*Adsorption of Insoluble Vapours on Water Surfaces. Part II.**

By D. C. Jones and R. H. Ottewill.

[Reprint Order No. 6488.]

The vertical film balance method has been adapted to determine the surface pressure–vapour pressure relations of some saturated aliphatic hydrocarbons on a water surface at the temperatures 0°, 7·5°, and 15°; the corresponding adsorption isotherms were calculated from the Gibbs equation. It has been found that the isotherms all fit fairly closely an equation to a rectangular hyperbola of the type $\Gamma_2^{(1)} = Bp/(1 - k_1p)$, which, passing through the origin, is convex to the vapour-pressure axis: they are, however, asymptotic to a value of p which is greater than p_0, and so cut the line $p = p_0$. These systems have, therefore, finite values of $\Gamma_2^{(1)}$ at saturation (or very near to it). The F–p curves all fit the equation

$$F = -(2{\cdot}303BRT/k_1)\log_{10}(1 - k_1p)$$

which is formally similar to that of Szyszkowski (*Z. phys. Chem.*, 1908, **64**, 385), but with corresponding changes of sign. Values of the thermodynamic quantities ΔG, ΔH, and ΔS have been computed: all the ΔH values are smaller than the corresponding heats of liquefaction, and the entropy values are consistent with the view that mobile gaseous adsorption films are produced. The ΔG values for the series of normal saturated aliphatic hydrocarbons C_5 to C_8 give an increase of *ca.* 420 calories per carbon atom: this is a quantitative statement of Traube's rule applied to the saturated aliphatic hydrocarbons themselves.

The experimental methods described in Part I * had the advantage of providing a fresh surface of the adsorbent for each determination of the lowering of surface tension, F $(= \gamma_0 - \gamma)$, γ_0 being the surface tension of the pure solvent, and one of these methods was independent of the contact angle (if any). Owing mainly, however, to the small values of F in these systems the further development of the problem needed a more sensitive method for their determination; *e.g.*, the maximum depression of the surface tension of water by *n*-heptane at 25° is *ca.* 2 dynes cm.$^{-1}$, whereas values of 45 dynes cm.$^{-1}$ occur on mercury surfaces at this temperature. After considerable experimentation the vertical-film balance was adapted, and gave a more precise means of determining F, especially at low surface pressures. The method is static but dependent on contact angle: this proved to be sensibly zero if used with a falling meniscus, *i.e.*, the partially immersed plate was continuously withdrawn from the surface as the vapour pressure of the adsorbate increased.

EXPERIMENTAL

Materials.—Some physical properties of each substance used were determined. B. p.s were observed in an apparatus similar to that described by Jones and Betts (*J.*, 1928, 1177); densities were determined in a two-limbed Sprengel-type pyknometer of 10 ml. capacity, and refractive indices by a Pulfrich refractometer for the sodium-*D* line.

Water. Many experiments were carried out with good conductivity water from a Bousfield still: subsequently it was found that the central supply of distilled water to the College had a surface tension equally as good, *viz.*, γ^{20} 72·79 dynes cm.$^{-1}$ (Harkins and Brown, *J. Amer. Chem. Soc.*, 1919, **41**, 499, give γ^{20} 72·8 dynes cm.$^{-1}$). It was drawn directly from the bottom of a large earthenware container and used in most experiments.

Hydrocarbons. n-Pentane, *n*-hexane, *n*-heptane, and *iso*octane (2 : 2 : 4-trimethylpentane) were supplied by the Anglo-Iranian Oil Company, Ltd., as 99·5% pure material. All were stored over phosphoric oxide, and then fractionated through a 3-ft. Towers column packed with glass helices; the middle half was used. Synthetic *n*-octane (B.D.H.) was treated with several portions of 25% oleum during two weeks, washed with dilute aqueous sodium hydroxide, and alkaline and acid permanganate, and dried (P_2O_5). The product was fractionated through a 12-in. column packed with glass helices, and the middle third was collected for use.

---

* Part I, preceding paper.

The physical properties were in good agreement with those reported by Forziati, Glasgow, Willingham, and Rossini (*J. Res. Nat. Bur. Stand.*, 1946, **36**, 129, Research Paper No. 1695) (see Table 1).

