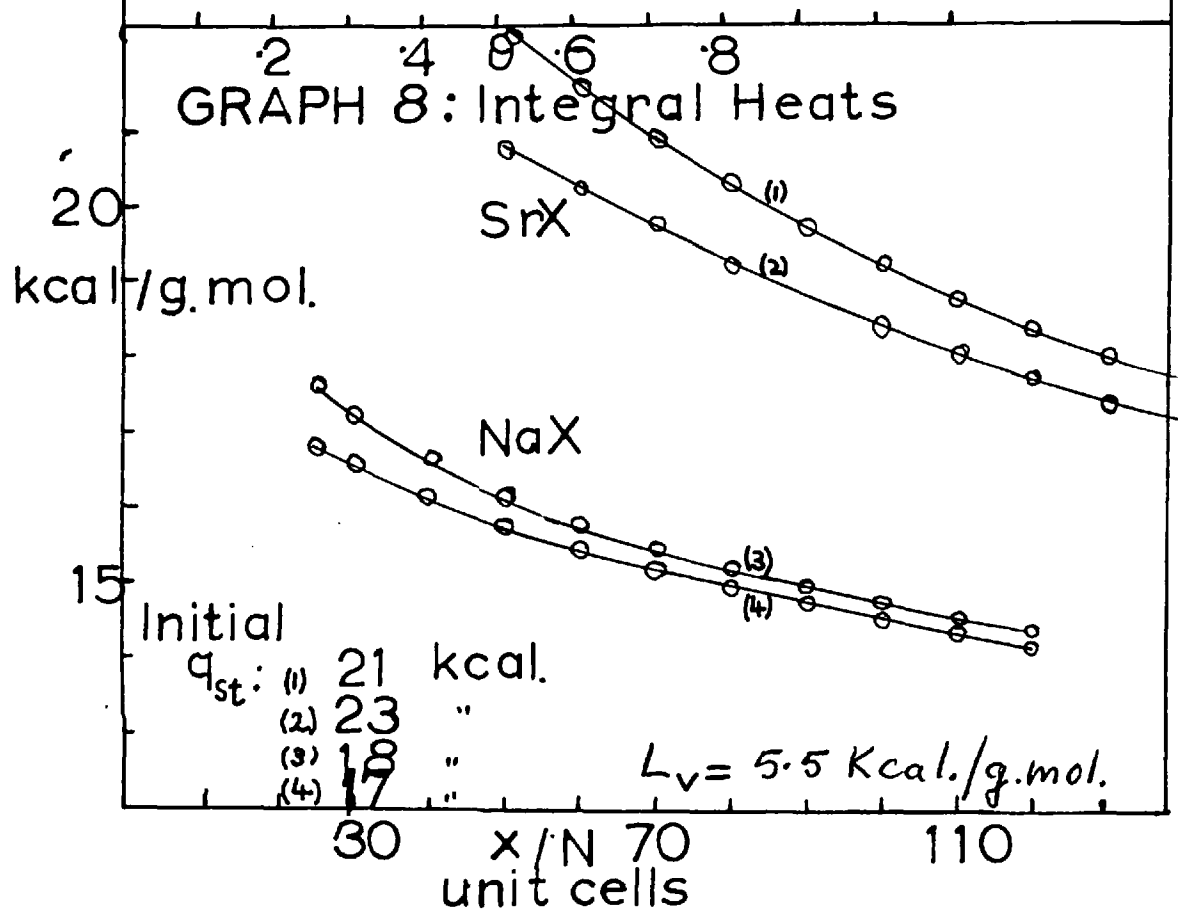
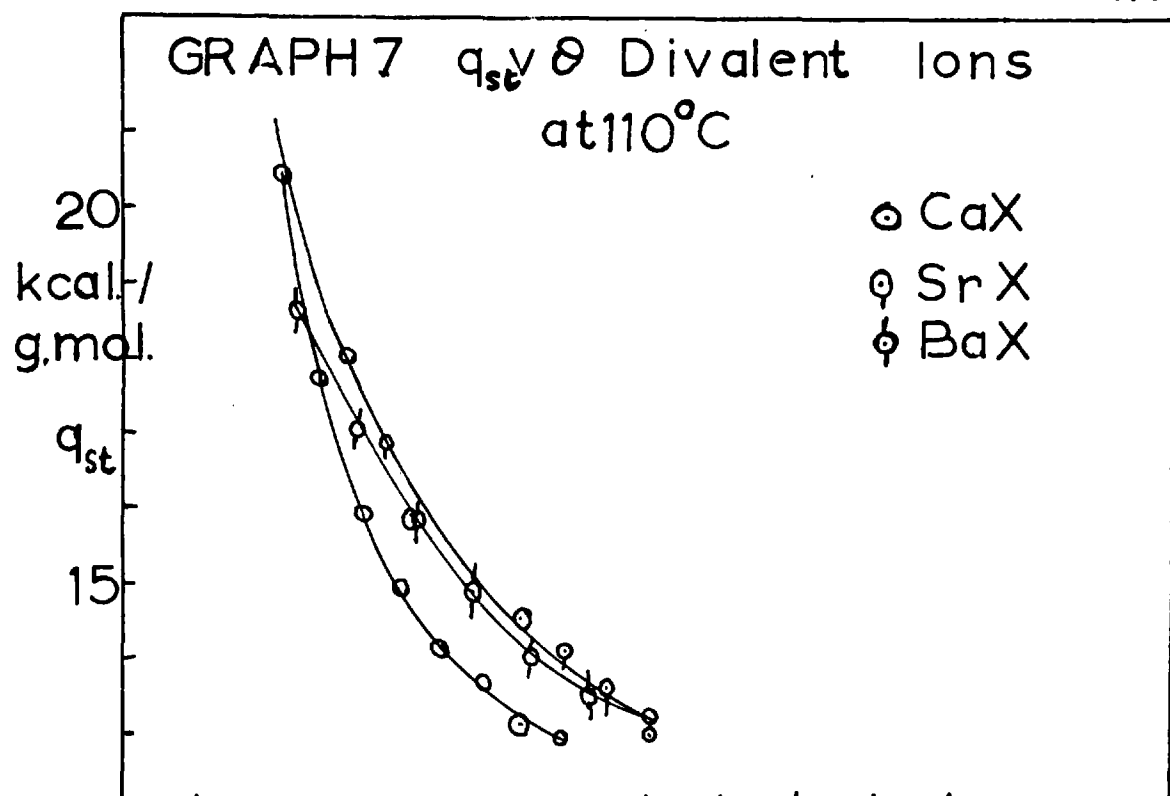
It is seen that the heats are very much higher than twice the latent heat and this may be interpreted to mean that there are substantial forces present in the crystal which have no counterpart in the liquid. Hirschfelder et al (87) apportion the energy of cohesion between two isolated ammonia molecules as follows:

Dispersion:		49.7%
Electrostatic:	1. Dipole/Dipole	45.0%
	2. Polarisation	5.3%

In the liquid the reaction field will increase the contribution from the electrostatic components.







In view of the ionic nature of the crystal, and the likelihood of strong electric fields being associated with this, one may tentatively ascribe the high heat of sorption to increased electrostatic interaction above that encountered in the liquid. This view is further supported by the substantial difference in the integral heats of ammonia on NaX and SrX, where much more intense fields are likely to occur.

3.2.2. Influence of the Cations

It is evident from the plots of ΔH_v vs x that the cation influences the heats quite markedly at low coverages. At higher coverages the isosteric heats for all forms appear to converge towards values which may be the same to within about ± 1 Kcal. The variation with coverage for NH_3 on the monovalent ion forms decreases with increase in the size of the ion present so that CsX is almost homogeneous while LiX is extremely heterogeneous. An attempt to explain this in terms of intermolecular forces will be made in a later section.

As may be seen in graph 6, at higher coverages the situation is more complex, with the curves of ΔH_v vs x for the various forms sometimes crossing each other. There does not appear to be any simple explanation of this. One might expect the electrostatic

forces to predominate at the lowest coverages and that in this region the forms with the smallest cations would have the highest heats, as is found experimentally in nearly all cases, while at higher coverages, where dispersion energies would be important, that the forms with the largest cations would have higher heats. Hence some intersection of the plots of ΔH_i vs x is to be expected.

However there are exceptions to this picture. The NaX plot lies above the KX plot for all coverages. Also the plots for the divalent ions Ca, Sr and Ba show that CaX lies below the other two for most of the coverage examined. The isosteric heats of NH_3 on SrX exceed those on the BaX and CaX, though the curve of ΔH_i vs x appears to be intersecting that for CaX at the lowest coverages. All three forms are strongly heterogeneous, the isosteric heat falling continuously from ~ 20 Kcal/mole at $\theta = .2$ to ~ 13 Kcal/mole at $\theta = .6$.

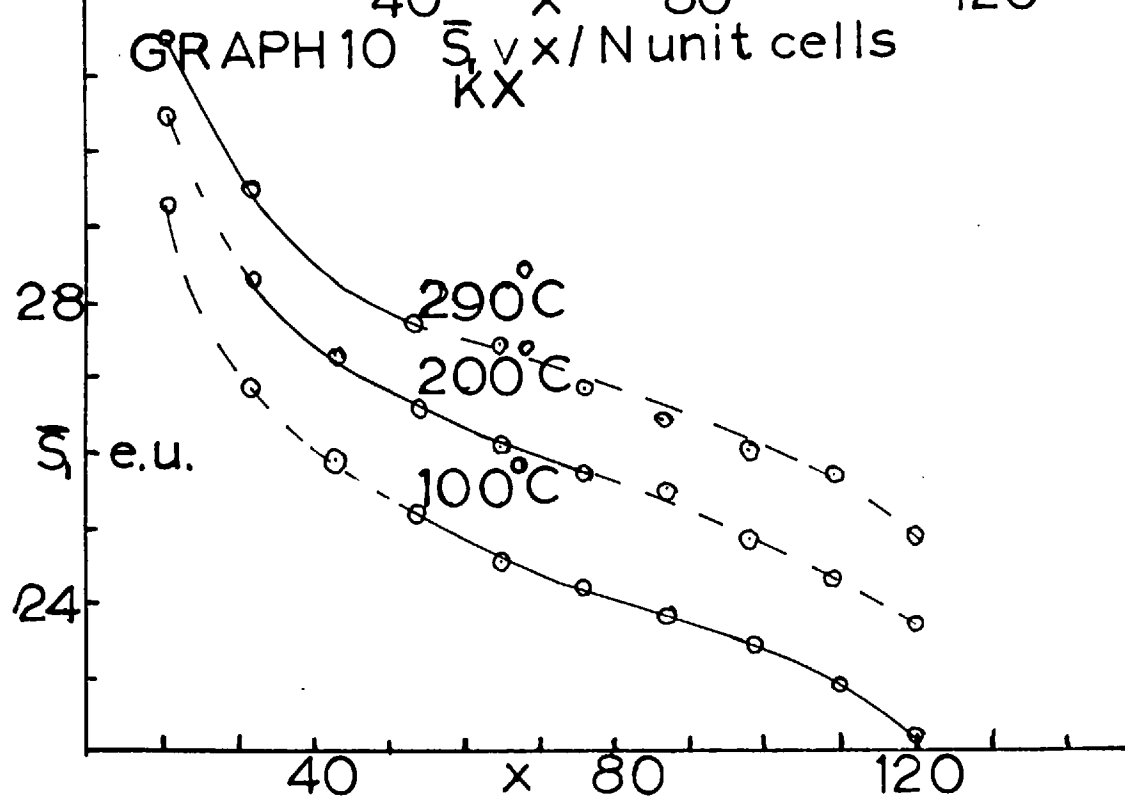
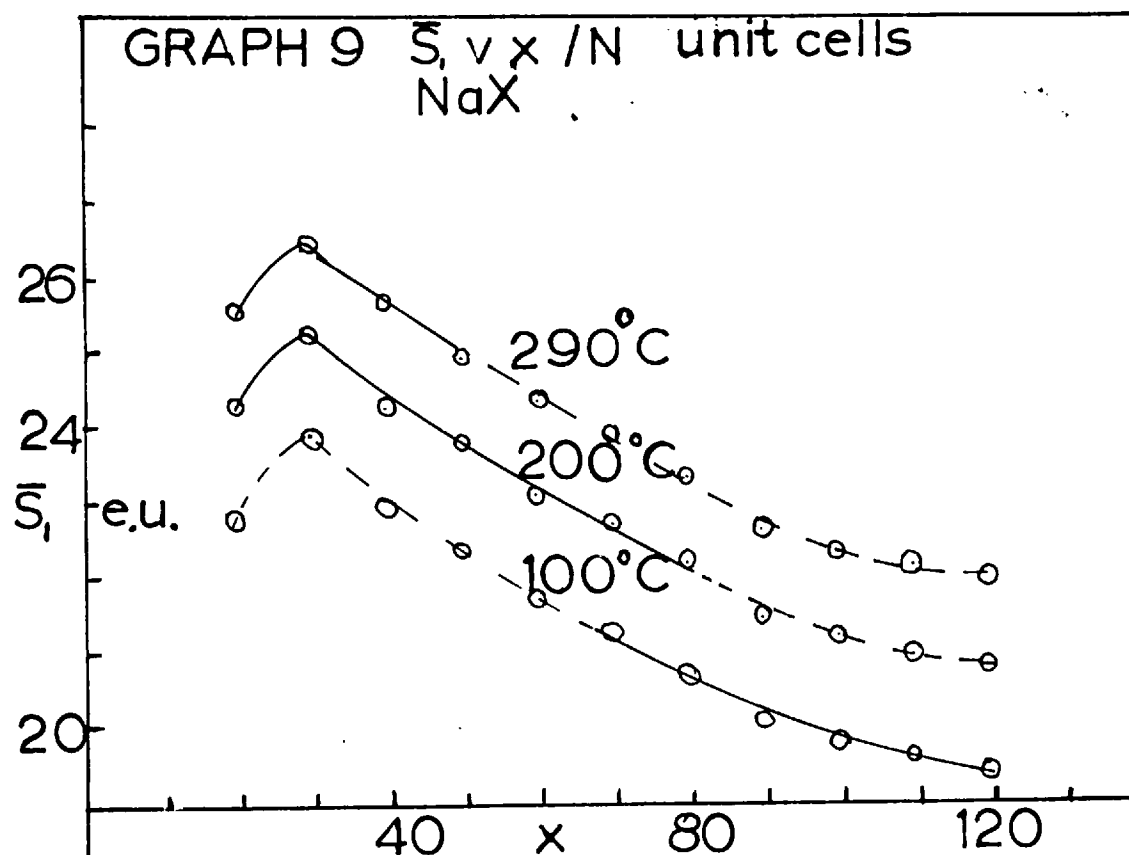
3.3.1. Entropy of the Sorbed Phase

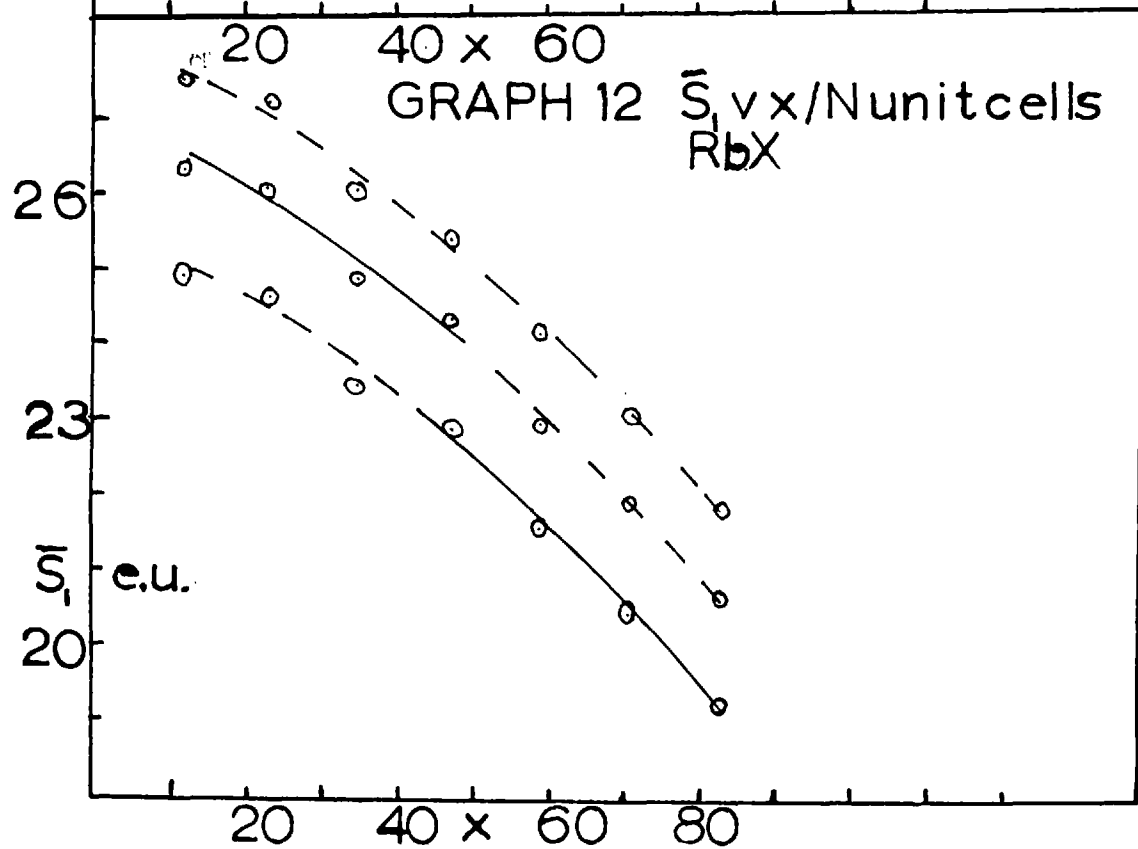
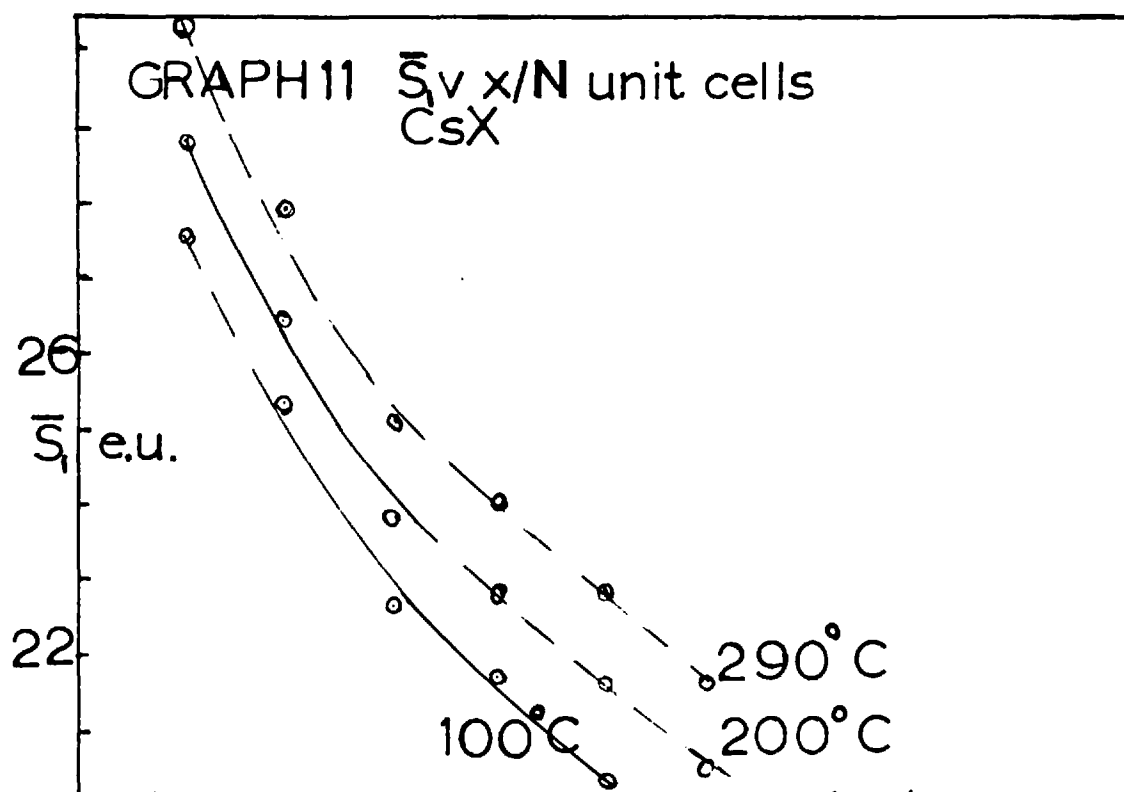
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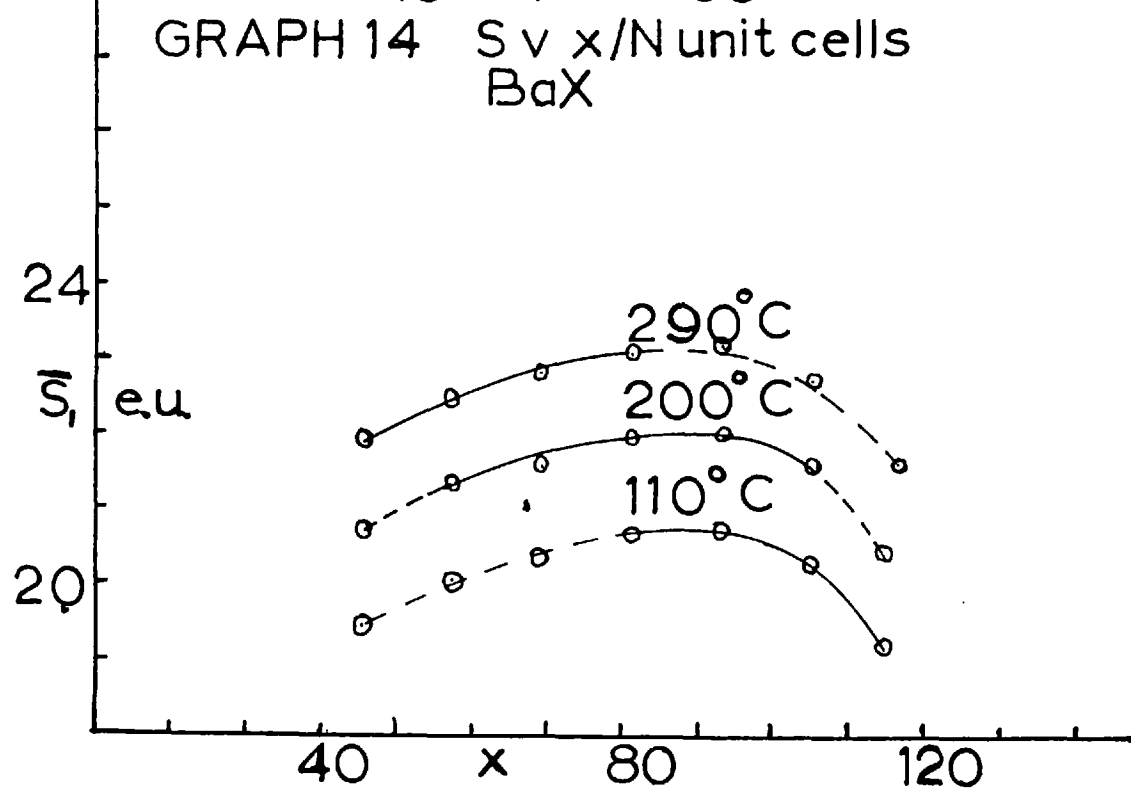
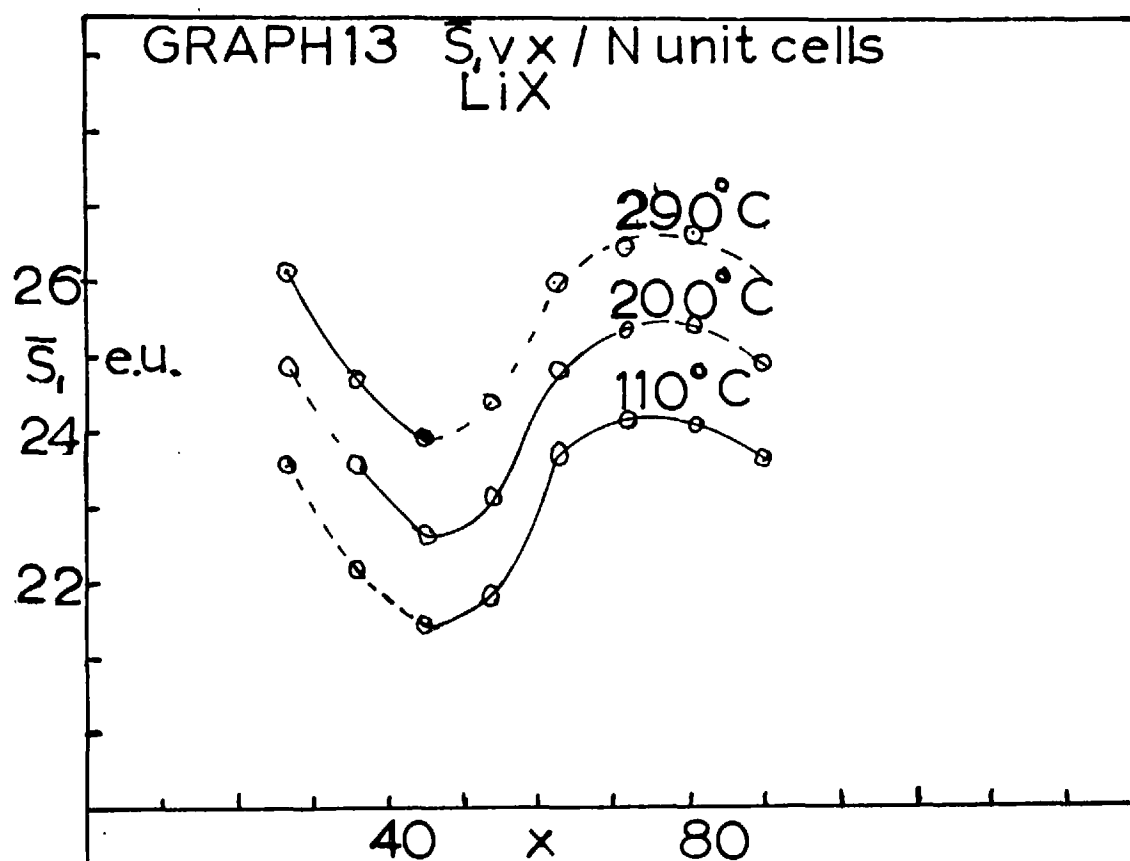
The differential molar entropies for ammonia sorbed on the various forms of faujasite were obtained from the isosteric heats, using the formula

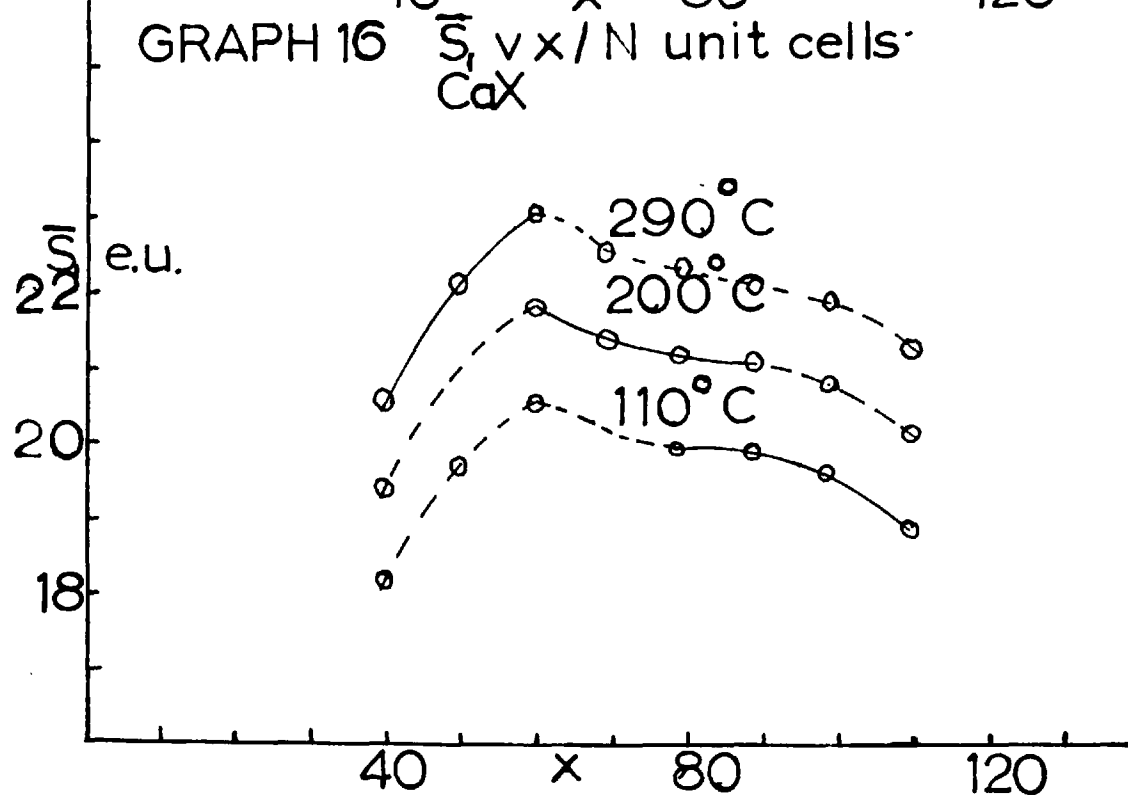
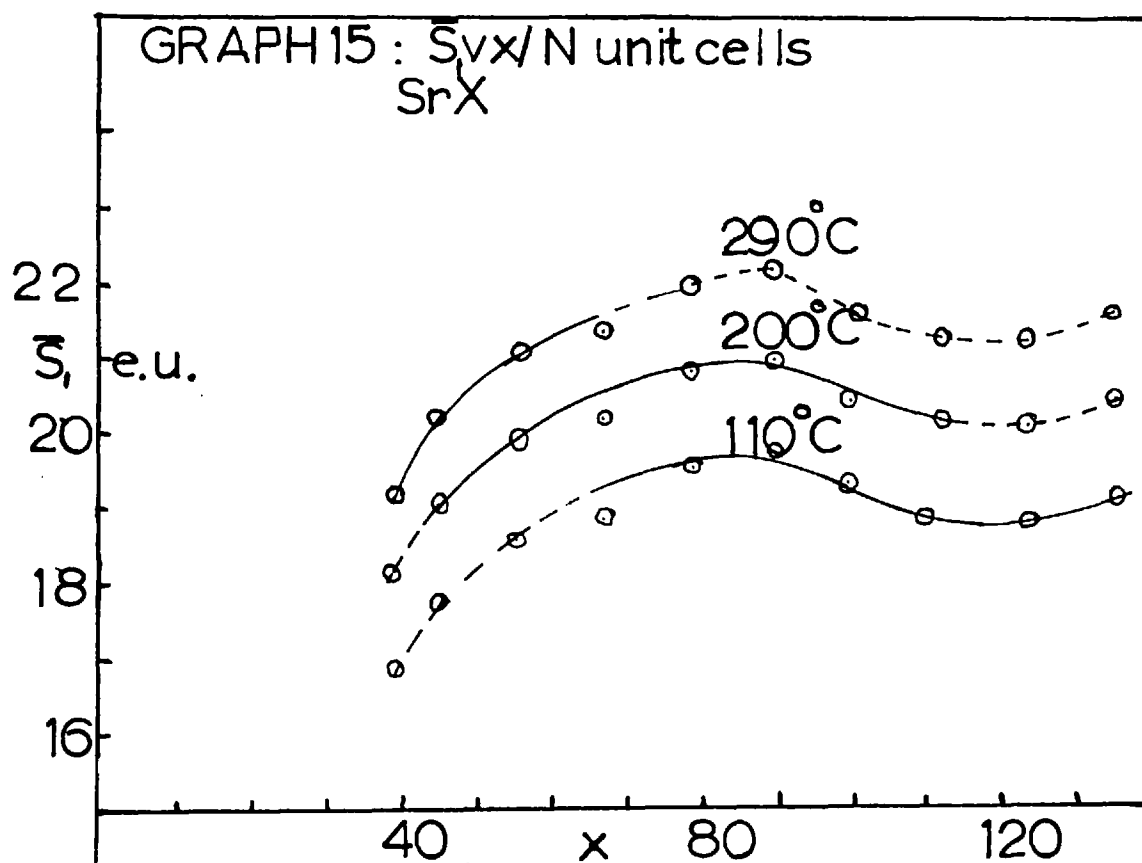
$$1. \quad \bar{S}_1 = \bar{S}_g^{\circ T} + R \ln \frac{p_0}{p} - \frac{q_{st}}{T}$$

* all entropies are quoted in cal./mol.deg.⁻¹ (e.u.)









where p is in cm. of Hg and q_{st} is in calories per g.mole. The entropy of gaseous ammonia at 1 atmosphere and any required temperature was obtained using the formula given by Spencer for the heat capacity of ammonia (21).

