318. *Polymolecular Adsorbed Films. Part I. The Adsorption of Argon on Salt Crystals at Low Temperatures, and the Determination of Surface Fields.*

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THE adsorption of the inert gases at low temperatures is interesting since there is the possibility of the formation of loose co-ordination compounds in which the inert gas acts

as a donor of electrons to an ion with an incomplete electronic shell, especially as Booth and Willson (*J. Amer. Chem. Soc.*, 1935, **57**, 2273, 2280) have shown that similar compounds are formed between argon and boron trifluoride. Such compounds would be expected to be stable at atmospheric pressure only at low temperatures. The results show that actually polymolecular films are built up. The mechanism of the formation of these films is of considerable interest, and a detailed analysis is given below. The method permits an estimate to be made of the field at the surface of the salt crystals. The lowering of the vapour pressure of argon by certain active catalysts has been observed by Hüttig and Juza (*Z. anorg. Chem.*, 1928, **177**, 313).

<div align="center">EXPERIMENTAL.</div>

The apparatus (Fig. 1) consisted of a quartz spiral spring of low sensitivity (1 g. $\equiv$ 4·146 cm.), to the end of which was attached a long quartz fibre. Higher sensitivity involves the use of a smaller load and a greater ratio of the weight of the containing vessel to that of the salt, and gives a less robust balance. A hook at the end of the fibre carried a thin Pyrex bulb weighing about 0·1 g. and containing finely powdered salt. Measurements of the upper end of the fibre relative to the reference point were made by a microscope reading to 0·001 mm. The maximum depressions with copper sulphate and aluminium sulphate were 0·25 and 0·40 mm. respectively

<div align="center">FIG. 1.</div>
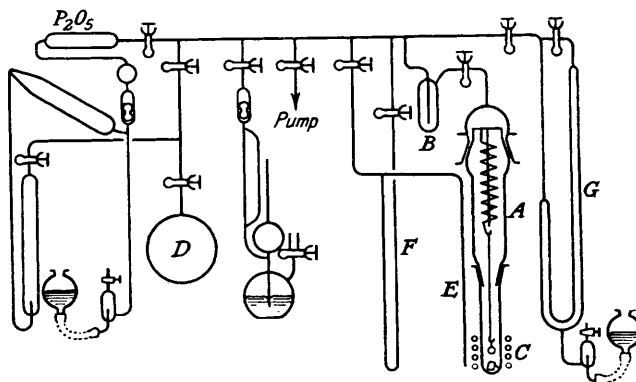
($\pm$ 0·002 mm.). The spring was contained in the case A with ground joints. The salt was always kept protected from vapours, when the tap on the case was open, by the liquid-air trap B. An electric heater C could be slid over the end of A. A small piece of radioactive glass prevented electrification of the quartz spring. The inert gas was contained in D, and could be circulated and kept dry by the Toëpler pump with a phosphoric oxide tube attached. Pressures could be read on the McLeod gauge and on the manometer G. All apparatus was cleaned by potassium permanganate and concentrated sulphuric acid, followed by sulphurous acid and water; Apiezon grease was used.

The apparatus was exhausted with the heater at about 200° for several hours, a higher temperature being unsuitable on account of a probable increase in surface, and readings of pointer and reference point were taken. Asbestos packing during heating prevented collapse of the tap grease. It is possible that molecules of gas tenaciously held on a few active points of the surface are not degassed, but this will not materially affect the results, which are concerned with adsorption on the main surface. Moreover, only a very small amount of material has to be degassed. On admission of argon at room temperature the balance was insufficiently sensitive to detect any adsorption. The bottom of the balance case was then cooled by liquid air, the bulb began to fall, and after about 20 minutes the motion ceased. The pressure was read before and after cooling. The time lag was due merely to conduction and not to slow adsorption, since it could be reduced to a few minutes by allowing cold gas to stream on to previously cooled solid. After allowance for buoyancy changes, the weight of the adsorbed gas could be calculated from the linear calibration curve of the balance. A separate experiment showed that adsorption on the glass was negligible, as was to be expected from the small ratio of glass to crystal surface, *viz.*, < 0·5%. On warming, the adsorbed film was rapidly desorbed and the system returned to

