

92. *The Heat of Adsorption of Ethyl Chloride and of Sulphur Dioxide on Sugar Charcoal.*

By S. JOHN GREGG.

The heats of adsorption were measured by a Bunsen ice calorimeter, and the adsorption isotherms determined, from very low pressures up to atmospheric for sulphur dioxide and up to the saturated vapour pressure for ethyl chloride, by a volumetric method.

The chief feature of the results was a sharp fall in the differential heat of adsorption of ethyl chloride, from about 11,500 cal./mole to near the latent heat of condensation 6,000 cal./mole, occurring within a narrow adsorption range and at pressures less than one-quarter of the saturated vapour pressure. The effect is ascribed

to the inception of a layer more than one molecule thick. Henry's law was not obeyed by either gas even at the lowest pressures studied, probably because the film was still not sufficiently dilute to behave as a perfect two-dimensional gas.

In preliminary experiments the differential heat of adsorption of ethyl chloride on charcoal was found to fall, within a narrow adsorption range and at pressures considerably below the saturated vapour pressure  $p_s$ , from some 12,000 cal./mole to near the latent heat of condensation, 6,000 cal./mole. Since the effect seemed to indicate a transition from a unimolecular to a thicker adsorbed layer, it was decided to investigate the system more fully by determining the adsorption isotherm from very low pressures up to  $p_s$ , and simultaneously measuring the heat of adsorption calorimetrically. The system sulphur dioxide-charcoal (where, it was anticipated, the behaviour would be simpler) was selected as a control.

#### EXPERIMENTAL.

*Materials.*—To minimise the well-known disturbing effects of mineral impurities, sugar charcoal—made by heating B.D.H. "Analytical Reagent" sucrose for  $1\frac{1}{2}$  hrs. in a silica tube in an electric furnace at  $550^\circ$ —was used as adsorbent. It was activated by passing over it a stream of air, at 0.8 l./hr., whilst heated to  $720^\circ$  in a silica tray in a tubular electric furnace for 6 hrs.; it was then sieved through 180 mesh. Since the sucrose is specified to contain  $> 0.02\%$  of mineral matter, the ash content of the charcoal should not exceed 0.04%.

The sulphur dioxide from a syphon was redistilled in a high vacuum, and the middle fraction only retained. The ethyl chloride (B.D.H. pure) was passed in succession through traps cooled severally to  $-60^\circ$ ,  $-110^\circ$ , and  $-182^\circ$ ; the  $-110^\circ$  condensate was fractionally redistilled in a high vacuum, and the middle fraction alone retained. The vapour pressures of each gas agreed at a number of temperatures with the values from Landolt and Börstein's Tables within  $\pm 1\%$ .

*Procedure.*—The usual volumetric method was used, successive measured volumes of gas at known pressure and temperature being admitted from a gas burette into the dead space in contact with the charcoal, or withdrawn therefrom into a vessel of known volume, the quantity adsorbed being obtained as the difference between the sum of the amounts admitted and the amount remaining unadsorbed in the dead space. The apparatus was all-glass (Monax) with mercury cut-offs to control the movement of gas. Dead-space pressures exceeding some 0.5 cm. were read on an ordinary mercury manometer with wide limbs (ca. 1.2 cm. diam.), and lower pressures on a three-stage McLeod gauge. All levels were read by an accurate cathetometer, and the deviations of the gases from Boyle's law were corrected for in all calculations.

The heat,  $q$ , evolved by each increment in the amount adsorbed was measured by having the charcoal bulb enclosed in the inner tube of a Bunsen ice calorimeter, the intermediate space being filled with mercury to promote thermal conduction from charcoal to ice sheath. The change in volume of the sheath (and thus  $q$ ) was obtained in terms of the change in weight of a tared crucible containing mercury, into which the ground-off end of the capillary of the calorimeter dipped. In order to minimise thermal errors due to expansion or compression after leaving the burette, the gas was made to pass through a worm coil immersed in a water-bath at a known temperature immediately before entering the adsorption bulb.