The differential molar entropies were obtained for the various forms of faujasite which were examined and are shown as full lines in graphs 9, 10, 11, 12 and 13 for monovalent ion forms at various temperatures. $\bar{S}_1$ for the divalent ion forms is shown in graphs 14, 15 and 16, also at various temperatures. The dotted sections are discussed in the next section.

Half Standard Entropy of Sorption

This is not the differential entropy of the sorbed phase but is the difference in entropy between that of the ammonia in a standard state in the gas phase (chosen as 1 atm. pressure) and in equilibrium in the crystal. This entropy, ΔS° , is shown in Table 5 for NaX, CaX and CsX and as can be seen from the table for a given amount sorbed ΔS° is independent of temperature. This was found to be true quite generally and has been shown by Barrer and Sutherland (46) to have the following basis:

$$2. \quad \Delta\mu_1^\circ = \Delta H_1^\circ - T\Delta S_1^\circ .$$

TABLE 5

CaX	290°C	260°C	230°C	200°C	170°C	140°C	110°C
x = 60 mgm/gm							
$\bar{S}_g^0$	49.79	49.42	49.03	48.63	48.22	47.79	47.35
$\bar{S}_1$	21.32	20.99	20.56	20.18			
ΔS^0	28.47	28.43	28.47	28.45			
x = 80 mgm/gm							
$\bar{S}_1$			21.42	20.99	20.62	20.23	19.75
ΔS^0			27.61	27.64	27.60	27.56	27.6
x = 100 mgm/gm							
$\bar{S}_1$				20.18	19.66	19.23	18.89
ΔS^0				28.45	28.56	28.56	28.46
CsX	230°C	200°C	180°C	160°C	140°C	120°C	100°C
x = 30 mgm/gm							
$\bar{S}_1$		27.21	26.98	26.47	25.97	25.76	25.65
ΔS^0		21.82	21.65	21.88	22.11	22.03	21.85
x = 50 mgm/gm							
$\bar{S}_1$				21.07	20.81	20.48	20.35
ΔS^0				27.01	26.98	27.02	26.85
NaX	290°C	260°C	230°C	200°C	180°C	160°C	140°C
x = 40 mgm/gm							
$\bar{S}_1$	25.64	25.9	24.80	24.33	24.13	23.93	
ΔS^0	24.15	24.52	24.23	24.30	24.22	24.15	
x = 80 mgm/gm							
$\bar{S}_1$			23.22	22.73	22.42	22.12	21.84
ΔS^0			25.81	25.90	25.93	25.96	25.95
x = 100 mgm/gm							
$\bar{S}_1$					20.69	20.38	20.08
ΔS^0					27.39	27.41	27.42

3. But (a) $\Delta\mu_1^0 = RT \ln P/p_0$, and (b) $\Delta H_1^0 = \Delta H_1$ for an ideal gas. On rearranging (2)

$$4. \quad \Delta S_1^0 = - \frac{\Delta H_1}{T} + R \ln P/p_0$$

Differentiating this w.r.t. T for a constant amount sorbed the R.H.S. is identically zero, because of the Clausius Clapeyron equation for the isosteric heat of sorption.

This relationship may therefore be used to obtain the differential entropy of the sorbate at any temperature once the half standard entropy of sorption and the entropy of the gas in a standard state in the gas phase at that temperature are known since

$$5. \quad \Delta S_1^0 = S_g^{oT} - \bar{S}_1.$$

$\bar{S}_1$ values have been obtained in this way and are plotted in the dotted portions of graphs 9 - 16. Further, if the heat is assumed to be independent of temperature the pressure may be calculated for the particular amount sorbed whose entropy is known. This latter use of the relationship is the same as extrapolating the $\ln p$ vs $\frac{1}{T}$ plot and hence is less ^{exact} than using the relationship to obtain the differential molar entropy at any temperature, though the error is within that of the experiment.

As may be seen from figures 9 and 13 the differential molar entropy of ammonia on the energetically

heterogeneous monovalent ion forms of faujasite (i.e. NaX, LiX) passes through a maximum at an intermediate coverage and then decreases with coverage. The partial molar entropy of NH_3 on the more homogeneous forms (i.e. KX, RbX, CsX) does not pass through a maximum (see graphs 10, 11 for KX and CsX) but decreases continually with increasing coverage. The partial molar entropy of ammonia on LiX is anomalous in that it shows a minimum as well as a maximum. The differential entropy of ammonia on the divalent ion forms also shows the maximum, followed by a decrease with increasing coverage, though the entropy on SrX appears to have two maxima (see graph 15).

3.3.2. Comparison with Entropy of Liquid Ammonia

The integral molar entropy may be obtained from plots of $\bar{S}_1$ vs. amount sorbed by use of the relationship

$$\bar{S}_1 = \frac{1}{n_1 - n_2} \int_{n_2}^{n_1} \bar{S}_1 dn$$

The integral molar entropy has been obtained for ammonia on several of the sorbents at several temperatures using this equation performing the integration graphically. The results are listed in Table 6.

In comparing these quantities it should be noted that they were not all obtained in 'corresponding states'. In order to do this they should all be obtained at the same θ and for comparison with the entropy of liquid it would be best to obtain this for $\theta = .5$, where any configurational term (or the translational term) would be a minimum or at least more comparable for the several forms. This is not the case in Table 6 where the entropy has been obtained between these amounts sorbed indicated. The quantities listed in Table 6 are not the 'integral' quantities of adsorption thermodynamics which would require an extrapolation of $\bar{S}_1$ to zero x ; however this should not alter the final result very much, as was also the case when obtaining the integral heats. On the more homogeneous faujasites (CsX, RbX, KX) the extrapolation of $\bar{S}_1$ to zero coverage would cause some increase in $\tilde{S}_1$ but in these cases the extrapolations are for very small ranges of x . For the heterogeneous forms (NaX, CaX, BaX, SrX) $\bar{S}_1$ is decreasing at low coverages and extrapolation to zero would decrease $\tilde{S}_1$.

The integral molar entropies of ammonia at 100° or 110° in the various sorbents are all smaller than the entropy of the liquid at the same temperatures. The entropies of the liquid and of the sorbate are made up of configurational, vibrational, librational

rotational and interaction terms. In the crystal the configurational term would probably be greater as the density is smaller; however the interaction energy term would be smaller in the sorbed phase. The smaller entropy of the sorbed phase is what would be expected if there are permanent electric fields in the crystal which would tend to orientate a dipole. In view of this it is to be expected that the divalent forms, possessing the stronger fields, would cause the entropy of ammonia to be smaller in these systems, as is actually the case. The difference between the integral molar entropies of liquid ammonia and of ammonia sorbed in NaX at 100°C, between the coverages indicated in Table 6 is 2.7e.u. while in the divalent forms the differences are between 4.0e.u. (for BaX) and 5.2 (for SrX) at 110°C. In KX the integral molar entropy is slightly larger than the entropy of the liquid at 100°C, by .5e.u. The integral molar entropy of ammonia in CsX is very close to that of ammonia in NaX at all temperatures examined, which may partly be accounted for by the fact that CsX is only 57% exchanged.

TABLE 6
 $\tilde{S}_1$ (e.u.)

LiX	NaX	KX	CsX	CaX	SrX	BaX	S_L	T°C
	21.39	24.62	21.76				~~24.07~~	100°C
23.13				19.71	18.92	20.28	24.23	110°C
24.23	22.81	26.11	23.03	20.99	21.34	21.57		200°C
25.47	23.99	27.32	24.20	22.15	22.54	22.35		290°C
n_2 27	20	10	10	40	40	40	mgm/N. unit cells	
n_1 110	110	100	90	110	135	110		

3.4. Thermodynamic Properties of the Sorbents

3.4.1. Free Energy Changes of the Sorbent

The thermodynamic properties of the sorbents may be obtained from the isotherm data via the argument outlined in section 1.3.1.2. This leads to the following equation for $\Delta\mu_2$ in which the molar unit of the sorbent, following Barrer (32), will be taken to be $\frac{1}{192}$ part of a unit cell.

$$1. \quad \Delta\mu_2 = V_M P - \frac{RTM}{m} \int_0^P \frac{x}{p} dp .$$

This assumes that the gaseous sorbate behaves as an ideal gas and that the sorbent does not swell on sorption; the latter assumption is not important as the second term in equation (1) is much larger than the first at all times. The integration may be carried out graphically. Because x/p becomes very large for small p , it is necessary to choose a reference standard state other than the empty sorbent. The chosen state was one in which the sorbent contained s^* mgm/N unit cells for the three forms (LiX, KX, SrX) which were examined. Equation (1) now reads:

$$2. \quad \Delta\mu_2^S = \mu_2^S - \mu_2^S = V_M(P_2 - P_1) - \int_{P_1}^{P_2} \frac{RTM}{m} \frac{x}{p} dp$$

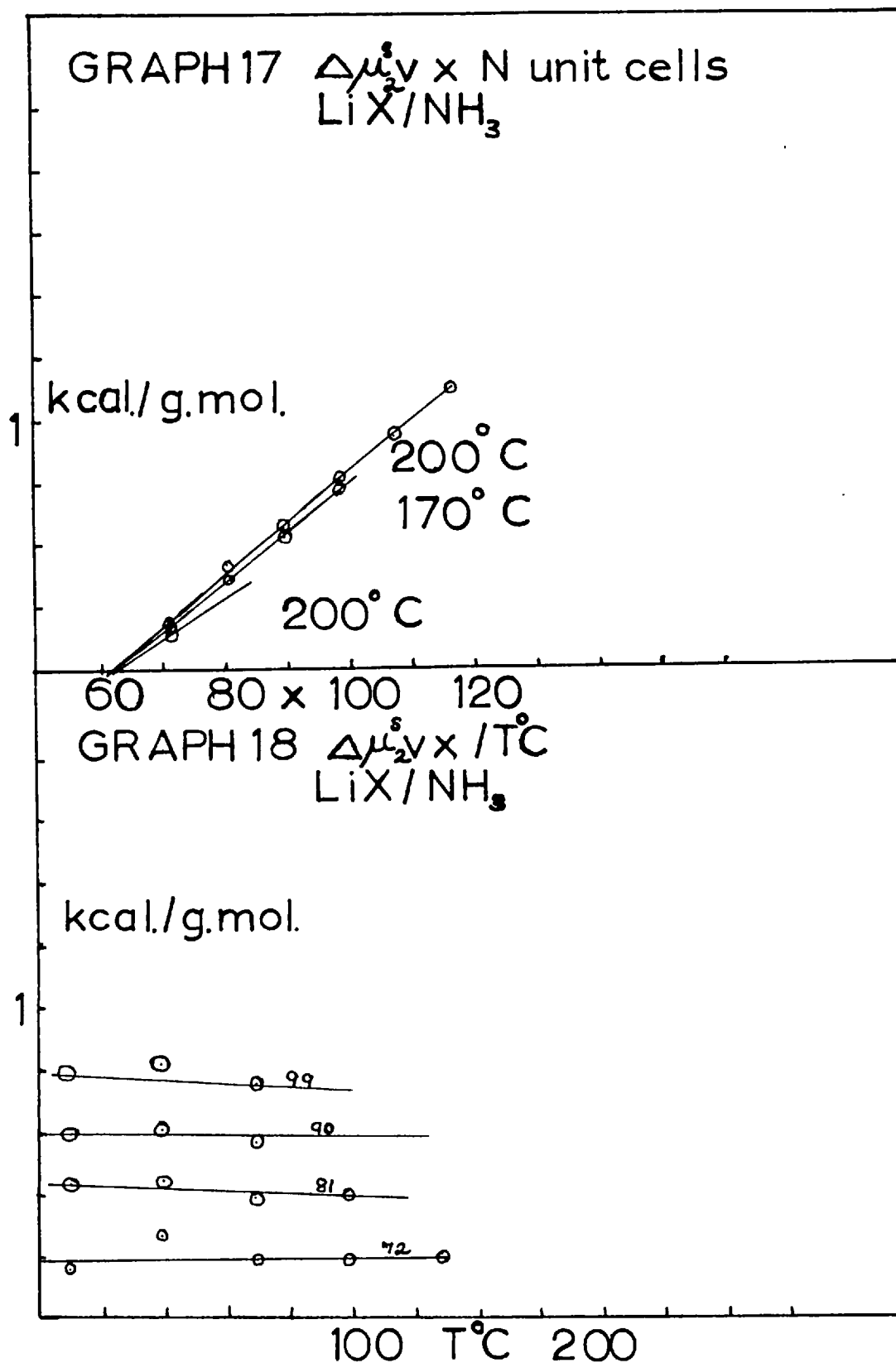
* $s = 63.3$ mgm/N unit cells.

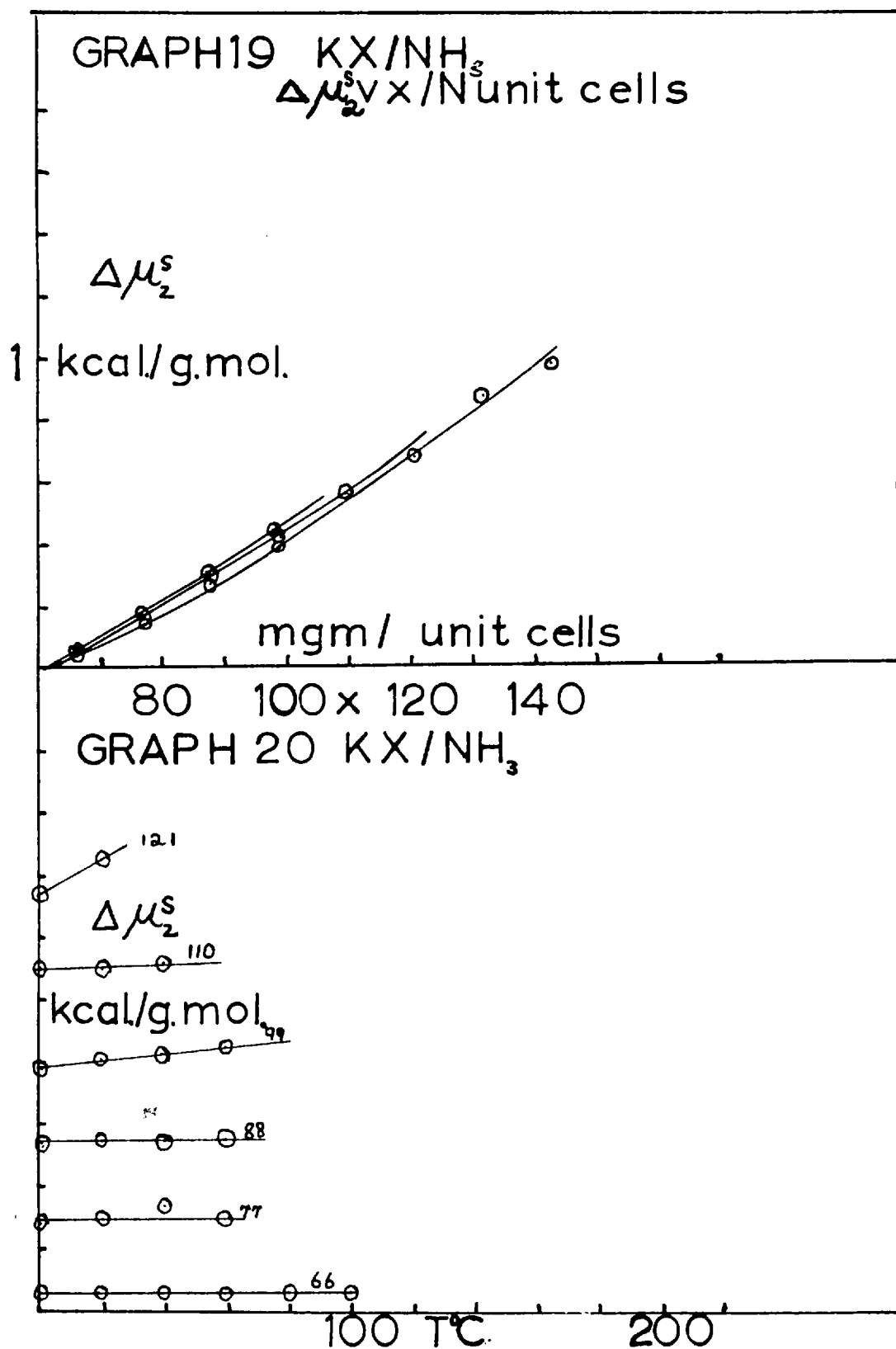
where P_1 is the equilibrium P at s mgm/N unit cells. At the lowest temperatures it was necessary, in one or two instances, to obtain the equilibrium pressure for s mgm/sorbed per N unit cells from the relationship outlined in section 3.3.1 using the temperature invariance of ΔS° and assuming ΔH to be independent of temperature. This is an approximate procedure, but the error involved in it should be within the experimental error. The contribution to the total integral of $\int \frac{x}{p} dp$ from those parts of the integral which involve temperature extrapolated values of p is small at the coverages for which the integrals were obtained and which are shown in graphs 17, 19, 21, except for one or two of the lowest coverages. The results are shown in graphs 17, 19 and 21, showing that the changes are small in all cases and are never more than two kilocalories.

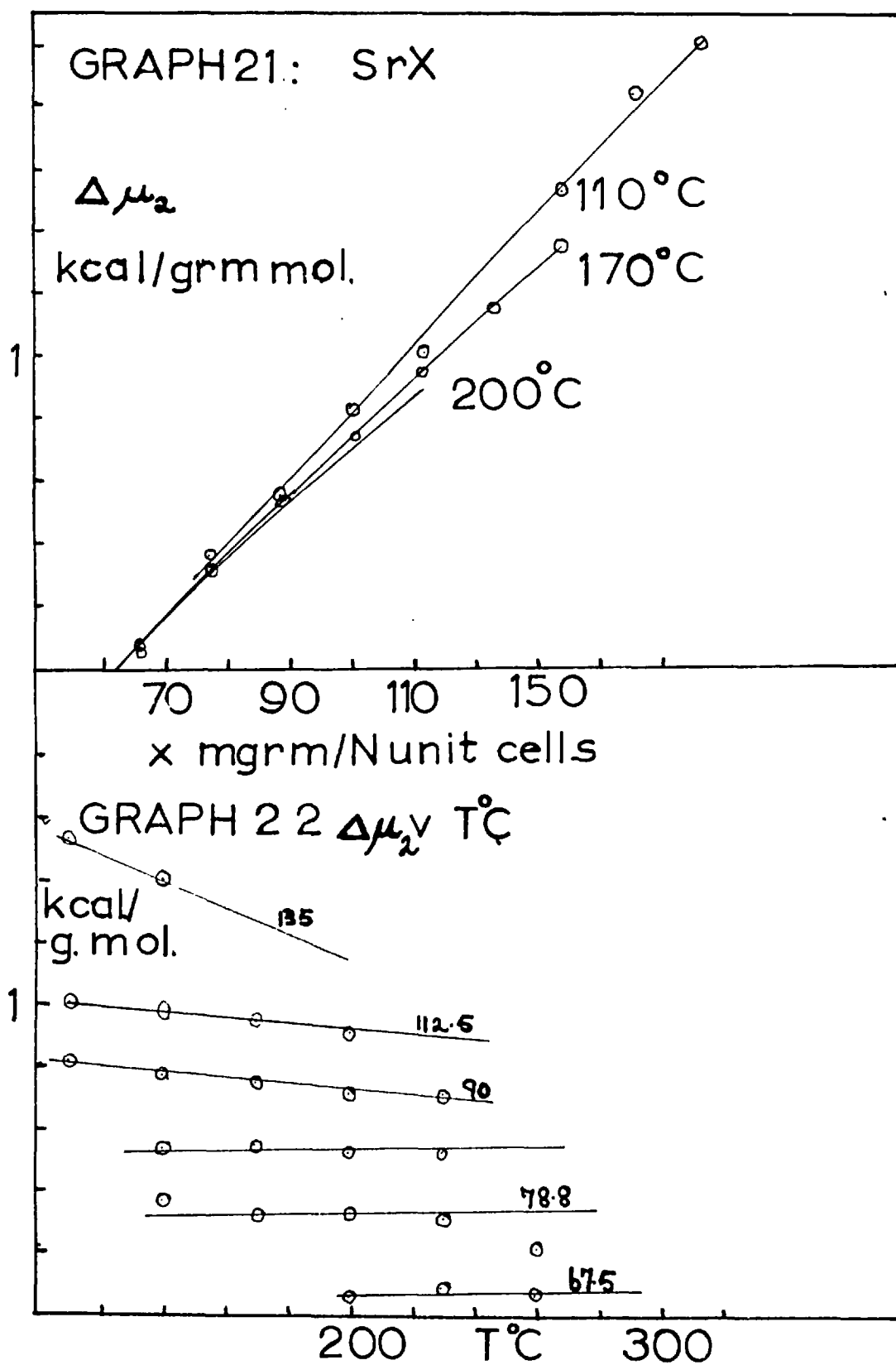
The partial molar entropy of the sorbent may be obtained from the following standard relationship:

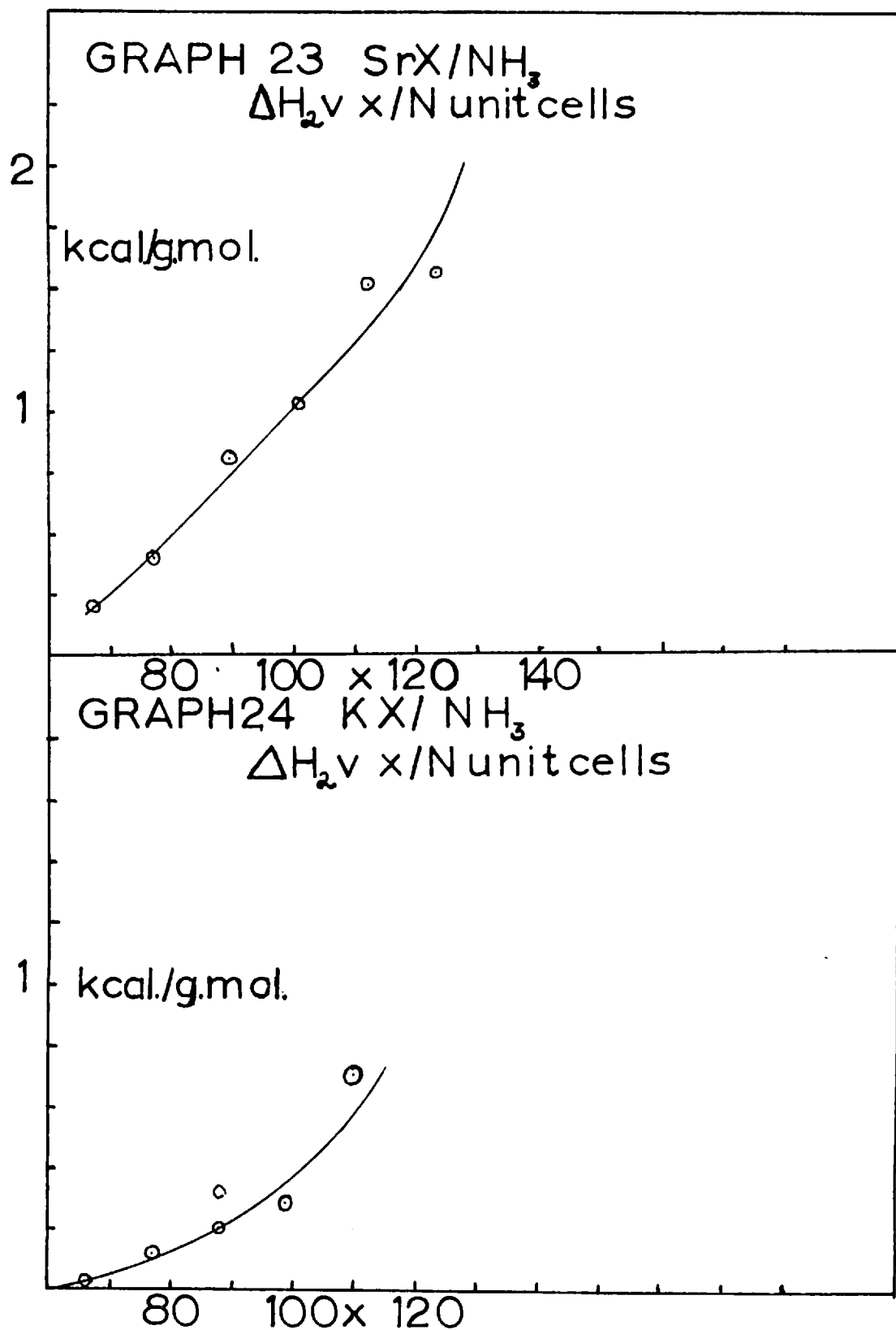
$$3. \quad \frac{\partial(\Delta\mu_2^S)}{\partial T} = -\Delta S_2^S$$

Plotting $\Delta\mu_2^S$ against T, the slope is ΔS_2^S . Plots are shown of $\Delta\mu_2^S$ against the temperature in graphs 18, 20 and 22, which show the slopes to be very small; the determination of the entropy of the sorbent by this method is too inaccurate to be worth evaluating.









3.4.2. Enthalpy Changes of the Sorbent

The enthalpy change of the sorbent may be obtained via the Gibbs Helmholtz relationship,

$$\frac{\partial}{\partial \left(\frac{1}{T}\right)} \left(\frac{\mu_2 - \mu_2^S}{T} \right) = \bar{H}_2 - \bar{H}_2^S = \Delta \bar{H}_2^S$$

by plotting $\frac{\Delta \mu^S}{T}$ against $\frac{1}{T}$; the slope of this plot is the enthalpy change, assuming that this is independent of temperature. The results are shown in graphs 24,25 which show that in the two cases examined (KX, SrX) the changes are not very large and are positive in sign, that is the opposite to the change in enthalpy of the sorbate.

3.4.3. Interpretation of Changes in Sorbent

In order to discuss changes in the thermodynamic properties of the sorbents further it is necessary to give a molecular interpretation to these changes; to do this the statistical thermodynamic treatment developed for clathrates (88) will be used. The situation of guest molecules in clathrates is not exactly analogous to the situation of guest molecules in faujasite. In the former case one, and only one, guest molecule occupies, and is localised in, one cavity. These

cavities are then sites of an ideal Langmuir type.