its initial state. The temperature of the liquid air could be read to $0.01°$ by means of the argon vapour-pressure thermometer E in conjunction with the manometer F. A comparison with a platinum-resistance thermometer afforded a check, showing that the gas was pure (it was supplied by the British Oxygen Co. as spectroscopically pure). The temperature of the liquid air could be maintained constant for sufficient time by bubbling in nitrogen from a cylinder, and thereby reducing the partial pressure of oxygen in contact with the liquid. Values taken at temperatures slightly different from those of the six isotherms given could be corrected by a small extrapolation, by using a graph of pointer depression against pressure of argon thermo-meter for constant pressure of the adsorbed film.

The copper sulphate was obtained by dehydrating A.R. pentahydrate for some hours at $350°$ until no change of weight occurred. The weighings showed that there was no loss of sulphur trioxide. The potassium chloride and aluminium sulphate were A.R. salts, and were dried just before use. Crystals were powdered finely in an agate mortar, and were graded by using the graticule described by Patterson and Cawood (Faraday Society Discussion on Smokes, April 1936) in conjunction with an eyepiece ($\times$ 12) and a 0.66-in. objective. The fine powder was dusted on to a microscope cover-slip by means of a clean camel-hair brush. The graticule was calibrated by means of a micrometer scale, the values given by Patterson and Cawood being used. In the counting, obvious aggregates were not included, since what was needed was the mean size of constituent crystallites.

Results were found to be reproducible. A summary is given on p. 1471.

Theoretical.—The formation of thick films will be studied on the assumption that the first film of adsorbed atoms is polarised by the positive ions of the salt, the influence of the negative ions being relatively small, owing, in general, to their larger size. The first layer polarises the second, and this in turn can attract a third layer. In this way a thick film is built up with gradually decreasing polarisation as the distance from the surface increases. The calculation is greatly simplified by the rapid decay of the field due to an ionic crystal, or to a plane array of dipoles, as the distance increases ; the decay is ap-proximately exponential and is thus much more rapid than that due to a single dipole. Hence, only the influence of adjacent layers on one another need be considered.

The field due to the crystal will be taken as constant with small variations in tem-perature. The crystal induces a dipole μ in the first adsorbed layer. In addition, the dipoles induced in the second layer polarise the first layer in the same direction. All induced dipoles are, of course, perpendicular to the crystal surface. The potential due to a dipole sheet with uniformly spaced dipoles distant a_1 apart may be shown (Bradley, *Phil. Mag.*, 1931, **11**, 449) to be given by

$$\phi(z) = 4\frac{E}{a_1}\sum_{l=1}^{\infty}\sum_{m=1}^{\infty} e^{-2\pi(l^2+m^2)^{\frac{1}{2}}z/a_1}\left[1 - e^{-2\pi(l^2+m^2)^{\frac{1}{2}}\delta/a_1}\right]/(l^2+m^2)^{\frac{1}{2}}$$
$$+ 4\frac{E}{a_1}\sum_{l=1}^{\infty} e^{-2\pi lz/a_1}[1 - e^{-2\pi l\delta/a_1}]/l \quad . \quad . \quad (1)$$

where z is the distance at right angles to the sheet for a point directly under one dipole, E is the electronic charge, and δ the dipole length, *i.e.*, $\delta E = \mu_2$, if we consider the dipole sheet due to the second layer. If α is the polarisability of an argon atom, then μ_1, the total induced moment of an atom in the first layer, is equal to $\mu - \alpha(d\phi/dz)_{z=b}$, z being equated to b, the diameter of an argon atom. With sufficient accuracy

$$\left(\frac{d\phi}{dz}\right)_b = -\frac{16\pi^2\mu_2}{a_1^3}\left[\sum_{l=1}^{\infty}\sum_{m=1}^{\infty}(l^2+m^2)^{\frac{1}{2}}e^{-2\pi(l^2+m^2)^{\frac{1}{2}}b/a_1} + \sum_{l=1}^{\infty}le^{-2\pi lb/a_1}\right].$$

Hence $\mu_1 = \mu + k\mu_2$, where k is a constant of zero dimensions.

