"The Study of Multilayer Formation on Ionic Adsorbents"

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MULTILAYER FORMATION ON IONIC ADSORBENTS.

PART I. INTRODUCTION

General

The object of this study has been to initiate work on the adsorption of polar vapours by crystalline heteropolar solids. This is of interest inasmuch as it can provide information on the mechanism of multilayer formation - in particular, the part played by the surface in promoting the formation of layers above the first. It is generally agreed that the primary step in the process of heterogeneous nucleation of a condensed phase from the vapour, i.e. the production of a crystal seed, is the formation, first of a monolayer of the vapour, then of several layers, on the surface of the nucleant. From this standpoint, it would be expected that the formation of several layers at low relative vapour pressures would characterize an adsorbent which could act as an efficient nucleating agent. The results of this study are thus of obvious importance.

The general method of approach to the problem is to study the effect on the adsorption isotherms, of varying the crystal lattice parameters and the electrical distribution within a surface plane, thereby modifying the adsorbent - adsorbate forces, by varying the adsorbent itself. By using a series of adsorbates, e.g. water, methanol and ethanol, the intermolecular forces within the adsorbed layer may be varied enabling the influence of polarity and steric considerations to be assessed.

Water itself is a case of obvious practical importance. In view of the fact that silver iodide, which has an ice-like crystalline structure, is a good nucleating agent for water vapour, it has been suggested that in general, structural similarity between the nucleating agent and the condensed phase of the adsorbate, is a pre-requisite for the growth of the seed crystal. The validity of this generalisation is open to question and it is therefore desirable to investigate the adsorption of water vapour on a range of solids, both known nucleating agents and others, in order to arrive at a better understanding of the phenomenon of nucleation.

Review of Previous Work on Adsorption by Heterpolar Surfaces

The published work in this field is not extensive and such data as are available often do not permit the energetics of the process to be evaluated.

Durau (1) was one of the first to study quantitatively adsorption on ionic crystals. At 18°C, he obtained isotherms for methane, ethane, prepane, sulphur dioxide and nitrous oxide on Sodium Chloride; a later publication (2) gives results at the same temperature for nitrogen, hydrogen, carbon monoxide, carbon dioxide and nitric oxide. The small adsorptions, apart from carbon dioxide, and the high pressures employed did not lead to great accuracy in the isotherms. Hydrocarbon vapours and acetone adsorptions were reported for lead chloride as adsorbent (3,4) and ethane and propane on potassium permanganate (5). Though heats of adsorption were calculated in the latter case, their interpretation was obscured by the alleged occurrence of chemisorption.

Frazer (6) using an optical method due to Rayleigh, examined the adsorbed layer of water on polished and freshly cleaved samples of rock salt and concluded that the layer was unimolecular. Silverman (7) using the same method obtained isotherms at a number of temperatures for methanol on rock salt. Calculation of heats of adsorption from the Clausius-Clapeyron equation yielded values of 7 K.Cals. for the first layer and 2 K. Cals for higher coverages.

Whipp (8) measured the uptake of iodine vapour by potassium iodide and explained the isotherms obtained on the basis of a loosely bound second layer in which the molecules of iodine were considered to be similar to those in the surface layer of pure iodine. Bradley (9) followed the slow adsorption of HCl gas on potassium chloride andinterpreted his results on the basis of a rapid surface adsorption followed by diffusion into the interior along cracks in the crystal structure, rather than simply by a slow surface adsorption. The experimental data were inadequate to separate the two mechanisms on thermodynamic grounds.

Herbert (10) studied the slow adsorption of ammonia and sulphur dioxide on sodium chloride but found difficulty in ascribing an equilibrium value of the amount adsorbed at a particular pressure. It was doubtful whether surface adsorption was the only effect occurring, but assuming that this was the case, the maximum adsorption corresponded to about seven layers. Tompkins (11) measured the adsorption of ten gases on sodium chloride at liquid air temperatures and found that, in the case of non-polar gases, there was a parallelism between their adsorbabilities and polarizabilities.

Some measurements at higher temperatures again revealed the slower process reported by earlier workers. Durau and Schratz (12) again investigated the adsorption of propane and sulphur dioxide on sodium chloride, finding that for the latter gas, the isosteric heats of adsorption (6.3 and 7.5 K. Cals for two temperature ranges) were of the same order of magnitude as the heat of vaporisation. But Herbert's results seemed to indicate that these calculations were based on pre-equilibrium adsorption values. In a re-investigation of the ammonia-sodium chloride system, Tompkins (13) obtained data on the fast initial adsorption from which he derived a heat of adsorption of 6.3 K. Cals. The kinetics of the slower adsorption process was also studied for which an energy of activation of 6.3 K. Cals was obtained. The mechanism proposed was a fast primary adsorption followed by desorption from the surface and diffusion into the bulk phase, thus accounting for the coincidence of the two heats.

Crawford and Tompkins (14, 15) obtained isotherms for sulphur dioxide, ammonia, carbon dioxide and nitrous oxide on barium fluoride and calcium fluoride at a series of temperatures between -78°C and 120°C, thus enabling heats of adsorption to be calculated from the Clausius-Clapeyron equation and the B.E.T, equation. A decrease of heat adsorption with increasing coverage was found and this was compared with theoretical calculations and discussed in terms of surface inhomogeneities.

Tompkins and Young (16, 17) made a detailed examination of the adsorption of carbon monoxide, nitrogen, argon and oxygen and the mixtures (nitrogen + argon) and (argon + oxygen) on caesium iodide. From the results, the variation in heats of adsorption during the filling of the first layer were obtained.

The shape of these curves was explained in terms of heterogeneity, lateral interactions of molecules in the adsorbed layer and due to the onset of second-layer formation. Comparison with theoretically calculated adsorption energies were good. Young (18) measured the heats of adsorption on two crystal faces of potassium chloride by suitably modifying the crystal habit and found good agreement with the theoretical calculations in the two cases.

The theoretical calculation of adsorption potential to which reference has already been made, was first carried out by Lenel (19) and more thoroughly by Orr (20, 21). These calculations were concerned mainly with rare gas-alkali halide systems and took into account dispersion and induction forces, the contribution of the latter to the total interaction energy being relatively small. Orr's treatment involved the use of the Kirkwood equation for calculation of the dispersion energy and included, in addition to the ion-induced dipole interaction, a term for the repulsive potential. In this way it was found that for argon adsorbed on the 100 plane of potassium chloride, the adsorption energy was greater when the argon was situated above the centre of a lattice square. Further, the variation of adsorption energy with increasing surface coverage viz. an initial fall in $-\Delta H$ followed by an increase could be explained since the electrostatic interaction energy between adsorbed molecules in the first layer was smaller than their Van der Waals attraction, thereby giving rise to a maximum at monolayer coverage. In contrast to this, Crawford and Tompkins (14), for sulphur dioxide on barium fluoride, found that the electrostatic contribution to the total energy was so large due to the permanent dipole and high polarizability of SO_2 and the double positive charge on the barium ion, that it outweighed the Van der Waals attraction forces with the result that the $-\Delta H$ curve fell during the filling of the first layer. Young (22) repeated Orr's detailed calculations for the adsorption of argon on the (111) face of potassium chloride and showed that there was a significant difference in the values obtained.

Bielanski and Tompkins (23) investigated the sorption of water vapour by dehydrated potash alum and observed reversible first layer adsorption followed by a diffusion into the crystal governed by the extent of multilayer formation occurring at higher pressures.

The adsorption of water vapour by silver iodide has been reported by Coulter and Candella, who obtained isotherms at 16°C, 34°C and 50°C. The results were complicated by the anomolous shape of the isotherms which was attributed to the hydration of a surface impurity. After allowing for this (by substraction of the amount of water taken up in the phase transition), the isotherm obtained was Type III of the Brunauer classification (24) - in which the isotherm is convex to the pressure axis; that is, the adsorption is small until high relative pressures of water vapour are attained. This is puzzling in view of the known efficiency of silver iodide in the nucleation of water vapour. Surface areas calculated from the adsorption data by the B.E.T., Harkins - Jura and Hüttig methods were all less than 0.1 $m^2\ g^{-1}$. Heats of adsorption calculated from the B.E.T. equation were 0.4 to 1 K. Cal greater than the heat of liquefaction whilst the isosteric heats were about 1 K. Cal less.