To carry out a run, the charcoal, contained in the adsorption bulb which had been previously fused on to the apparatus (blowing being through a phosphoric oxide tube), was out-gassed for several days, usually at  $250^\circ$ , till the dead space pressure was ca.  $10^{-5}$  mm. It was then cooled, sulphur dioxide or ethyl chloride admitted up to a dead-space pressure of some 5 cm., and left to stand for some hours, being finally out-gassed, first at room temperature and then at a higher temperature, usually  $150^\circ$ . When the pressure had again fallen to ca.  $10^{-5}$  mm., the heater was removed, and the connection to the pumps closed when the charcoal had cooled to room temperature; pressure was now unreadable. (This "flushing-out" technique is recommended by Burrage, *J. Physical Chem.*, 1933, **37**, 510, 735.) The calorimeter was now raised into position, and when after an hour or so the calorimeter showed a steady rate of drift, the first charge of gas was admitted from the burette. Readings of the pressure and weighings of the crucible were taken at intervals till the former was nearly or quite constant. This equilibrium was never completed in less than an hour and often required much longer (see detailed results).

*Results.*—Let  $q_2$  cal. be the heat evolved when the number of c.c. (at N.T.P.) adsorbed by the  $w$  g. of charcoal increases from  $wx_1$  to  $wx_2$  (after correction for the heat given up by  $wx_2 - wx_1$  c.c. in cooling from room temperature to  $0^\circ$ ); then the approximate differential heat of adsorption  $\Delta H_2$  for the adsorption range  $wx_1$  to  $wx_2$  is given by  $\Delta H_2 = q_2 \times 22414/w(x_2 - x_1)$  cal. per mole of gas. Results are recorded, in Figs. 1 and 2, as a plot of  $x$  the adsorption in c.c. (at N.T.P.) per gram of charcoal—against  $\log_{10} p$ , where  $p$  is the equilibrium dead-space pressure in cm. of mercury; and also as a plot of  $\Delta H_2$  against the corresponding average value of  $x$ , viz.,  $(x_1 + x_2)/2$ . Experimental points are numbered in the order in which they were determined. The lines in Fig. 2 and the upper part of Fig. 1 merely join related points and do not necessarily indicate the best curve. The main source of error in  $q$  is the "drift" in the calorimeter, i.e., the change in weight of the mercury due to thermal leaks between the calorimeter and its surroundings, and possibly also to a slow alteration in the volume of the calorimeter itself. To minimise the drift the water was boiled out under reduced pressure *in situ* before forming the ice sheath, the ice in the outer ice bath (a large thermos flask) was made from distilled water and was constantly stirred, and the calorimeter, which had its own vacuum jacket fused on, was made small—12 cm. long by 5 cm. outside diameter—and of Pyrex glass in order to reduce volume changes due to elastic after-working of the glass. These measures did not entirely eliminate the drift, however, and it had to be determined before ( $B$ ) and after ( $A$ ) each measurement of  $q$ , the calculated drift for the duration of the measurement (based on the average of  $A$  and  $B$ ) being subtracted from the total change in the weight of the mercury. Sometimes  $A$  and  $B$  differed considerably, and this led to some uncertainty in the value of  $q$ . The percentage error from this source is greater where the increments  $\Delta x$  are small, as is often the case at the higher pressures; this error varies from about  $\pm 1\%$  for the best cases to 5–10% for the worst. Although undesirably large, the error could be reduced only by increasing the values of  $\Delta x$ , i.e., by spacing the experimental points more widely; but this would no longer have given even an approximation to the differential heat of adsorption in those ranges where this quantity varied rapidly with  $x$ , i.e., in exactly those regions which it was desired to study most closely.