TABLE 1. *Physical constants of aliphatic hydrocarbons.*

	n_D^{20}	n_D^{20} (N.B.S.)	B. p./760 mm. (± 0·05°)	B. p./760 mm. (N.B.S.)	d_4^{25}	d_4^{25} (N.B.S.)
n-Pentane	1·3576	1·35745	35·95°	36·073°	0·6208	—
n-Hexane	1·3749	1·37486	68·90	68·740	0·6550	0·65481
n-Heptane	1·3875	1·38764	98·30	98·426	0·6796	0·67949
n-Octane	1·3974	1·39743	125·60	125·665	0·6987	0·69849
2 : 2 : 4-Trimethylpentane	1·3914	1·39145	99·15	99·238	0·6877	0·68777

Vapour Pressures.—n-*Pentane.* These were calculated from equation (1) with the values $A = 27{\cdot}691$ and $B = 7{\cdot}558$ (I.C.T.) :

$$\log_{10} p_{\text{mm.}} = -(0{\cdot}05223/T)A + B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

n-*Hexane.* These were calculated similarly, with the values $A = 35{\cdot}162$, $B = 8{\cdot}399$ from $-20°$ to $-10°$, and $A = 31{\cdot}679$, $B = 7{\cdot}724$ from $-10°$ to $+15°$ (I.C.T.).

n-*Heptane and* n-*octane.* Values were interpolated from a $\log_{10} p_{\text{mm.}}$ against $1/T$ graph (I.C.T.)

2 : 2 : 4-*Trimethylpentane.* Values were interpolated from a $\log_{10} p_{\text{mm.}}$ against $1/T$ graph from the values given by Stull (*Ind. Eng. Chem.*, 1947, **39**, 517).

The Vertical-film Balance.—This has been used in conjunction with (*a*) an analytical balance and (*b*) a torsion balance. The analytical balance was a Sartorius beam balance with a sensitivity of two divisions per mg., modified so that the plate suspension, an aluminium rod, could be hung, together with a counterpoise (W) (see Fig. 1), in place of one balance pan. A mirror of 100 cm. radius of curvature was fixed at the mid-point of the top of the beam, and was used with a galvanometer lamp and scale. The balance was mounted on a rigid platform screwed to the top of the thermostat (T_1) containing the adsorption vessel. The torsion balance was made here and employed a phosphor-bronze torsion wire 12 cm. long, 0·012 cm. in diameter, firmly soldered into chucks at each end, one of which could be rotated through 180°. A small aluminium arm at the centre point of the wire carried a galvanometer mirror of 100 cm. radius of curvature. At one end of the arm was a small hook for attaching the plate suspension, and at the other, a small plunger, dipping into a well, allowed oil damping to be applied when required.

(a) *The analytical balance method.* The surface pressure is given in this case by the expression

$$F = k\Delta P/2(t + w) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

(see Harkins and Anderson, *J. Amer. Chem. Soc.*, 1937, **59**, 2189) where ΔP is the scale deflection, t the thickness of the plate, w the width of the plate, and k a constant which can be measured experimentally. The values of F obtained by this method are independent of any inaccuracies in the balance construction, since these are covered by k. However, k includes a density term and must therefore be measured at each temperature.

For a pure liquid at constant temperature, it may be shown that $k = g\Delta W/\Delta P$. In order to determine k, the plate is suspended in the liquid adsorbent, at the correct temperature, and the balance equilibrated. By further successive increments in weight, ΔW, a graph of ΔW against ΔP can be obtained over the range of ΔP required, and k obtained from the slope.

(b) *The torsion balance method.* It has been shown by Addison and Hutchinson (*J.*, 1948, 930) that

$$F = K_1\Delta P + K_2\Delta\phi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\Delta\phi$ is the decrease of torque; $K_1[= (g\rho twl)/4(t + w)L]$ and $K_2[= 1/2(t + w)]$ are constants for the apparatus and a given plate, L being the distance between the mirror on the balance and the scale, and l the distance from the centre of the torsion wire to the point of suspension of the plate. Since the torsion wire is fixed at both ends, the torque depends only on the vertical movement of the plate, which was measured by means of the attached mirror, lamp, and scale. The wire was so arranged that lifting of the plate involved a decrease of torsion.

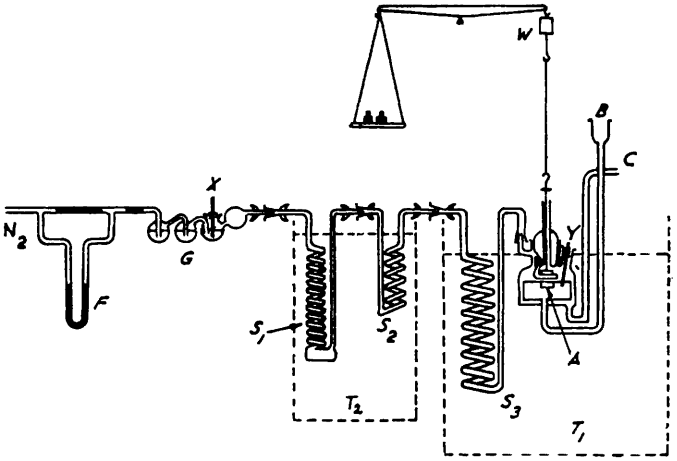
For calibration, a small pan was suspended from the arm; weights were added to this in small increments of *ca.* 5 mg., and the corresponding scale deflections, ΔP, read. The weights were then removed carefully, in small increments, and the ΔP values again obtained. The wire was replaced if any hysteresis was found. The relation between $\Delta\phi$ and ΔP was linear over the range used, and therefore, $\Delta\phi$ being put equal to $K_3\Delta P$, equation (3) may be written