Low (25) employed an unusual experimental technique to study the adsorption of water vapour by Germanium dioxide. After allowing the solid to attain equilibrium with water vapour at a particular temperature, the adsorbed water was desorbed at 350°C as water vapour + hydrogen, into a calibrated volume where its pressure was measured. Isosteric heats were obtained and were observed to fall with increasing coverage from about 14.4 K.Cal at low monolayer coverages to about 11 K.Cals ($\simeq$ heat of liquefaction) after two layers had been adsorbed. The thermodynamics of the system was discussed in terms of recent theories of multi-layer adsorption.

Since 1937 there have been several theoretical approaches to a mathematical formulation of the adsorption isotherm involving the concept of multilayer formation. The first, that of Brunauer, Emmett and Teller (26), though it makes several simplifying assumptions is still of great useparticularly in the estimation of the surface area of solids. It regards adsorption on the first and subsequent layers to be of the Langmuir type. A gas molecule is localized to a given point on the solid surface and it can either remain in this position or return to the gas phase; there is no mutual interaction amongst adsorbed molecules and the heat of adsorption in the second and higher layers is equal to the heat of liquefaction.

Several modifications of the B.E.T. isotherms have been proposed, notably by Hill who took into account lateral interactions. By considering that the energy of a higher layer is not merely the heat of liquefaction, but contains an additional term due to the forces transmitted from the surface, Hill (27), Frenkel (28) and Halsey (29) have arrived at essentially the same isotherm, which predicts a stepwise increase of amount adsorbed as a function of pressure for a uniform surface. As soon as a surface distribution of energies in the first layer is introduced, the isotherm is smoothed out and the steps no longer appear. Singleton and Halsey (30) were able to detect these in the adsorption of xenon by graphitized carbon black known to be of uniform surface. The xenon was deposited on the surface, layer by layer, with a pronounced point of inflection (or step) corresponding to the completion of each layer. Halsey developed this further into a new technique for examining the multilayer region, with the idea of overcoming the difficulty of examination of adsorption at pressures approaching the condensation pressure. This consists of depositing firstly a layer or layers of a more condensable gas ("pre-freezing") followed by determination of an isotherm of a less condensable gas. An example of this is to be found in the adsorption of argon on pre-frozen xenon on carbon, anatase and silver iodide. It was shown that distinguishable stepwise isotherms were obtained up to six layers of pre-adsorbed xenon on carbon showing that surface forces (Van der Waals) were still operative at this distance; thereafter, the isotherms were indistinguishable. In the case of anatase and silver iodide, the steps were less evident and the isotherms coincident after two pre-adsorbed layers. It thus seems from those realts that the structure of the underlying solid isimportant and that in the case of anatase and silver iodide, only a few layers of xenon can be stablished; thicker layers are unstable both with respect to the bulk solid and thinner layers.

In a later publication, Karasz, Champion and Halsey (31), applied the same procedure to prefrozen layers of ice on anatase and silver iodide. The argon isotherms were indistinguishable after three layers on anatase and one layer on silver iodide. From the latter fact, they concluded that the growth of layers of ice on silver iodide does not take place under equilibrium conditions and that the two surfaces are energetically incompatible.

The work of Young, Chessick, Healey and Zettlemoyer (32) on the adsorption of water vapour by graphon, though not strictly relevant in this context, has some interesting features worthy of note. Heats of adsorption were obtained from a single water isotherm (Type III) and heat of immersion data. This decreased with increased coverage of the surface from about 10 K. Cals, passed through a minimum befor increasing gradually to the heat of liquefaction. Differential entropy values were also derived, these also passing through a minimum corresponding to the B.E.T. monolayer coverage as obtained from the water isotherms. This was 1/1500 of the B.E.T. monolayer coverage from nitrogen adsorption, i.e. the second layer began to form when only a small fraction of the total surface was filled. The interpretation was based on the hypothesis that the hydrophobic graphon surface contained some hydrophilic sites of high but non-uniform energy. After adsorption of the first layer on these sites, a second layer seemed to form in preference to adsorption on the surrounding hydrophobic area. It was not surprising that the heat of adsorption was found to be less than the heat of liquefaction as on this picture the adsorbed molecules are isolated on the surface and the possibility of hydrogen bonding, which contributes largely to the high heat of liquefaction of water, is precluded. For the same reason, the entropy is higher than for liquid water. The sites responsible for water adsorption were thought to be surface oxide; a suggestion which was confirmed in a later paper (33) when the number of such sites was increased by controlled oxidation. The water isotherms were observed to change progressively from Type III to Type II whilst the ratio $\frac{V_m \text{ (water)}}{V_m \text{ (nitrogen)}}$ increased from 1/400 to 1/8 during the oxidation.

The work to be described in this report has been aimed at obtaining adsorption data for water vapour on sodium chloride. The attempt has met with limited success because of experimental difficulties associated with accurate measurements involving water vapour.

PART II THE ADSORPTION OF WATER VAPOUR ON SODIUM CHLORIDE

There are two general methods for studying the adsorption of gases or vapours on solids. One involves measurement of the pressure of the vapour before and after adsorption in a constant volume system and calculation of the amount adsorbed from the resulting change in pressure. In the case of water vapour this presents three difficulties:

(i) That of accurately determining the pressure of water vapour;

(ii) The adsorption of water vapour on to the glass walls of the vacuum system in which the measurements are carried out;

(iii) The non-ideality of water vapour to the gas laws.

The second method, the one adopted in the work to be described is to weigh directly the amount adsorbed using a balance of adequate sensitivity. It would seem that wall adsorption could not interfere with these measurements. A pressure measurement is therefore not necessary for the calculation of amount adsorbed, although the equilibrium vapour pressure is required. Instead of measuring the latter directly, use may be made of the known equilibrium vapour pressure of water as a function of temperature; for the purpose of this work the pressure range covered entailed the use of a cryostat.

The sodium chloride adsrobent was required in the form of small crystals thus giving a large surface area; precipitation from solution and sublimation have been used. A conventional B.E.T. gas adsorption apparatus using Krypton at -183°C was employed for surface area determination; the latter was also determined by a gravimetric technique.

Experimental Details

(a) Spring Balance

The quartz fibre helical spring semi-microbalance was of the Mcbain-.Bakr type (90 turns, diameter 2 cms, sensitivity 200 cmo/gm. Maximum load 200 mg.). A long silica fibre attached to the spring, suspended on aluminium foil bucket containing the adsorbent, the temperature of which during the adsorption runs was 30 to 40°C below room temperature; hence the isolation of the bucket to minimise convection currents. Spring extensions were observed on a graticular eyepiece of a vertically mounted travelling microscope. Readings were made to ± 0.1 eyepiece divisions corresponding to ± 2.5 μg. Interference resulting from the accumulation of electrical charge on the surface of the pyrex adsorption vessels was overcome by slight ionisation of the gas inside the adsorption vessel by means of a soft β-emitter (S^{35}) placed inside.

(b) Cryostat

Adsorptions were carried out in the range -20°C to + 10°C and hence the thermostat for controlling the water vapour pressure in the system was operated between -50°C and 0°C. In order to obtain a 1% control on pressure, it was necessary to control the cryostat temperature to ± 0.05°C. A 'soft' Dewar vessel containing acetone was surrounded by a silvered Dewar containing acetone-cardice mixture to provide permanent refrigeration of the former. A mercury toluene thermoregulator, which was designed so that the mercury was outside the cryostat, operated an electronic relay which in turn switched a heater on and off as required.

(c) The Vacuum System

A conventional vacuum system was used employing greased taps throughout. The general layout of the apparatus is shown in Fig. 1. A rotary oil pump and a mercury diffusion pump provided a vacuum of approximately 10^{-4} mms. of mercury. The spring was suspended in a long pyrex tube and an extension to this constituted the adsorption tube which accommodated the bucket. A thermostat controlled at the temperature of adsorption surrounded the adsorption tube. Rubber supports were used for mounting all glass apparatus in order to minimise the transmission of vibration. Water was distilled from a reservoir on to glass wool in the ice bulb immersed in the cryostat so giving a large surface area of ice. A Krypton bulb, a manometer, a dosing volume and adsorption bulb constituted the section for B.E.T. area determination. The Macleod gauge (3 mm. bore capillary and 30 c.c. bulb; covering the pressure range 10^{-2}mm to 20 mm. of Hg.) was placed between the two sections of the apparatus. In order to check the pressure of water vapour in the system, it was later jacketted at 100°C with a doubled walled pyrex tube the air gap between the two walls being electrically heated. Heights in the Macleod capillary were read on a cathetometer telescope with vernier scale.

(d) Preparation of Sodium Chloride Adsorbent

Preparation by rapid precipitation through adding a saturated aqueous solution to a large volume of alcohol (34) yielded cubic crystals of 1 to 5 μ The B.E.T. areas (of the order 0.1 $m^2 g^{-1}$) were not large enough to enable the powder to be used in the gravimetric techniques.