Making the usual assumptions for Langmuir type sorption which are probably very accurate in this case, the change in chemical potential in going from the empty sorbent to the equilibrium state, for inclusion of guest molecules in sites (cavities) of one type only,

$$1. \quad \Delta\mu_2 = \mu_2 - \mu_2^0 = \frac{RT}{m} \ln(1-\theta)$$

where m is the ratio of the number of structural units to that of cavities (sites) (θ is here the fraction of cavities occupied).

The sorption of ammonia is assumed to be confined to the supercages in faujasite, where not one but a cluster of ammonia molecules may be sorbed and may have contact with clusters in neighbouring cavities. However if the volumes of the faujasite cavities can be arbitrarily divided into sites for one guest molecule only, then the same treatment can be applied to sorption in faujasite; it should be noted that in doing this molecular interactions between the sorbate molecules are ignored, which is very reasonable for the clathrate systems but is probably not realistic for sorption in faujasite.

The change in chemical potential of the sorbent in going from the pure sorbent to the equilibrium state is now given by

$$2. \quad \Delta\mu_2^0 = \frac{n_{\text{sat}}}{24} RT \ln(1-\theta)$$

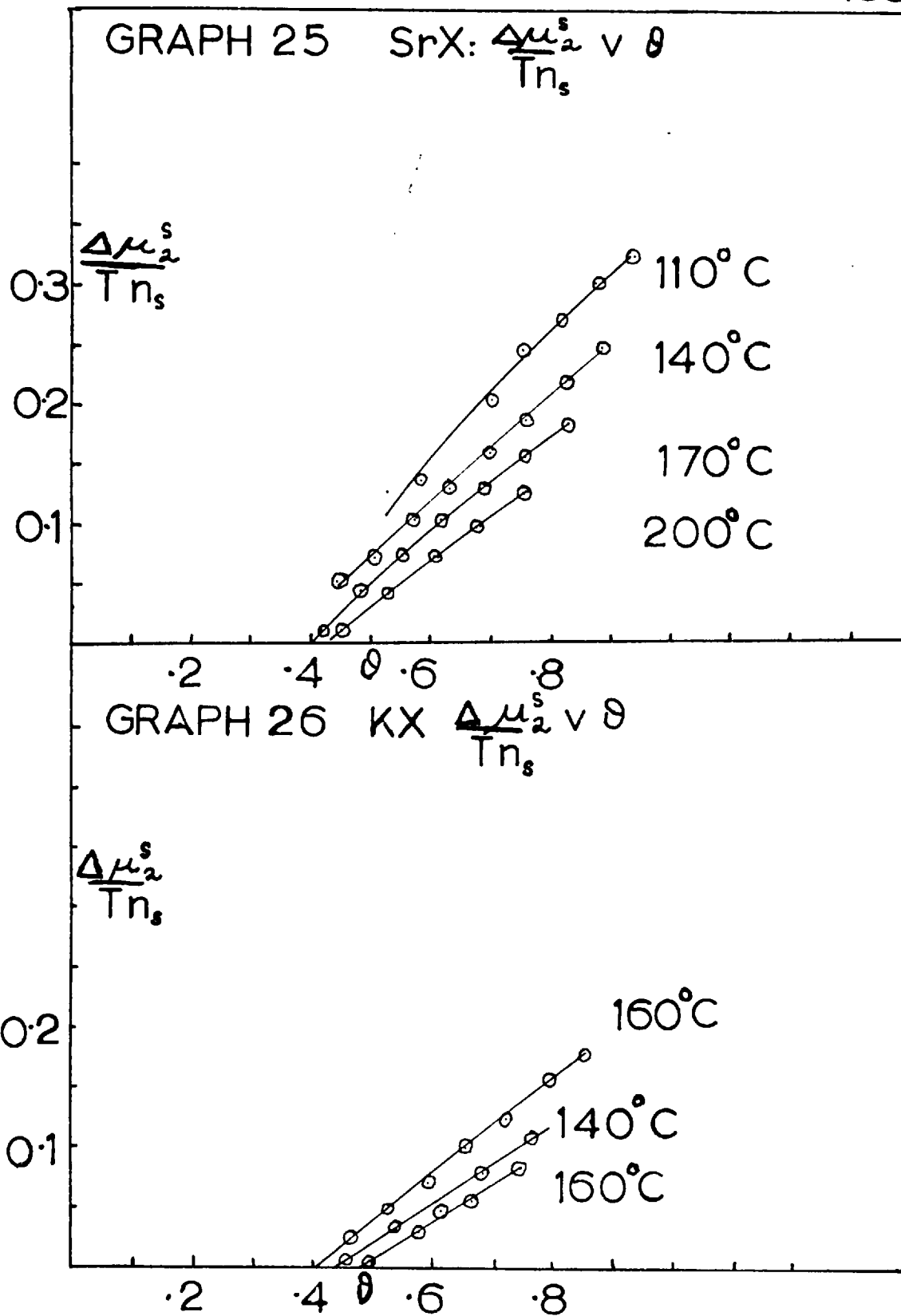
where $n = \frac{24}{n_{\text{sat}}}$; n_{sat} = no. of molecules sorbed per cage at saturation. n_{sat} is taken to vary with temperature and need not be a whole number; the temperature variation of n_{sat} violates one of the original Langmuir assumptions. Following from equation (2) a plot of $\frac{\Delta\mu_2^0}{Tn_{\text{sat}}}$ against θ should yield a universal curve independent of the sorbent. As $\Delta\mu_2^0$ was not obtainable, plots of $\frac{\Delta\mu_2^S}{Tn_{\text{sat}}}$ against θ were obtained and are shown in graphs 25 and 26 for SrX and KX from which at once it is obvious that this model will not hold for sorption of ammonia on SrX and KX. In fact for $\Delta\mu_2^S$ the change in chemical potential of the sorbent is given by

$$\Delta\mu_2^S = \frac{n_{\text{sat}}}{24} RT (\ln(1-\theta) - \ln(1-\theta_s))$$

where θ_s is the value of θ at s mgm/N unit cells, which will be temperature dependent because the saturation values are. However the variation of θ_s with temperature is not very large (e.g. for SrX between 200°C and 110°C it varies from .3891 to .2916, a change of .100 or of log .13). Another possible cause of the discrepancy could be that sorption is occurring in the sodalite cages as well as the supercages; the

calculation of the change in chemical potential of the sorbent would then be given by a different expression, involving separately the degree of filling in both types of cages, quantities which could not be obtained from the experimental data.

Finally one should note that these changes in the thermodynamic properties of the sorbent cannot be related directly with perturbations of the sorbent; all that may be said is that any changes which require much energy cannot occur, if the changes in the thermodynamic properties are small.



4.1. Thermal Expansion of the Sorbate at Constant ϵ

As was shown in section 1.3.3 the thermal expansion of the sorbed fluid at constant ϵ near saturation is given

$$-\frac{1}{x}\left(\frac{\partial x}{\partial T}\right)_{\epsilon} = \alpha_i - \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{\epsilon}$$

where ϵ is the free energy change on sorption in going from the liquid to the sorbate, i.e. $\epsilon = RT \ln \frac{p_{V.P.}}{p}$, where $p_{V.P.}$ is the saturated vapour pressure of the liquid at that temperature. Hence this relationship can only be used at temperatures below the critical, which effectively confines discussion to the volumetric data obtained for ammonia on NaX in the temperature range 0°-70°C. The equilibrium pressures for various arbitrary free energy changes were calculated at the various temperatures; from the amount sorbed at these equilibrium pressures the coefficient of thermal expansion was calculated, equating $\left(\frac{\Delta x}{\Delta T}\right)_{\epsilon}$ with $\left(\frac{dx}{dT}\right)_{\epsilon}$.

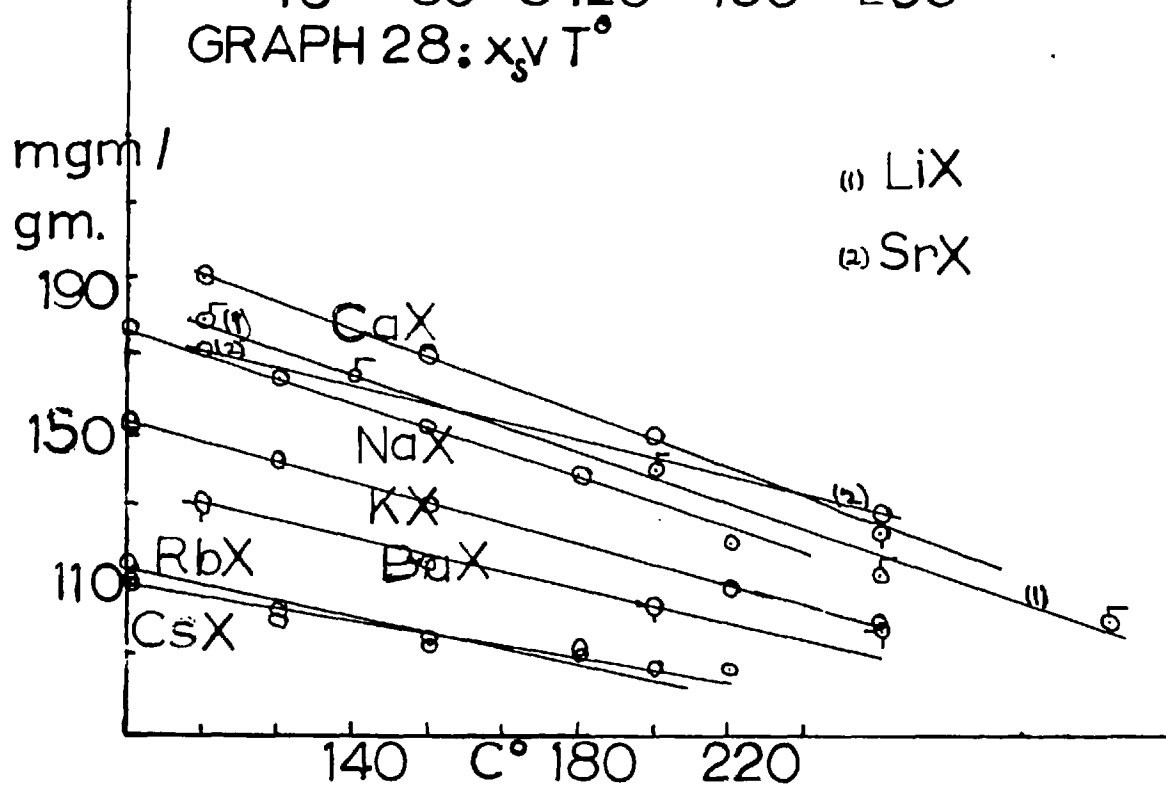
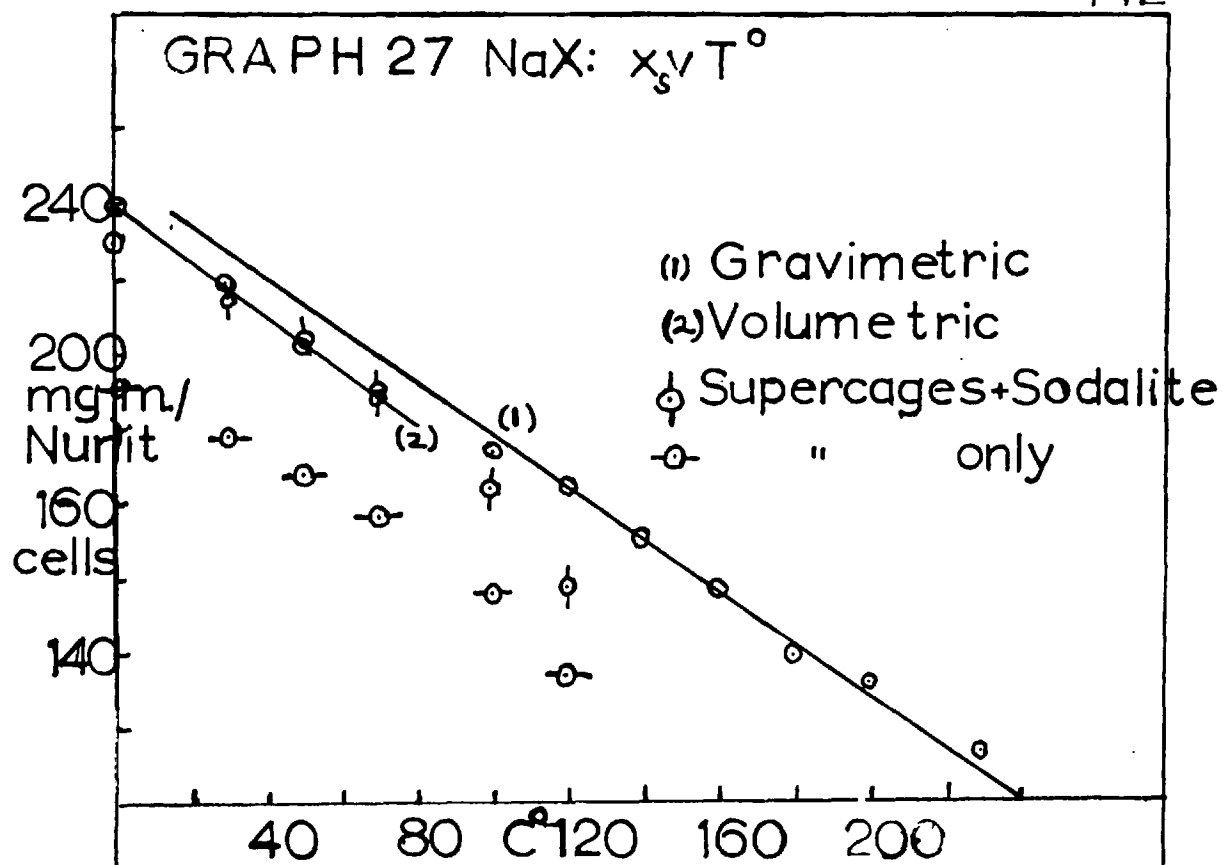
The results are shown in Table 7 as α_{ϵ} where the coefficient of expansion of the bulk liquid, α_L , is also shown for the various temperatures. The values of α_{ϵ} fluctuate considerably, as would be expected since the determination of α_{ϵ} involves Δx , a small quantity which cannot be obtained with accuracy.

In general α_C is smaller than α_L by about a third; this is similar to results obtained for the hydrocarbons and fluorohydrocarbons in faujasite (8,9), though in the latter two cases α_C approaches α_L more closely.

TABLE 7
 α at constant ϵ

Kcal./g. mol.	0°C	30°C	50°C	70°C
x at $\epsilon = 4000$	153.9	144.9	138.1	135.4
α_{C_4}	.0016	.0025	.0012	
x at $\epsilon = 3500$	166.3	157	149.7	144.4
$\alpha_{C_{38}}$	.0012	.0026	.0018	
x at $\epsilon = 3000$	187	173.4	165	159.5
α_{C_3}	.0027	.0026	.0017	
α_L	.0025	.0030	.0036	

x =mgm./gm. sorbent.



4.2. Saturation Values

For the temperature range in these studies it was not possible to obtain an experimental value for the saturation capacities of NH_3 on the crystals. Three methods were used to estimate these quantities:

- (1) the limiting slopes of P/x v. p plots, or by assuming the sorbate has the same co-volume as the liquid and calculating the intracrystalline volume from
- (2) the dimensions of the sorbent
- (3) the volume of liquid water, equated with the water content of the crystal.

All values quoted in this section are in terms of mgm/gm. of outgassed sorbent.

The plots of P/x v. p were in general curves; the apparent saturation values, x_s , obtained from the limiting slopes are shown in graph 28, cases of $\leq .50$ being ignored. If the data obey Langmuir's isotherm, this method has some theoretical significance; otherwise the plots are empirical. x_s , in nearly all cases, shows a good linear relationship with the temperature from which α_s , the coefficient of thermal expansion, may be obtained. In general α_s is very close to α_L of the liquid (table 9) at temperatures below the critical. Sorption of NH_3 on NaX will now be discussed in some

detail as data was obtained for it from 0°C to 290°C employing a volumetric system from 0-70°C and the McBain balance between 100-290°C.

x_s for NaX at all the temperatures examined are shown in graph 27 from which it is obvious that there is a discrepancy between the results from the two methods of measurement. However, it is not great, being ~ 5 mgm/N unit cells, which is approximately 3%, the size of the experimental error and not therefore of great significance. α_s was obtained at various temperatures from the slopes of the lines in graph 27 and these are tabulated in table 8; α_s from the two sets of data are very similar to one another and to α_L .

The results calculated from the co-volume of liquid NH_3 and the calculated volume of the super cages only are shown in table 8 where the values obtained assuming sorption occurs in the sodalite cages too are also shown. The latter case is seen to be in quite good agreement with the previous method for obtaining x_s at temperatures not too close to the critical temperature. The results calculated on equating the intracrystalline free volume with the volume of liquid water in the hydrated crystal are shown in table 8 and graph 27 and agree quite well with those calculated assuming sorption in the sodalite cages and supercages. All

the saturation capacities based on the co-volume of liquid NH_3 give values which are too low for temperatures close to the critical, since the law of rectilinear diameters results in a rapid decrease in the density of the liquid as the critical temperature is approached; a comparable decrease is not to be expected in the sorbed phase on approaching the three dimensional critical temperature.

The data seems to point to sorption occurring in the sodalite cages and a sample of sodalite was exposed to NH_3 to see whether sodalite was accessible to NH_3 . No sorption occurred in two days at room temperature but on heating the sample to $\sim 130^\circ\text{C}$ a considerable quantity (~ 20 mgm/gm. anhydrous sodalite) was sorbed, equilibrium being established finally after ~ 5 -6 hours. There are differences between the sodalite cages in faujasite and those in a sodalite crystal. The former, being surrounded by wide channels, are all immediately accessible to a sorbate whereas in sodalite itself, diffusion through a succession of cages is necessary for a molecule to penetrate to the interior cages. Also in sodalite not all the 6 rings are blocked by Na ions, which is the case in faujasite. If NH_3 does enter the sodalite cages then this implies cationic movements inside the crystal as a result of sorption.

The x_s for various crystals show no simple relation to the water content which is not to be expected as Bratt (103) showed that water has different molar volumes in the various crystals; equating the intracrystalline volume with the water content is therefore an approximation. There is also some intersection of x_s v. T plots for the various forms (e.g. SrX, with CaX, LiX) but in general the data is consistent with a picture of a fluid filling a container as has previously been found by Barrer and Reucroft for SF_6 and CF_4 in NaX (8) and Barrer et al (9), for hydrocarbons in NaX. Though the methods of obtaining the saturation capacities are not entirely satisfactory, it is not unreasonable to suppose that the values estimated are accurate to $\sim 5\%$.

TABLE 8

$T^\circ\text{C}$	x_s	a_s	a_L	$x_s^\#$	$x_s^\#$	$x_s^\#$
0°C	238	.0029	.0025	190	217	229
30°C	219	.0031	.0030	177	203	214
50°C	201	.0031	.0036	167	192	202
70°C	188	.0036	.0039	156	179	188
100°C	174	.0038	.0067	136	156	164
120°C	164	.0038		115	131	138
140°C	150	.0044				
160°C	137	.0048				
180°C	120	.0055				

$\#$ supercages only. $\#$ supercages + sodalite cages.
 $\#$ from water content.

TABLE 9

	110°C	140°C	170°C	200°C	
<u>CaX</u>					
x_s	190	163	143	118	
a_s	.0042	.0049	.0054	.0067	
<u>BaX</u>					
x_s	129	116	104	90	
a_s	.0033	.0037	.0041	.0048	
<u>SrX</u>					
x_s	181	164	146	129	
a_s	.0033	.0037	.0041	.0046	
<u>LiX</u>					
x_s	177.5	158	138.5	119	
a_s	.0037	.0041	.0047	.0055	
	100°C	120°C	140°C	160°C	180°C
<u>KX</u>					
x_s	151	140.5	130	120	110
a_s	.0034	.0037	.0040	.0043	.0047
<u>RbX</u>					
x_s	112	103.5	95	87	
a_s	.0038	.0040	.0044	.0048	
<u>CsX</u>					
x_s	110	103.5	97	90.5	84
a_s	.0029	.0031	.0034	.0036	.0039

N.B. All values cited as mgm. per gm. of anhydrous zeolite.

5.1. Statistical Models for the Sorbate

In this section an attempt will be made to interpret the isotherm data in terms of the equilibrium equations predicted by various statistical models for limiting cases for sorption on energetically homogeneous sorbents. As NH_3 on CsX was the only energetically homogeneous system examined the interpretation is, rigorously, restricted to this system. However as a first approximation this approach was applied to the heterogeneous systems also with a view to establishing the direction and extent of the deviations. The isotherm equations predicted by the various statistical models and the methods of testing them are shown in Table 10. In each case the isotherm quotients should be independent of θ and the isotherm should be reproduced using the appropriate equations. The tests are those recommended by Garden, Kington and Laing (89) except that used for equation 4. Previously this equation has been tested using an arbitrary value of α , presumably because it was feared that the complicated expression in θ for K_v would make a plot of $\log K_v \theta$ an insensitive test; while this may be so, it was found to be quite adequate in these studies.

The form of the isotherm is a test of the free energy predicted by a statistical model. Recalculation of the isotherm using one value for each quotient or

TABLE 10.

Tests of Isotherm Equations

Isotherm equation	Plot against θ	Result
1. $p = K_L \frac{\theta}{1-\theta}$	$\frac{p(1-\theta)}{\theta}$	K_L independent of θ
2. $p = K_{BW} \frac{\theta}{1-\theta} e^{-b\theta}$	$\log \frac{p(1-\theta)}{\theta}$	Straight line, intercept K_{BW} , slope $-b$
3. $p = K_V \frac{\theta}{1-\theta} e^{\frac{\theta}{1-\theta}}$	$\frac{p(1-\theta)}{\theta} e^{-\frac{\theta}{1-\theta}}$	K_V independent of θ
4. $p = K_{VW} \frac{\theta}{1-\theta} e^{\left(\frac{\theta}{1-\theta} - a\theta\right)}$	$\log \left[\frac{p(1-\theta)}{\theta} e^{-\left(\frac{\theta}{1-\theta}\right)} \right]$	Straight line intercept K_{VW} , slope $-a$

constant then constitutes a test between the equilibria observed experimentally and that predicted by a particular statistical model. A more sensitive test may be applied using the entropies predicted by the various limiting models on homogeneous sorbents for simple monatomic or even diatomic molecules. However, in more complicated molecules with large amounts of entropy associated with internal vibrations (usually not important at experimental temperatures) and rotations, this test loses a lot of its sensitivity. In many cases there is sufficient entropy to correspond with several different distributions of the entropy among the various degrees of freedom. This is only true if the vibrational entropy is very similar in magnitude to the translational entropy. In the NH_3/CsX system the vibrational and translational entropies are very different.

Restricting any discussion to homogeneous sorbents, the entropies $\bar{S}_1$ predicted by the various models may in certain circumstances^{*} be factorised as below:

1. $\bar{S}_1 = \bar{S}_c + {}_c\bar{S}_{th}$
2. $\bar{S}_1 = {}_1\bar{S}_T + {}_1\bar{S}_{th}$
3. $\bar{S}_1 = {}_2\bar{S}_T + {}_2\bar{S}_{th}$

^{*} These are that the configurational entropy can be defined. Only true in homogeneous systems.

The quantities $\bar{S}_C$, ${}_1\bar{S}_T$, ${}_2\bar{S}_T$ are the partial molar configurational and translational entropies associated with a localised model or a model with one or two free translations.

The thermal entropies obtained from these equations must be positive; for simple monatomic sorbates they must also be independent of θ , though this is not necessary for more complicated molecules. Finally the thermal entropy must lead to a reasonable value of the frequency of vibration.

Garden, Kington and Laing originally proposed estimating the frequency of vibration from the value 1×10^{12} computed by Orr for A on KCl by use of the following equation due to Hill (40):

$$4. \quad \nu_2 = 1 \times 10^{12} \left(\frac{\Delta E_2}{\Delta E_A} \frac{m_A}{m_2} \right)^{\frac{1}{2}}$$

where the subscript $_2$ refers to any sorbate molecule for which ΔE^* is known. This assumes simple harmonic vibrations and that the frequency of vibration is proportional to $(\Delta E)^{\frac{1}{2}}$; ΔE is obtainable from ΔH . Hill (40) had shown there are theoretical reasons for expecting this to be true; however there is some experimental evidence which indicates that ν is proportional to ΔE rather than $(\Delta E)^{\frac{1}{2}}$ (86). The entropy associated with this frequency can then be calculated treating the system as one composed

$^*\Delta E_A = 1.5 \text{ Kcal/mol. for A on KCl.}$

of Einstein oscillators for which the entropy is

$$5. \quad \tilde{S}_V = R \left[u(1-e^{-u})^{-1} - \ln(1-e^{-u}) \right]$$

where $u = \frac{h\nu}{kT}$.

This is obviously a highly approximate procedure but no direct experimental methods are available for measuring ν . Apart from the approximations mentioned previously it is assumed that the vibrations are monochromatic, which is probably unrealistic, particularly so in the case of localised sorption where the two vibrations parallel to the surface will be very different from that of the vibration at right angles to the surface. However, as the frequency calculated is a mean frequency it is not incompatible with a range of frequencies and probably gives a fair indication of the vibrational entropy.

In the original treatment Garden, Kington and Laing found $\bar{S}_{th}$ to be independent of θ and therefore could equate:

$$6. \quad \bar{S}_{th} = \tilde{S}_{th} = \tilde{S}_V$$

In this study $\bar{S}_{th}$ varies with θ and therefore could not be equated with $\tilde{S}_{th}$; however neglecting interactions between vibrations and rotations $\bar{S}_{th}$ may be factorised as below:

$$7. \quad \bar{S}_{th} = \bar{S}_V + \bar{S}_R + \bar{S}_I$$

TABLE 11

Test of Entropies predicted by Models

$\bar{S}_{c,T}$	Plot against θ	Desired result
1. $\bar{S}_c = -R \ln \frac{\theta}{1-\theta}$	$\bar{S}_1 - \bar{S}_c = \bar{S}_{th}$	Positive Predict reasonable
2. ${}_2\bar{S}_T = R \left[\ln \frac{2\pi kT}{h^2} \frac{a(1-\theta)}{\theta} + 1 - \frac{\theta}{1-\theta} \right]$	$\bar{S}_1 - {}_2\bar{S}_T = {}_2\bar{S}_{th}$	Positive Predict reasonable
3. ${}_1\bar{S}_T = R \left[\ln \frac{(2\pi kT)^{\frac{1}{2}}}{h} \frac{l(1-\theta)}{\theta} + \frac{1}{2} - \frac{\theta}{1-\theta} \right]$	$\bar{S}_1 - {}_1\bar{S}_T = {}_1\bar{S}_{th}$	Positive Predict reasonable

where $\bar{S}_V$, $\bar{S}_R$ and $\bar{S}_I$ are the partial molar vibrational rotational and internal entropies. In view of the heat data $\bar{S}_V$ may be equated with $\tilde{S}_V$ and the vibrational entropy calculated, even though $\bar{S}_{th}$ varies with θ . The variation in $\bar{S}_{th}$ may then be explained in terms of $\bar{S}_R$, which is physically reasonable.

5 1.1. Entropy of Ammonia

In the temperature range of interest the entropy of gaseous ammonia may be expressed as below

$$1. \quad \tilde{S} = \tilde{S}_T + \tilde{S}_R + \tilde{S}_I$$

where $\tilde{S}_T$ is the translational contribution, $\tilde{S}_R$ the rotational contribution, and $\tilde{S}_I$ the internal vibrational contribution. Calculations show that $\tilde{S}_I$ contributes a very small amount to the total entropy. Unless there is a large shift in the internal vibrational frequencies, which is unlikely, these modes will make a negligible contribution to the entropy of the ammonia in the sorbed phase. Accordingly the entropy of the sorbate will be examined in terms of the configurational or translational, rotational and external vibrational entropies (i.e. entropies associated with vibrations against the crystal).

The molar entropy of ammonia was calculated for 1 atmosphere pressure at 100°C. assuming that the only contributions to the entropy arose from translational

and rotational motion (97). The value calculated was 47.13 e.u. compared with the value of 47.20 obtained using Spencer's formula (21). The difference can be attributed to the internal vibrational entropy. This shows that the internal degrees of freedom may be ignored. The rotational entropy was also calculated at 100°C and 180°C, the values being 10.5 e.u. and 10.8 e.u. respectively.