$$F = (K_1 + K_2K_3)\Delta P \qquad \qquad (4)$$

To calculate K_1, the distances l and L have to be measured mechanically; the analytical balance method was, therefore, preferred, although the torsion balance method was used extensively later.

Contact Angle.—It is essential when using the vertical-film balance that zero contact angle should be obtained and maintained. This was accomplished by keeping the plate completely immersed in distilled water and attaching the plate whilst still wet. After a few minutes in the surface the excess of water drained from the top of the plate and zero contact angle was obtained. It was usual, after the balance had reached equilibrium in the clean surface, to allow the plate to drain, otherwise a slight drift in readings was observed (see also Addison and Hutchinson, *loc. cit.*). Since in the adsorption experiments the surface tension always decreased, the plate rose out of the surface and zero contact angle was maintained.

FIG. 1.



Cleaning of Plates.—The glass plates were heated in chromic acid until it boiled gently, thoroughly rinsed, boiled, and again rinsed, all in distilled water, and then kept completely immersed in it until immediately before use.

Adsorption Apparatus.—This is illustrated in Fig. 1. A stream of nitrogen from a cylinder was washed, dried ($CaCl_2$) to prevent accumulation of water in the organic phase in the bubbler, and passed through the flow-meter (*F*) into the bubbler (*G*) where it became saturated with adsorbate vapour at room temperature or higher. The gas stream then passed through the spirals S_1 and S_2 contained in a large Dewar flask (T_2), used as a variable thermostat, where excess of vapour was condensed out (the experiments were below room temperature) so that the nitrogen stream, passing through spiral S_3 and into the adsorption vessel, *A*, contained a partial pressure of vapour corresponding to the temperature of T_2. As the vapour passed into the adsorption vessel, the surface tension changed slowly until equilibrium was reached for that partial pressure. Spiral S_2 was used merely to test whether effective condensation had occurred in S_1. This was checked at the end of each experiment, but no condensate was ever found in this spiral. Spiral S_3 was used to bring the vapour to the temperature of the adsorbent. Whilst this work was in progress (see Ottewill and Jones, *Nature*, 1950, **166**, 687), Dean and Hayes (*J. Amer. Chem. Soc.*, 1951, **73**, 5583) independently developed a similar apparatus for measuring the sorption of vapours on monolayers.

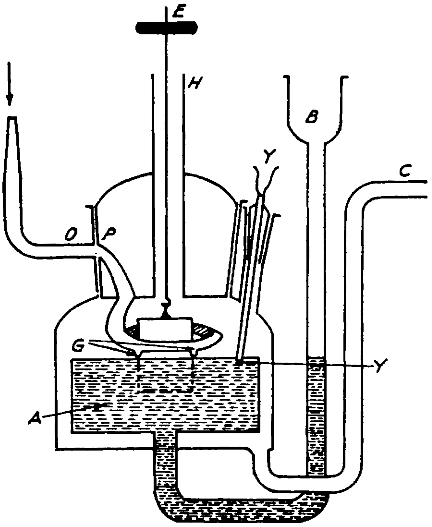
The adsorption experiments were carried out at several degrees below room temperature, to avoid condensation of the adsorbate vapour before it reached the adsorption vessel, in a small room with close-fitting windows and door, since good results by this method are only obtained if draughts and mechanical disturbances are absent.

X and Y (Fig. 1) were thermistors (type 1512/300, Standard Telephones and Cables, Ltd.); Y recorded the temperature of the adsorbent surface, X that of the last bulb in the bubbler, since evaporation sometimes lowered the temperature here. Adjustment was made if the temperature difference between this and the adsorbent surface became less than 5°.