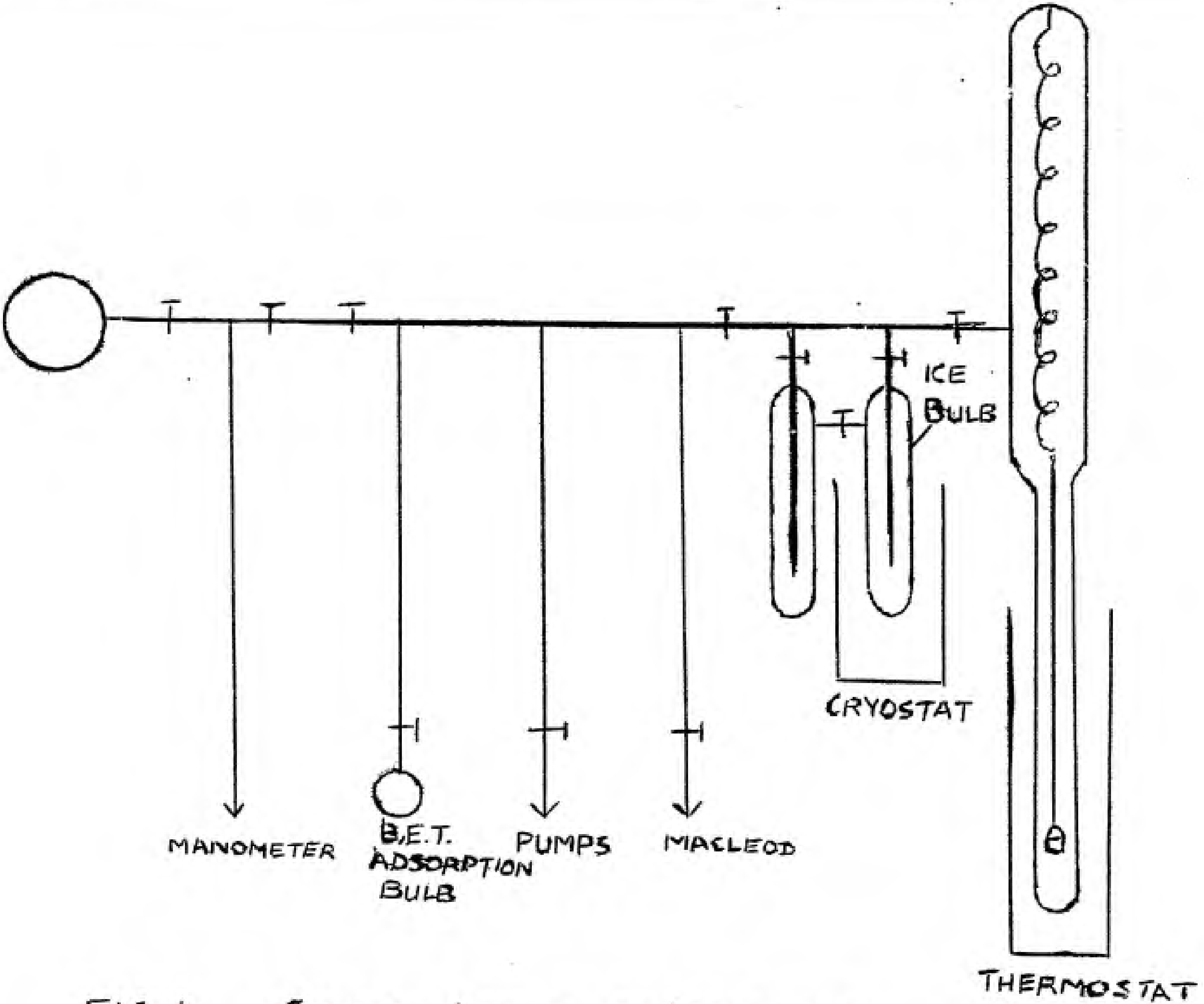


FIG. I. GENERAL LAYOUT OF APPARATUS.

A fine powder was prepared by an electrostatic precipitation technique described by Young and Morrison (35). A.R. grade sodium chloride was heated above its melting point in a platinum crucible and a current of dry nitrogen blown over the surface. The resultant stream of gas containing microcrystalline sodium chloride was passed upwards through a long pyrex tube (5 ft. length, 4in. diameter) along the axis of which was mounted a tungsten wire. This was connected to a high voltage D.C. supply obtained from the rectified output of a motor car ignition coil which had a circuit-breaker and a 6 volt battery in its primary circuit. 10 K.V. used for the first runs was found to be inadequate and it was therefore augumented by using a simple voltage doubling circuit to give 17.5 K.V. The outer wall was surrounded by a sheath of aluminium foil which was earthed. Deposition of the sodium chloride occurred on the wall of the pyrex tube. Removal by means of a circular brush, preferably in a current of dry nitrogen, with minimum exposure to air resulted in the production of suitably sized crystals. Electron micrographs showed the crystals to be well formed cubes of dimensions 0.75 to 1   It was found that a nitrogen flow rate of 40 litres per min. and 17.5 K.V. potential difference between the wire and the walls were the conditions giving the most satisfactory results. Details of the runs carried out before arriving at this conclusion have been given in an interim report.

(e) Procedure

(i) Area Determinations by B.E.T. method

The Krypton isotherms at $-183^{\circ}C$ were obtained by sharing gas at a known initial pressure and volume into the adsorption bulb. From the volume of the latter and the final equilibrium pressure attained, it was possible to calculate the amount adsorbed. At a later stage the adsorptions were measured gravimetrically; this had the advantage that surface areas could be checked 'in situ' between measurements of the water vapour isotherms. The results obtained were in good agreement with those obtained by the pressure measurement procedure.

(ii) Water Vapour Adsorptions

Preliminary outgassing of the salt and the glass walls of the apparatus proved to be important and as a result of experience, it was found that 60 hours degassing at 180°C was necessary. For a given temperature of the adsorption tube thermostat, the cryostat temperature was adjusted during a run to give a range of $^{P}/P_{o}$ values. The cryostat was fixed at a temperature corresponding to a required water vapour pressure which was then measured on the jacketted Macleod gauge. In this way it was possible to check that the water vapour pressure was of the correct order of magnitude and to safeguard against errors being introduced by the slow attainment of water vapour equilibrium above ice. The latter was, however, avoided by approaching the equilibrium from the higher temperature. The actual value of the equilibrium pressure used was derived from tables, the Macleod gauge being found to be not sufficiently reproducible for this purpose. After attainment of constant pressure conditions, the ice bulb was opened to the adsorbent and spring extension noted as a function of time.