5.2.1. Analysis of Ammonia on CsX

The equations predicted by the various statistical models of the sorbate were tested by the methods shown in Table 10 at three representative temperatures. The various plots are shown in graphs 29-34 at 100°C, 140°C, and 180°C. The Langmuir quotient, K_L , increases with coverage while the Volmer quotient, K_V , passes through a broad maximum and then declines to negligible values at higher coverages. The plot of $\log K_L$ v θ gives a straight line at each of the temperatures examined; the slope of the line is positive and the equation which produces this plot is of the form

$$1. \quad p = K \frac{\theta}{1-\theta} e^{b\theta}$$

The intercept of this line at $\theta = 0$ gives K while b is

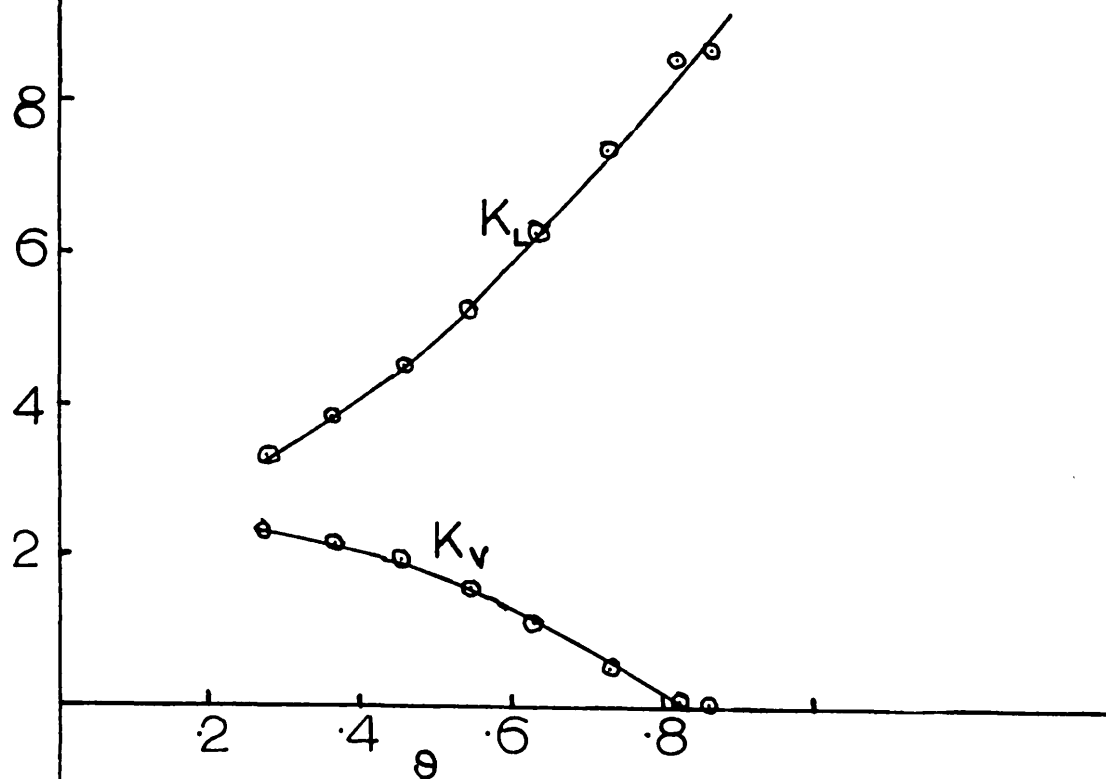
obtained from the slope. This has the same form as the Bragg Williams equation (2 in Table 10) but the exponential term is positive. If this isotherm was the Bragg Williams equation, then this positive exponential term would indicate repulsion between the sorbate molecules; however there is no decrease in the heat terms to support this view. Therefore the change was attributed to entropy changes in the sorbate and the equation has the form:

$$2. \quad p = \frac{\theta}{1-\theta} K e^{f(\theta) - \frac{CW}{kT} \theta}$$

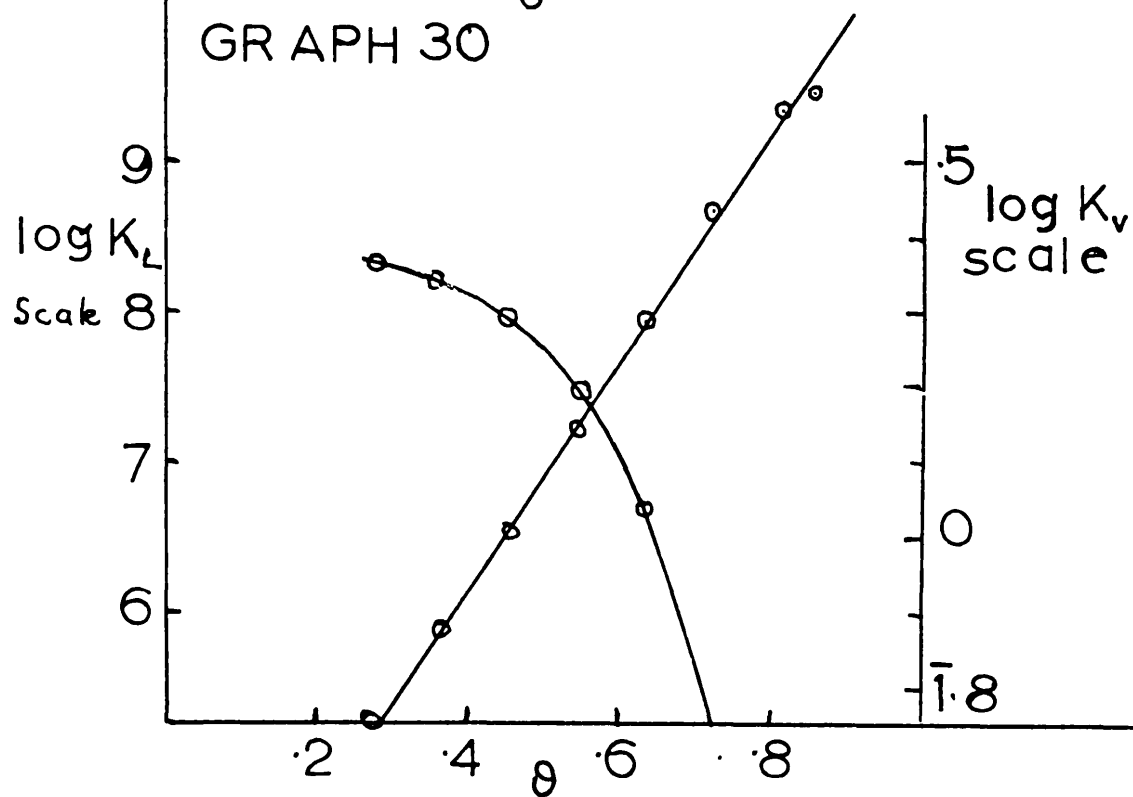
This type of equation had previously been found to describe the isotherm data for SF₆ and CF₄ sorption on NaX by Barrer and Reucroft (8).

The equation was further tested by recalculating the isotherm from equation 1 using the constants K and b derived from the slopes and intercepts of the plots of $\log K_L$ v θ . As may be seen from graph 36 this simple equation predicts the isotherm with considerable accuracy. It might be noted that the agreement of the calculated with the experimental isotherm is quite sensitive to the value of x_s . In all calculations the values were taken from the graph of the 'apparent' x_s against temperature not the actual results of the p/x v p plots. The constants K and b were not so sensitive to the choice of

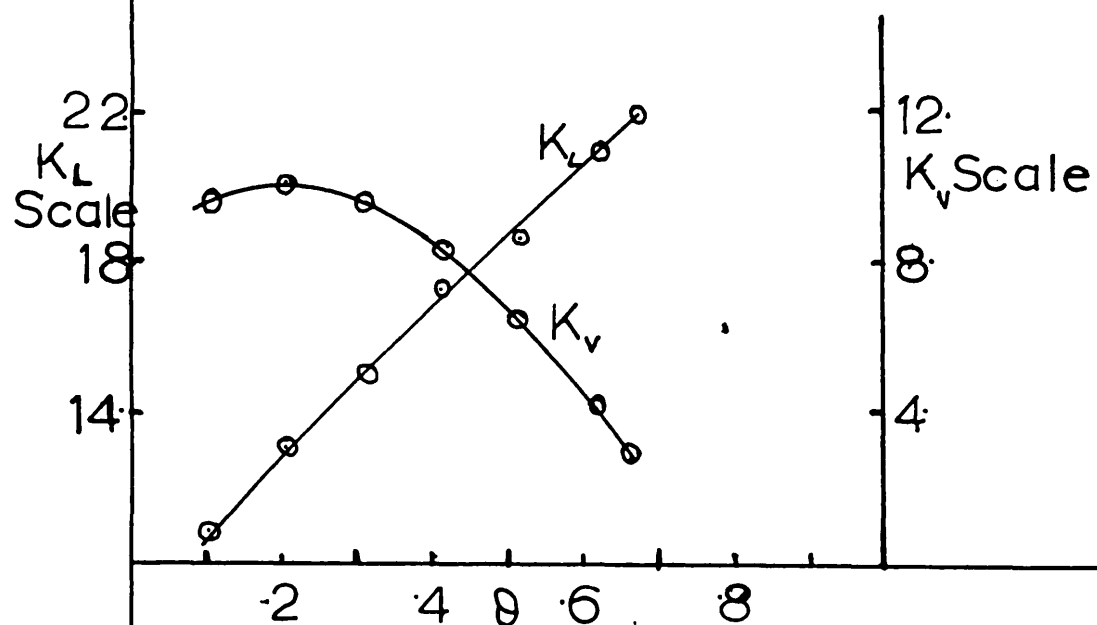
GRAPH 29



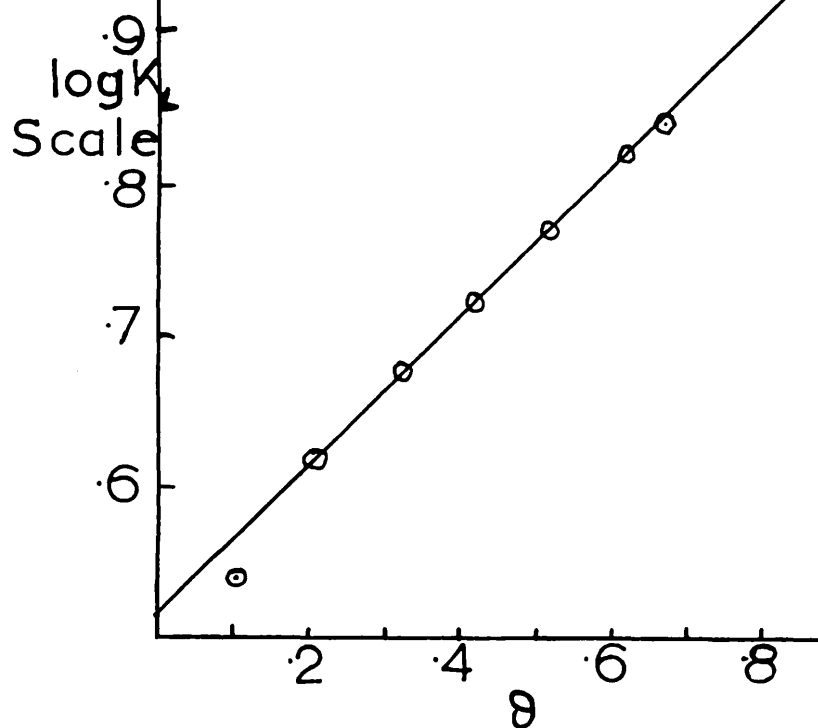
GRAPH 30



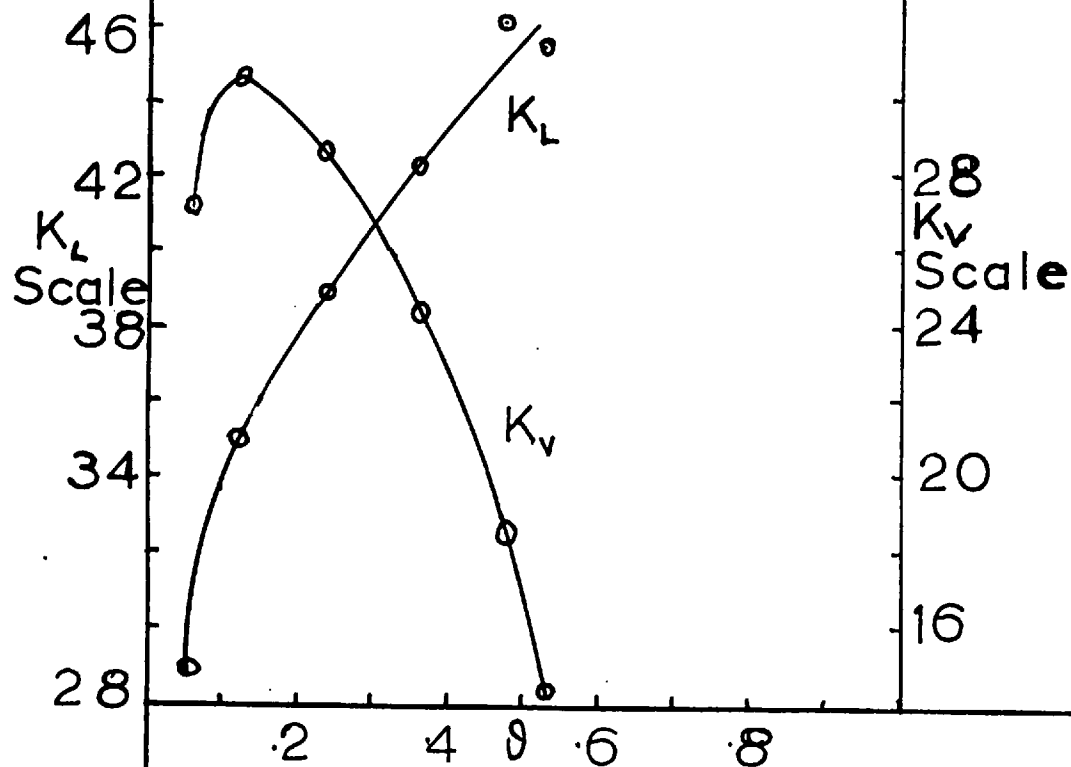
GRAPH 31



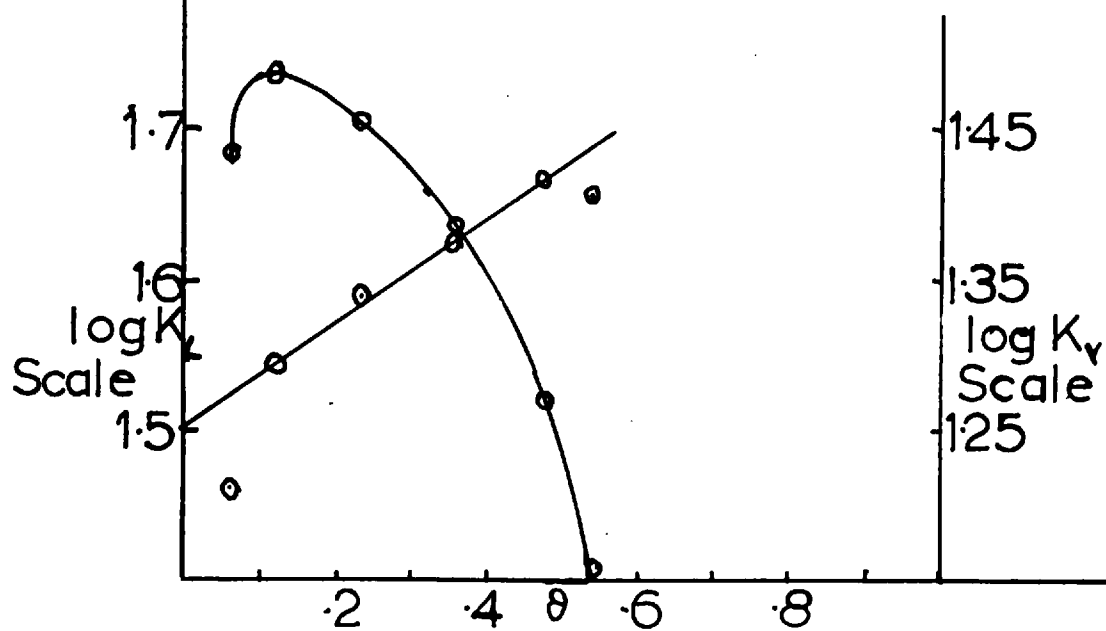
GRAPH 32



GRAPH 33



GRAPH 34



GRAPH 35 Isotherm recalculation

160

calc. points Δ

exp. " $\circ$

calc " Δ

at 180°C $x=90\text{mg./g.}$ $b=1.013$ $K=34.09^k$

100 mgm./gm.

50

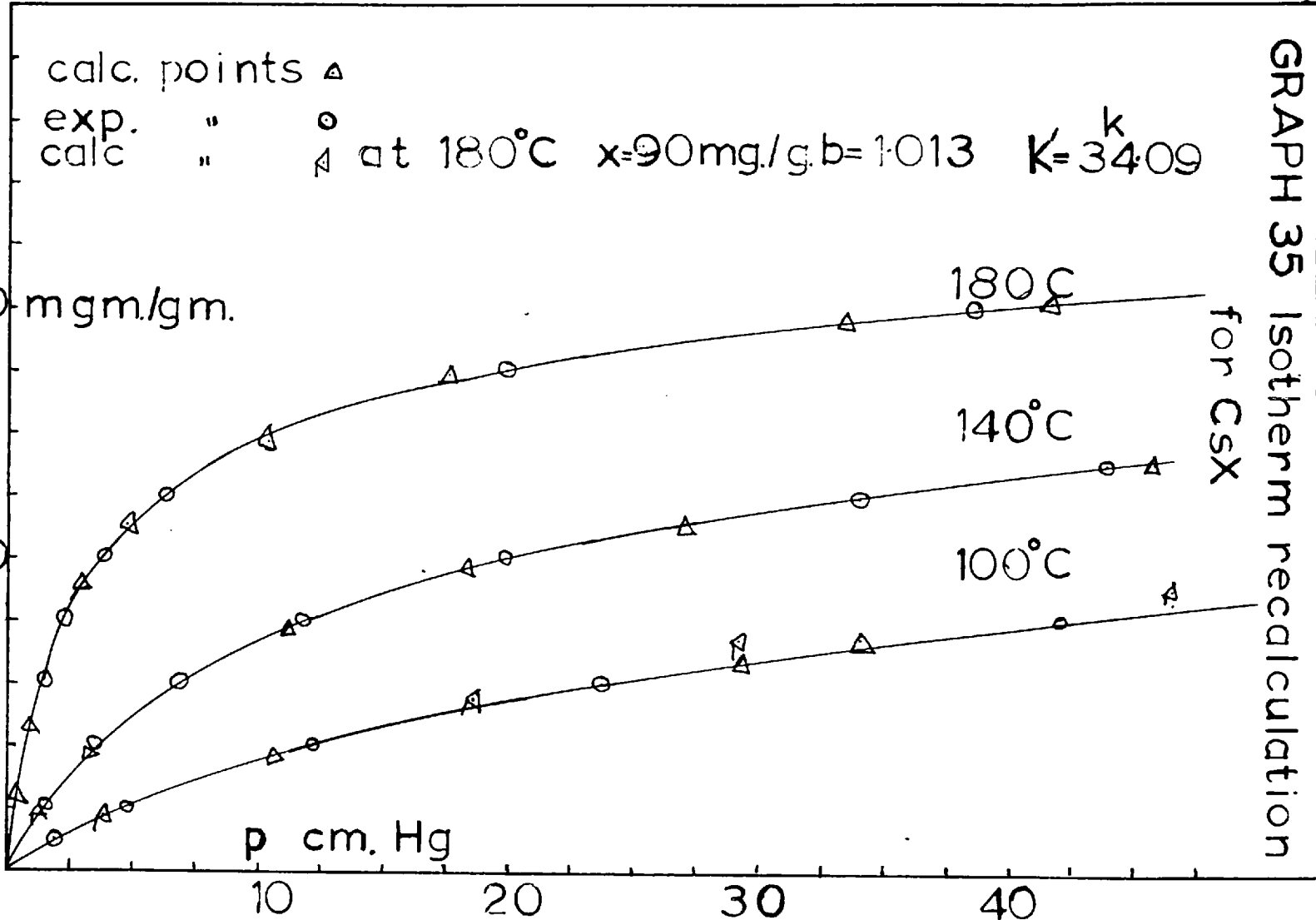
p cm. Hg

180°C

140°C

100°C

for CSX



x_s . In graph 36 calculated points are shown at 180°C for two cases, one $x_s = 84$ from the graph of x_s v T , the other $x_s = 90$ from the actual result of plotting p/x v p . The agreement is seen to be much better with the former. In view of the uncertainty of the values of x_s it is suggested that there may be several combinations of the three parameters x_s , K and b which could reproduce the experimental isotherm equally well.

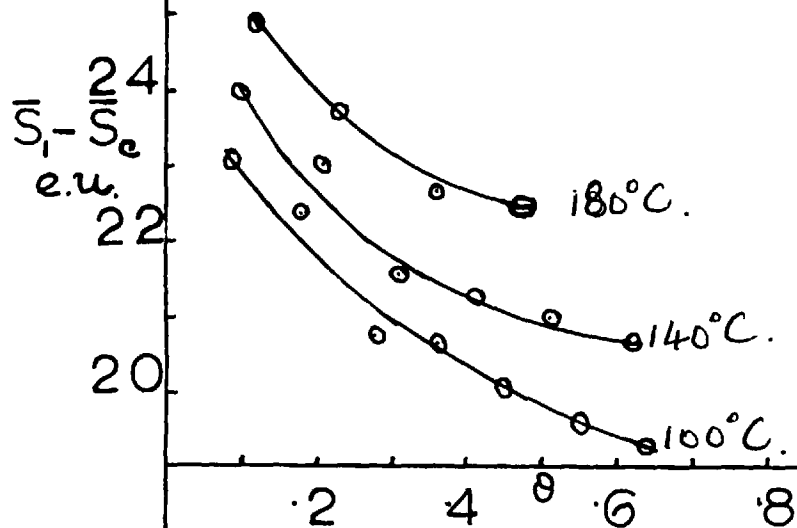
5.2.2. Entropy of Ammonia in CsX

The isotherms predicted by mobile models do not produce agreement with the isotherm data except possibly at the lowest coverages; this may be due to the naive equations of state (8) chosen to represent free translation. To examine the entropy predicted by these models is more sensitive than testing the free energy data.

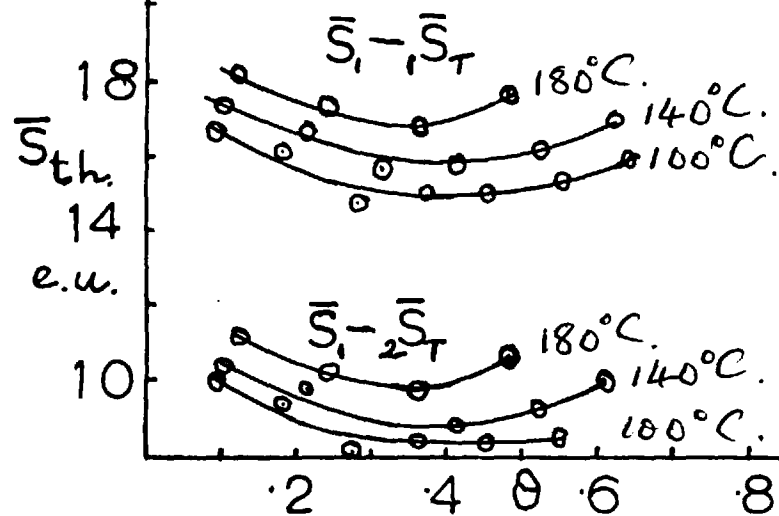
The partial molar entropies at each of the three temperatures were factorised as below for the various limiting cases:

$$\begin{aligned}
 1. \quad \bar{S}_1 - \bar{S}_c &= {}_c\bar{S}_{th} = {}_3\bar{S}_V + \bar{S}_R \\
 2. \quad \bar{S}_1 - {}_2\bar{S}_T &= {}_2\bar{S}_{th} = {}_1\bar{S}_V + \bar{S}_R \\
 3. \quad \bar{S}_1 - {}_1\bar{S}_T &= {}_1\bar{S}_{th} = {}_2\bar{S}_V + \bar{S}_R
 \end{aligned}$$

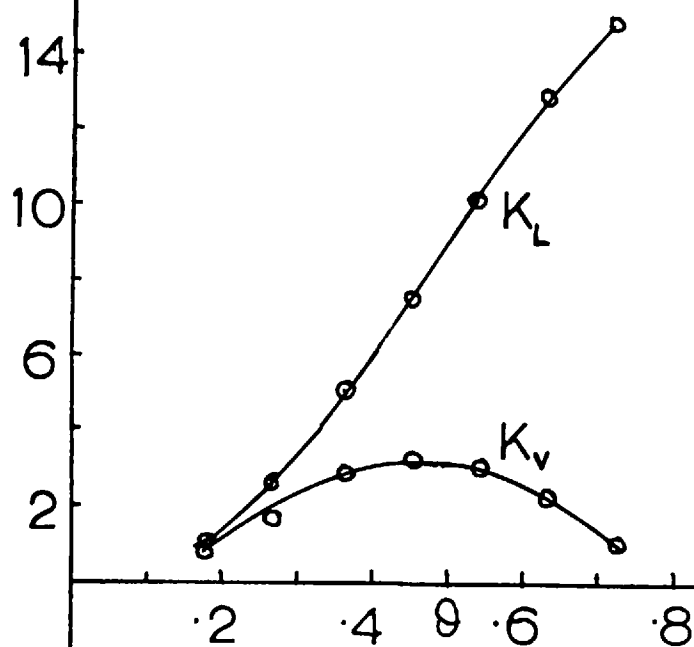
GRAPH 36



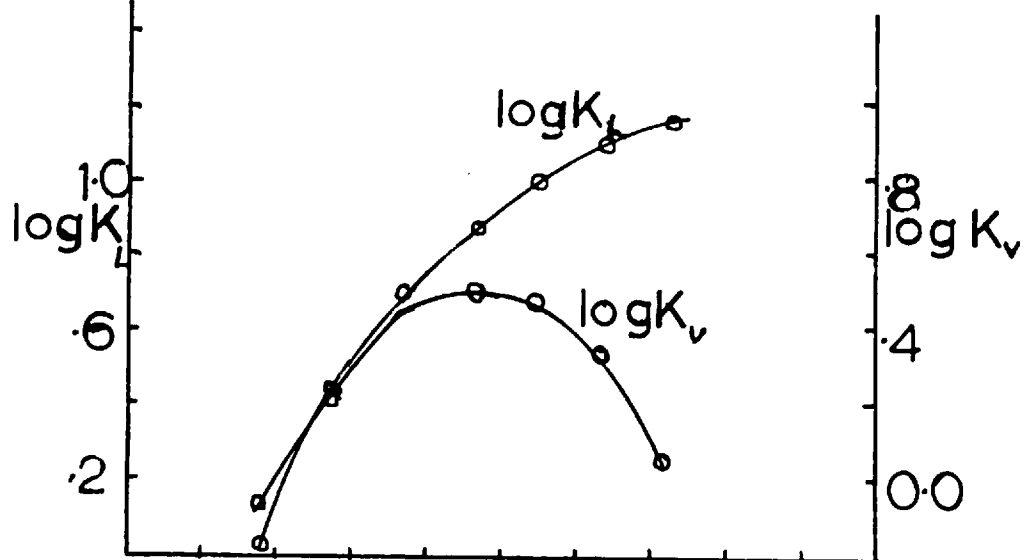
GRAPH 37



GRAPH 38



GRAPH 39



Plots of the thermal entropies for equations 1-3 are shown in graphs 36, 37; ${}_c\bar{S}_{th}$ is positive and strongly dependent on θ while for a considerable range in θ ${}_1\bar{S}_{th}$ and ${}_2\bar{S}_{th}$ are positive and independent of θ , though they rise somewhat at higher coverages, after passing through a shallow minimum at $\sim .35 \theta$.

In order to take the analysis further the partial molar vibrational entropy was assumed equal to the integral molar vibrational entropy; justification for this may be that heat is independent of coverage (although the total thermal entropy, which includes the rotational term, may not be). This is reasonable since the vibrational frequency has been assumed (89) to depend on $(\Delta E)^{\frac{1}{2}}$.

The frequency of vibration was then estimated from the procedure outlined in Section 5.1, and the entropy associated with this frequency at each temperature obtained using the tables in reference (90). The results are listed in Table 12.

TABLE 12
Integral Vibrational Entropies

$T^{\circ}\text{C}$	${}_1\tilde{S}_V$	${}_2\tilde{S}_V$	${}_3\tilde{S}_V$
100°C	3.235	6.47	9.705
140°C	3.42	6.84	10.26
180°C	3.59	7.18	10.77

The remainder of the thermal entropy after subtracting the calculated vibrational entropy is shown in Table 13 for the three cases at 100°C and for the two coverages indicated, the residual entropy being that associated with rotation. As a molecule with two degrees of translation would also be expected to be a free rotator the model predicting two degrees of translational freedom may be eliminated because the predicted rotational entropy is too small for this model.

TABLE 13.

θ	${}_c\bar{S}_{th}-{}_3\tilde{S}_V$	${}_1\bar{S}_{th}-{}_2\tilde{S}_V$	${}_2\bar{S}_{th}-{}_1\tilde{S}_V$
.1	13 e.u.	10.1	6.8
.6	10 e.u.	9.1	5.2

On the other hand the rotational entropy at $\theta = .1$ predicted by a localised model is greater than can be accounted for by even a free rotator while at $\theta = .6$ the rotational entropy predicted by this model would still be effectively free. For localised sorption hindered rotations, with a consequent decrease in entropy, are to be expected; Hill (105) has estimated

the barrier to rotation to be $\sim \frac{\Delta E}{3}$, which in this case is ~ 4 Kcal compared to $RT = 0.7$ Kcal. In the cases of dipoles in strong fields the potential energy barriers to rotation may be even greater than $\frac{\Delta E}{3}$.

It is possible that the vibrational entropy has been underestimated. In calculating the vibrational entropy the vibrations were assumed to be three fold degenerate. The estimate may be reasonable for the vibration perpendicular to the surface but much too high for vibrations parallel to the surface, where the potential energy barriers will be very much smaller. The entropy at 100°C has been calculated for three arbitrary values of ΔE using equation 5 in Section 5.1 to obtain $\mathcal{V}$. It should be noted that in assuming the vibrations parallel to the surface to be different from the vibration perpendicular to the surface, the original reason for equating $\bar{S}_V = \tilde{S}_V$ (i.e. the invariance of ΔH_1) is no longer applicable. However the integral and differential vibrational entropies are assumed to be equal as a first approximation since the frequencies of the vibrations parallel to the surface should not vary very much with coverage.