The essential details of the adsorption vessel are shown in Fig. 2. Down the centre of stopper is the tube, *H*, for the plate suspension; the orifice (*P*) connects with the inlet in the socket (*O*). Vapour entering passed through the stopper to the four uniform jets, *G*. They were about 3 mm. above the liquid level in the trough, a distance at which no disturbance of the surface was caused at the flow rates used, and good contact between vapour and surface was obtained. The water was contained in trough *A*, which enabled a clean surface to be formed by overflowing from *B* (see Harkins and Jordan, *J. Amer. Chem. Soc.*, 1930, **52**, 1751), excess being drawn off *via C*. The vessel itself was mounted on a rigid stand, which could be adjusted in both horizontal and vertical planes, to ensure that the trough was horizontal, and the suspension tube vertical.

The Dewar thermostat, consisting of a 5-l. Dewar flask, was controlled to 0·01°. Alcohol was normally used as the bath liquid, cooled when necessary to low temperatures by the addition of powdered "Drikold" and well stirred. Blank experiments, with water as the bath liquid, showed that the use of alcohol had no effect on the adsorption experiments. Near saturation the bath temperature could be easily increased in steps of 0·1° by a fine screw adjustment of the regulator. Temperatures were read on a $-40°$ to $+15°$ thermometer graduated in 0·1°, readable to 0·02°, which had been calibrated against an N.P.L.-standardised thermometer.

FIG. 2.



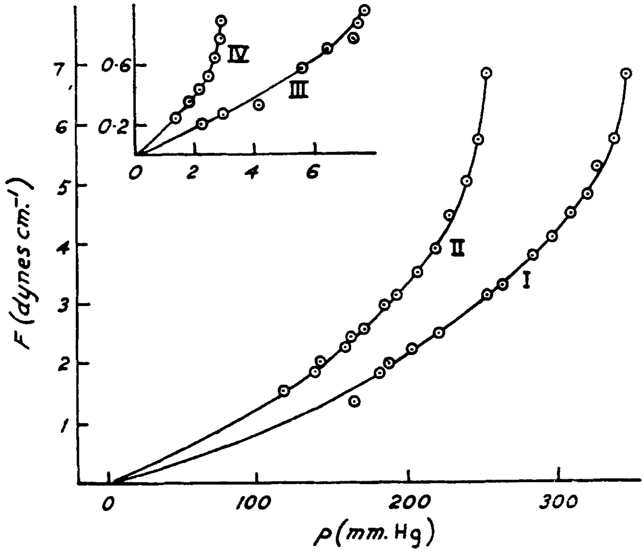
The main thermostat bath for use below room temperature was similar to that of Benford and Ingold (*J.*, 1938, 929) and Benford (*J. Sci. Instr.*, 1936, **13**, 14). The evaporator cylinder of an Electrolux refrigerator, unit type 42A2, having an absorption rate of 5×10^4 cal. hr.$^{-1}$ at 0°, at an input of 400 w, was inserted into a copper sleeve projecting into the thermostat bath. The sides and bottom of the tank were insulated with a 2″ layer of glass-wool. The refrigerator was adjusted to keep the bath 2—3° below the desired working temperature.

Determination of Adsorption Isotherms.—After temperature equilibrium had been established, and a clean surface prepared by flushing with water at the same temperature, the stopper, with the wet plate suspended through *H* by a fine aluminium suspension, was inserted. After adjustment of the stopper for coincidence between *O* and *P* (see Fig. 2), the suspension was attached to the balance, thus pulling the plate up through the surface, and the balance released and equilibrated. With the same plate the weight on the balance necessary for equilibrium was predetermined. The plate was then allowed to drain, and the scale reading P_1, corresponding to the surface tension of the clean surface γ_0, read. Meanwhile the temperature of the Dewar thermostat was adjusted to *ca.* $-30°$, and the needle valve on the nitrogen cylinder was carefully and slowly adjusted to give a slow stream of bubbles until the flow-meter registered the correct value.

As the nitrogen carried the adsorbate vapour over the surface, the scale reading gradually decreased, owing to the fall in γ on adsorption, and eventually became constant at a reading P_2 corresponding to the surface tension of the film-covered surface. Owing to the displacement of the air originally present, a lag of some minutes elapsed before this reading became constant. From the values of $\Delta P(= P_1 - P_2)$, F was calculated from equation (2) or (4).

The temperature of the Dewar thermostat was increased until the saturation vapour pressure was reached and a complete adsorption isotherm was thus obtained. At lower surface pressures increments of 2° or 3° were usual, but near saturation the temperature was raised slowly in steps of 0·1° or 0·2°, since in this region large changes in surface pressure occur with small changes of partial pressure. For this reason accurate values in the neighbourhood of saturation were more difficult to obtain, and very close thermostatic control of both thermostats was essential. With *n*-pentane at 0° it was found impossible to obtain a reproducible value at saturation, and an "instability" of the type noted by Cassel and Formstecher (*Kolloid Z.*, 1932, **61**, 18) seemed to occur. This trouble was not encountered, however, at the other temperatures, or with the other adsorbates.