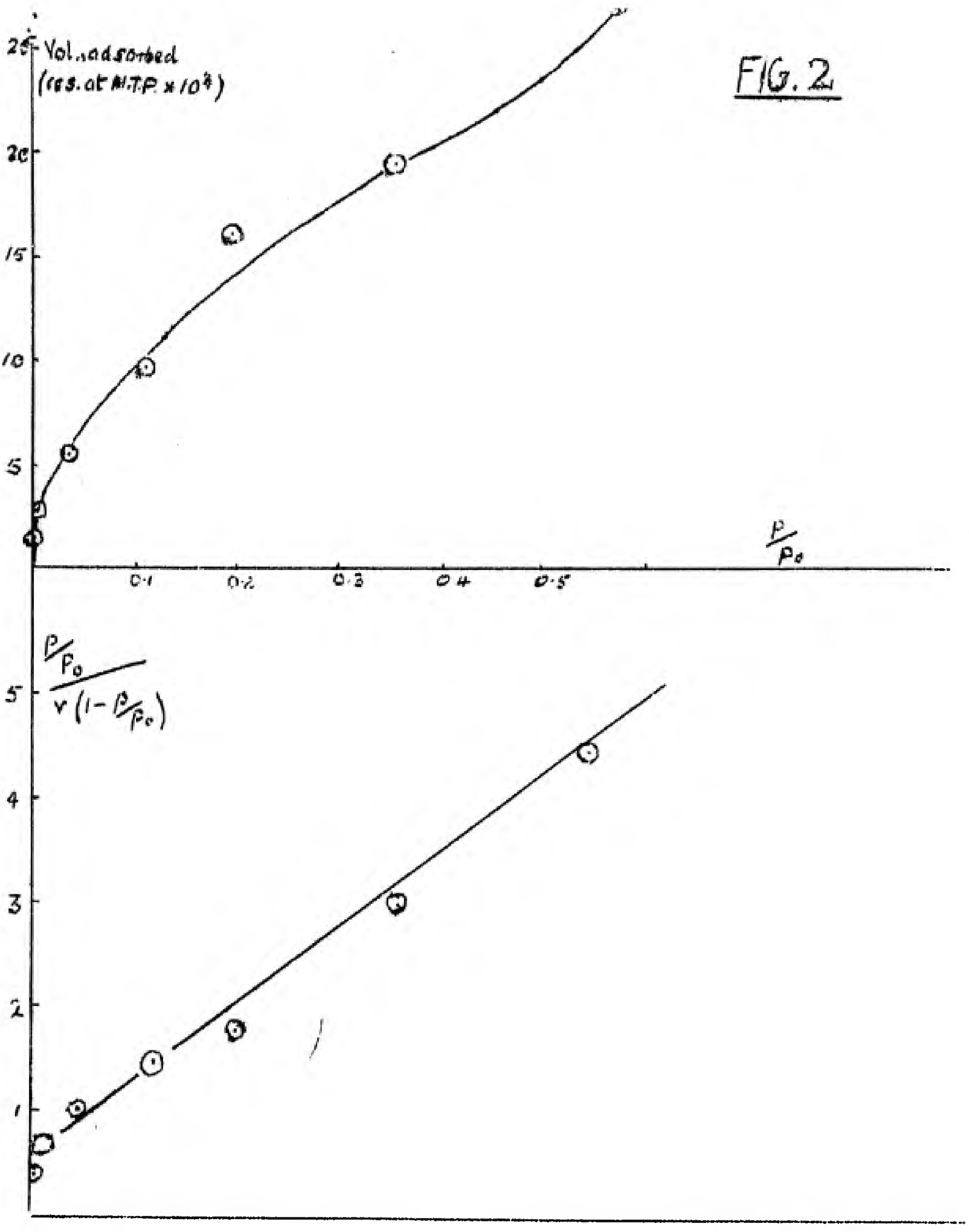
Results

Krypton was used for the surface area measurements at $-183^{o}C$ in preference to nitrogen because of the higher saturation vapour pressure of krypton at this temperature, a fact which makes for greater accuracy in the calculation of the amount adsorbed. A typical isotherm is shown in Fig. 2 together with a B.E.T. plot. From the slope and intercept of the latter, the surface area was calculated.

It was necessary at an early stage in the work to ascertain whether the conditions of outgassing of the adsorbent were such as to cause a significant decrease in area. A series of surface area measurements was therefore made to determine the effect of various pre-adsorption treatments on the sodium chloride prepared by electrostatic precipitation. The results for one such sample are given in Table 1, from which it may be seen that no loss in area is suffered as a result of exposure of the salt to water vapour at approximately 5 mms. pressure. Further, no loss of area is encountered as a result of outgassing at $110^{o}C$. The fourth determination shows the degree of reproducibility of the surface area measurement.

Though the above method and the results obtained by means of it were perfectly satisfactory in assessing the surface areas of powders obtained during the electrostatic precipitation runs, it became necessary at a later stage to obtain area values for samples on which water adsorptions had been made. The krypton isotherms were therefore obtained gravimetrically thus avoiding the necessity of removing the salt from the apparatus. The results of such a determination are given in Figure 3.

FIG. 2



25
Vol. adsorbed
(ccs. at N.T.P. × 10⁴)
20
15
10
5
0·1
0·2
0·3
0·4
0·5
p/p₀
p/p₀ / v(1 − p/p₀)
5
4
3
2
1

FIG. 3

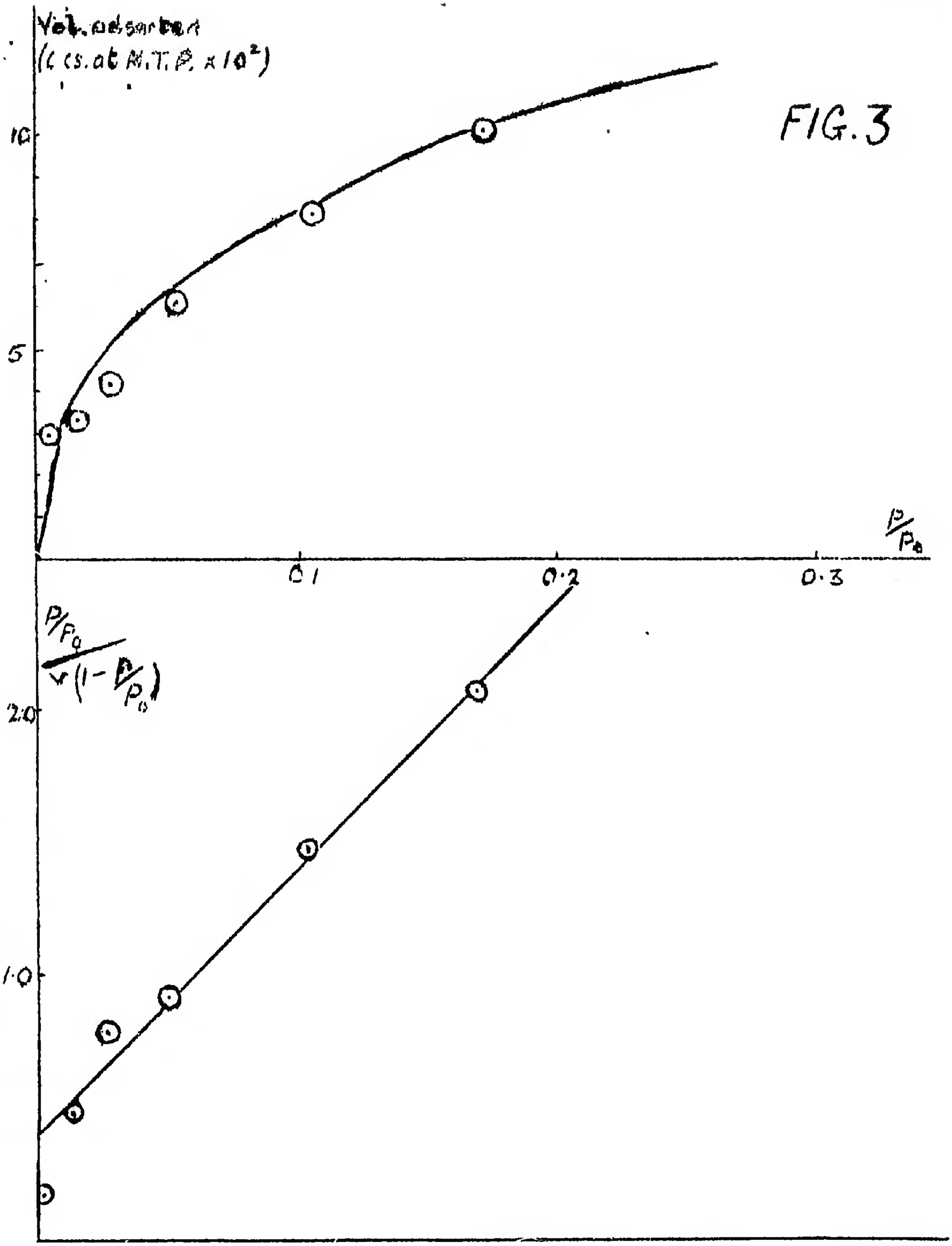


Table 1.

Treatment	Area $(m^2.g^{-1})$
Outgassing at room temperature for 24hrs.	1.17
Doses of water vapour at equilibrium pressures of 0.05mms., 0.15mms., 1.25mms. and 4.6mms. were successively admitted to the sample. This was followed by outgassing at room temperature for 24hrs.	1.22
Previous sample outgassed at 110°C for 12 hrs.	1.69
Previous determination repeated after pumping off krypton at room temperature	1.47

An attempt was made initially to obtain water vapour adsorption isotherms at -23°C. As a result of several runs in which the assessment of equilibrium adsorption was ambiguous, it was concluded that there were three factors responsible.

(i) there was slow adsorption on the glass walls of the apparatus.

(ii) the adsorption on the salt itself was slow.

(iii) there was slow attainment of the water vapour-ice equilibrium.

By carrying out the adsorptions at higher temperatures, the rate of the second process was considerably increased. The occurrence of slow adsorption on glass caused the pressure to fall on opening the ice bulb to the adsorption tube and slow attainment of the ice-water vapour equilibrium meant that there was a time interval before the pressure reached the appropriate value for a particular cryostat temperature. Thus it was necessary to check approximately that the water vapour pressure had attained its equilibrium value by means of the jacketted Macleod gauge. By employing the rigorous outgassing conditions already noted, it was possible to obtain reasonably satifactory adsorption characteristics.