The values of the rotational entropies in columns 4 and 5 of Table 14(b) are calculated by subtracting from the thermal entropy the entropies obtained

for two vibrations parallel to the surface for the potential energy barriers indicated plus one vibration perpendicular to the surface, as calculated previously. It is seen that if the sorbate is localised, in order to predict a reasonable value of the rotational entropy, the potential energy barriers for motion along the crystal must be very small (of the order of ~ 1 Kcal). The distinction between translational motion and vibrational in terms of the entropy (and indeed physically) becomes very slight (${}_1\bar{S}_T$ at 100°C for $\text{NH}_3 = \sim 6.6$ e.u.; see Table 14 for ${}_1\bar{S}_V$). In Table 14(b) the entropy for rotation is given, assuming one degree of translational freedom and calculating the vibrational entropy for one vibration parallel, for the potential energy barriers indicated, and one vibration perpendicular to the surface as calculated previously. This gives values for the rotational entropy very similar to those calculated for the localised model. However the isotherm data indicates that the thermal entropy of the sorbate is changing markedly with coverage. The localised model predicts this while the model with one translation does not (see graphs 36 and 37); the localised model is therefore to be preferred, though for such low potential barriers to translations the distinction between the two cases is somewhat blurred. The variation of $\bar{S}_R$ with coverage

TABLE 14.

(a)				(b)			
T = 100°C				$\theta = .1$	$\theta = .6$	$\theta = .1$	$\theta = .6$
ΔE		${}_1\tilde{S}_V$	${}_2\tilde{S}_V$	${}_c S_{th} - {}_3\tilde{S}'_V$	${}_c S_{th} - {}_3\tilde{S}'_V$	${}_1\bar{S}_{th} - {}_2\tilde{S}'_V$	${}_1\bar{S}_{th} - {}_2\tilde{S}'_V$
1	.500 Kcal	6.26	12.52	6.9	3.9	7.1	5.1
2	1.5 Kcal	5.16	10.32	9.14	6.14	8.4	7.4
3	6 Kcal	3.85	7.9	11.56	8.56	9.5	8.5

then accounts for the variation of $\bar{S}_{th}$ with θ .

It should be noted that the values of the rotational entropies are differential quantities while the calculated value of 10.6 e.u. at 100°C is an integral quantity; the two cannot be compared directly unless the dependence of $\tilde{S}_R$ on θ is known explicitly. It should also be noted that at higher coverages the vibrations parallel to the surface may increase in frequency thus decreasing the entropy, which may mean that the values of $\bar{S}_R$ suggested in Table 14 are too low; in this case, strictly, the partial molar vibrational entropy should be obtained and used in calculating $\bar{S}_R$.

5.3. Analyses of Ammonia on KX, NaX, Bax

Isotherm data:

Various isotherms were examined for each of these three systems. In addition to those of Table 10 various other more approximate or empirical isotherms were tested; these isotherm equations and the methods of testing them are shown in Table 15.

As can be seen from graphs 36-53 none of the isotherm equations give any reasonable agreement with the experimental isotherms. Qualitatively the plots of K_L and K_V v θ are similar to the plots of those for the CsX/NH₃ but there is no simple equation such as that which describes the CsX/NH₃ equilibria. An equation of the form

$$p = \frac{\theta}{1-\theta} K e^{-\left(\frac{\Delta H - T\Delta S^\circ}{RT}\right)}$$

gave good agreement with terms of the experimental isotherm for NaX at 100°C; at this temperature

$$-\left(\frac{\Delta H - T\Delta S^\circ}{RT}\right) \text{ can be represented by } \left[\frac{-\Delta H + T\Delta S^\circ}{RT} \right] = -6.44 + 5.18\theta.$$

K was obtained from the experimental data at one pressure.

At the other temperatures examined the variation of

$-\left(\frac{\Delta H - T\Delta S^\circ}{RT}\right)$ with coverage was not linear and the equation is then of no practical use. In view of the divergence of K_L and K_V with increasing coverage an equation with

an exponential term which varies somewhat less than $e^{-\frac{\theta}{1-\theta}}$ with θ should be able to represent the isotherm data. However it is to be doubted if anything very useful would follow from this approach.

Entropy of ammonia sorbed on NaX, KX and BaX:

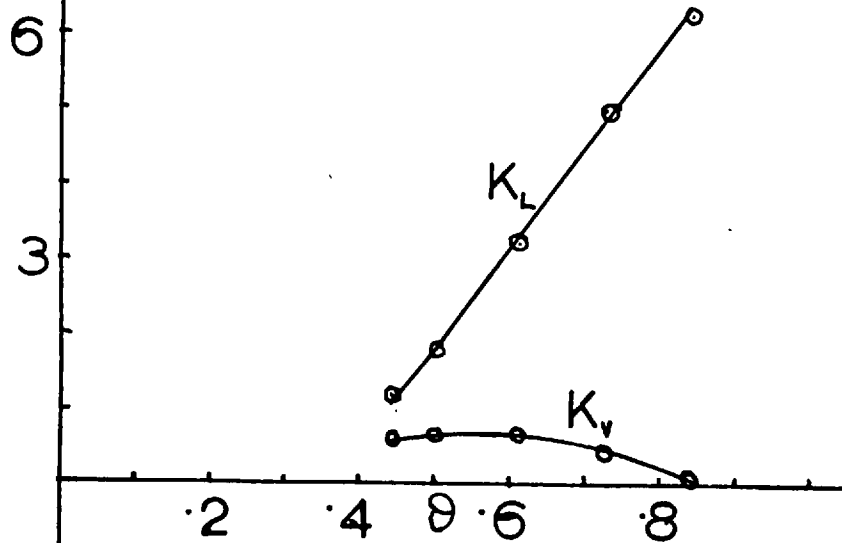
These three sorbents, NaX, KX, and BaX are all, in varying degrees, heterogeneous. Any factorisation of the entropy would therefore be arbitrary since there is no expression which rigorously represents the entropy of a sorbate on a heterogeneous sorbent. Accordingly the entropy cannot be examined in terms of the entropy predicted by the various statistical models for the motion of the sorbate.

Qualitatively it can be said that the statistical model for the sorbate which gives the best agreement with the experimental data for CsX would also apply^{here}; the heterogeneity of the sorbent makes it extremely difficult to take the argument any further.

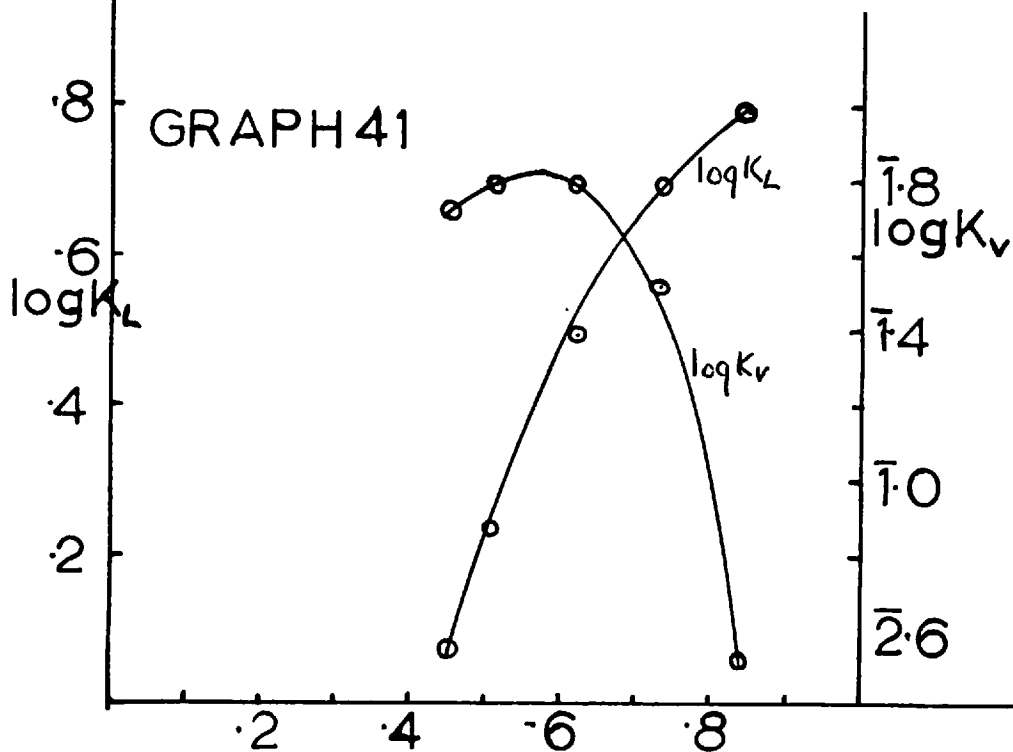
TABLE 15

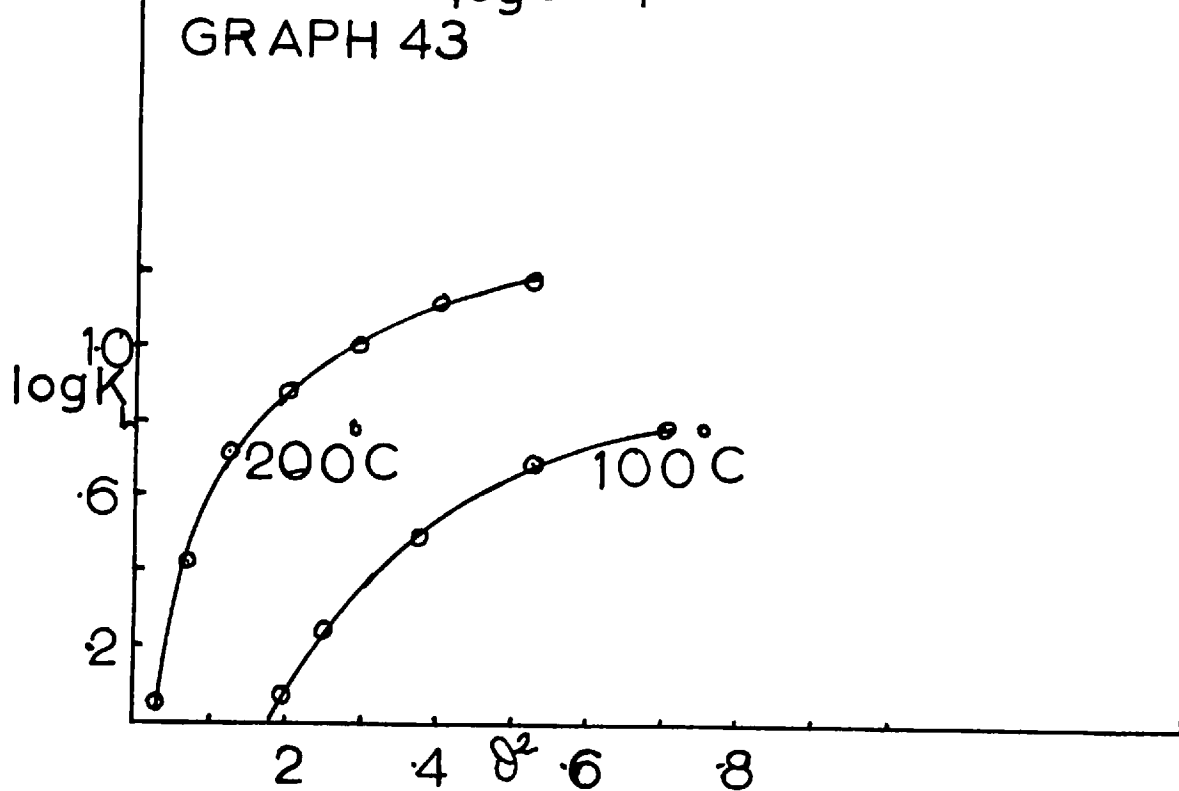
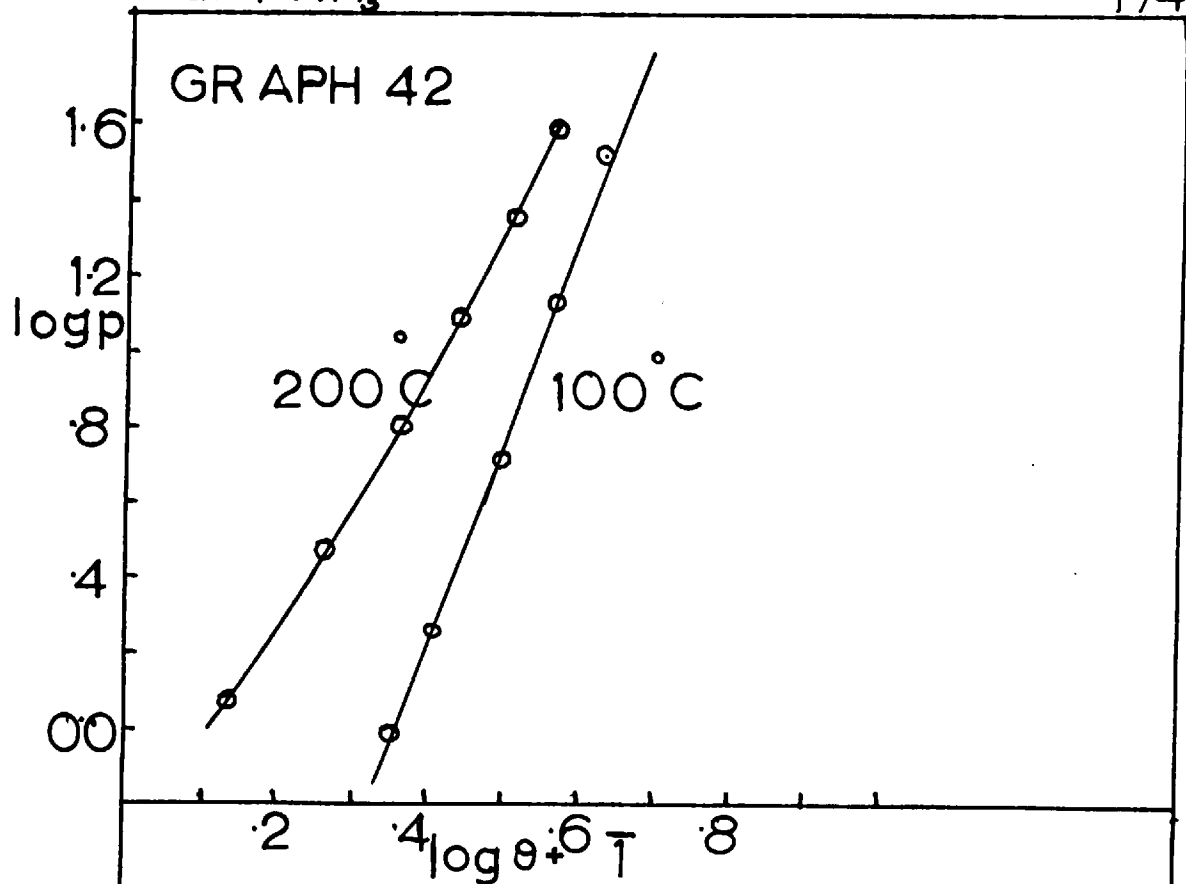
Equation	Test Plot	Desired Result	Basis
1. $\theta = kp^h$ Freundlich	$\log p \text{ v } \log \theta$	Straight line, slope h	Localised model heterogeneous sorbent
2. $p = \frac{\theta}{1-\theta} K e^{+b\theta^2}$	$\log K_L \text{ v } \theta^2$	Straight line, slope b	Empirical
3. $\log \frac{p(1-\theta)}{\theta} = K' \theta$	$\log K \text{ v } e^\theta$	Straight line, slope K'	Empirical
4. $p = K e^{a(1-\theta)}$ Brunauer Temkin	$\log p \text{ v } 1-\theta$	Straight line, slope a , intercept K	Mobile model on a heterogeneous surface
5. $p = \frac{\theta}{1-\theta} K e^{-a+b\theta}$	Obtain a, b from $\frac{\Delta H}{T} \Delta S^\circ \text{ v } \theta$; straight line	Recalculate iso- therm, obtaining K from one experi- mental point	General thermo- dynamics

GRAPH 40

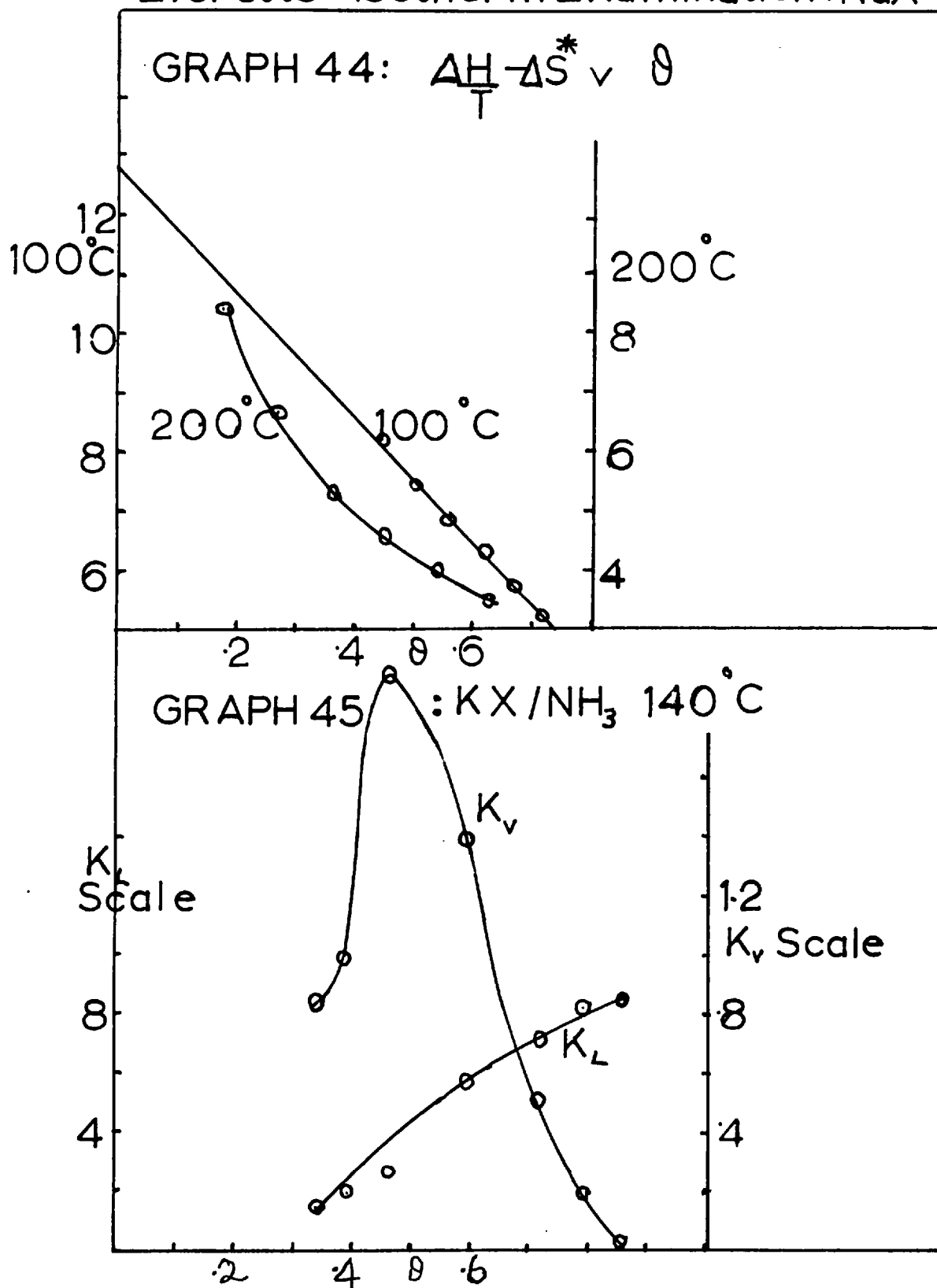


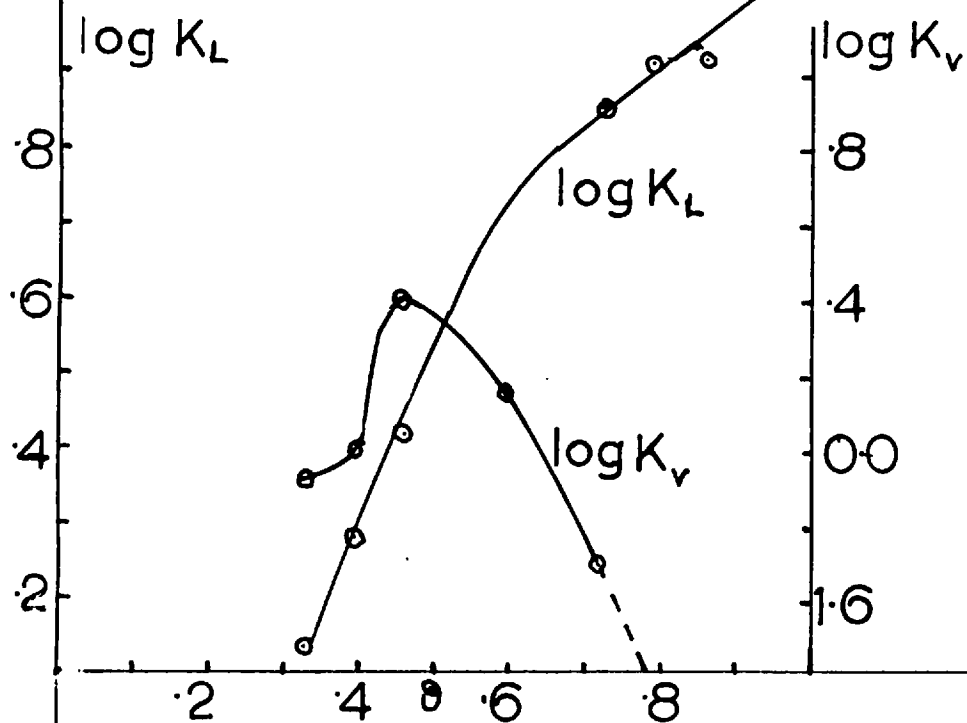
GRAPH 41



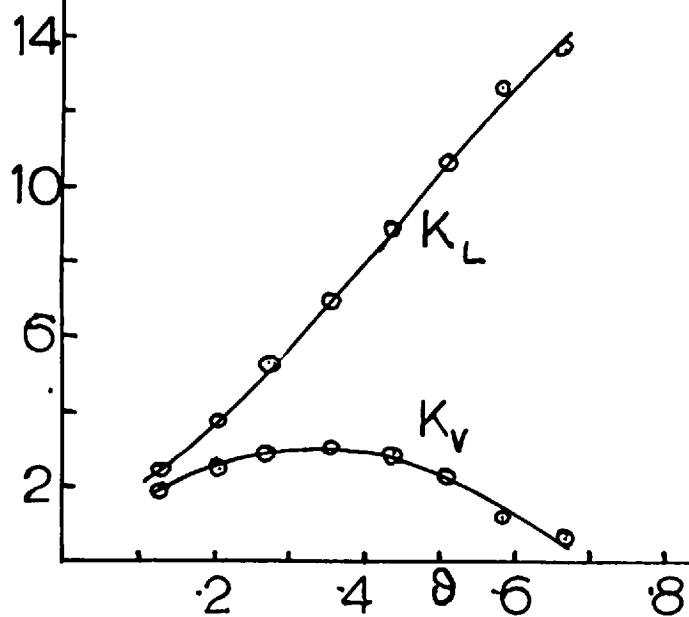


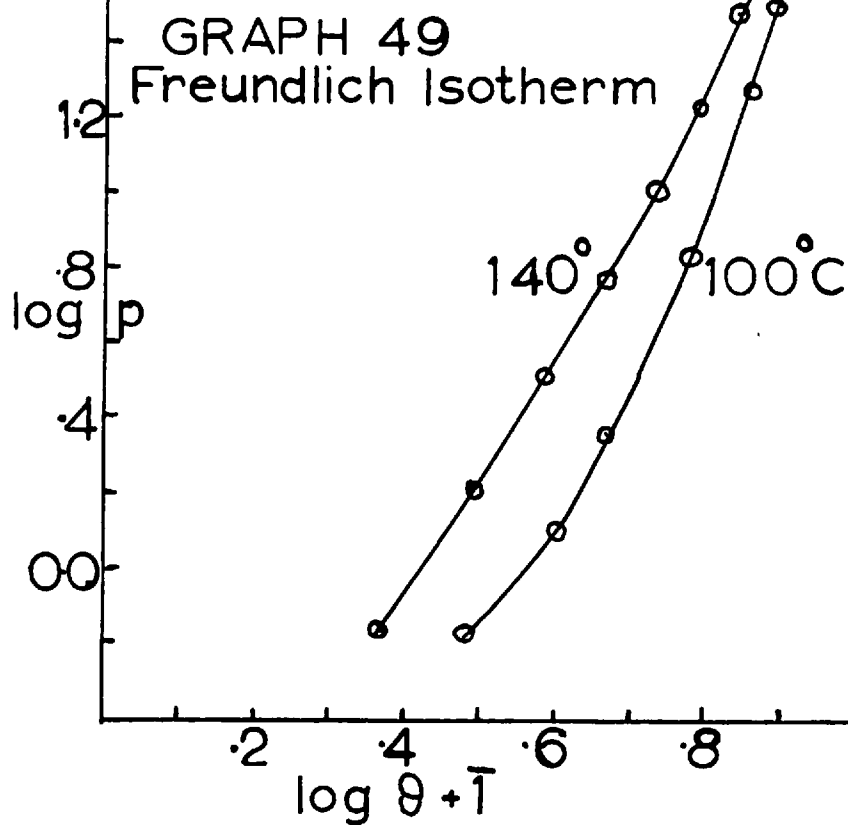
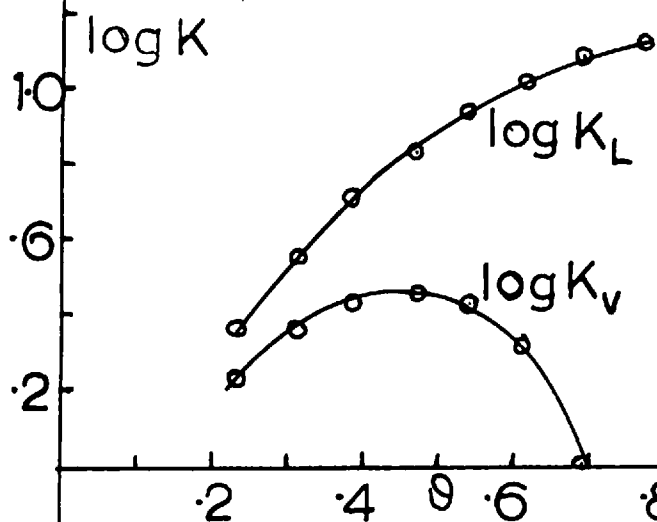
Everett's Isotherm Examination: NaX