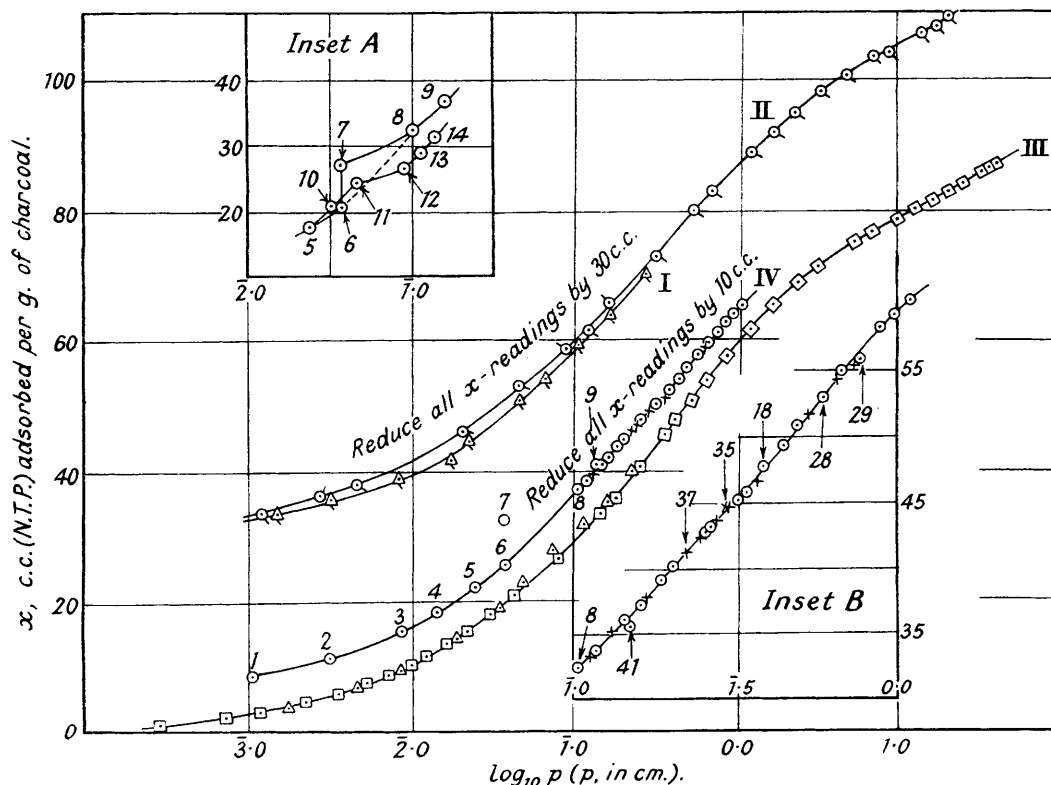
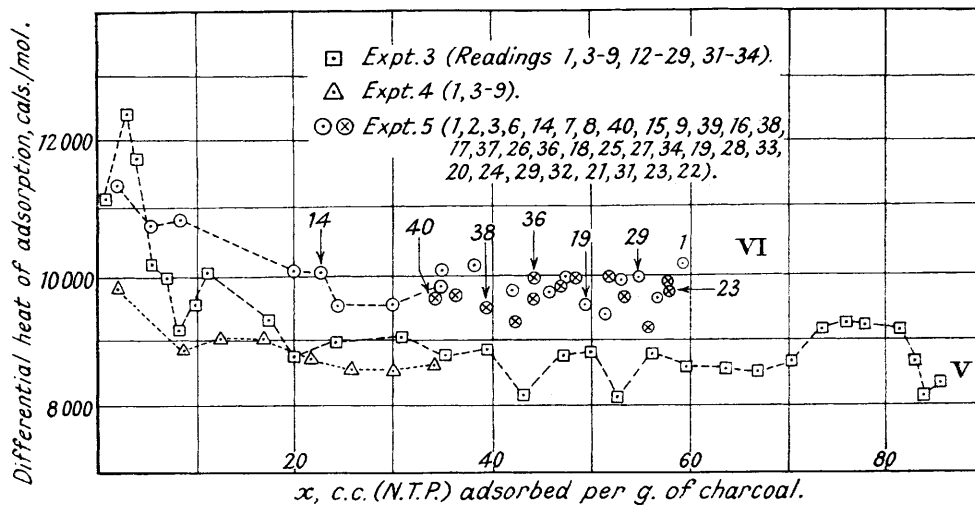
*Experiments with sulphur dioxide.* Expt. 1. (Fig. 1, Curve I.) 1.076 G. of charcoal. Out-gassed at  $250^\circ$ . Equilibration  $1\frac{1}{2}$ —2 hrs. No heat measurements.