Similarly $\qquad\qquad \mu_2 = k(\mu_1 + \mu_3) \qquad \mu_{m-1} = k(\mu_{m-2} + \mu_m)$
$$\mu_3 = k(\mu_2 + \mu_4) \qquad\qquad \mu_m = k\mu_{m-1}$$

All induced dipoles are in the same direction. Hence

$$\mu_{m-1} = k^2\mu_{m-1} + k\mu_{m-2} \text{ or } \mu_{m-1}(1 - k^2) = k\mu_{m-2}$$

Similarly $\mu_{m-1} = [k/(1-k^2)]^{m-2}\mu_1$

Hence $\mu_m = k\mu_{m-1} = k[k/(1-k^2)]^{m-2}\mu_1$

and $\mu_m = k\mu_{m-1} = k[k/(1-k^2)]^{m-3}\mu_2 = k[k/(1-k^2)]^{m-3}(\mu_1-\mu)/k$

Hence $k[k/(1-k^2)]^{m-2}\mu_1 = [k/(1-k^2)]^{m-3}(\mu_1-\mu)$ or $(\mu_1-\mu)(1-k^2)=k^2\mu_1$

and $\mu_m = \mu k[k/(1-k^2)]^{m-2}(1-k^2)/(1-2k^2)$

The value of μ_q for $q = 1$ to $(m-1)$ is given by

$$\mu_q = \mu[k/(1-k^2)]^{q-1}(1-k^2)/(1-2k^2)$$

The energy for the m layers per g.-mol. is given by

$$E_m = N\sum_1^{m-1}\mu_q^2/2\alpha + N\mu_m^2/2\alpha + E_0$$

where N is Avogadro's number and E_0 represents the mutual energy of the atoms due to repulsive and van der Waals forces. Hence

$$E_m = \frac{N\mu^2}{2\alpha}\sum_1^{m-1}\frac{k^{2q-2}}{(1-k^2)^{2q-4}(1-2k^2)^2} + \frac{N\mu^2}{2\alpha}\frac{k^{2m-2}}{(1-k^2)^{2m-6}}\frac{1}{(1-2k^2)^2} + E_0.$$

The energy required to remove the last layer is $E_m - E_{m-1}$. It may be shown that

$$E_m - E_{m-1} = \frac{N\mu^2}{2\alpha}\left(\frac{1-k^2}{1-2k^2}\right)^2\left[\frac{k^{2m-4}(1+k^2) - k^{2m-4}(1-k^2)^2}{(1-k^2)^{2m-4}}\right] + E'_0$$

where the last term allows for the repulsive and the van der Waals forces for a single layer. Hence

$$E_m - E_{m-1} = \frac{N\mu^2}{2\alpha}\frac{k^{2m-2}}{(1-2k^2)^2}\frac{(3-k^2)}{(1-k^2)^{2m-6}} + E'_0$$