FIG. 3.



I, *n*-Pentane (15·0°); II, *n*-pentane (7·5°); III, *n*-octane (15·0°); IV, *n*-octane (0°).

All the isotherms were repeated in quadruplicate with good agreement. Blank experiments with water in the bubbler and in the trough had demonstrated that the passage of nitrogen alone had no appreciable effect on the film balance.

RESULTS AND DISCUSSION

The experimental results are given in Table 2. Fig. 3 illustrates the form of the F–p curves obtained in all these cases.

The adsorption excess $\Gamma_2^{(1)}$, referred to later in this paper as Γ, is given by the Gibbs equation

$$\Gamma_2^{(1)} = \frac{-\mathrm{d}\gamma}{\boldsymbol{R}T\,.\,\mathrm{d}\ln a_2} = \frac{\mathrm{d}F}{2{\cdot}303\boldsymbol{R}T\,.\,\mathrm{d}\log_{10} p_2} \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

It can be assumed that the vapours will obey the perfect-gas laws adequately, and also that Dalton's law can be applied with sufficient accuracy to the vapour phase. From a

TABLE 2.

F is expressed in dynes cm.$^{-1}$, p in mm. Hg.

n-Pentane				*n*-Hexane					
7·5°		15°		0·0°		7·5°		15°	
F	p	F	p	F	p	F	p	F	p
1·50	118·3	1·82	181·6	0·60	16·46	0·72	26·67	0·79	38·42
1·85	139·0	1·92	187·1	0·89	22·88	0·83	30·62	1·00	47·86
1·99	143·2	2·19	204·2	0·93	24·66	0·94	34·47	1·13	51·17
2·27	159·6	2·45	220·8	1·08	26·67	1·13	38·15	1·19	54·20
2·43	162·6	3·09	253·5	1·18	29·24	1·32	44·87	1·28	57·02
2·52	171·0	3·26	264·2	1·36	31·62	1·56	50·35	1·41	61·09
2·96	186·2	3·76	284·4	1·40	33·04	2·15	59·16	1·54	65·16
3·08	193·2	4·08	296·5	1·75	36·82	2·53	62·23	1·61	66·76
3·52	207·0	4·47	309·7	2·05	40·65	3·26	65·61	1·73	71·12
3·89	219·3	4·80	321·4	2·46	43·25	3·65	66·53	1·83	74·13
4·44	229·6	5·24	328·1	2·80	44·36			2·04	77·45
5·01	241·0	5·71	338·8	3·42	46·00			2·44	84·14
5·69	248·9	6·81	346·7					2·66	88·72
6·83	254·1							2·83	91·62
								3·53	95·94

n-Heptane								*n*-Octane			
0·0°		7·5°		15°				0·0°		15°	
F	p	F	p	F	p	F	p	F	p	F	p
0·32	4·87	0·34	7·16	0·36	9·25	1·07	22·60	0·24	1·35	0·20	2·24
0·40	5·57	0·43	7·85	0·43	11·18	1·11	23·23	0·35	1·79	0·27	2·94
0·48	6·35	0·53	9·28	0·51	13·34	1·17	23·26	0·43	2·15	0·34	4·18
0·58	7·35	0·70	11·45	0·58	15·40	1·29	25·12	0·52	2·45	0·57	5·59
0·67	8·30	0·78	12·71	0·66	16·10	1·46	26·00	0·65	2·69	0·71	6·41
0·77	9·27	0·95	14·66	0·70	17·38	1·68	26·50	0·76	2·86	0·77	7·23
0·85	9·62	1·02	15·35	0·73	17·95	1·75	27·16	0·89	2·94	0·88	7·48
1·05	10·60	1·09	15·74	0·79	18·67					0·97	7·69
1·07	10·86	1·24	17·04	0·89	20·23						
1·34	11·18	1·56	17·58	0·94	21·58						
1·67	11·45	1·63	17·68	1·04	22·05						

2 : 2 : 4-Trimethylpentane											
0·0°				7·5°				15°			
F	p	F	p	F	p	F	p	F	p	F	p
0·58	5·88	1·56	9·48	0·58	7·43	1·91	15·76	0·79	13·40	2·11	23·23
0·63	6·21	1·92	10·69	0·74	9·08	2·73	18·20	0·96	15·17	2·41	25·35
0·84	7·18	2·74	12·09	0·85	10·67	2·83	18·24	1·04	16·11	2·82	26·24
1·07	8·32	3·41	12·70	0·95	10·86	3·41	19·21	1·10	17·54	3·08	27·99
1·12	8·39	4·07	13·06	1·25	12·91	3·88	19·82	1·43	20·37	3·32	28·18
				1·66	15·38			1·87	22·86	3·90	29·58