Expt. 2. (Fig. 1, Curve II.) At the end of Expt. 1 the charcoal was out-gassed at  $250^\circ$ , whereupon owing to a breakage some air entered and remained for some hours in contact with the hot charcoal. This probably altered its state of activation slightly. After repair, the charcoal was out-gassed and flushed out. Equilibration  $1\frac{1}{2}$ —2 hrs. No heat measurements.

Expt. 3. (Fig. 1, Curves III and V.) Fresh sample of charcoal (3.80 g.). Out-gassed at 190°, and flushed out. Equilibration 1½—2 hrs. Probable error in  $\Delta H$  usually  $\pm 2$  to  $\pm 3\%$  but *ca.*  $\pm 6\%$  in readings 3, 4, 7, 18, 28, 29, 31, 34.

Expt. 4. (Fig. 1, Curves III and V.) At the end of Expt. 1 some air entered. The charcoal was then out-gassed first at 15° then at 190°, but not flushed out. Probable error in  $\Delta H$ ,  $\pm 1\%$  to  $\pm 2\%$ . Equilibration 1—2 hrs. The

FIG. 1.



△ Expt. 1 (Readings 1-12); ○ Expt. 2 (Readings 1-23); □ Expt. 3 (Readings 1-36);  
 △ Expt. 4 (Readings 1-10); ○ Expt. 5 (Order of readings after 7 is 8; 40, 14, 39, 15, 41; 9, 38, 43, 16, 37; 25, 44, 17, 36, 35; 46, 26, 45, 34, 18, 23, 27, 19, 24, 28; 22, 20, 23, 31, 29; 21, 30, 22).  
 ○ Obtained by adding gas. ⊙ Obtained by withdrawing gas.