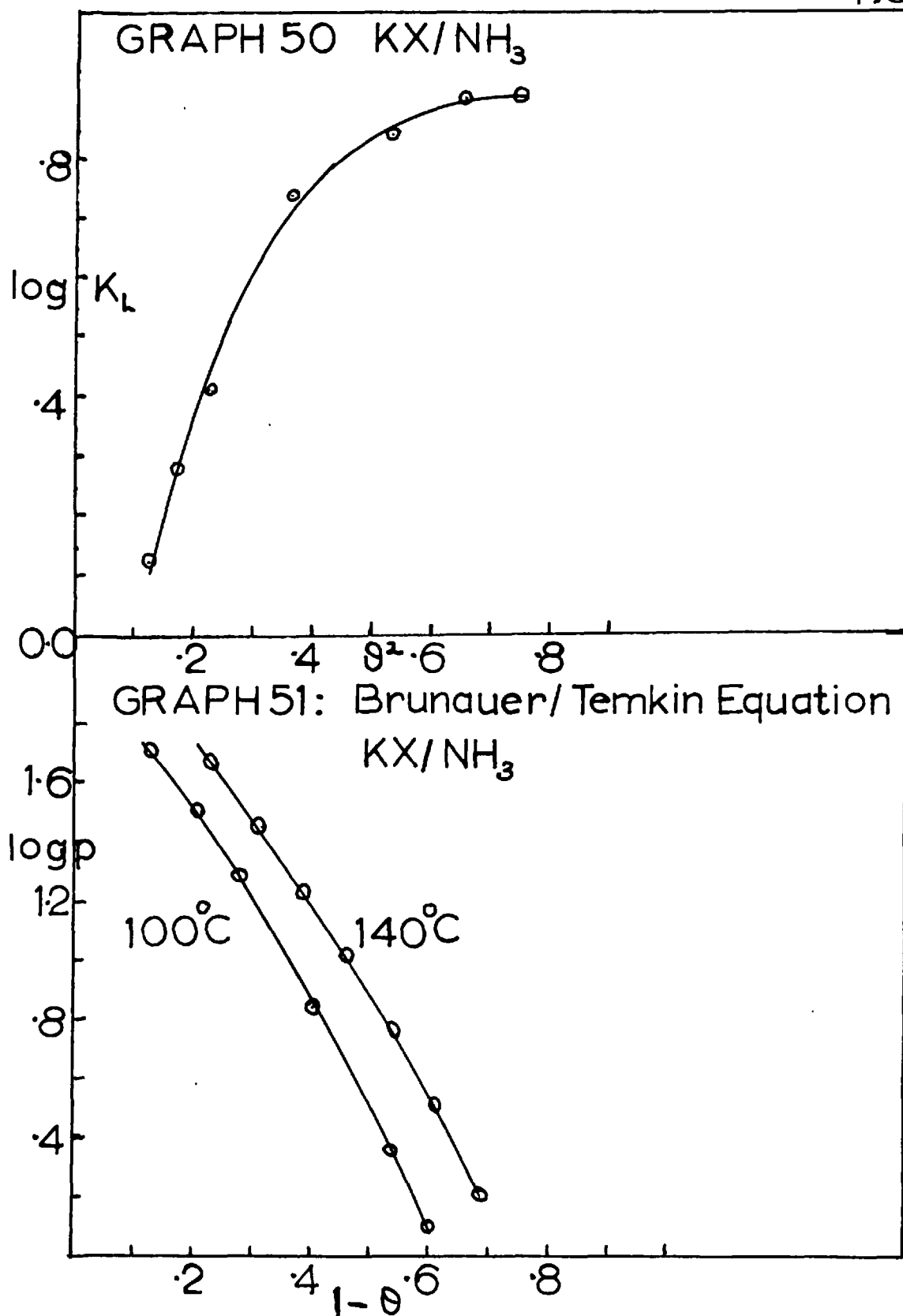


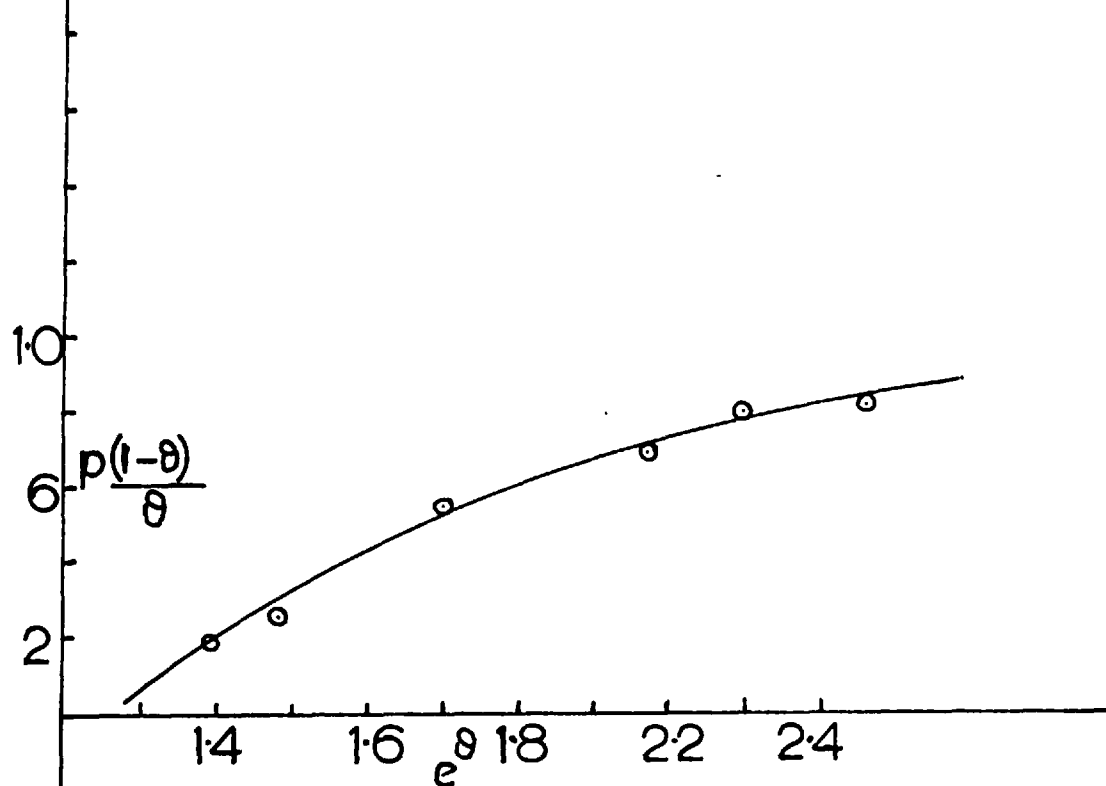
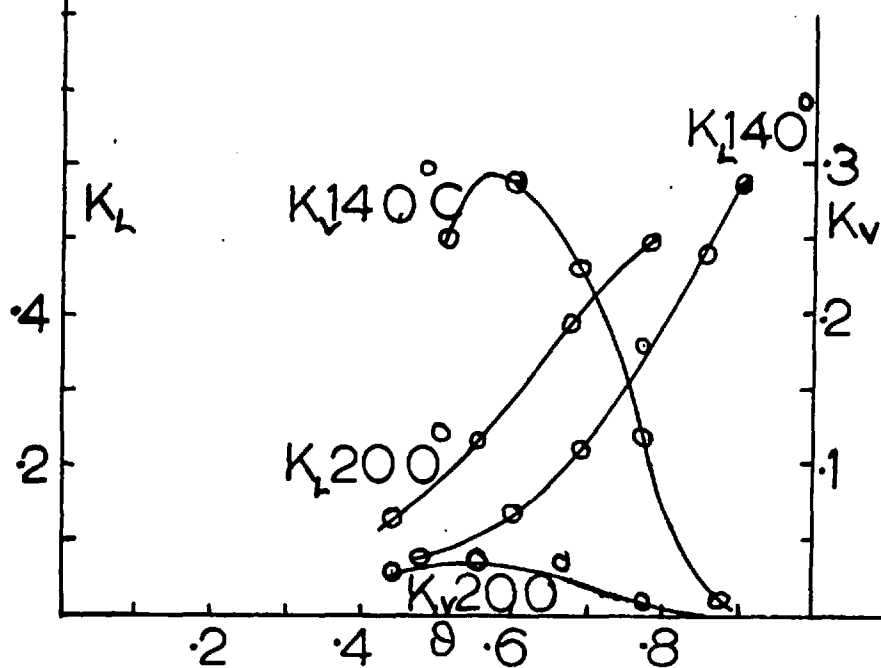
GRAPH 46: KX/NH₃ 100°C

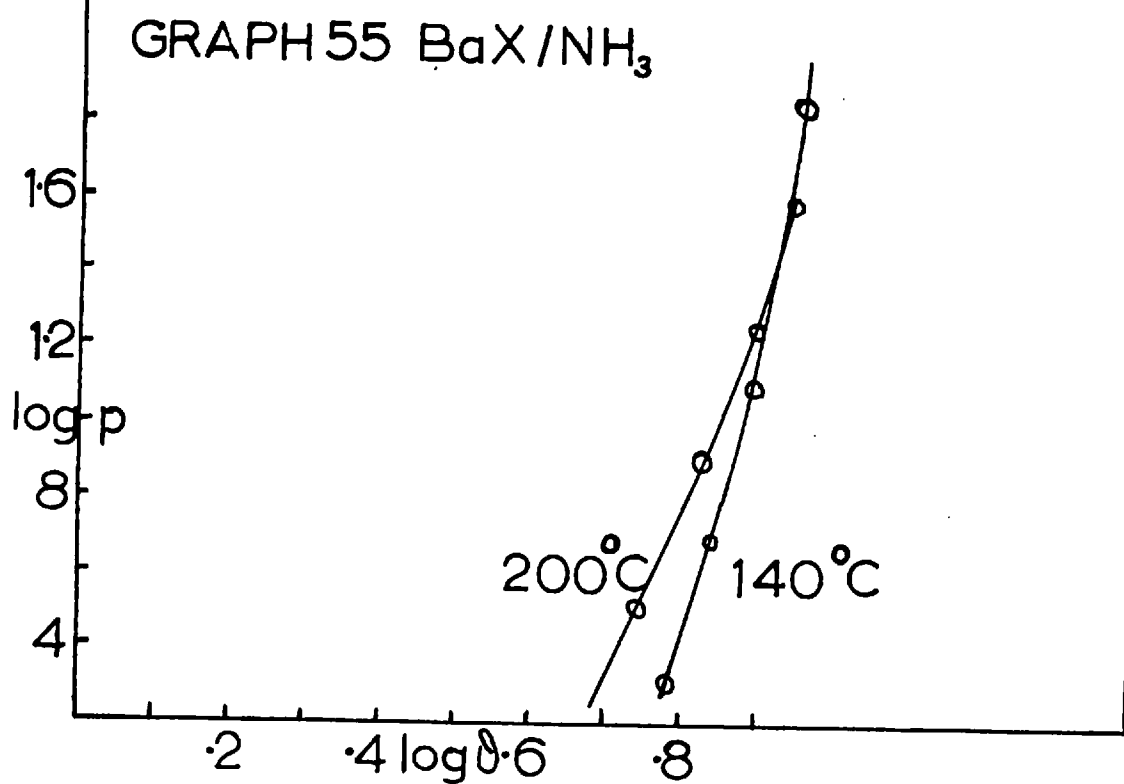
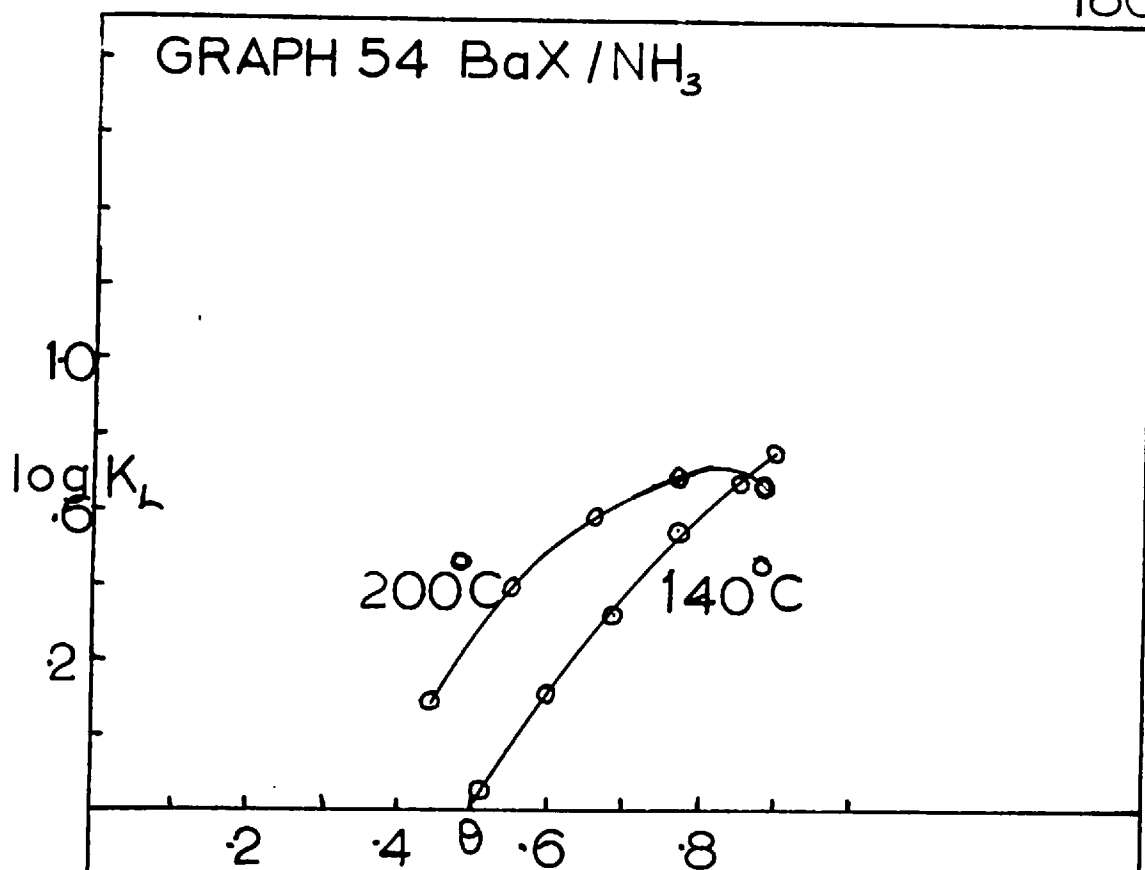
GRAPH 47: 140°C KX



GRAPH 48: KX/NH₃ 140°C.



GRAPH 52 KX/NH₃GRAPH 53 BaX/NH₃



6. Intermolecular Forces.

Calculations have been made for the dispersion, repulsion, field dipole and polarisation energies of a probe ammonia molecule with the oxygen atoms and sodium ions of two adjacent supercages of NaX. In the dispersion and repulsion calculations ammonia was assumed to be a spherical particle of $1.7\text{\AA}$ radius, the interaction being assumed to be the result of centro-symmetric forces. $1.7\text{\AA}$ is the radius of a freely rotating ammonia molecule. The field-dipole interaction was calculated for an ideal dipole situated at the centre of the ammonia molecule. This model is a highly idealised one but the other approximations in the calculations would make any other sophistications futile.

6.1. Sorbate-Sorbate Interactions

Interaction energies have been obtained for two isolated ammonia molecules using a Lennard Jones potential to represent the dispersion energy and assuming the molecules to possess a point dipole and quadrupole. The average energies of interaction of two dipoles and also of two quadrupoles were obtained at r_e , the equilibrium distance for two ammonia molecules ($r_e = 2r_{\text{NH}_3}$), and at $2r_e$; the interaction energy of two dipoles for three

relative orientations are also shown in table 17 (the three orientations of the dipoles are shown in figures (i), (ii) and (iii) of table 16). The interaction energies were obtained for polarisable and non-polarisable molecules. In addition the effect on two polarisable dipoles in an external field of the strength calculated for the field at a position inside a cage of NaX has been examined.

The formulae used to calculate the various interactions are shown in table 16. The results are shown in table 17. The dispersion energy was obtained from two values for the constant A , from the London formula and also from the Kirkwood Muller equation. The London formula gives values which appear to be too small and will not be discussed further; all values for the dispersion energies refer to those obtained from the Kirkwood Muller value of A .

The average dipole/dipole interaction at 100°C (table 17b) is seen to be somewhat smaller than the dispersion energy (0.6 v. 0.8 Kcal/gm.mole). The maximum negative (attractive) interaction for two dipoles (obtained in position (i)) is 1.6 Kcal/gm. mole while the maximum repulsion energy for two dipoles is 0.8 Kcal/gm.mole for the position shown in figure -iii/ of table 16. The repulsive counterpart of figure (i) is thought not to

occur in sorption and will not be considered here. The effect of polarisation on the dipole/dipole interaction of two isolated molecules is seen to be small (table 17b). While the non-polarisable case is the lower limit for attraction, it is an upper limit for the repulsion energies between isolated molecules. It is seen from table 17 that two non-polarisable molecules will not develop a nett repulsion potential even though the dipoles are orientated in the most unfavourable position (as in figure (iii)), the attraction of the dispersion forces almost exactly counterbalancing the repulsion between the dipoles in this case.

The interaction energy of the two quadrupoles for two ammonia atoms was found to be completely negligible (the value of Q was taken as 1.3×10^{-26} e.s.u. to obtain an upper limit for this interaction). The maximum value of the interaction of the dipole/quadrupole term was found to be large enough to contribute slightly to the total interaction energy (0.08 Kcal/gm.mole against 0.8 Kcal. for the dispersion forces).

The effect of an external field was examined by assuming the field to polarise the molecules but also assuming that the dipoles do not depolarise each other. The polarisation of the molecules by the field was assumed to be given by:

TABLE 16.
Interaction Formulae

Energy Term	Formula
Dispersion	$E_D = A \left(\frac{1}{r^6} - \frac{r_e^6}{2r^{12}} \right)$
London	$A_L = \frac{3}{4} a^2 E$
Kirkwood Muller	$A_{KM} = \frac{3mc^2 a \chi}{r^6}$
Dipole/Dipole	
1. In position(i)	$- \frac{2m^2}{r^3}$
2. " " (ii)	$- \frac{m^2}{r^3}$
3. " " (iii)	$+ \frac{m^2}{r^3}$
4. Dipole/Dipole Polarisable Position (i)	$- \frac{2m^2}{r^3 \left(1 - \frac{a}{r^3} \right)}$
5. Dipole/Dipole Average	$- \frac{2}{3} \frac{m^2 m^2}{r^6} \frac{1}{kT}$
6. Dipole/Quadrupole Average	$- \frac{1}{kT} \frac{m^2 Q^2}{r^8}$
7. Q/Q Average	$- \frac{1}{kT} \frac{7}{40} \frac{Q^4}{r^{10}}$

Figure (i)

↑

↑

Figure (ii)

↑↓

Figure (iii)

↑↑

TABLE 17
Sorbate-Sorbate
Energies (Kcal./g.mol.)

	r_e	$2r_e$	position
(a)			
(L) $E_D(L)$	-.33	-.01	
(KW) E_D	-.81	-.03	
(b) Electrostatic			
$E_{m/m}$	-1.58	-.20	1
$E_{m/m}$	-.79	-.10	2
$E_{m/m}$	+.79	+.10	3
$E_{m/m}$	-1.79		1
$E_{m/m}$ (av.)	-.56	.07	
(c)			
$E_{Q,Q}$	0	0	
$E_{m,Q}$	.08	0	
E_{mm}^F	+1.00		3

$$n^* = n + \alpha F$$

This overestimates the polarisation effect but it will be used as a first approximation. The field strength assumed was that calculated for a point inside a NaX cage where $F = .197 \cdot 10^6$ e.s.u./cm. (see section 6.3). The results are shown in table 17c; the dipole term is now seen to be much bigger than the dispersion term at r_e . Repulsion energies between sorbed ammonia molecules would therefore be possible; however, as the polarisation effect is greatly overestimated by these calculations it appears that the repulsion between adjacent molecules will not be large.

Finally the calculations show that all interactions between molecules at a distance of $2r_e$ apart are very small (see Table 17). This would indicate that only nearest neighbour interactions are important.

6.2. Dispersion and Repulsion Forces

The total dispersion and repulsion forces at any point between a probe molecule and a sorbent can be obtained from:

$$E_D + E_R = A \sum_i \left(\frac{1}{r_i^6} - \frac{r_e^6}{2r_i^{12}} \right)$$

where $r_e = r_{\text{NH}_3} + r_0$

or $r_e = r_{\text{NH}_3} + r_{\text{Na}^+}$

for interaction with the oxygen atoms and the sodium ions respectively, and r_i is the distance between the point considered and a sorbent atom. To evaluate $E_R + E_D$ in equation (1) summations of $\frac{1}{r_i^6}$ and $\frac{1}{r_i^{12}}$ must be made to include all relevant atoms of the sorbent. For points on a line joining the centres of two adjacent cages in NaX it is sufficient to obtain $\sum_i \frac{1}{r_i^6}$ for all the oxygen atoms and cations that go to make up the two cages and $\sum_i \frac{1}{r_i^{12}}$ for those few atoms closer than $2r_e$ to the probe molecule. This line continues from the centre of the supercage up to the centre of a 6-ring of oxygen atoms in the wall where a sodium ion is positioned. Systematically the path is shown in figure 17. The positions on this line are fairly representative of all those that occur in the cage. When the centre of one cage is taken as origin the centre of one adjoining cage is $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and the coordinates of any point on the line joining these two centres may be written as (ppp) where p is a variable parameter. This line, (ppp), is chosen because it is particularly easy to obtain r_i^2 and hence $\frac{1}{r_i^6}$, for any point on it. The data for calculating r_i^2 were obtained from reference 13 with the assistance of Dr. Kerr. The actual summations for the oxygen atoms were made by Dr. Crawford (91).

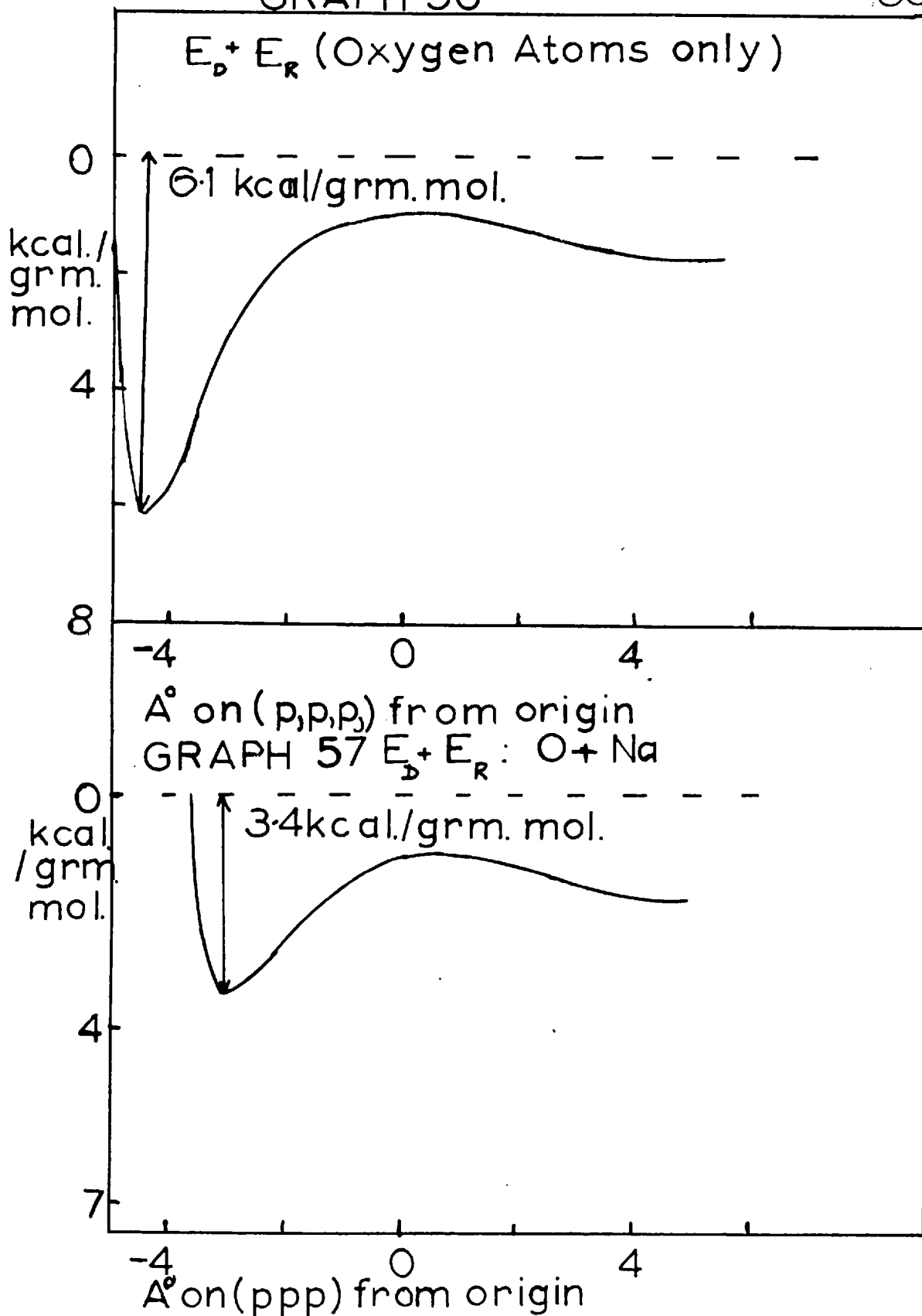
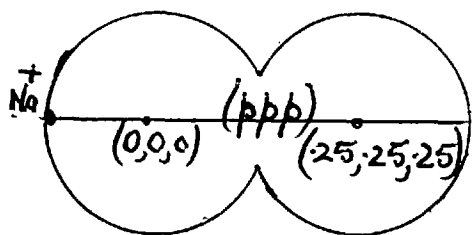


TABLE 18
 Constants for dispersion energy calculations

	NH_3/O	NH_3/Na^+	Units
r_0	3.1	2.65	$\text{\AA}$
A_L	$1.886 \cdot 10^{-45}$	$1.355 \cdot 10^{-45}$	Kcal/gm.mole
A_{KM}	$2.422 \cdot 10^{-45}$	.3066	Kcal/gm.mole
α	$3.90 \cdot 10^{-24}$	$.19 \cdot 10^{-24}$	cm^3 per atom
χ	$20.9 \cdot 10^{-30}$	7.0	cm^3 per atom
E	13.55	47.06	volts

Figure 17



$$\sum_i \frac{1}{r_{i6}^6} \text{ and } \sum_i \frac{1}{r_{i12}^2} \text{ were used to obtain the}$$

dispersion energies from equation 1. A was obtained from the London and Kirkwood-Muller formulae; in general the London formula gave values which were too small and all the results shown are those calculated using the Kirkwood Muller formula unless otherwise stated. The equilibrium distances between the sorbate and the oxygen or cation were taken to be the sum of the radii; the radius of ammonia was taken as the van der Waals radius. This is a value for the freely rotating molecule which is unlikely to be the case here. The constants used in the calculation are shown in table 18.

Graph 56 shows the dispersion interaction energy at points on (ppp) for the framework oxygen atoms only, ignoring the cations. At the equilibrium position, which was obtained graphically, the probe molecule is at a distance of r_e from each of the six oxygen atoms of the 6 ring. This is therefore a favourable position for dispersion interaction, the minimum potential energy being 6.1 Kcal/gm.mole (the London formula gives 4.5 Kcal/gm.)

In graph 57 the interaction of the cations is included. They contribute very little to the total dispersion energy but the introduction of a cation into the centre of the 6 ring moves the equilibrium position

away from the wall and hence reduces the interaction between the oxygen atoms and the probe molecule. The minimum potential energy is now 3.4 Kcal/gm.mole of which the cations contribute 0.2 Kcal/gm.mole. Thus the nett effect of the cations is to reduce the interactions of the oxygen atoms at equilibrium.

Previously it has been tacitly assumed that the molecule may be represented by a centrosymmetric force field, which is unrealistic for a non-rotating molecule, since ammonia has four atoms in it; the dispersion forces may therefore be non-central. The true equilibrium position lies between the positions shown since the molecule would not be rotating freely; it is not possible to be more precise than this. These uncertainties together with those noted in section 1.4.1 for evaluating A make it impossible to regard these energies as other than qualitative or semi-quantitative.

6.3. Electrostatic Interaction Energies

To evaluate the electrostatic interaction energies of a molecule with a dipole at points near a sorbent requires a knowledge of the electrostatic potential produced by the sorbent at a series of points near its surface; the potential gradient may then be obtained

graphically. If the charge distribution in the sorbent is known then the electrostatic potential at any point may be calculated from

$$1. \quad \phi = - \sum_i \frac{e_i}{r_i}$$

where r_i is the distance between the i^{th} charge and the position considered. Using eq. 1 the electrostatic potential for a single supercage was evaluated for points along the line (ppp), chosen both because the field must lie along this line, from symmetry, and because r_i is particularly easy to compute for points on this line (ppp). Any variation in ϕ other than along (ppp) is ignored; for a molecule of the size of ammonia it would be possible for it to interact with fields in several directions at once. Here it is assumed to be a point dipole. A particular, arbitrary, charge distribution was assumed. Details of the charge distribution are given in the next section. A simple calculation for the electrostatic potential produced ^{by} the charges in each of the adjacent cages, treating the cages as a series of point multipoles, showed that they produced a negligible potential outside their own cage. The potential for a single cage should therefore be a reasonable representation of the potential in NaX.

Charge distribution

In each supercage there are 10 cations and 48 oxygen atoms. The cationic charge is assumed to be carried on the 10 cations while the nett anionic charge is assumed to be shared equally among the oxygen atoms. Those atoms shared with other cages were assumed also to share their charges equally with the other cages so that the cages considered remained electrically neutral. The charge distribution adopted then is:

24 oxygen atoms with $\frac{10}{48} e^-$ each

48 " " " $\frac{5}{48} e^-$ each

8 cations with $1 e^-$ each

12 " " $\frac{1}{6} e^-$ each.

(Cations in the connecting cages, shared with five other cages).

The charge distribution seems reasonable in view of the polar nature of Na^+ bonds and the non-polar nature of Si-O and Al-O bonds.