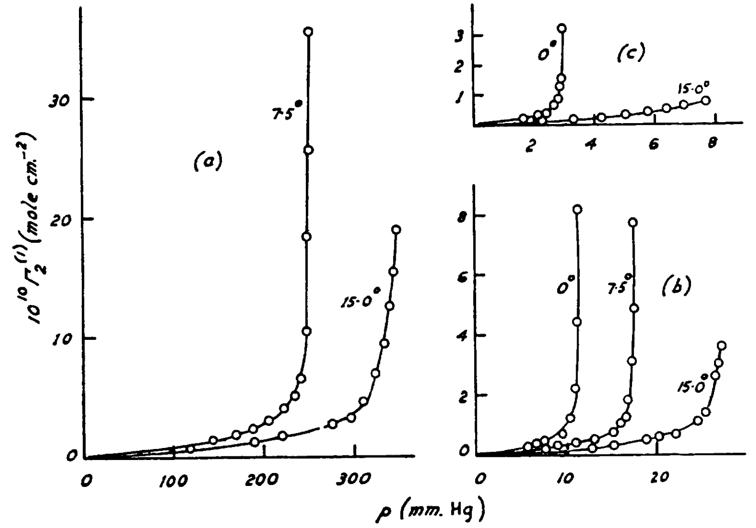
graph of F against $\log_{10} p_2$, the values of $dF/d \log_{10} p_2$ were determined mechanically, at various F values, and Γ calculated from the equation (5). The isotherms are shown in Figs. 4 and 5. For the hydrocarbons it was found that, at constant vapour pressure, the adsorption decreases with increasing temperature; at the same vapour pressure and the same temperature, the adsorption increases markedly with the length of the hydrocarbon chain; at the same temperature, the order of adsorption at similar values of p/p_0, including saturation, is $C_5 > C_6 > C_7 > C_8$, and 2 : 2 : 4-trimethylpentane is intermediate between *n*-hexane and *n*-heptane.

In all the cases investigated the adsorption isotherms can be expressed fairly accurately by the empirical equation

$$\Gamma = Bp/(1 - k_1 p) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

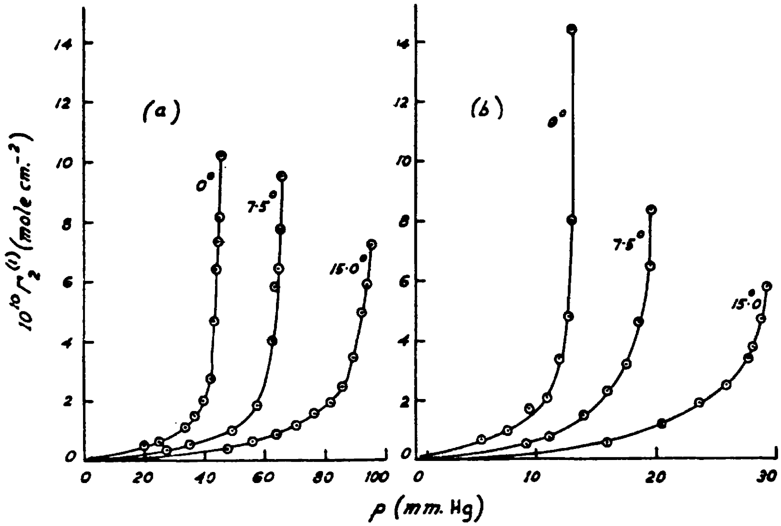
where B and k_1 are constants. This is an equation to a rectangular hyperbola, whose asymptotes are $\Gamma = -B/k_1$ and $p = 1/k_1$; the curve to the equation passes through the origin and is convex to the p axis. Fig. 6 shows the good linear relationship of Γ/p and Γ for *n*-pentane and *n*-octane, and in Fig. 7*b* are the experimental and calculated curves for 2 : 2 : 4-trimethylpentane. In all cases $1/k_1$ is greater than p_0, and therefore at saturation, or very near it, a finite value for the adsorption is obtained. An isotherm of this form is obtained in the B.E.T. model only for unrestricted adsorption, and in the special case when $c = 1$ (or $\sigma_1 = \sigma_2 = \sigma_3$, etc.); the absence of the point of inflection for this case, realisable or not, follows from the equality of σ_1, σ_2, etc. (see Jones, *J.*, 1951, 126). It should be noted, however, that this model requires the asymptote equation to be $p = p_0$ (since $\sigma_2\mu$ is put equal to p/p_0). The experimental data, as is to be expected, do not fit this model. The type of deviation is instructive, however; values of c ($= \sigma_1/\sigma_2$) can be chosen so that the experimental data fit the theory approximately at the lower pressures, and a rough agreement can be extended in some cases even up to $0{\cdot}6p/p_0$, but the theoretical curve deviates increasingly from the experimental as the pressure increases further, so that when p/p_0 is 0·8 the theoretical adsorption is much greater than the experimental. This is because these

Fig. 4



a, *n*-Pentane; *b*, *n*-heptane; *c*, *n*-octane.