Fig. 4 shows a typical set of curves for adsorptions at 0°C. It may be seen that equilibrium was attained in 20 to 30 mins. at most whilst at lower pressures the equilibrium value was reached after 3 to 5 mins. A summary of isotherms obtained from such curves is given in Table 2 and Fig. 5 for 0°C and Table 3 and Fig. 6 for 10°C. The 0°C isotherm represents the results for two separate runs. The best curves through these points were obtained and the results plotted in Fig. 7 with pressure as abcissae.

TABLE 2.

0^o Isotherms

Cryostat Temp. (^oC)	p. (mms.)	P/po	Adsorption in microscope eyepiece divisions (.1 div. ≡ 25μg)				
			1	2	3	4	5
- 30	.286	.063			.31	.35	.26
- 25	.476	.104			.34	.42	.33
- 22	.640	.140		.41	.35		
- 20	.776	.169	.40			.52	.39
- 19	.854	.187		.48			
- 18	.939	.205			.43		
- 16	1.132	.247		.60			
- 15	1.241	.271	.50			.67	.53
- 13	1.490	.325		.72			
- 12	1.632	.355			.63		
- 10	1.950	.425	.90	1.00			.85
- 8	2.326	.507			1.02	1.47	
- 5	3.013	.656		1.70	1.33		1.84
- 4	3.280	.714	1.75				

TABLE 3. 10^oC Isotherms

Cryostat Temp. (^oC)	p. (mms.)	P/po	Adsorption (miscroscope divisions) (.1 div. ≡ 25μg).	
			1	2
- 30	.286	.031	.21	
- 25	.476	.052	.36	.38
- 20	.776	.084	.40	
- 15	1.241	.135		.50
- 10	1.950	.212	.61	.61
- 5	3.013	.302	.85	.87
- 1	4.217	.457		1.14
3	5.685	.615		1.66

FIG. 4.

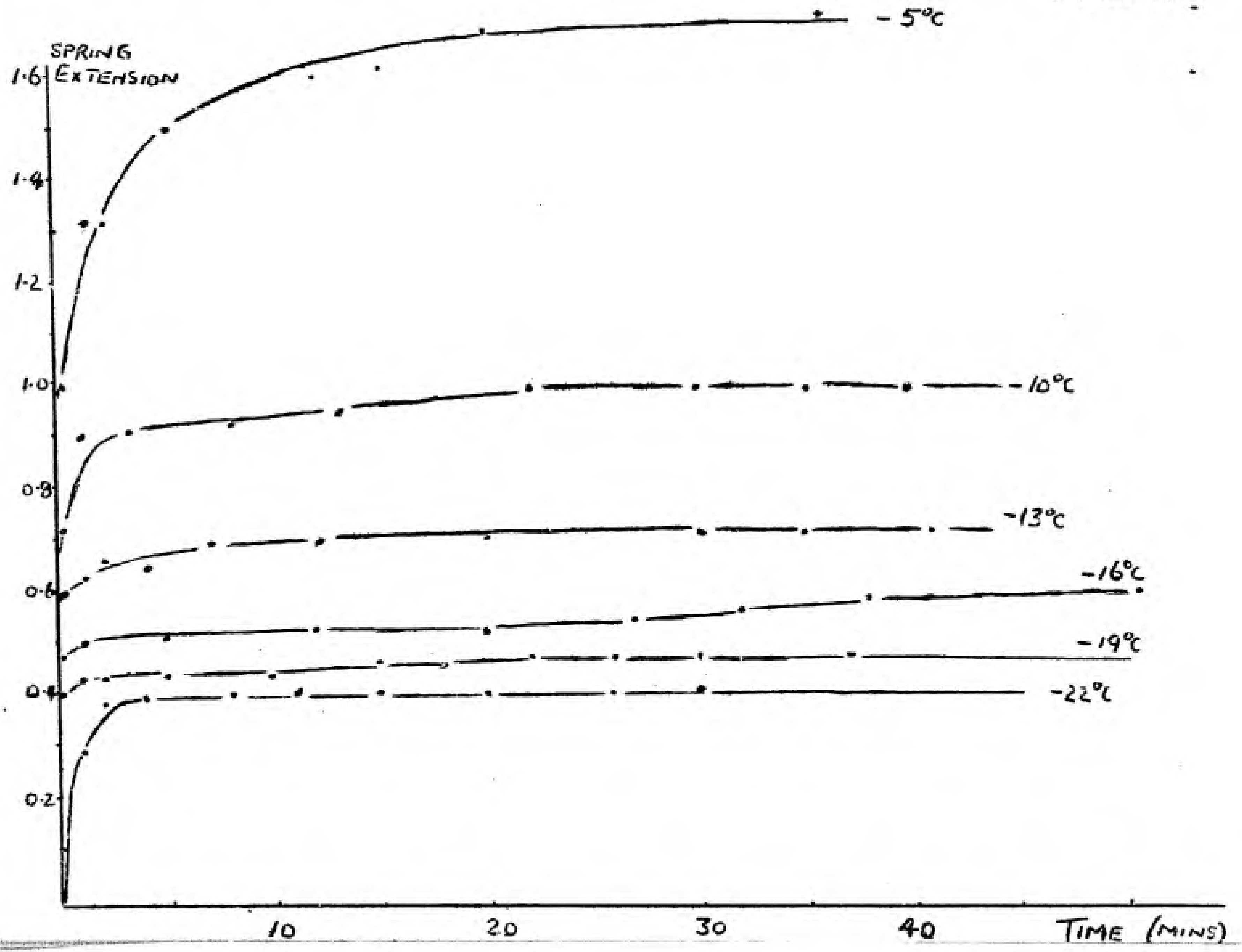

SPRING EXTENSION
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
10
20
30
40
TIME (MINS)
-5°C
-10°C
-13°C
-16°C
-19°C
-22°C

FIG. 5.