Apart from the approximation in the charge distribution the positions of 4 of the cations are unknown and their charges were placed symmetrically, $\frac{2}{3}$ of an electronic charge at the centre of each of six 4 rings of oxygen atoms. It is thus seen that there are many approximations in this calculation. $\sum_i \frac{e_i}{r_i}$ was obtained for all

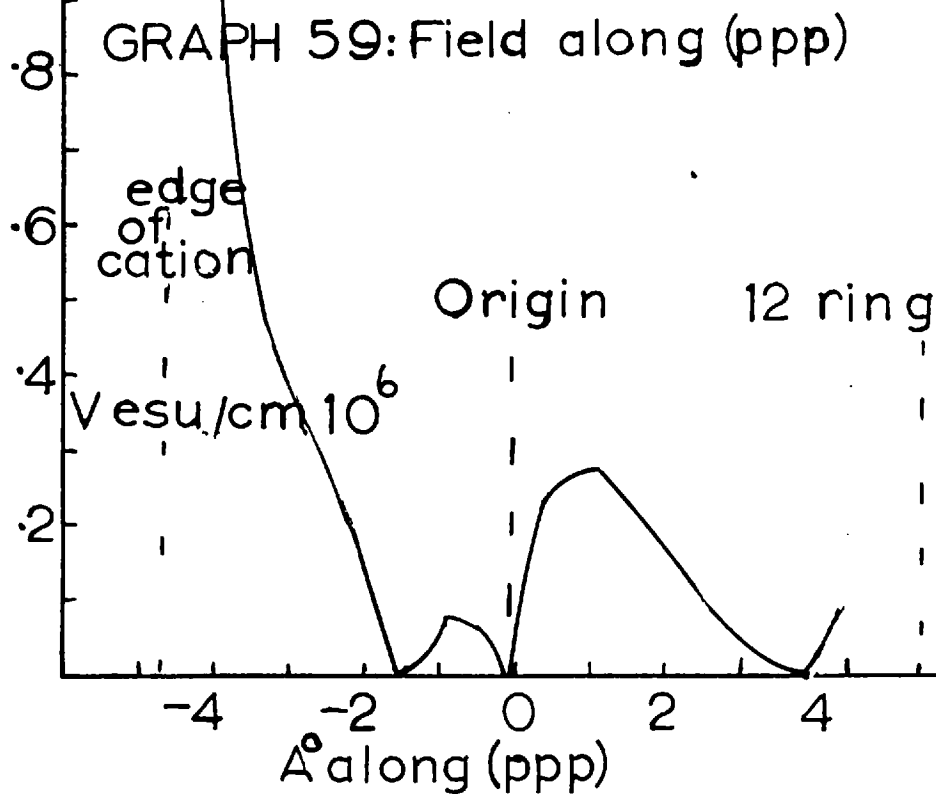
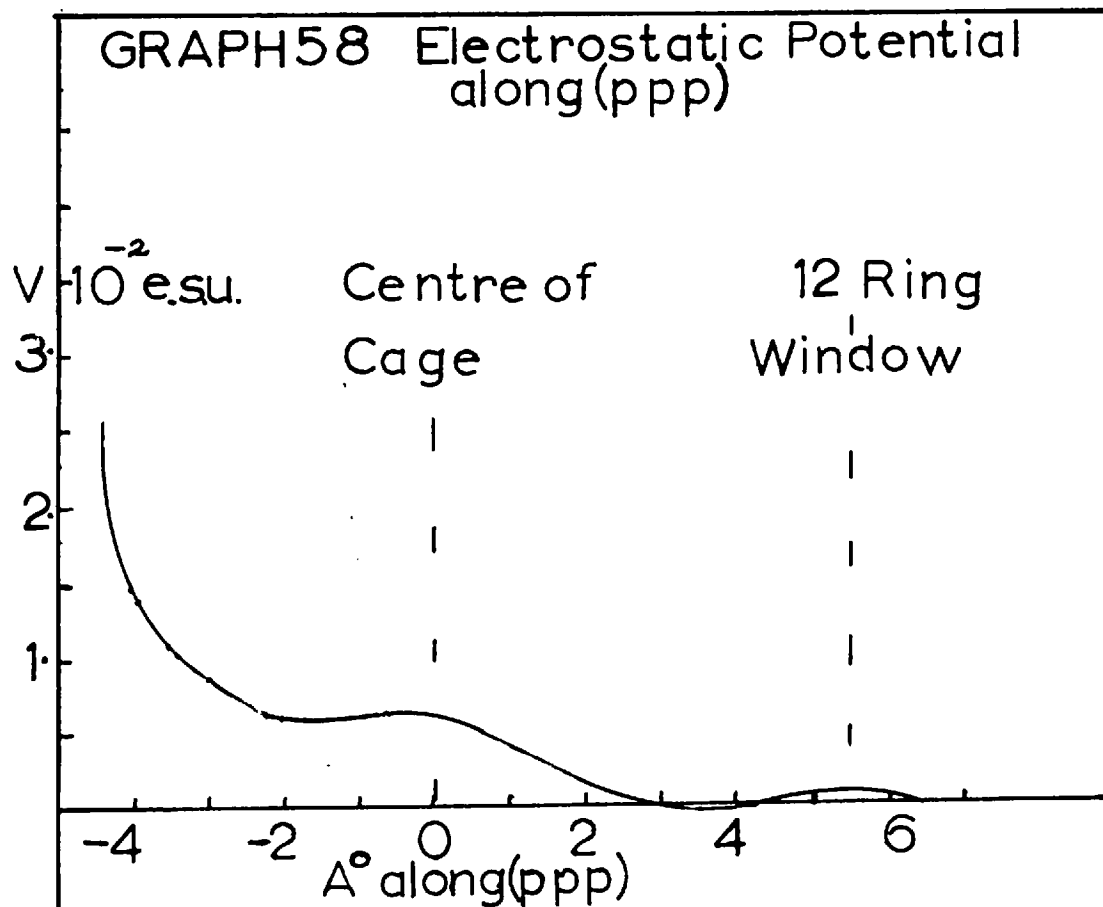
the oxygen atoms and sodium ions for a series of points on (ppp). The results are shown in graph 58 which shows that there is a small positive potential along most of the line (ppp) in the cage which increases very rapidly as the wall is approached at the point occupied by the cation at the centre of the 6 ring of oxygen atoms.

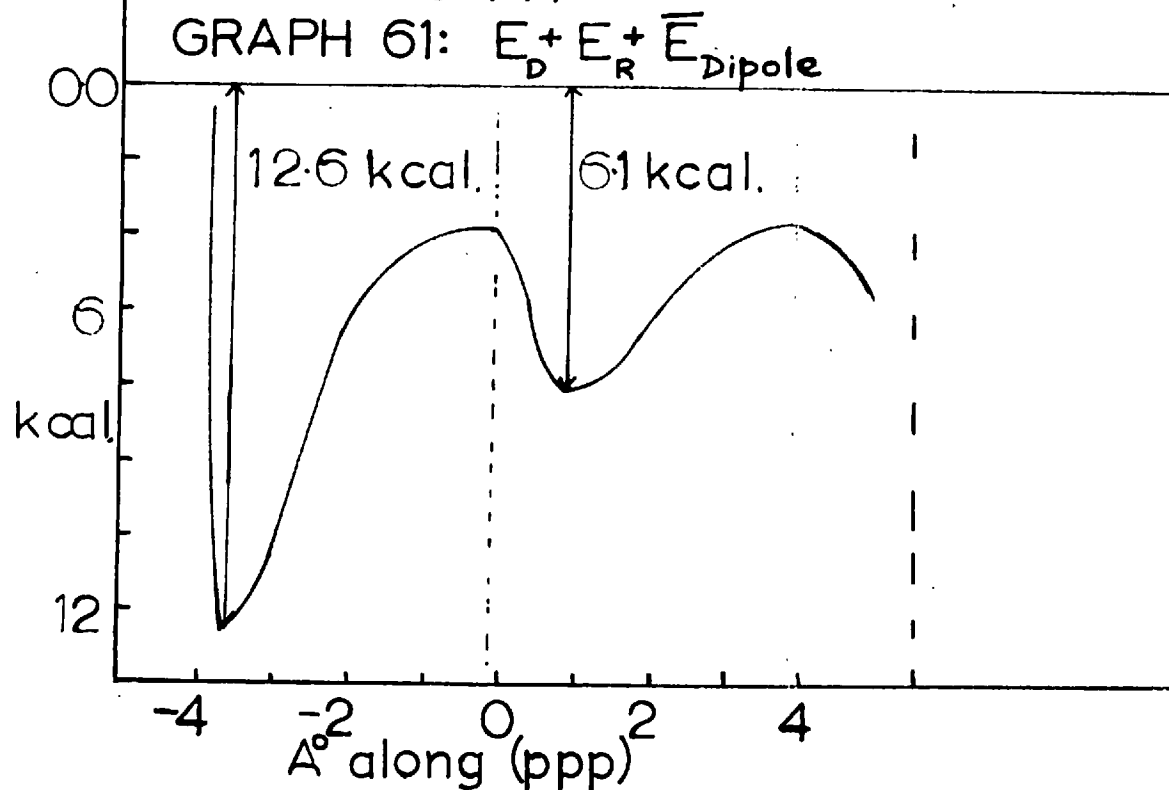
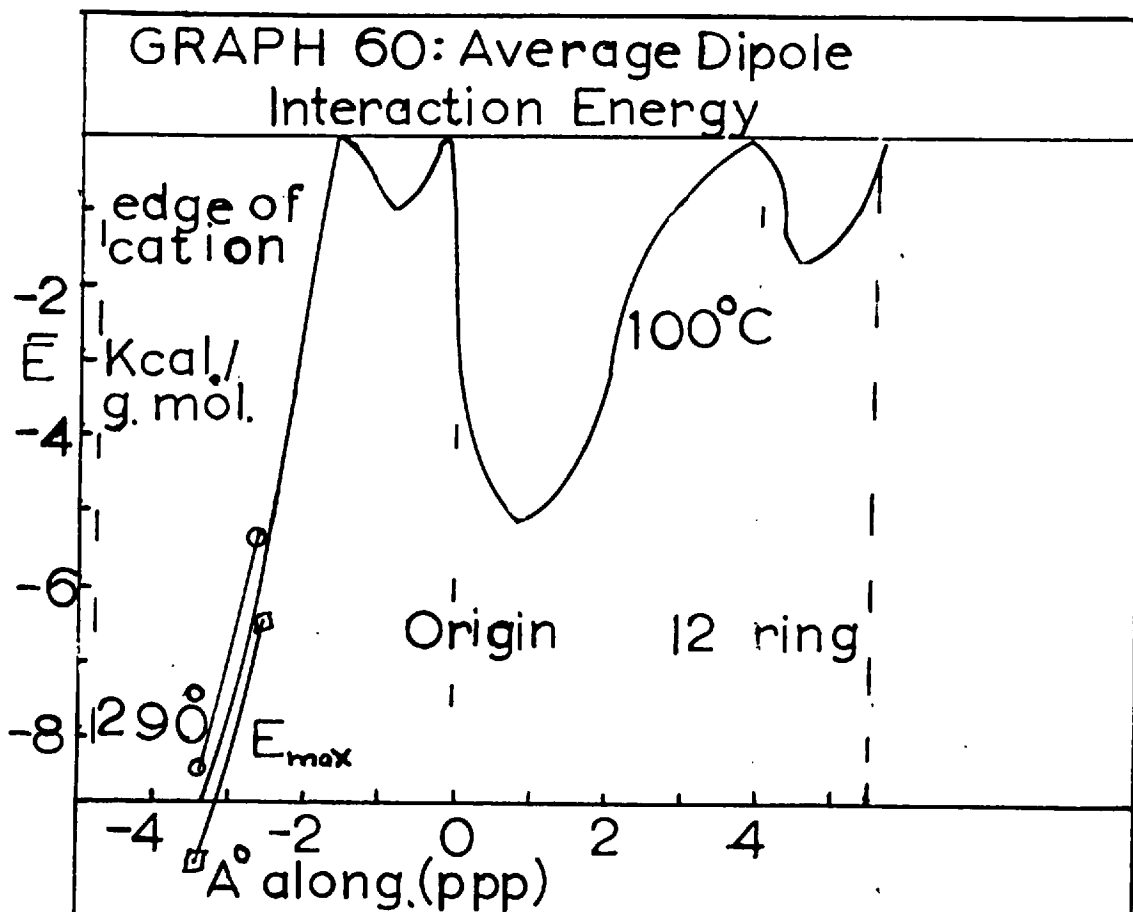
The field at each point was obtained from the slope of the graph of ϕ v. distance along (ppp) and a plot of the field v. distance along (ppp) is shown in graph 59. This is not a very accurate procedure for obtaining the field but the error should be less than 10%. The average interaction energy of an ideal dipole was then obtained at 100°C using equation 5a of section 1.4.2 and tables for the Langevin function. The results are shown in graph 60. It is seen that there is a strong interaction near the centre of the cage as well as a very strong interaction near the wall immediately above a cation. Near the equilibrium point the average dipole energy is ~ 9 Kcal/gm.mole which is much larger than the dispersion energy contribution (~ 3 Kcal $\pm$ 1.3 Kcal). The barrier to a complete rotation about an axis at right angles to the surface would involve the dipole in a repulsion with the field, leading to an energy barrier of the order of 19 Kcal/gm.mole (graph 60). It is thus apparent that two rotations for ammonia sorbed in these positions will be substantially hindered.

Also shown in graph 60 is the maximum energy of interaction of the dipole with the field for two points (the difference between $\bar{E}_m^{100^\circ\text{C}}$ and maximum E_m is ~ 0.8 Kcal/gm.mole). $\bar{E}_m$ at 290°C is also shown at two points in graph 60; the difference between $\bar{E}_m^{290^\circ}$ and $\bar{E}_m^{100^\circ}$ is ~ 0.4 Kcal/gm.mole at the positions indicated in graph 60. This change in $\bar{E}_m$ with temperature would produce a similar change in q_{st} ; very approximately, in view of the relationship between q_{st} and the energy of the sorbate:

$$2. \quad \Delta q_{st} = \Delta \bar{E}_m$$

assuming the other interaction energies to be independent of temperature. The value of Δq_{st} between 290°C and 100°C is given as ~ 0.4 Kcal/gm.mole. Though this variation in q_{st} is quite large it was not measured, experimentally, since no value of q_{st} was obtained over the entire temperature range from 290°C to 100°C . Over a range of 100°C the variation would be $\sim .2$ Kcal, i.e. ± 0.1 Kcal/gm.mole and this is less than the experimental error in q_{st} . As most heats were obtained over a temperature range of 100°C it is therefore expected that the temperature coefficient of q_{st} was unobtainable from these experiments.





6.4. Electrostatic, Dispersion and Repulsion Energies

The sum of the dispersion, repulsion and average of dipole interaction energies are plotted in graph 61 which shows that the dipole affects the equilibrium position quite markedly shifting it $0.5\text{\AA}$ closer to the cation. This apparent shift may be due to the inadequacy of the repulsion term in the Lennard Jones potential. However, it only increases the total interaction energy by 1 Kcal, but it alters the relative contributions of the various forces as shown in table 19.

TABLE 19
Interaction Energies at r_0

Equilibrium position (on ppp) $\text{\AA}$	$E_D + E_R$	$\bar{E}_m$	Total
-3.05	2.75	8.7 (100°C) (8.38)(290°C)	11.45
-3.55	1.92	10.9 (100°C) (10.5)(290°C)	12.82

In view of the undue shift of the equilibrium on including the dipole energy all that may be said from these figures is that the interaction energy from these forces amounts to ~ 12 Kcal and that the dipole interaction is predominant. This value is approximately equal to the residual

value for the heats, and one concludes that the high initial heats are caused by the cations whose positions are unknown. These cations would be likely to lie in the channels and presumably would be more exposed than the cations in the centres of 6 rings of oxygen atoms thus allowing a more energetic interaction with a dipole. The polarisation energy, which will be discussed in section 6.6 would raise the interaction energy markedly at the equilibrium position in graph 61 by 5.2 Kcal/gm. mole. This seems unduly high as it would indicate that there are eight sites per cage (i.e. 80 mgm. of NH_3/N unit cells) with interaction energies of the order 17.5 Kcal/gm. mole. The number of sites associated with the high initial heats in NaX would be much less than 8 per cage since the heterogeneity dies away so quickly. In addition in CsX, which shows no heterogeneity, some of the sites in the 6 rings would be occupied by sodium ions. In view of this it is thought that the polarisation energies calculated are too large.

6.5. Calculations for other Cationic Forms

No rigorous extension of the calculations of the electrostatic field can be made for any of the other cationic forms of faujasite since the positions of the cations are unknown. However, if it can be assumed for monovalent ions that the centres of the 6 rings of oxygen atoms are occupied by the exchanging ion then, qualitatively, it is possible to make suggestions about the relative importance of the various types of forces. In the cases of partially exchanged forms (RbX, CsX) it is likely that the positions in the 6 rings are occupied by sodium ions as Freeman and Stamires (92) have recently adduced evidence showing that these are the most stable of the cationic sites in NaX and hence least likely to be exchanged. It is therefore likely that most of the exchange occurs with these cations whose positions were not established by Shoemaker and Broussard (13). Calculations have been made for LiX and KX for the line (ppp), since it is likely that these cations will occupy the same sites as does sodium in the NaX form. LiX is assumed to differ only in the equilibrium position possible for ammonia since Li^+ has a smaller radius, 0.6 Å as against .95 Å for Na^+ . K^+ , because of its size, ($r = 1.33 \text{ Å}$), cannot fit in the middle of the 6 ring and projects out towards the centre of the cage; hence the equilibrium position of

ammonia shifts both because of the size of the cation and because the equilibrium position of K^+ is changed slightly.

The values of the average dipole field interactions at 100°C have been calculated at the equilibrium positions on (ppp), assuming $r_e = r_{\text{ion}} + r_{\text{NH}_3}$ for the two cases. The results are shown in table 19 where the values of the different energy terms are also listed. While this may not be the true equilibrium point, the final value of the interaction energy will not be very different, as was the case with NaX. Again the cations contribute very little to the total interaction energy but they control the dispersion interaction between the probe molecule and the oxygen atoms. The dipole-field term is seen to vary quite sharply with the cation present.

TABLE 19.

	Oxygen $E_D + E_R$	Ions $E_D + E_R$	$\bar{E}_\mu$	$\bar{E}_{\text{Total}}$	Position on o p p p A
LiX	4.35	.25	10.7	14.67	- 3.5
KX	2.7	.3	8.0	11.0	- 2.77

6.6.1. Polarisation Energy

The dipole induced by a field of not too high strength in a polarisable molecule may be represented by

$$1. \quad m_{\text{ind}} = \alpha F$$

where α is the mean polarisability, ignoring any anisotropy. However, at high field strengths it has been suggested that the induced dipole may be better represented by

$$2. \quad m_{\text{ind}} = \alpha_0 F + \beta F^3$$

where β is a constant. Coulson et al (93) have suggested β is positive which means that the induced dipole increases very rapidly at high F . Buckingham and Pople (94), for non polar molecules have related β to the Kerr constant for the molecule concerned which would result in a maximum value for m_{ind} induced if the Kerr constant, and hence β is negative. The Kerr constant is negative for ammonia and if the above argument holds for ammonia as well as non polar gases, then on differentiating equation 2 w.r.t. F the maximum value of m_{ind} is obtained at

$$3. \quad F_m^2 = \frac{\alpha_0}{3\beta},$$

and the maximum polarisability by

$$\alpha_m = \frac{2}{3} \alpha_0.$$

The value of the induced dipole would then be $\leq \frac{2}{3}a_0F$.

6.6.2. Polarisation Energy (2)

The polarisation energy for an ammonia molecule with the field in a cage in NaX was assumed to be given by

$$4. \quad E_p = -\frac{1}{2}a_0F^2$$

The values obtained using this formula for positions on (ppp) at various distances from the cation in the centre of the 6 ring are shown in table 20 where the polarisation energies at several distances from a cation are shown for a point particle of polarisability 2.28×10^{-24} . It is seen that E_p on approaching a cation in a cage is very much smaller than for an isolated cation at all distances. In the cage by the time the probe molecule is at a position $\sim 3.5\overset{\circ}{\text{A}}$ from the cation the polarisation energy is very small. The nett effect of the cage then is to provide a small "background" potential which decreases the potential gradient markedly as a cation is approached.

The actual magnitude of the polarisation energies at the equilibrium position seems somewhat large, being 5.2 Kcal/gm.mole. Even allowing that the maximum value is

$$E_p = -\frac{2}{3}\left(\frac{1}{2}a_0F^2\right)$$

E_p would still be 3.7 Kcal/gm.mole. Similar results were found by Barrer and Bratt (24) when they considered the interactions of water with various charge arrays. The results here are much more reasonable but are still too large. Attempts were made to allow for the actual size of the molecule by averaging the field over the whole molecule; this made E_p between 10 and 100 times as large as previously. It would be possible to modify

TABLE 20
 E_p for a cage and a cation.

Cage (a)		Isolated ion (b)	
Distance from cation on (ppp)	E_p Kcal/gm.mole	Position (from ion)	E_p Kcal/gm.mole
1.9	11.67	$2\overset{\circ}{\text{A}}$	23.6
2.65	3.4	$3\overset{\circ}{\text{A}}$	4.6
3.25	1.5	$4\overset{\circ}{\text{A}}$	1.48
3.53	0.1		

Equilibrium position = $2.2\overset{\circ}{\text{A}}$. The equilibrium position between NH_3 and the Na^+ associated with a 6-ring is $\sim 2.2\overset{\circ}{\text{A}}$ (graph 61).

the polarisation energies by assuming that the induced dipole approaches a limit as Barrer and Bratt did in an empirical way. The only rigorous conclusion to be drawn

however is that the approximation

$$m_{\text{ind}} = \alpha F$$

breaks down at these high fields (i.e. fields of the order 1.10^6 e.s.u./cm). Until a rigorous theory is developed which predicts why and how the polarisation energy varies with the field strength it does not seem advantageous to pursue the matter further.

An alternative explanation could be that the quadrupole in ammonia is aligned so that it has a positive interaction with the field gradient when the dipole is in equilibrium. This could then balance the polarisation; very approximate calculations of the field gradient show the quadrupole term to be smaller than the polarisation term by a factor of 2.

6.6.3. Polarisation Energy (3)

The polarisation energy in sorption is the result of interactions of the sorbent molecule with the electrostatic field at sites on the sorbent. The importance of this form of energy of interaction depends on the fields at the sorbent, the radius of the molecules, which determines whether a molecule has access to any recessed sites of high electrostatic field, and on the polarisability per unit volume of the sorbate. The intensity

of polarisation, rather than the total polarisability of a molecule, has been suggested by Barrer (95) as the best guide in judging the order of polarisation energies. The polarisations per unit volume for various molecules are shown in table 21 and their sorption data on NaX support the view of the importance of the intensity rather than the total polarisation. Thus I_2 has a high intensity and it also has a very high initial heat on NaX (47) while CF_4 and SF_6 (8) with the next largest polarisabilities show no initial heterogeneity; in these cases their sizes contribute also to the diminution of the polarisation by excluding them from any recessed sites with high fields.

TABLE 21.
Polarisability/unit vol.

	V_m liq	a_m	$\frac{a_m}{V_m}$	$T^\circ C$
NH_3	17.9	1.373	.049	- 10°C
I_2	63.5	7.685	.121	+183
SF_6	76.5	3.74	.049	60
CF_4	44.9	2.21	.049	-184
H_2O	18.8	.89	.049	100
A	28.3	.98	.035	-187

7. CoX Data.

The CoX data are listed in Appendix 1.

The sorption of ammonia on this system was irreversible and X-ray examination after sorption established that the lattice had disintegrated. Colour changes of CoX were noted both with the amount of water in the crystal, during outgassing, and also with the amount of ammonia sorbed.

The colour of the outgassed CoX was royal blue and the first colour change, to grey, occurred at ~50mgm./gm. sorption; the second change was to brown and occurred at ~100mgm./gm. The first colour change was not reversed on decreasing the amount sorbed, but the second change was. These amounts sorbed are closely related to the number of ammonia molecules per cobalt ion. Since CoX was 80%* exchanged, these amounts sorbed correspond to 5 and 10 per supercage which would mean approximately 1 and 2 molecules per cobalt ion. The colour changes were therefore ascribed to ammine formation by the cobalt ions.

* Analysis showed that the CoX was 80% exchanged.

8. Summary of Results and Discussions.

Isotherms have been obtained for ammonia sorbed on various ion-exchanged faujasites between 100°C . and 290°C .; in addition, isotherms have been obtained for ammonia on NaX between 0°C . and 70°C . The various forms of faujasite have been analysed to determine the extent of exchange. From the reversible isotherms the isosteric heats, the partial molar entropies and the half standard entropies have been calculated.

The cations influenced the energetic heterogeneity of the sorbents at low coverages; at higher coverages, all the heats converge to approximately the same value. The most heterogeneous forms were the forms containing divalent ions; the forms containing monovalent ions were increasingly homogeneous as the size of the ion increased, the data for CsX showing this sorbent to be homogeneous. The integral heats were obtained from the isosteric heats for ammonia on NaX and SrX and comparison with the latent heat showed them to be between 2.5 and 3.5 times as large as the latter. This was ascribed to interaction of the dipole of ammonia with the field inside the crystal.

The half standard entropies for a given

amount sorbed were obtained and their temperature invariance demonstrated. They were then used to predict the partial molar entropies of ammonia on the various faujasites at temperatures for which the partial molar entropies were otherwise unobtainable. Integral molar entropies of ammonia on each form were obtained at various temperatures between the limits of the amounts sorbed for which heat data were available and compared with the entropy of liquid ammonia and with one another. The entropies are very close to one another and are somewhat smaller than the entropy of the liquid at 100°C. or 110°C., except for the entropy on KX which was slightly larger than S_L at 100°C.

Efforts were made to estimate the saturation capacities of ammonia for each form, as these quantities were not obtainable directly, using the limiting slopes of p/x v. p plots at several temperatures and also, for NaX, from the co-volume of the liquid and the intracrystalline volume of the crystal. The thermal expansions of ammonia were obtained on each form and compared to that of liquid ammonia. For ammonia on NaX the thermal expansion of ammonia was also obtained at constant Polanyi potential.

Using the estimated saturation capacities

an attempt was made to interpret the isotherm data in terms of various limiting models for motion of the sorbate. For the heterogeneous forms no model, or even empirical equation, gave any agreement with the experimental data. For CsX it was possible to interpret the data in terms of a localised model which had two soft vibrations parallel to the surface and had hindered rotational degrees of freedom. The difference between such soft vibrations and free translations is somewhat blurred.

The free energy and enthalpy changes of the sorbents were obtained, for LiX, KX and SrX, with respect to the same standard state in order to compare these changes. This state was chosen arbitrarily as it was impossible to obtain changes relative to the empty sorbents. In all cases the changes were small; the enthalpies were opposite in sign to those of the sorbate.

The data on CoX showed hysteresis associated with colour changes and accompanied by a breakdown of the lattice.

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APPENDIX 1.ISOTHERM DATA.

P= cm. of Mercury

x= mgm./gm, (outgassed)

LiX/NH₃290°C

<u>P</u>	<u>x</u>
3.500	0.0310
10.702	0.0396
19.474	0.0460
29.51	0.0507
39.438	0.0543
49.380	0.0576
54.464	0.0587
44.785	0.0564
35.034	0.0527
24.300	0.0483
14.315	0.0424
6.916	0.0356
4.680	0.0325
0.597	0.0239
9.664	0.0381
17.255	0.0441
34.110	0.0518

260°C

<u>P</u>	<u>x</u>
1.376	0.0294
4.237	0.0387
9.614	0.0453
19.486	0.0535
29.000	0.0586
39.355	0.0628
50.124	0.0665
54.015	0.0675
44.325	0.0646
35.099	0.0611
24.909	0.0568
15.161	0.0505
7.384	0.0425
2.161	0.0323
0.714	0.0265
0.322	0.0241

230°C

<u>P</u>	<u>x</u>
1.409	0.0371
5.421	0.0496
10.890	0.0574
19.208	0.0669
29.830	0.0708
39.485	0.0747
49.241	0.0787
54.928	0.0802
45.280	0.0774
34.656	0.0729
24.759	0.0683
14.169	0.0609
19.269	0.0652
7.520	0.0535
3.345	0.0446
0.757	0.0321
0.375	0.0285

200°C

<u>P</u>	<u>x</u>
1.373	0.0460
5.708	0.0608
10.485	0.0681
19.351	0.0768
31.208	0.0829
40.252	0.0882
49.489	0.0918
59.325	0.0953
55.605	0.0942
44.800	0.0906
35.526	0.0866
25.146	0.0795
15.206	0.0739
7.031	0.0643
3.093	0.0549
0.413	0.0367
0.832	0.0426

Lix/NH₃170°C

<u>P</u>	<u>x</u>
1.125	0.0534
5.004	0.0698
10.486	0.0800
19.000	0.0891
29.412	0.0975
39.892	0.1038
50.769	0.1091
59.463	0.1127
55.147	0.1112
44.551	0.1069
35.660	0.1025
25.336	0.0949
14.533	0.0854
7.208	0.0761
3.080	0.0670
0.914	0.0546
0.378	0.0434
4.108	0.0682

140°C

<u>P</u>	<u>x</u>
1.302	0.05850
5.135	0.0759
9.073	0.0868
18.383	0.01017
29.138	0.01129
39.762	0.01201
49.967	0.01261
58.919	0.01296
54.585	0.01280
44.935	0.01237
35.515	0.01199
24.885	0.01119
15.208	0.01016
13.805	0.099
7.736	0.0894
2.510	0.0748
0.868	0.0660
0.500	0.0613

110°C

<u>P</u>	<u>x</u>
1.140	0.0776
4.420	0.0959
8.882	0.1106
18.945	0.1275
28.286	0.1366
38.752	0.1432
49.596	0.1493
58.950	0.1521
55.293	0.1514
44.630	0.1470
34.764	0.1418
25.022	0.1363
15.100	0.1252
7.816	0.1101
2.286	0.0923
0.481	0.0726

NaX/NH₃290°C

<u>P</u>	<u>x</u>
1.115	0.0113
3.265	0.0182
6.363	0.0226
11.870	0.0278
24.773	0.0365
35.885	0.0417
47.530	0.0455
55.824	0.0474
50.472	0.0464
40.418	0.0432
32.214	0.0398
18.965	0.0335
14.430	0.0302
9.939	0.0269
5.075	0.0212
2.355	0.0156
0.126	0.0009

NaX/NH₃

260°C

<u>P</u>	<u>X</u>
1.455	0.0184
3.461	0.0259
7.574	0.0309
11.485	0.0354
20.108	0.0429
30.903	0.0490
41.770	0.0544
53.232	0.0584
47.436	0.0564
37.763	0.0551
26.634	0.0472
15.731	0.0398
4.432	0.0266
3.123	0.0237
0.983	0.0163

230°C

<u>P</u>	<u>X</u>
0.362	0.0159
2.859	0.0296
6.793	0.0384
17.217	0.0514
32.453	0.0619
42.774	0.0672
53.374	0.0707
60.193	0.0734
56.039	0.0718
47.473	0.0689
24.956	0.05788
12.751	0.0475
4.635	0.0351
1.885	0.0269

200°C

<u>P</u>	<u>X</u>
0.121	0.017
1.753	0.0345
7.224	0.0458
23.119	0.0704
34.020	0.0772
43.741	0.0818
52.351	0.0857
48.305	0.0841
39.604	0.0804
29.168	0.07498
18.469	0.0669
12.241	0.0602
7.444	0.0549
4.620	0.0464
2.660	0.0390
0.621	0.0247