The above calculation takes no account of the energy associated with the lateral repulsion of dipoles in a layer, for which a small correction is required. By straightforward summation this is given approximately as $\frac{1}{2}N.4\mu^2(1 + \frac{1}{3} + \frac{1}{4} \ldots)/a_1^3 = 4N\mu^2/a_1^3$ per g.-mol. (Bradley, *Trans. Faraday Soc.*, 1934, **30**, 596). Hence, since one layer only need be considered, with sufficient accuracy,

$$E_m - E_{m-1} = N\mu^2\left(\frac{1}{2\alpha} - \frac{4}{a_1^3}\right)\frac{(3-k^2)}{(1-2k^2)^2}\frac{k^{2m-2}}{(1-k^2)^{2m-6}} + E'_0 = H_m \quad . \quad (2)$$

where H_m is the latent heat of evaporation for the mth layer. If p_m is the pressure of the gas in equilibrium with the adsorbed film of m layers, then $RT \log p_m = H_m + AT$, where A is a constant. But $RT \log p_0 = H_0 + BT$, where B is a constant and H_0 is the latent heat of evaporation of the pure liquid; other terms in the vapour-pressure equation may be neglected. Hence

$RT \log (p_0/p_m) = H_m - H_0 + (A-B)T$

$$= N\mu^2\left(\frac{1}{2\alpha} - \frac{4}{a_1^3}\right)\frac{(3-k^2)}{(1-2k^2)^2}(1-k^2)^4[k/(1-k^2)]^{2m-2} + E'_0 - H_0 + (A-B)T$$

or $T \log_{10}(p_0/p_m) = K_1K_2^m + E'_0 - H_0 + (A-B)T$

where $K_1 = \frac{N\mu^2}{2\cdot303R}\left(\frac{1}{2\alpha} - \frac{4}{a_1^3}\right)\frac{(3-k^2)}{(1-2k^2)^2}\frac{(1-k^2)^6}{k^2}$ and $K_2 = [k/(1-k^2)]^2$.

The weight of the adsorbed film may be put proportional to m for a thin film relative to the dimensions of a crystallite, or $ab = m$, where a is the number of g.-mols. of argon adsorbed per g.-mol. of salt, and b is a constant. Naturally, the building up of the layers is not a discontinuous process, and the pressure will vary continuously during the formation of any layer; the calculation merely selects points, *viz.*, those for complete films, on a

smooth curve. It follows that $T \log_{10}(p_0/p_a) = K_1 K_3{}^a + E'_0 - H_0 + (A - B)T$, where $K_2{}^b = K_3$. We may put $E'_0 = H_0$. We may also put $A = B$; since K_3 is less than 1, a becomes infinite when $p_a = p_0$, *i.e.*, when a bulk liquid is built up. Hence finally,

$$T \log_{10}(p_0/p_a) = K_1 K_3{}^a \quad \cdots \quad \cdots \quad (3)$$

De Boer and Zwikker (*Z. physikal. Chem.*, 1929, *B*, **3**, 407) deduce a similar result by a consideration of the free energies of adsorbed films, putting $dF/dp = 0$. They include another constant in equation (1), giving $a = \infty$ when $p_a \neq p_0$.

Equation (3) requires a flat **S** shaped curve which is actually observed. If a loose compound were formed, a would increase at constant pressure until the maximum amount of compound were formed. The adsorbed film may be regarded as a series of compounds changing in composition and equilibrium pressure as the adsorption continues; theoretically the addition of each molecule of argon changes the compound.

The calculation is readily extended to allow for the polarisation due to negative as well as positive ions, when there will be two values of μ on the surface, and two inter-penetrating dipole lattices. However, in the examples below, the sulphates will certainly obey the simple theory given, since the radii of cupric and sulphate ions are approximately 0·6 and 3·5 A. respectively.

RESULTS AND DISCUSSION.

(a) *Argon on Anhydrous Copper Sulphate.*—The mean surface of the crystallites was $5 \cdot 75 \times 10^{-6}$ sq. cm. (the crystals being regarded as spheres). The density, determined by using carbon tetrachloride in the pyknometer, was 3·605 at 25·4°, in agreement with published values. In Table I are given the values of a in g.-mols. per g.-mol. of copper sulphate for pressures p_a, in mm., at the absolute temperatures T. The values of a are compared with those calculated as below from equation (3).