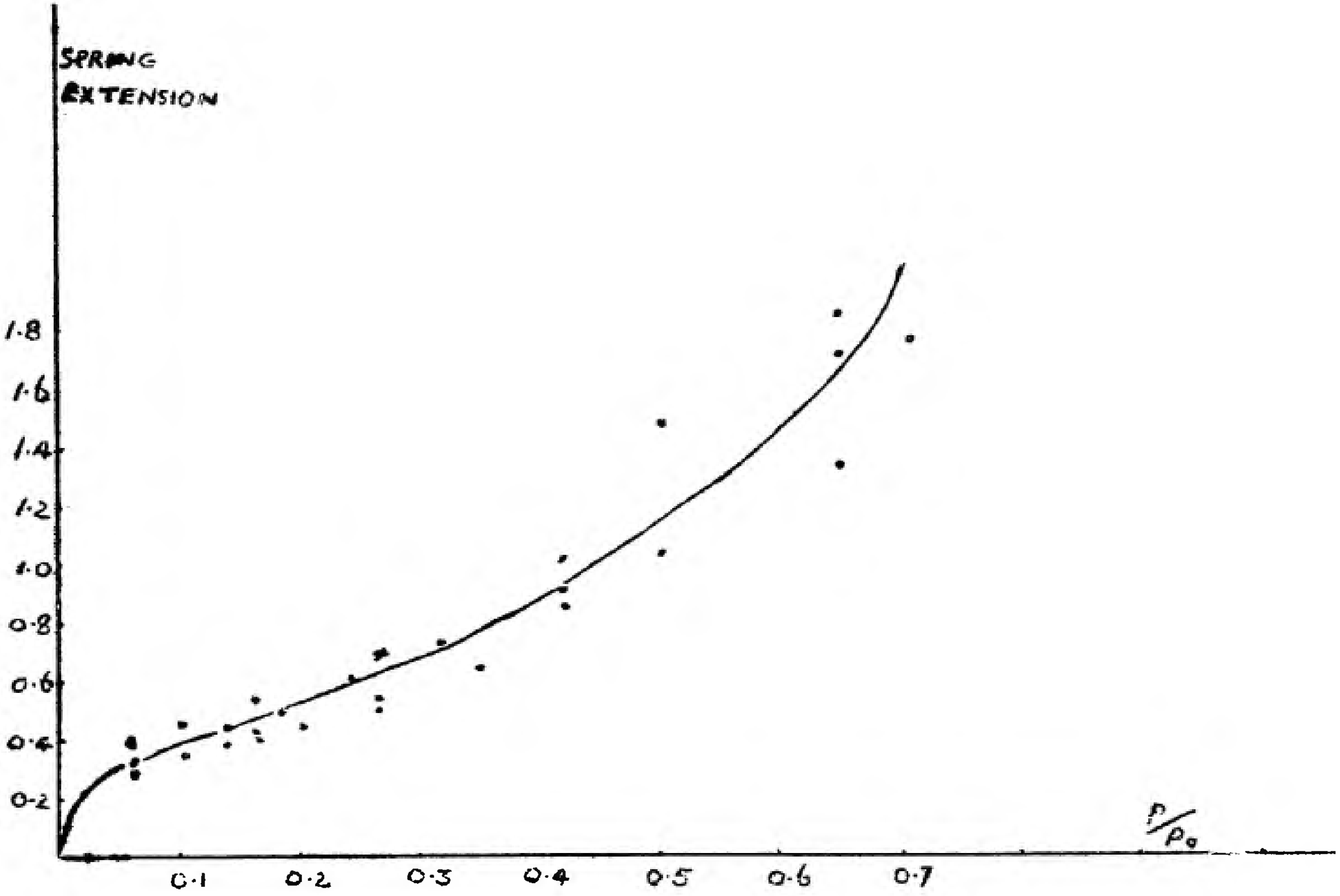

SPRING
EXTENSION
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.1
0.2
0.3
0.4
0.5
0.6
0.7
p/p_0

FIG. 6.

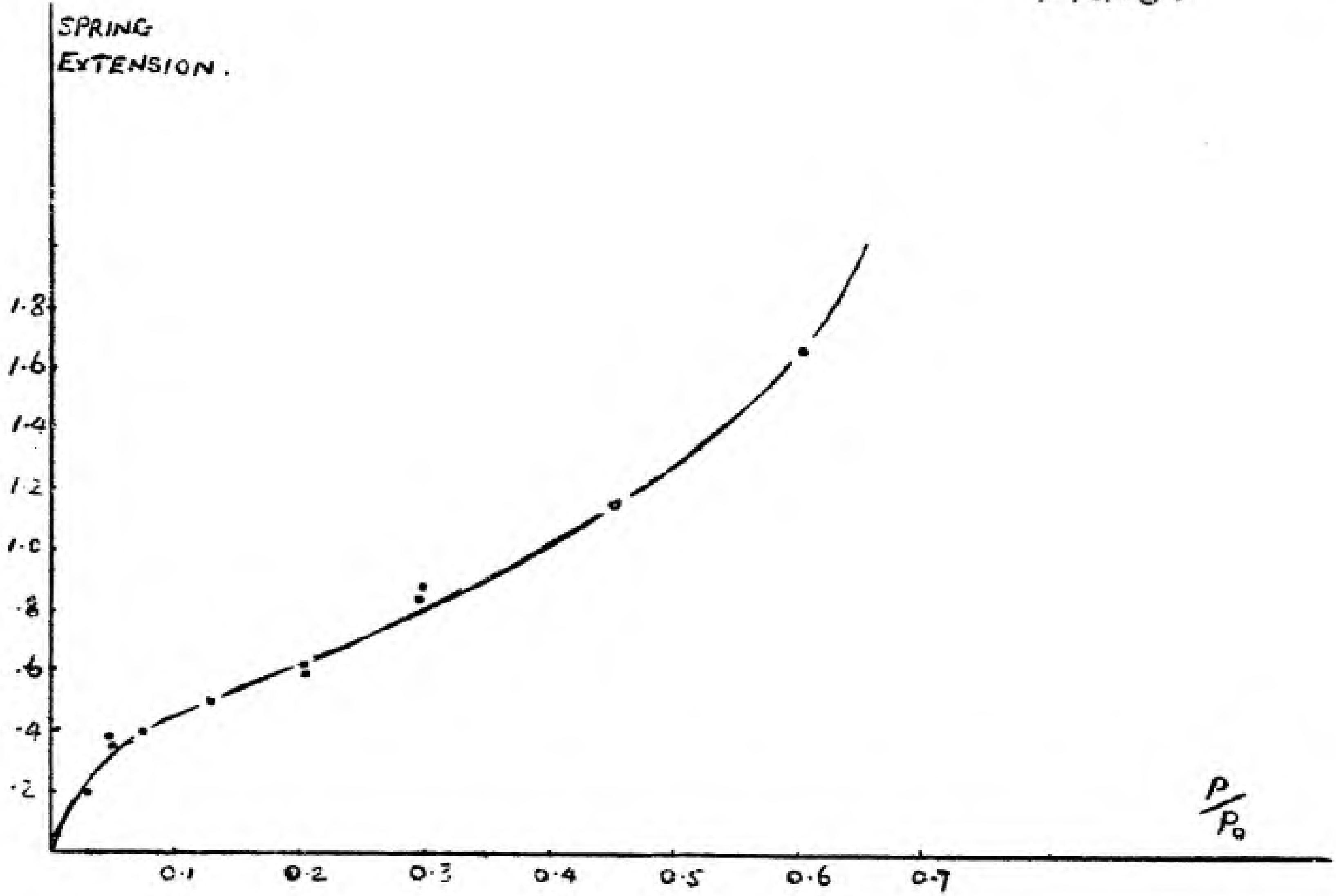
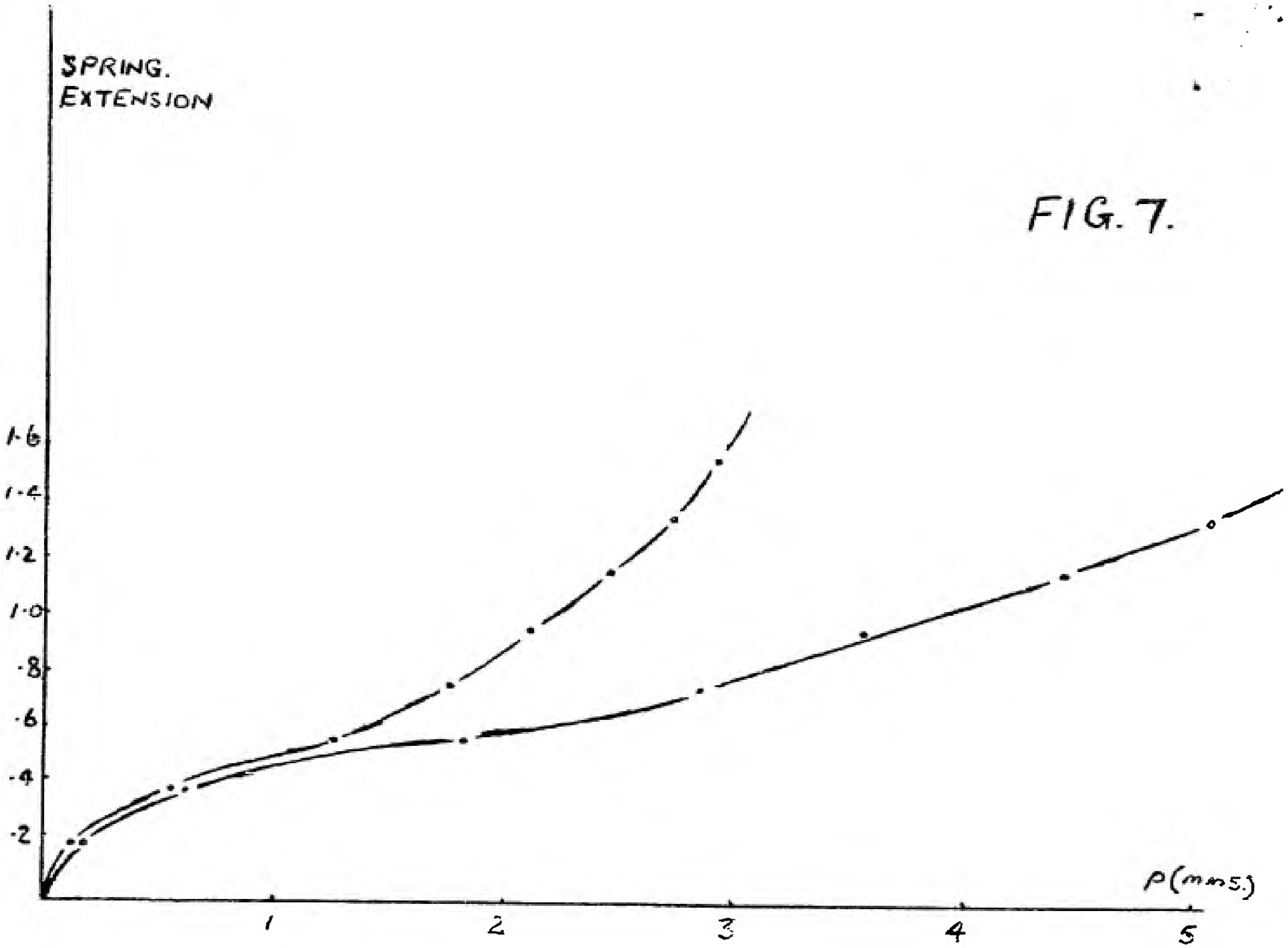


FIG. 7.