180°C

<u>P</u>	<u>X</u>
0.398	0.0278
3.381	0.0506
5.716	0.0581
9.778	0.0663
19.144	0.0776
31.709	0.0869
43.003	0.0933
53.548	0.0981
45.838	0.0952
36.668	0.0913
28.548	0.0855
14.96	0.0741
8.142	0.0626
3.755	0.0486
4.556	0.0552
0.976	0.0363

NaX/NH₃

160°C

<u>P</u>	<u>X</u>
1.025	0.0447
3.504	0.0613
6.243	0.0697
16.800	0.0867
28.446	0.0965
38.111	0.1038
50.003	0.1098
43.054	0.1067
33.966	0.1012
23.710	0.0938
13.570	0.0831
7.757	0.0737
3.801	0.0647
1.760	0.0523
0.345	0.0342

120°C

<u>P</u>	<u>X</u> X
0.888	0.0665
3.463	0.0855
7.050	0.0989
14.363	0.1136
28.764	0.1278
41.364	0.1350
51.137	0.1397
46.252	0.1379
35.470	0.1250
22.093	0.1324
10.249	0.1068
4.542	0.0910
1.475	0.0730
0.469	0.0567

140°C

<u>P</u>	<u>X</u>
0.852	0.0540
3.624	0.0734
7.815	0.0859
13.790	0.0969
21.999	0.1065
33.972	0.1162
45.206	0.1226
52.749	0.1260
40.056	0.1199
29.568	0.1134
16.450	0.0997
6.276	0.0838
0.623	0.0494
1.893	0.0666

100°C

<u>P</u>	<u>X</u>
0.095	0.0810
3.031	0.0988
6.016	0.1126
12.702	0.1274
21.405	0.1383
31.163	0.1458
42.871	0.1512
47.980	0.1533
35.357	0.1483
25.998	0.1427
16.086	0.1335
8.117	0.11988
5.550	0.1125
2.016	0.0933
0.593	0.0735

KX/NH₃290°C

<u>P</u>	<u>X</u>
2.738	0.0085
6.342	0.0133
10.343	0.0165
20.000	0.0221
30.174	0.0265
40.113	0.0295
41.894	0.0303
35.160	0.0275
24.991	0.0244
16.004	0.0200
8.820	0.0155
4.545	0.0118
0.793	0.0059

230°C

<u>P</u>	<u>X</u>
4.617	0.0205
12.385	0.0312
21.069	0.0389
30.363	0.0448
39.999	0.04936
46.612	0.0522
34.989	0.0474
25.434	0.0414
14.493	0.0334
9.223	0.0279
6.454	0.0240
1.786	0.0138
0.5	0.0089

260°C

<u>P</u>	<u>X</u>
2.043	0.0108
11.281	0.0218
21.005	0.0289
31.402	0.0337
40.083	0.0381
43.173	0.0392
35.069	0.0362
25.760	0.0317
15.561	0.0256
8.368	0.020
8.443	0.0196
5.019	0.0160
0.989	0.0084
4.665	0.0153
12.332	0.0225
20.263	0.02844
30.300	0.0341
41.510	0.0389
2.891	0.0128

200°C

<u>P</u>	<u>X</u>
2.328	0.0226
10.340	0.04025
21.306	0.0518
29.617	0.0580
40.535	0.0637
46.446	0.0667
36.038	0.0617
25.696	0.0556
17.537	0.0486
4.962	0.0304
0.434	0.0124
8.063	0.0368

KX/NH_3
180°C

<u>P</u>	<u>X</u>
2.134	0.0320
9.842	0.0483
19.981	0.0604
30.337	0.0682
41.084	0.0741
49.723	0.0782
43.615	0.0755
35.102	0.0710
25.390	0.0649
15.935	0.0562
8.116	0.04497
2.838	0.0315
0.745	0.0187
3.225	0.0326

140°C

<u>P</u>	<u>X</u>
4.408	0.0552
9.452	0.0685
21.448	0.0844
32.027	0.0930
44.774	0.0996
53.093	0.1030
48.733	0.1014
39.291	0.09700
28.786	0.0909
15.260	0.0772
9.846	0.0699
6.005	0.0608
0.515	0.0269
2.115	0.0439

160°C

<u>P</u>	<u>X</u>
1.356	0.0298
5.475	0.0486
10.174	0.0586
19.985	0.0711
26.607	0.07898
42.962	0.0865
53.804	0.0909
48.312	0.0888
36.747	0.0836
25.212	0.0762
15.806	0.0670
6.870	0.0526
3.045	0.0402
0.819	0.0246

120°C

<u>P</u>	<u>X</u>
2.500	0.0588
9.274	0.0830
21.689	0.1001
31.748	0.1074
44.159	0.11396
52.642	0.1177
48.457	0.1159
37.389	0.1105
25.644	0.1028
13.487	0.0914
7.578	0.0792
4.336	0.0688
0.666	0.0338

KX/NH₃

100°C

<u>P</u>	<u>x</u>
1.775	0.06574
10.200	0.0982
18.824	0.1101
29.725	0.1194
41.185	0.1256
52.583	0.1304
47.137	0.1284
35.002	0.1226
24.667	0.1155
14.570	0.1051
1.418	0.0713
7.011	0.0910
0.364	0.0412

260°C

<u>P</u>	<u>x</u>
1.830	0.0035
10.764	0.0084
30.106	0.0166
19.925	0.0132
30.107	0.0166
38.656	0.0196
49.313	0.0230
33.834	0.0183
24.355	0.0145
14.774	0.0109
4.384	0.0050

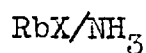
250°C

RbX/NH₃

290°C

<u>P</u>	<u>x</u>
1.881	0.0015
9.743	0.0049
19.936	0.0087
29.208	0.0119
39.749	0.0127
49.676	0.0146
44.929	0.0135
34.046	0.011
24.205	0.0085
14.388	0.0058
4.809	0.0025
4.082	0.0026
16.321	0.0069
27.820	0.0100
21.452	0.0084
8.538	0.0044

<u>P</u>	<u>x</u>
4.097	0.0066
11.235	0.0132
20.474	0.0195
30.129	0.0246
39.935	0.0284
49.746	0.0320
44.817	0.0307
34.830	0.0269
25.443	0.0225
15.040	0.0163
1.386	0.00373



200°C

<u>P</u>	<u>x</u>
1.768	0.0078
9.936	0.0208
19.209	0.0293
29.560	0.0356
39.452	0.0418
49.929	0.0462
44.405	0.0438
34.823	0.0401
24.658	0.0337
14.727	0.0271
4.037	0.0141
0.461	0.00431
9.967	0.0219

170°C

<u>P</u>	<u>x</u>
9.493	0.0302
19.755	0.0423
29.468	0.0496
39.615	0.0546
49.046	0.0582
58.756	0.0628
53.473	0.0609
44.855	0.0580
34.003	0.0533
24.841	0.0478
15.422	0.04009
2.414	0.0169
5.260	0.0239

140°C

<u>P</u>	<u>x</u>
1.346	0.0198
10.770	0.0490
19.640	0.0587
28.986	0.0648
38.446	0.0692
49.819	0.0727
58.053	0.0751
53.441	0.0744
44.962	0.0715
36.520	0.0685
23.950	0.0622
15.010	0.0546
6.867	0.0424
3.382	0.0312
0.547	0.0142

120°C

<u>P</u>	<u>x</u>
1.541	0.0298
10.210	0.0616
19.938	0.0719
29.498	0.0776
39.583	0.0816
48.796	0.0844
58.889	0.0867
55.302	0.0857
45.717	0.0834
34.347	0.0799
24.390	0.0751
14.629	0.06800
7.636	0.0574
3.303	0.0440
0.748	0.0243
10.051	0.0616

RbX/NH₃100°C

<u>P</u>	<u>x</u>
1.011	0.0383
4.484	0.0612
10.394	0.0736
19.009	0.0819
29.340	0.0876
39.925	0.0912
49.743	0.0938
59.021	0.0959
54.478	0.0951
34.798	0.0896
45.117	0.0925
14.897	0.0785
7.524	0.0692
2.322	0.0513
0.624	0.0317
1.285	0.0417
2.230	0.0499

CsX/NH₃290°C

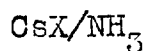
<u>P</u>	<u>x</u>
1.947	0.00068
9.253	0.0018
20.432	0.0041
29.518	0.0058
40.605	0.0079
49.185	0.0093
44.816	0.0087
35.238	0.0069
15.291	0.0033

260°C

<u>P</u>	<u>x</u>
2.001	0.0011
9.256	0.0037
19.520	0.0068
30.380	0.0099
39.699	0.0120
49.891	0.0145
44.115	0.0132
33.642	0.0106
24.903	0.0083
14.265	0.00471
2.396	0.0012
14.092	0.0050
21.696	0.0073
36.128	0.0111
29.053	0.0089
10.283	0.0042

250°C

<u>P</u>	<u>x</u>
1.986	0.0013
9.534	0.0058
18.948	0.0107
29.884	0.0149
38.876	0.0184
49.381	0.0218
44.812	0.0204
34.886	0.0171
24.740	0.0132
14.605	0.0087
6.081	0.0039



200°C

<u>P</u>	<u>x</u>
2.34	0.0036
9.810	0.0118
19.508	0.193
29.275	0.0254
39.427	0.0304
49.700	0.0342
44.762	0.0324
34.755	0.0279
24.929	0.0237
15.357	0.0164
6.031	0.0079

180°C

<u>P</u>	<u>x</u>
1.747	0.0039
10.184	0.017
19.693	0.0262
29.960	0.0328
38.591	0.0382
48.244	0.0412
52.352	0.0452
34.491	0.0369
45.398	0.0425
25.739	0.0308
16.047	0.0241
4.506	0.0111
10.403	0.0185
18.544	0.0263
29.810	0.0339
40.814	0.0401
50.056	0.0441
1.046	0.0045

160°C

<u>P</u>	<u>x</u>
2.100	0.0083
10.31	0.0353
19.018	0.0359
28.339	0.0454
39.067	0.0499
50.289	0.0548
56.151	0.0569
44.703	0.0524
25.135	0.0414
34.149	0.0474
14.661	0.0317
8.083	0.0221
4.837	0.0162
0.330	0.0038

140°C

<u>P</u>	<u>x</u>
1.665	0.0120
9.770	0.0288
19.624	0.0397
29.840	0.0506
39.426	0.0559
1.146	0.0095
11.020	0.0415
16.073	0.0444
49.054	0.0609
55.300	0.0688
44.088	0.0649
59.847	0.0630
34.730	0.06075
25.251	0.0549
19.585	0.0499
30.532	0.0582
14.962	0.0445
9.671	0.0363
7.142	0.0312
5.882	0.0215
3.086	0.0188
0.498	0.0062

CeX/NH₃120°C

<u>P</u>	<u>X</u>
1.529	0.0156
10.859	0.0328
19.959	0.0642
29.767	0.0713
40.389	0.0766
50.817	0.0800
58.681	0.0817
53.668	0.0808
25.085	0.07796
34.967	0.0684
34.630	0.0738
14.734	0.0587
8.029	0.0468
6.098	0.0415
4.051	0.0339
1.490	0.0198

100°C

<u>P</u>	<u>X</u>
1.408	0.0308
5.562	0.0569
19.124	0.0793
10.429	0.0689
29.890	0.0862
40.413	0.0904
50.070	0.0933
59.488	0.0957
55.310	0.0944
45.338	0.0922
35.487	0.0887
25.174	0.0838
15.560	0.0763
7.575	0.0639
4.482	0.0536
2.4	0.0430
0.813	0.0265

SrX/NH₃290°C

<u>P</u>	<u>X</u>
0.908	0.0297
4.720	0.03987
9.746	0.0466
19.448	0.0527
29.465	0.0569
38.949	0.0607
48.594	0.0629
54.535	0.0647
42.799	0.0613
33.554	0.0583
23.858	0.0548
14.871	0.0501
2.340	0.0350
0.375	0.0253

260°C

<u>P</u>	<u>X</u>
0.808	0.0341
4.851	0.0474
10.574	0.0551
19.655	0.0622
29.275	0.0671
40.406	0.0718
49.872	0.0758
54.814	0.0769
45.198	0.0740
35.180	0.0697
24.813	0.0655
15.275	0.0596
7.673	0.0524
2.550	0.0432
0.253	0.0289

SrX/NH₃230°C

<u>P</u>	<u>X</u>
0.958	0.0422
4.201	0.0549
8.825	0.0627
19.724	0.0728
29.680	0.0797
39.729	0.0846
49.110	0.0884
54.980	0.0908
44.846	0.0868
35.255	0.0825
25.366	0.0772
15.554	0.0706
6.825	0.0613
1.104	0.0449
0.236	0.0347

170°C

<u>P</u>	<u>X</u>
1.165	0.0651
4.194	0.0835
10.583	0.0938
19.630	0.1049
29.158	0.1126
39.540	0.1179
50.135	0.1235
55.400	0.1252
44.792	0.1214
34.950	0.1163
25.450	0.1104
14.854	0.1005
7.574	0.0896
2.568	0.0731
0.498	0.0579

200°C

<u>P</u>	<u>X</u>
1.00	0.045
4.890	0.0669
10.206	0.0770
18.953	0.0865
29.537	0.0944
39.685	0.1026
47.400	0.1053
54.968	0.1066
45.263	0.1029
35.137	0.0983
14.488	0.0830
24.582	0.0921
8.204	0.0742
1.831	0.0544
0.304	0.0447

140°C

<u>P</u>	<u>X</u>
0.936	0.0761
4.682	0.0989
10.272	0.1126
19.410	0.1245
29.358	0.1324
39.131	0.1373
49.3	0.1418
55.206	0.1431
45.292	0.140
35.019	0.1356
24.426	0.1299
15.581	0.1218
7.739	0.1086
2.534	0.0923
0.357	0.0686

SrX/NH₃110°C

<u>P</u>	<u>x</u>
0.780	0.0942
4.266	0.1196
19.401	0.1447
10.558	0.1549
29.241	0.1516
39.700	0.1556
49.660	0.1580
54.573	0.1601
44.926	0.1577
35.280	0.1542
25.438	0.1486
14.632	0.1430
7.881	0.1309
2.546	0.1119

260°C

<u>P</u>	<u>x</u>
1.273	0.0250
5.248	0.0364
10.040	0.0421
19.502	0.0491
29.884	0.0546
40.167	0.0581
49.666	0.0612
44.430	0.0596
33.869	0.0566
24.345	0.0521
14.885	0.0462
6.724	0.0388
2.439	0.0301
0.465	0.0198

BaX/NH₃290°C

<u>P</u>	<u>x</u>
1.595	0.0197
5.380	0.0296
11.785	0.0355
21.861	0.0416
29.720	0.0453
37.197	0.0480
49.521	0.0515
42.483	0.0496
34.359	0.0459
16.064	0.0392
24.818	0.0434
7.452	0.0323
2.377	0.0238
0.502	0.0145

230°C

<u>P</u>	<u>x</u>
0.289	0.0246
1.522	0.0341
4.709	0.0434
10.031	0.0511
18.754	0.0589
29.503	0.0645
39.311	0.0695
48.963	0.0722
42.928	0.0706
36.103	0.0687
25.187	0.0633
14.844	0.0569
7.555	0.0489
2.316	0.0388
0.418	0.0272

BaX/NH₃200°C

<u>P</u>	<u>x</u>
1.063	0.0406
4.956	0.0539
9.932	0.0612
18.235	0.0707
30.174	0.0772
39.289	0.0808
50.413	0.0835
43.780	0.0821
34.384	0.0790
24.419	0.0750
15.059	0.0686
7.699	0.0598
10.626	0.0641
2.523	0.0483
0.588	0.0367

170°C

<u>P</u>	<u>x</u>
0.359	0.0422
1.418	0.0528
4.587	0.0659
10.372	0.0757
19.501	0.0830
29.781	0.0878
39.236	0.0913
49.058	0.0939
53.832	0.0947
44.371	0.0931
32.641	0.0892
24.823	0.0870
14.857	0.0812
7.244	0.0722
2.491	0.0593
0.477	0.0441
10.841	0.0767

140°C

<u>P</u>	<u>x</u>
0.510	0.0562
1.606	0.0677
4.605	0.0794
9.941	0.0873
19.003	0.0942
29.451	0.0993
39.540	0.1026
50.620	0.1046
54.295	0.1054
44.383	0.1036
34.633	0.1011
24.599	0.0974
14.397	0.0920
7.769	0.0855
2.773	0.0748
0.577	0.0574
0.294	0.0511

110°C

<u>P</u>	<u>x</u>
0.121	0.0555
0.989	0.0793
5.403	0.0948
10.184	0.1010
19.751	0.1078
29.226	0.1112
38.049	0.1142
50.153	0.1173
54.289	0.1182
44.800	0.1158
34.704	0.1130
24.792	0.1097
14.951	0.1045
7.365	0.0977
2.482	0.0879
1.759	0.0834
0.451	0.0695

CaX/NH₃290°C.

<u>P</u>	<u>X</u>
0.433	0.0507
5.151	0.0457
10.129	0.0491
20.146	0.0549
29.191	0.0583
39.274	0.0608
49.597	0.0637
45.218	0.0626
55.016	0.0602
24.679	0.0573
13.031	0.0539
6.781	0.0455
0.553	0.0519

260°C.

<u>P</u>	<u>X</u>
1.508	0.0413
4.510	0.0485
19.277	0.0596
29.620	0.0644
41.524	0.0662
50.536	0.0694
57.412	0.0710
45.053	0.0682
35.195	0.0667
14.827	0.0590
25.192	0.0637
9.488	0.0555
7.076	0.0537
3.992	0.0486
0.517	0.0401
5.713	0.0511
1.175	0.0431
18.765	0.0602

230°C.

<u>P</u>	<u>X</u>
0.557	0.0426
4.404	0.0558
9.157	0.0596
19.711	0.0681
28.765	0.0715
39.418	0.0755
48.965	0.0782
58.575	0.0810
54.541	0.0805
44.519	0.0778
55.032	0.0745
25.151	0.0710
14.415	0.0655
7.652	0.0597
4.467	0.0569
2.050	0.0517
0.546	0.0418

200°C.

<u>P</u>	<u>X</u>
0.900	0.0528
4.761	0.0641
10.420	0.0709
19.317	0.0769
28.984	0.0832
39.209	0.0878
49.200	0.0918
59.192	0.0950
51.976	0.0927
33.254	0.0856
25.251	0.0816
42.443	0.0891
14.204	0.0749
7.348	0.0684
2.076	0.0596

CaX/NH₃170°C.

<u>P</u>	<u>X</u>
1.128	0.0625
9.902	0.0802
4.476	0.0719
19.423	0.0897
29.216	0.0966
39.761	0.1027
49.578	0.1074
58.843	0.1119
54.751	0.1102
45.433	0.1063
35.237	0.1014
24.905	0.0950
7.490	0.0777
15.421	0.0874
0.288	0.0552
2.580	0.0685
29.151	0.0972

140°C.

<u>P</u>	<u>X</u>
0.769	0.0685
5.689	0.0820
9.456	0.0959
19.324	0.1093
28.880	0.1180
29.297	0.1250
49.942	0.1308
59.879	0.1350
54.950	0.1336
33.978	0.1230
25.301	0.1167
15.657	0.1056
23.600	0.1139
33.668	0.1211
7.849	0.0943
5.365	0.0884
2.666	0.0307
0.452	0.0663

110°C.

<u>P</u>	<u>X</u>
1.514	0.0895
5.456	0.1087
9.947	0.1201
18.792	0.1347
29.297	0.1462
38.946	0.1526
50.330	0.1586
59.088	0.1615
55.527	0.1602
23.756	0.1419
44.707	0.1571
33.273	0.1506
15.430	0.1321
7.772	0.1174
2.408	0.0984
0.524	0.0813
9.821	0.1198
19.233	0.1361
28.619	0.1452

Volumetric Data NaX/NH₃70°C.

<u>P</u>	<u>X</u>
4.859	0.1241
38.694	0.1674
51.301	0.1730
49.578	0.1683
42.899	0.1658
36.870	0.1630
30.951	0.1601
23.438	0.1555
19.454	0.1531
15.285	0.1472
10.725	0.1417
7.448	0.1366
5.218	0.1301
3.517	0.1217
2.222	0.1116
1.264	0.1001

NaX/NH₃50°C.

<u>P</u>	<u>X</u>
0.216	0.1063
19.176	0.1764
24.778	0.1730
30.655	0.1773
48.994	0.1854
42.688	0.1994
35.176	0.1816
22.982	0.1729
15.506	0.1665
12.551	0.1625
8.992	0.1570
7.357	0.1541
5.054	0.1478
2.614	0.1349
1.589	0.1253
0.977	0.1152

30°C.

<u>P</u>	<u>X</u>
2.316	0.1602
9.473	0.1798
17.070	0.1893
30.068	0.1956
49.965	0.2042
53.350	0.2030
44.178	0.2011
35.788	0.1994
25.873	0.1955
16.686	0.1892
13.353	0.1856
7.734	0.1808
4.982	0.1707
3.251	0.1645

0°C.

<u>P</u>	<u>X</u>
0.200	0.1538
6.980	0.2065
12.093	0.2131
20.529	0.2200
40.315	0.2251
54.651	0.2286
47.014	0.2281
39.737	0.2262
33.509	0.2251
27.733	0.2224
20.594	0.2198
14.266	0.2161
10.867	0.2122
8.597	0.2091
4.640	0.2007
2.406	0.1916
1.399	0.1855

CoX/NH₃290°C.

<u>P</u>	<u>X</u>
1.185	0.0227
4.761	0.0303
11.496	0.0368
19.622	0.0393
30.143	0.0425
38.616	0.0449
49.207	0.0478
44.480	0.0480
55.229	0.0453
24.833	0.0432
14.865	0.0406
29.460	0.0447
19.383	0.0420
7.450	0.0376
2.501	0.0316
0.666	0.0267
10.123	0.0375

CoX/NH₃260°C.

(Check isotherm)

290°C.

<u>P</u>	<u>x</u>
3.120	0.0358
9.559	0.0421
19.608	0.0469
29.742	0.0507
39.632	0.0547
41.147	0.0582
44.185	0.0570
34.755	0.0549
25.050	0.0523
15.184	0.0487
7.643	0.0442
1.798	0.0370
4.586	0.0413
10.116	0.0455
20.297	0.0499
29.953	0.0532
2.334	0.0379
40.052	0.0557
0.399	0.0265

<u>P</u>	<u>x</u>
3.270	0.0300
11.311	0.0370
21.362	0.0409
33.721	0.0434
44.991	0.0455
15.460	0.0422
1.005	0.0287
30.836	0.0468

200°C.

<u>P</u>	<u>x</u>
1.590	0.0429
5.587	0.0509
11.379	0.0569
18.294	0.0623
30.106	0.0684
40.562	0.0722
44.999	0.0729
52.820	0.0760
35.082	0.0707
25.002	0.0672
15.753	0.0620
10.790	0.0590
20.052	0.0650
4.898	0.0517

230°C.

<u>P</u>	<u>x</u>
0.372	0.0275
0.793	0.0349
5.566	0.0456
8.844	0.0495
18.945	0.0557
29.925	0.0603
48.561	0.0655
39.960	0.0631
45.346	0.0655
35.691	0.0632
24.536	0.0591
14.488	0.0547
8.530	0.0495
2.320	0.0440
4.078	0.0468
19.651	0.0572
39.856	0.0648
51.169	0.0677

170°C.

<u>P</u>	<u>x</u>
1.115	0.0506
5.284	0.0610
9.854	0.0674
21.519	0.0763
29.999	0.0783
38.913	0.0848
51.484	0.0886
30.599	0.0812
15.240	0.0748

CoX/NH₃Appendix 2170°C, Contd.Conversion Factors(Number of ~~mg.~~mg./N unit cells)

<u>P</u>	<u>X</u>
3,459	0.0607
19,661	0.0775
10,702	0.0709
39,616	0.0856

NaX	1.000
LiX	0.901
KX	1.099

140°C.

<u>P</u>	<u>X</u>
1,656	0.0643
4,990	0.0769
11,538	0.0881
18,907	0.0949
30,115	0.1018
39,227	0.1039
50,324	0.1080
42,274	0.1063
24,436	0.1016
7,424	0.0876
2,737	0.0761
9,029	0.0897
39,573	0.1050
20,010	0.1003
0,350	0.0659

RbX	1.150
CsX	1.385
CaX	0.980
SrX	1.125
BaX	1.192
CoX	1.020

110°C.

<u>P</u>	<u>X</u>
0,280	0.0710
4,302	0.0976
9,251	0.1114
19,680	0.1207
31,741	0.1247
38,652	0.1275
51,689	0.1298
45,249	0.1285
24,956	0.1242
7,371	0.1154
0,744	0.0947
20,081	0.1212
40,999	0.1263
11,811	0.1182

INTERMOLECULAR FORCES DATA.

<u>Oxygen Atoms.</u>		<u>Position</u>	<u>E.S.U.⁺</u>	<u>Position</u>
<u>* 1. r.</u>	<u>** 1 2r^{1/2}</u>	<u>on (ppp)A</u>	<u>Potential</u>	<u>on (ppp)A</u>
866.2	87443.	4.89	2.482	4.34
447.3	22154.	4.35	1.390	3.91
264.0	6125	3.1	1.060	3.47
164.4	1856.	3.26	0.881	3.04
113.7	659.6	2.72	0.720	2.60
77.5	229.4	2.17	0.578	1.97
59.5	96.6	1.63	0.560	1.74
49.4	-	1.09	0.631	0.43
44.17	-	0.54	0.620	0.00
42.17	-	0.00	0.550	0.43
41.88	-	0.54	0.300	1.30
43.84	-	1.09	0.135	1.97
47.4	-	1.63	0.055	3.04
52.24	-	2.17	0.021	4.34
58.01	-	2.72		
64.29	-	3.26		
70.09	-	3.81	<u>Field⁺⁺</u>	<u>Position</u>
75.64	-	4.89		<u>on</u>
72.96	-	5.44		<u>(ppp)A</u>
23.514	-	7.07		
			0.363	3.91
			0.197	3.25
			0.132	2.60
			0.087	2.17
			0.000	1.52
			0.034	0.87
			0.003	0.43
			0.013	0.00
			0.107	0.43
			0.114	1.30
			0.069	2.17
			0.023	3.04
			0.000	3.91
			0.036	4.34
			0.050	4.76

Cations

1.
r.

Position
on
(ppp)A

1
r.

23.34
5.948
1.540
1.559
0.124
0.034
0.041
0.030

5438.
350.8
23.00
2.888
-
-
-
-

4.34
3.91
3.47
3.04
2.17
0.00
2.17
4.34

0.363
0.197
0.132
0.087
0.000
0.034
0.003
0.013
0.107
0.114
0.069
0.023
0.000
0.036
0.050

3.91
3.25
2.60
2.17
1.52
0.87
0.43
0.00
0.43
1.30
2.17
3.04
3.91
4.34
4.76

* x 10⁴³
** x 10³⁶ cm.

***x

***x .4299.10⁴⁰

****x.1848.10³⁶ cm.

+ x 10² c.s.u.

++ x 10⁶ e.s.u./cm.

INTERMOLECULAR FORCES DATA.

<u>Oxygen Atoms.</u>		<u>Position</u>	<u>E.S.U.</u> ⁺	<u>Position</u>
<u>* 1. r.</u>	<u>** 1 2r^{1/2}</u>	<u>on (ppp)A</u>	<u>Potential</u>	<u>on (ppp)A</u>
866.2	87443.	4.89	3.482	4.34
447.3	22154.	4.35	1.390	3.91
264.0	6125	3.1	1.060	3.47
164.4	1856.	3.26	0.881	3.04
113.7	659.6	2.72	0.720	2.60
77.5	229.4	2.17	0.578	1.97
59.5	96.6	1.63	0.560	1.74
49.4	-	1.09	0.631	0.43
44.17	-	0.54	0.620	0.00
42.17	-	0.00	0.550	0.43
41.58	-	0.54	0.300	1.30
43.84	-	1.09	0.155	1.97
47.4	-	1.63	0.055	3.04
52.24	-	2.17	0.021	4.34
58.01	-	2.72		
64.29	-	3.26		
70.09	-	3.81	<u>Field</u> ⁺⁺	<u>Position</u>
75.64	-	4.89		<u>on</u>
72.96	-	5.44		<u>(ppp)A</u>
23.514	-	7.07		
			0.363	3.91
			0.197	3.25
			0.132	2.60
			0.087	2.17
			0.000	1.52
			0.034	0.87
			0.003	0.43
			0.013	0.00
			0.107	0.43
			0.114	1.30
			0.069	2.17
			0.023	3.04
			0.000	3.91
			0.036	4.34
			0.050	4.76

Cations

1.
r.

Position
on
(ppp)A

1.
r.

23.34
5.948
1.540
1.559
0.124
0.034
0.041
0.030

5438.
350.8
23.00
2.888
-
-
-
-

4.34
3.91
3.47
3.04
2.17
0.00
2.17
4.34

0.363
0.197
0.132
0.087
0.000
0.034
0.003
0.013
0.107
0.114
0.069
0.023
0.000
0.036
0.050

3.91
3.25
2.60
2.17
1.52
0.87
0.43
0.00
0.43
1.30
2.17
3.04
3.91
4.34
4.76

* x 10⁴³

** x 10³⁶ cm.

***x

***x .4299.10⁴⁰

****x.1848.10³⁰ cm.

+ x 10²¹ c.s.u.

++ x 10⁶ e.s.u./cm.