TABLE I.

p_a	$a \times 10^3$, obs.	$a \times 10^3$, calc.	p_a	$a \times 10^3$, obs.	$a \times 10^3$, calc.	p_a	$a \times 10^3$, obs.	$a \times 10^3$, calc.
	$T = 84 \cdot 5°$.			$T = 85 \cdot 1°$.			$T = 85 \cdot 8°$.	
100	8·0	7·8	50	6·7	5·9	17	4·0	4·1
200	10·2	10·0	100	7·3	7·3	50	6·3	5·6
300	12·3	12·3	200	9·6	9·5	100	6·9	6·9
402	15·4	15·0	403	14·5	13·8	200	9·1	8·9
463	16·9	17·5	480	15·9	16·4	402	13·5	12·8
502	20·4	19·8	550	20·1	20·5	480	15·0	14·9
536	24·1	24·2	580	22·0	24·6	550	17·2	17·6
						613	21·6	22·0
						642	23·7	27·9
	$T = 86 \cdot 5°$.			$T = 87 \cdot 2°$.			$T = 87 \cdot 9°$.	
25	3·3	3·7	17	4·2	3·4	15	2·8	2·2
50	5·9	5·0	50	5·4	4·8	50	5·0	4·4
100	6·5	6·6	100	6·1	6·1	100	5·5	5·6
200	8·5	8·6	200	8·4	8·0	200	8·0	7·4
400	12·6	12·5	400	11·7	11·4	400	10·6	10·4
480	14·2	14·2	480	13·3	13·0	480	12·5	11·8
550	15·9	16·2	550	15·1	14·6	693	16·6	17·0
613	19·3	19·6	642	18·0	17·8	750	19·7	20·4
665	24·0	24·0	700	20·7	21·5	770	20·3	22·4
687	25·5	28·0	730	25·5	25·6			

The curves are easily analysed. From equation (3)

$$\log_{10}[T \log_{10}(p_0/p_a)] = \log_{10} K_1 + a \log_{10} K_3 \text{ or } \log_{10} \log_{10}(p_0/p_a) = \log_{10}(K_1/T) + a \log_{10} K_3$$

Hence a plot of a against $\log_{10} \log_{10}(p_0/p_a)$ should give a straight line. In every case a good line was obtained, as is seen in Fig. 2, where, for convenience, only one temperature is considered; since K_1 and K_3 are nearly the same for all the curves, the lines for other temperatures lie very close to the line given; $\log_{10} K_3$ is calculated from the slope of this line, and $\log_{10}(K_1/T)$ is given by the value of $\log_{10} \log_{10}(p_0/p_a)$ for $a = 0$. The constants

are then used to calculate the values of a in Table I. Good agreement with experiment is observed, as may also be seen from Fig. 3, where the curves are calculated from equation (3), and the points are experimental. For clearness, only two curves are given. Results are summarised below :

T	84·5°	85·1°	85·8°	86·5°	87·2°	87·9°
K_1	377·5	360·5	336·5	279·8	293·0	286·3
K_3	0·796	0·794	0·796	0·813	0·803	0·796

The constants are calculated for the graphs of 10^3a, *i.e.*, $T \log_{10} (p_0/p_a) = K_1 K_3^{10^3a}$.