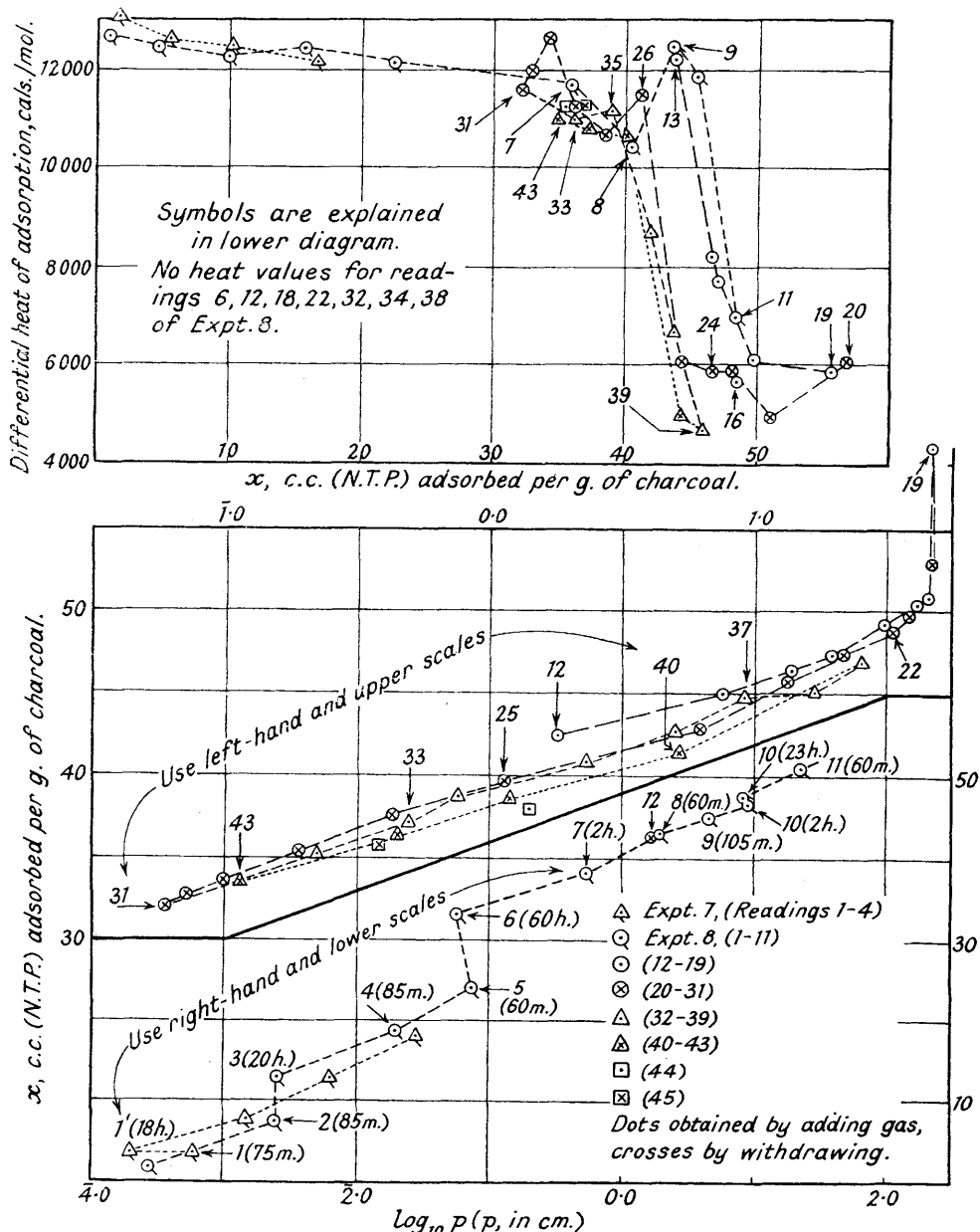
semilog isotherm points fall on exactly the same curve as those of Expt. 3, but the heat curve for Expt. 4 lies slightly above that for Expt. 3.

Expt. 5. (Fig. 1, Curves IV and VI.) At the end of Expt. 4 some air entered and remained for some hours in contact with the charcoal at 15°. Out-gassed at 15°, then at 190°, and flushed out. Equilibration 1—2 hrs. Probable error in  $\Delta H$  is  $\pm 1$  to  $\pm 2\%$  except reading (22), 3%; (33), 4%; (36), 7%.

In the region (6) to (9) the semilog isotherm showed anomalous behaviour (see Inset A). After (9), gas was accordingly withdrawn by pumping till  $p$  fell to a certain value [given by  $\log p = 2.412$ , point (10)] below the abnormal region, to find if, on re-adsorption, the abnormality could be reproduced [see points (10), (11), (12), (13), . . . ; point (10) was interpolated on to the curve (4)—(5)—(6)]. From Inset A it will be seen that, though the re-adsorption curve still exhibits some irregularity, the original feature is not exactly reproduced, and it remains undecided whether the effect is real or arises from an unsuspected experimental error.

To connect the remainder of the re-adsorption curve [points (14) . . . , see Curve IV and Inset B] with the earlier part [(1) . . . (10)], point (14) was interpolated between (8) and (9); a small but constant uncertainty ( $< 4$  c.c.) therefore attaches to all points from (14) onwards.

FIG. 2.