Discussion

The sample of sodium chloride used throughout for the water vapour adsorptions possessed a surface area, derived from krypton adsorption measurements, of 2.55 m^2g^{-1}. From the B.E.T. plot of the water vapour isotherms shown in Fig. 8, a value for Vm, i.e. the amount of water vapour required to cover the surface with a monolayer has been calculated. Hence it is possible to obtain a value for the 'effective surface area' of the water molecule in this particular system. The value obtained, 28.5 A^2, is abnormally large in terms of the real surface area calculated from the interatomic distances for the water molecule given by Pauling. (35) The O - H bond distance of 1A leads to an approximate surface area of 5A^2. It is therefore reasonable to deduce that the monolayer is not a hydrogen bonded structure similar to that of ice but consists of isolated water molecules with insufficient mobility to attain an ice-like structure. For a surface array of ions in the sodium chloride lattice, it is known that the position of minimum potential energy for an adsorbate atom or molecule is directly above the centre of a lattice square. On this basis a reasonable distribution of adsorbed water molecules on the 100 plane of the sodium chloride lattice would be such as to allocate one water molecule to each lattice square. The effective area of the water molecule is thus equal to the area of the lattice square. The latter, derived from Pauling's value of 2.814A (35) for the Na - Cl interationic distance, is 28.8A^2. The close agreement between this and the figure obtained from the experimental data is taken to be good confirmation of the model postulated. The picture of the first layer which emerges is therefore one of localized adsorption of single water molecules.

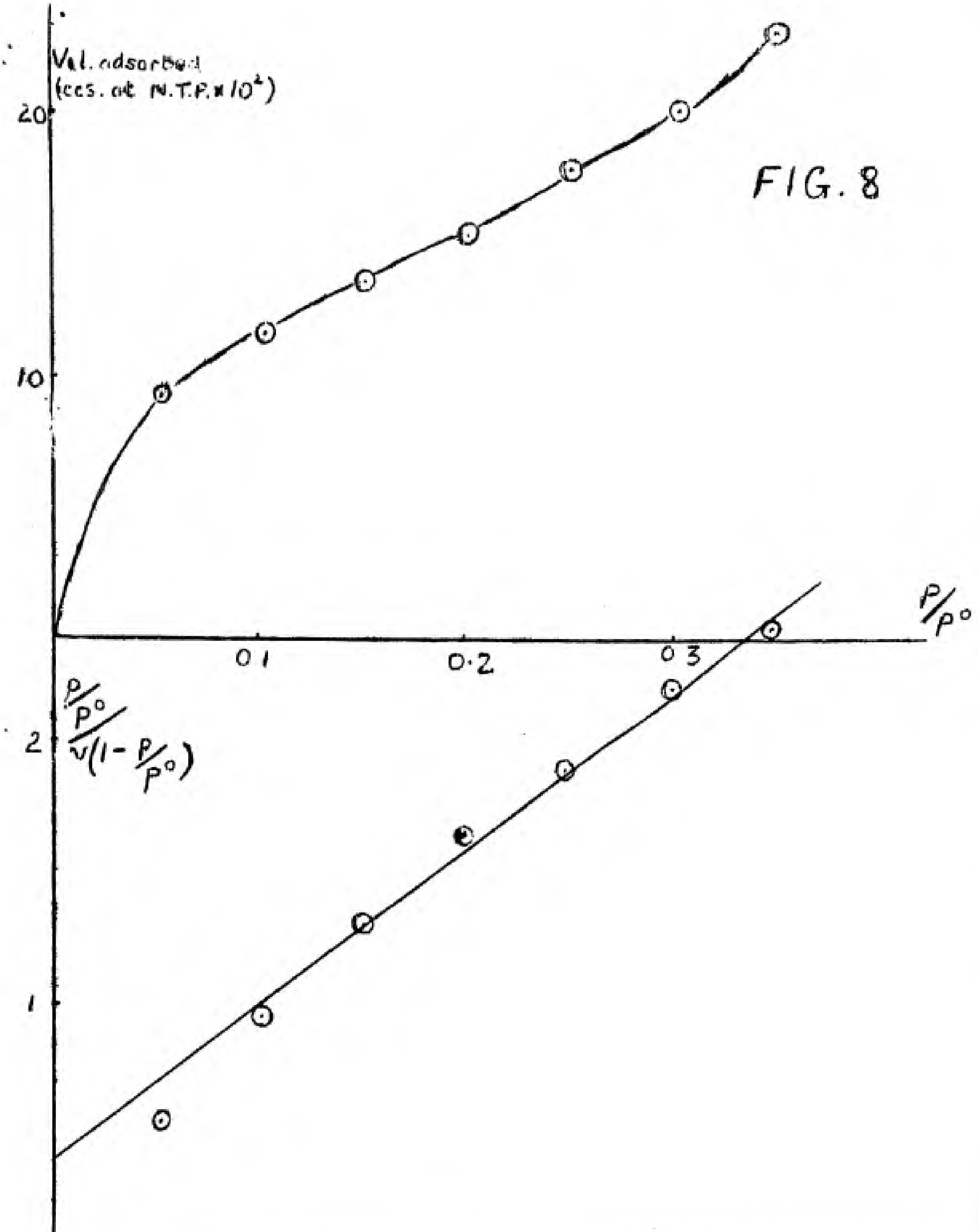


FIG. 8

Vol. adsorbed
(ccs. at N.T.P. × 10²)
20
10
0·1
0·2
0·3
p/p°
$\frac{p/p^\circ}{v(1-p/p^\circ)}$
2
1

From the application of the Clausius - Clapeyron equation to the data of Fig. 7, it is possible to calculate the heats of adsorption.

$$\ln \frac{P_1}{P_2} = \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad \ldots\ldots\ldots\ldots(1)$$

where P_1 and P_2 are equilibrium vapour pressures at temperatures T_1 and T_2. The value obtained relates to a particular amount adsorbed. The fraction of the surface covered at any stage can be obtained using the value of the crossectional area of the water molecule discussed above. A plot of heat of adsorption against the fraction of the surface covered is shown in Fig. 9. It is seen that the value of ΔH rises from about 4 to 5 K.Cal. at low coverages to about 9 to 10 K.Cals. at high coverages thus approaching the heat of liquefaction of water (9.7 K.Cals. per mole).

In order to assign values for the free energy and entropy of adsorption, it is necessary to designate a convenient reference state. For the present purpose, the vapour in equilibrium with liquid at the temperature under consideration is the most suitable. Free energy and entropy changes are therefore calculated for the transfer of one mole from the liquid to the adsorbed phase. The free energy change for this process is

$$\Delta G = RT \ln \frac{P_o}{P} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where P_o and P are the saturation and equilibrium vapour pressures respectively at the given temperature. The enthalpy change for the same process is given by $\Delta H_S - \Delta H_L$ where ΔH_L is the enthalpy change for the transfer of one mole of vapour to the surface and ΔH_L for the transfer to the liquid.

TABLE 4.

Adsorption (μg)	Fraction of surface covered (θ)	10°C		0°C		$\log . P_1/P_2$	$-\Delta H$ (K.Cals)
		P_1	P_1/P^0	P_2	P_2/P^0		
150	2.75	1.81	0.197	1.26	0.275	0.1580	5.57
200	3.63	2.86	0.310	1.76	0.385	0.2109	7.45
250	4.53	3.69	0.40	2.11	0.465	0.2427	8.55
300	5.41	4.42	0.48	2.45	0.535	0.2562	9.03
350	6.37	5.07	0.55	2.74	0.595	0.2684	9.39
400	7.29	5.54	0.61	2.92	0.640	0.2781	9.83

TABLE 5.