At pressures near the saturation values for the pure liquid a slight divergence is observable from the theoretical curve. This may be due to the filling up of pore space, *i.e.*, the adsorption is less than that calculated from the equation owing to the union of films formed from adjacent crystal surfaces. This may be partly counteracted by the fact that a is not proportional to m for thick films. It is noticeable that K_1 but not K_3 varies with T. The m. p. of argon is *ca.* 83·8° Abs., which is below the temperatures observed. There is no suggestion from the trend of the constants of the solidification of the film. It is hoped to take up this interesting point later with a more suitable example. A possible influence of temperature on K_1 may be due to the change in effective diameter of the argon
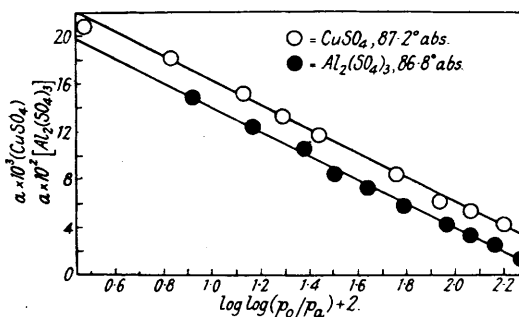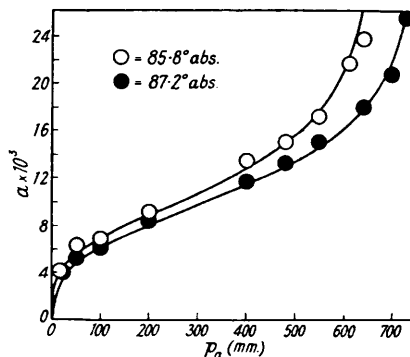
FIG. 2.

FIG. 3.

Curves calculated from equation (3) ; *points experimental.*

atom with temperature, in the liquid state, which would tend to cause a decrease in μ with increasing temperature, especially as the crystal field varies rapidly with the distance.

From the surface of the crystals and the density of liquid argon, the constant b may be calculated to be $2 \cdot 85 \times 10^3$; K_1 is taken to be 0·796. Hence $[k/(1 - k^2)]^2 = 0 \cdot 796^{1/2 \cdot 85}$, which gives $k = 0 \cdot 6075$. The values of H_m can be calculated from the equation $H_m = 2 \cdot 303 R K_1 K_3^{10^3a} + H_0$. This gives :

$a \times 10^3$	2	5	10	15	20
$H_m - H_0$	949	486	159	53	16

where $H_m - H_0$ is given in g.-cals. per g.-mol. Since $m = ab$, a value of $a \times 10^3 = 10$ corresponds with about 29 layers. As would be expected, the value of H_m gradually approaches that for the bulk liquid, *i.e.*, the latent heat of evaporation. The influence of the crystal surface is thus effective at some considerable distance from the surface.

From the equation for K_1 it is easy to calculate μ, the dipole induced in the first layer due to the crystal field. It is found that $\mu = 2 \cdot 31 \times 10^{-19}$ e.s.u., which corresponds with a surface field at the centre of the argon atom of $14 \cdot 1 \times 10^4$ e.s.u. The point at which the field is measured is approximately 2·5 A. from the centre of the copper ion. It is thus possible to map out the field by the use of other inert-gas atoms, it being assumed that variations with temperature are small.

(b) *Argon on Potassium Chloride.*—No formation of thick films was observed even at pressures near the saturation value for the bulk liquid. This may be expected on account

of the small polarising power of the alkali metals, and from the approximate equality of the ionic radii of potassium and chlorine. It is clear that the field due to a mixed dipole sheet with dipoles in two groups of approximate equality but opposite direction will be small. This suggested the use of a tervalent ion of high deforming power, *viz.*, $Al^{...}$. Aluminium sulphate is a convenient substance to use, since its hydrate can be dehydrated without loss of acid radical, and since the negative ion has a small polarising influence. The unimolecular adsorption of argon on potassium chloride has been considered by Lennard-Jones (*Trans. Faraday Soc.*, 1932, **28**, 333).

(c) *Argon on Aluminium Sulphate.*—The mean surface of the crystals was $3 \cdot 20 \times 10^{-6}$ sq. cm. Results are summarised in Table II, where the calculated values are obtained from equation (3). Linear plots of $\log_{10} \log_{10}(p_0/p_a)$ against a were obtained as before (see Fig. 2).