Fig. 5.



a, *n*-Hexane; *b*, 2 : 2 : 4-trimethylpentane.

curves are asymptotic at a value of p greater than p_0, so that the rapid adsorption increase occurs at a higher value of p than in the B.E.T. theory, and may be found, theoretically, above the saturation point. This could be interpreted, apart from the general unsuitability of the B.E.T. model, as due to either changes in the values of c as adsorption increases or the fact that $\sigma_2\mu$ is greater than p/p_0, which is the assumption made in the Anderson model (*J. Amer. Chem. Soc.*, 1946, **68**, 686). It has been found, however, that neither Anderson's equation nor that of Hüttig (*Monatsh.*, 1948, **78**, 177) gave agreement with the experimental results. Good agreement, up to 90% of saturation in some cases, was found with Barrer and Ferguson's equation (*Trans. Faraday Soc.*, 1950, **46**, 403, equation 22), which was obtained

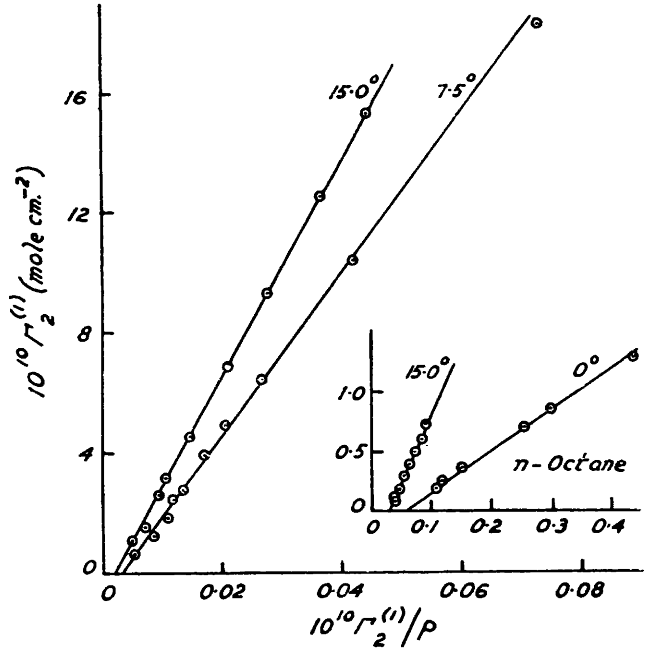
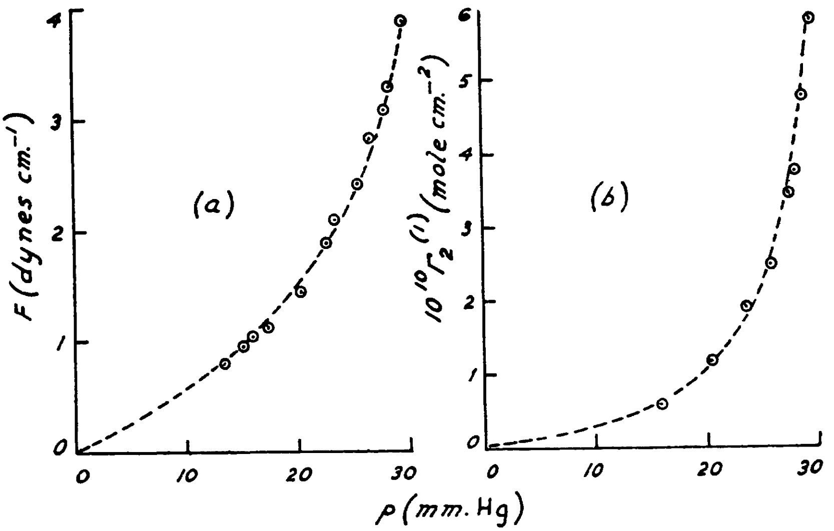


FIG. 6.
n-Pentane.
Inset : *n*-octane.

FIG. 7.



Broken lines represent calculated curves and circles experimental values.

by embodying Anderson's assumption into the Hüttig equation. This agreement would warrant further consideration of this model.