Though in this experiment gas was added and withdrawn in arbitrary order (see numbering of points), "both adsorption increasing" and "adsorption decreasing" points lie on the same curve within experimental limits, proving hysteresis to be sensibly absent.

Expt. 6. New sample of charcoal. Out-gassed at  $250^\circ$  and flushed out. This was a low-pressure experiment to test Henry's law. No heat measurements.

In all the three sulphur dioxide experiments for which heat data were obtained, it is seen (Fig. 1) that, as  $x$  increases from zero,  $\Delta H$  at first falls somewhat, then remains fairly constant over a considerable range of  $x$ ;  $\Delta H$  does not show the continual fall which is perhaps more usual (cf. McBain, "Sorption of Gases by Solids," 1932, Chap. XIV). It may increase slightly and then diminish at high values of  $x$  (see Curve V), but experimental error is rather large here.

*Experiments with ethyl chloride.* Expt. 7. (Fig. 2.) New sample of charcoal (3.72 g.). Out-gassed at 250°, and flushed out.

Expt. 8. (Fig. 2.) After four points of Expt. 7 had been taken, the system was out-gassed at 15° and left for four weeks; it was then flushed out with ethyl chloride and out-gassed at 150°. At all pressures, but particularly at <0.1 mm., there was extensive "drift" in both Expts. 7 and 8; *e.g.*, the pressure always fell appreciably on standing overnight [cf. points (1) and (1') of Expt. 7]. Owing to the impracticability of extending calorimetric measurements over many hours, and since  $\Delta H$  determinations were the primary object of the experiment, the next addition of gas was usually made after 1—2 hrs. [the actual times for points (1) to (11) are given in Fig. 2] even though pressure was still falling; consequently, the isotherm curve does not quite correspond to equilibrium conditions, though the deviation therefrom is much less at the right-hand than at the left-hand end.

Owing to a manipulative error at point (12), there is a small uncertainty, not exceeding 3 c.c., in the position of the semilog isotherm subsequent to point (12). Its general shape, and the values of  $\Delta H$ , are unaffected.

Calorimetric errors are very variable, being much greater at higher pressures where  $\Delta x$ , and therefore  $\Delta q$ , at each reading is small. For small adsorptions the probable error in  $\Delta H$  is  $\pm 2$  to  $\pm 3\%$ , increasing to as much as  $\pm 5$  to  $\pm 10\%$  for the larger adsorptions where  $p$  is approaching  $p_s$ .

The fall in  $\Delta H$  as  $x$  increases from zero, already noted for sulphur dioxide, is less marked with ethyl chloride; the data for intermediate adsorptions (say 10—30 c.c.) are too scanty to say whether  $\Delta H$  remains constant within experimental error or decreases slightly. The most striking feature of the ethyl chloride results, however, is the relatively sudden fall in  $\Delta H$  from about 11,500 cal./mole to near the latent heat of condensation, 6000 cal./mole, occurring within a narrow range of  $x$  [the low values of (21), (39), and (40) are probably due to experimental error]. The fall occurred on five runs, three with adsorption increasing and two with adsorption decreasing [see (10)—(11),  $\odot$ ; (13)—(14)—(15)—(16),  $\odot$ ; (24)—(25)—(26)—(27),  $\otimes$ ; (33)—(35)—(36)—(37)—(39),  $\Delta$ ; (39)—(40)—(41)—(42),  $\Delta$ ] and there can be no doubt as to the reality of the effect. It occurred at pressures of the order of 10 cm., *i.e.*, considerably below the saturated vapour pressure, *viz.*, 46.9 cm. Owing to the experimental necessity of having finite values of  $\Delta x$  there is an uncertainty of some 3 c.c. as to the exact value of  $x$  (say  $x_b$ ) at which the fall commences; but it seems clear that  $x_b$  varies somewhat from one run to another.