TABLE II.

p_a.	$a \times 10^2$, obs.	$a \times 10^2$, calc.	p_a.	$a \times 10^2$, obs.	$a \times 10^2$, calc.	p_a.	$a \times 10^2$, obs.	$a \times 10^2$, calc.	p_a.	$a \times 10^2$, obs.	$a \times 10^2$, calc.
	$T = 85 \cdot 0°$.			$T = 85 \cdot 4°$.			$T = 85 \cdot 9°$.			$T = 85 \cdot 8°$.	
6	2·4	1·2	18	2·5	2·8	6	1·6	1·1	10	1·3	1·3
24	3·4	3·0	63	4·3	4·6	9	2·1	1·5	27	2·4	2·4
49	4·4	4·1	100	5·0	5·5	19	2·8	2·3	55	3·3	3·4
102	5·3	5·6	194	7·0	7·3	50	3·9	3·6	98	4·2	4·4
176	7·1	7·3	303	8·9	9·2	87	4·8	4·6	204	5·8	6·2
263	9·4	9·0	396	11·3	11·1	172	6·3	6·3	314	7·3	7·6
390	12·7	12·3	503	14·0	13·9	246	7·7	7·5	394	8·4	8·8
444	14·4	14·1	600	17·3	18·9	290	8·2	8·2	480	10·5	10·2
530	17·1	18·3	633	18·6	24·1	330	9·0	8·9	595	12·3	12·3
562	18·6	22·0				370	10·3	9·7	690	14·9	14·8
						464	12·0	11·4			
						558	13·8	13·9			
						615	16·3	16·0			
						670	18·8	20·1			

The results when plotted give curves similar to those shown in Fig. 3. Analysis of the curves gives the following values for the constants :

T	$85 \cdot 0°$	$85 \cdot 4°$	$85 \cdot 9°$	$86 \cdot 8°$
K_1	218·4	259·4	230·0	223·1
K_3	0·805	0·787	0·791	0·792

The constants are calculated from the curves for 10^2a, *i.e.*, $T \log(p_0/p_a) = K_1 K_3^{10^2 a}$. Good agreement between theory and experiment is obtained.

The value of b is $9 \cdot 47 \times 10^2$, giving $k = 0 \cdot 615$. This gives $\mu = 1 \cdot 93 \times 10^{-19}$, and the field at the centre of the argon atom in the first layer $= 11 \cdot 8 \times 10^4$. The calculation of the surface field is dependent on a knowledge of the crystallite dimensions, but is not very sensitive to changes in the latter. A reduction of surface in the case of copper sulphate from $5 \cdot 75 \times 10^{-6}$ to $1 \cdot 5 \times 10^{-6}$ reduces the value of μ from $2 \cdot 31 \times 10^{-19}$ to $0 \cdot 99 \times 10^{-19}$.

The radius of the $Al^{...}$ ion is $0 \cdot 55$ A., so the argon atoms in the first layer are at about the same distance from the cation for adsorption on copper sulphate and aluminium sulphate. The field in the latter case is smaller, notwithstanding the increased ionic charge, probably because of the greater crystal spacing; *e.g.*, the density of copper sulphate ($3 \cdot 6$) is considerably greater than that of aluminium sulphate ($2 \cdot 7$).

It appears that thick films of this type can be built up only on crystals with cations which have incomplete electronic shells, with which is associated the tendency to form co-ordinate and covalent links. It is hoped in subsequent work to extend the scope of this inquiry over a wider field.

SUMMARY.

By means of a quartz spiral balance, the adsorption of argon at 84·5—88° Abs. on finely powdered anhydrous copper sulphate and aluminium sulphate and on potassium chloride has been studied. Except with the last, thick films were built up. The theory of the formation of thick films by polarisation is discussed. Results agree with the equation given by theory, *viz.*, $T \log(p_0/p_a) = K_1 K_3^{a}$, where p_0 and p_a are the saturation pressures

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of the bulk liquid and the adsorbed liquid film, and K_1 and K_3 are constants. The dipole moments induced in the adsorbed atoms and the fields at the surface due to the crystals are calculated.