Free Energies and Entropies at 0°C

Fraction of surface covered (θ)	$-\Delta H_s$ (K. Cals)	$\Delta H_s - \Delta H_1$ (K. Cals)	p mms.	$\log p/p^0$	$-\Delta G = RT \ln p/p^0$ (cals.)	$\Delta S = \frac{(\Delta G - \Delta H)}{T}$ (cals/deg.)
2.73	5.57	4.15	1.26	0.5604	702	17.8
3.63	7.43	2.29	1.76	0.4153	517	10.6
4.53	8.55	1.17	2.11	0.3365	419	5.8
5.41	9.03	0.69	2.45	0.2716	338	3.8
6.37	9.39	0.33	2.74	0.2250	278	2.2
7.29	9.83	-0.11	2.92	0.1954	157	0.18

The entropy change for the transfer of one mole of liquid to the adsorbed phase is therefore given by

$$\Delta S = - \left(\frac{\Delta G - \Delta H}{T}\right) \quad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

The results of these calculations are shown in Tables 5 and 6 and Fig. 9. It is seen that as a consequence of the heat of adsorption being less than the heat of liquefaction, the enthalpy change for the transfer of water from the liquid to the adsorbed phase is positive. Since the free energy change is negative, it follows from equation (3) that the entropy change for the process must be positive. At the lowest coverage for which a value is available, ΔS is approximately 20 e.u. This is about 8 e.u. less than the Trouton constant for water which may be taken as the entropy change for the transfer of 1 mole from liquid to vapour. The loss of 8 e.u. from the gaseous phase to the adsorbed phase is abnormally low in comparison with that for the adsorption of water vapour on silica or ferric oxide. (more than 30 e.u.). In the latter case, the adsorbed layer is more ice-like than liquid water whereas for adsorptions on sodium chloride, the entropy evidence indicates a freedom intermediate between liquid and gas. Kemball's super-mobile adsorption (36), where the adsorbed layer behaves as a 'two-dimensional gas' deprived of translational movement at right angles to the surface, would be acceptable on entropy grounds since the loss of one translational degree of freedom corresponds to a ΔS of approximately 10 e.u. This is not acceptable on the basis of the model already postulated where the water molecule is adsorbed above the centre of lattice squares. But, if the water molecule retains vibrational freedom

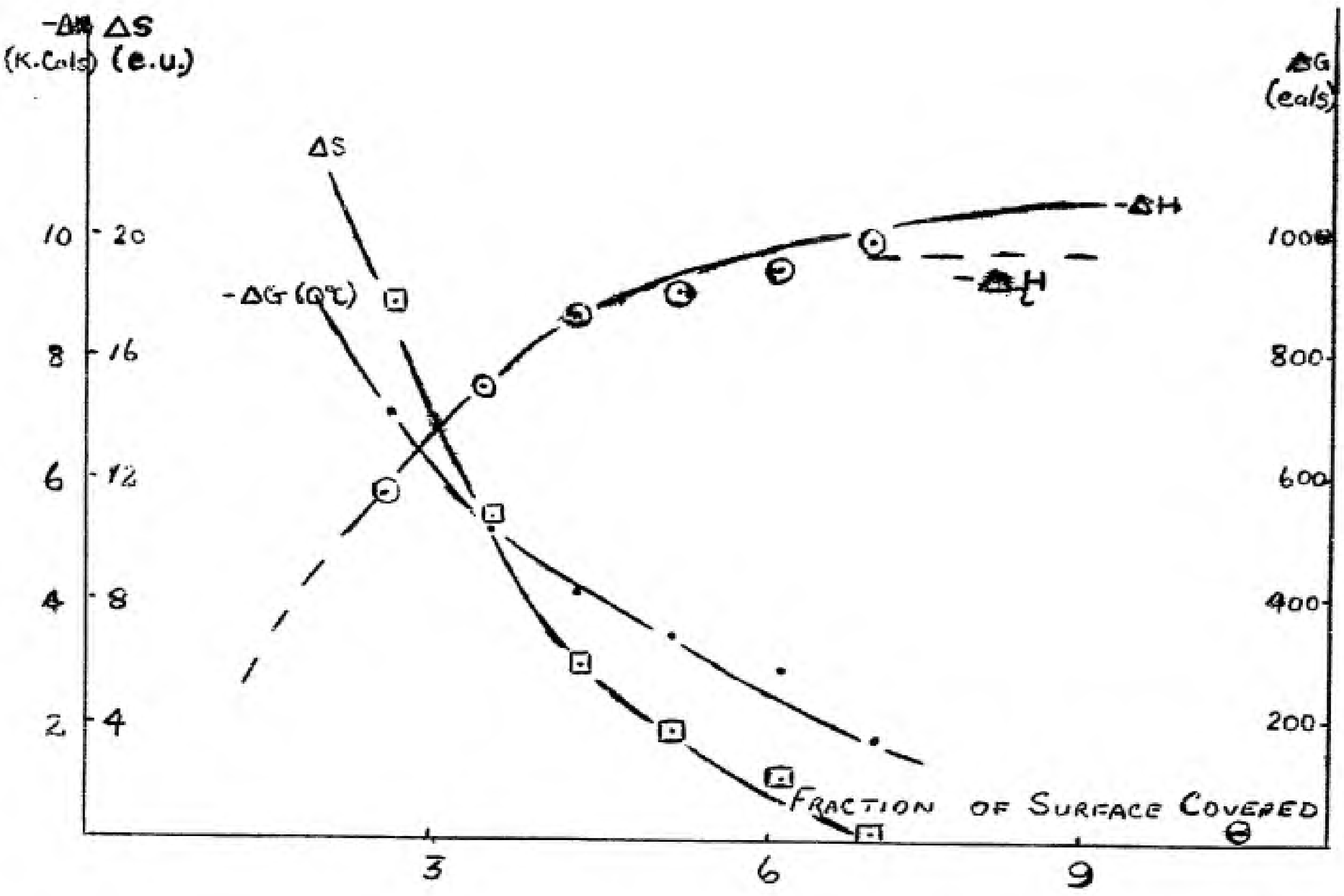

-ΔH ΔS
(K.Cals) (e.u.)
ΔG
(cals)
ΔS
-ΔG (0°C)
-ΔH
-ΔH
10 20
8 16
6 12
4 8
2 4
1000
800
600
400
200
3
6
9
Fraction of Surface Covered
Θ

FIG. 9.

TABLE 6.

Free Energies and Entropies at 10°C

Fraction of surface covered (θ)	$-\Delta H$ (K. Cal.)	$\Delta H_s - \Delta H_l$ (K.Cal.)	p mms.	$\log p/p^o$	$-\Delta G = RT \ln p/p^o$ (cals.)	$\Delta S = \frac{(\Delta G - \Delta H)}{T}$ (cals/deg.)
2.75	5.57	4.15	1.813	0.7058	911	17.9
3.63	7.43	2.29	2.86	0.5078	655	12.6
4.53	8.55	1.17	3.69	0.3972	514	5.95
5.41	9.03	0.69	4.42	0.3188	411	3.88
6.37	9.39	0.33	5.07	0.2592	334	2.33
7.29	9.83	-0.11	5.54	0.2207	285	0.64

perpendicular to the surface, the loss of entropy from the gas phase is much smaller - a vibrational frequency of 5×10^{11} sec.$^{-1}$ would be associated with an entropy of approximately 5 e.u. Since the molecule can also vibrate in the potential well on the surface, vibrational frequencies of 1 to 2×10^{11} sec.$^{-1}$ in two directions at right angles and parallel to the surface would account for the entropy loss.

Hence it is possible to account for the adsorbed phase having an entropy of 20 e.u. above that of the liquid or 8 e.u. below that of the gas if a model is adopted where the adsorbed layer is, in effect, a highly extended liquid layer in which the vibrational frequency parallel to the surface is much reduced and compared with liquid water and there is also a weak vibration at right angles to the surface.

The formation of a second layer probably takes place above gaps in the first layer and in such a way as to make hydrogen bonding likely. This is reflected in the decrease in free energy and entropy and increase in $-\Delta H$. A continuation of this process results in the attainment of a liquid water structure after about six or seven layers. The latter value is, however, probably high since more molecules can be accomodated in the second layer than in the first and similarly more in the third than the second so that a more accurate figure for attainment of a liquid water structure would be three to four layers.

In conclusion, it may be stated that two main features have emerged. In the first place, the first-layer adsorption is dependent on the lattice parameters of the crystal and secondly, that the transmission of forces from the adsorbent does not occur to an appreciable extent since the heat of liquefaction of water after the adsorption of about three to four layers.

In the light of these deductions, it would therefore be logical to make further investigations using adsorbents of smaller lattice spacings and also those containing higher valent ions in the surface plane; knowledge of the effect of homo-ionic as compared with hetero-ionic surface planes would also be valuable. Finally, it would be useful to correlate the structure of the first layer with that of the higher layers since the ultimate objective is to obtain an ice-like structure with as few layers of adsorbate as possible.

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