Curves drawn through the "adsorption increasing points" (13)—(20) and the "adsorption decreasing" points (21)—(32) respectively do not coincide, the difference being slightly but definitely greater than experimental error. This lack of coincidence is not ordinary adsorption hysteresis, however, for the value of  $x$  at a given  $p$  value is *less* on the "decreasing" than on the "increasing" curve, not greater.

*Discussion.*—In an earlier communication (J., 1942, 696) reasons have been advanced for the belief that the fall in the differential heat of adsorption just noted denotes the completion of a monolayer of ethyl chloride and the inception of a thicker layer.

In the same paper it was also explained how, by measuring the area under the semilog isotherm from zero pressure up to a given pressure  $p$ , the values of  $FA$  and  $FS$  corresponding to  $p$  can be obtained ( $F$  = surface pressure of adsorbed film;  $A$  = area occupied per molecule of adsorbate;  $S$  = area of adsorbent per g.); and  $FA$ — $FS$  curves are there given for Expts. 3 and 8. In Expt. 3 the experimental readings extend to very low pressures, so the summation from zero pressure is particularly accurate. The remaining sulphur dioxide experiments all give  $FA$ — $FS$  curves of the same general shape as does Expt. 3. The reciprocal of the slope of the rectilinear portion of the  $FA$ — $FS$  curve gives the monolayer capacity  $x_0$  of the charcoal, *i.e.*, the number of c.c. (N.T.P.) which can be adsorbed in a completed monolayer:

Expt. No.	2.	3.	5.	8.
$x_0$ .....	113 $\pm$ 3 *	119 $\pm$ 3	136 $\pm$ 3	47 $\pm$ 2
Charcoal No.† .....	X b	X a	X c	XII b

\* Erroneously given as 135  $\pm$  3 in *loc. cit.*, p. 701. † Quoted in *loc. cit.*, p. 701.

Despite the fact that the readings extended to very low pressures, in no case did the relationship between  $x$  and  $p$  become accurately linear, as shown by the following data:

	Expt. 2.				Expt. 3.					
$x$ .....	3.72	6.02	8.07	16.19	0.85	2.38	3.16	4.70	6.0	7.52
$p \times 10^3$ .....	1.24	2.83	4.69	20.9	0.29	0.72	1.17	2.21	3.56	5.25
$(x/p) \times 10^{-3}$ .....	3.02	2.14	1.74	0.78	2.96	3.3	2.7	2.14	1.69	1.22
	Expt. 6.									
$wx$ .....	0.915	1.854	2.289	3.091	3.412					
$p \times 10^3$ .....	0.099	0.195	0.265	0.382	0.408					
$(wx/p) \times 10^{-3}$ .....	9.2	9.5	8.7	8.1	8.4					

( $w$  = about 3 g., exact weight unknown. Expts. 1, 4, and 5 give results very similar to Expts. 2 and 3. Ethyl chloride shows a much more rapid fall in  $x/p$ .)

The results are not, however, to be taken as disproving the widely held view that, in absence of impurities, all adsorption follows "Henry's law"  $x = kp$  ( $k$  = constant) at very low pressures: application of the Gibbs adsorption equation shows that the isotherm can have this linear form only when the adsorbed film is so dilute that it can behave as a two-dimensional perfect gas (Langmuir, *J. Amer. Chem. Soc.*, 1917, 39, 1888). For surface films of fatty acids on water such behaviour is approached, though not reached, when the area per molecule is 4000 Å.<sup>2</sup> (Adam and Jessop, *Proc. Roy. Soc.*, 1926, A, 110, 423), *i.e.*, some 200 times greater than the incompressible area per molecule. An equivalent dilution in the present films on charcoal, where  $x_0 \approx 125$  c.c., would be  $x = 0.6$  c.c.; and with an adsorbate like sulphur dioxide, with its considerable external field, it is likely therefore that obedience to the linear law would be found only at pressures lower than those studied in Expts. 1—5. It is satisfactory that in Expt. 6, where the film dilutions are rather higher, the deviations of  $x/p$  from constancy do not greatly exceed experimental error.