Equation (2) when combined with that of Gibbs gives

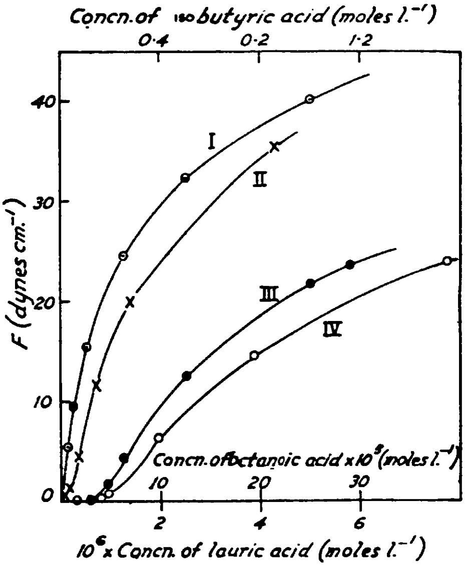
$$\mathrm{d}F = BRT\,\mathrm{d}p/(1 - k_1p)$$

and on integration

$$F = -(2{\cdot}303BRT/k_1)\log_{10}(1 - k_1p) \quad . \quad . \quad . \quad . \quad . \quad (7)$$

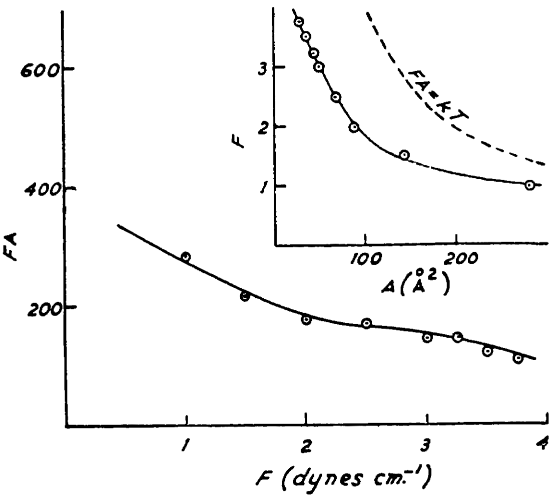
Fig. 7*a* illustrates the agreement obtained between the observed and calculated results from equation (7) for 2 : 2 : 4-trimethylpentane. This equation, save for two sign changes, is identical with that of Szyszkowski (*Z. Phys. Chem.*, 1908, **64**, 385), which agrees with his results for the lower fatty acids on water. His equation, when combined with that of Gibbs, gives the Langmuir adsorption isotherm (Case I) (Langmuir, *J. Amer. Chem. Soc.*, 1918, **40**, 1361) which is also a rectangular hyperbola, but concave to the p axis; it approaches a limiting monolayer adsorption asymptotically.

FIG. 8.



I, *iso*Butyric acid (18°); II, octanoic acid (25°); III, lauric acid (18°); IV lauric acid (29°).

FIG. 9.
2 : 2 : 4-Trimethylpentane.



In these experiments no evidence was obtained of any approach to an adsorption limit in the realisable part of the isotherm. Frumkin's work (*Z. phys. Chem.*, 1925, **116**, 482) on the adsorption of the fatty acids, octanoic and lauric, on very dilute hydrochloric acid, provides an important comparison with this work; Fig. 8 shows the F–concentration curves that he obtained with these acids. The corresponding *iso*butyric acid curve, determined by Szyszkowski (*loc. cit.*), and which obeys his equation, is also shown. The effect of the attraction of the hydrocarbon chain is seen as the series is ascended, with corresponding deviations from the Szyszkowski equation, until the curve becomes (as for the C_8 acid) *convex* to the concentration axis (cf. the present work). As the concentration increases, however, they show a point of inflection and at higher concentrations again obey the Szyszkowski equation, thus indicating an approach to a limiting value of adsorption. In this work no evidence of this was found; in fact, $\mathrm{d}\Gamma/\mathrm{d}p$ continually increases up to (or very near to) the saturation pressure.

The surface area per molecule, A, was calculated from $A = 1/\Gamma N$, and the F–A and FA–F relations were studied. Fig. 9 shows the results obtained for 2 : 2 : 4-trimethylpentane at 15°. In the F–A curves, very similar to the P–V curves for gases, the values of A for a given value of F are always less than those corresponding to the perfect-gas equation; this is shown also in the FA–F relation, which is reminiscent of real-gas curves at low pressures, where the attractive correction is predominant, and where, over small pressure ranges, the FA–F curves are approximately linear. It can be shown from a surface equation of condition, analogous to that of van der Waals

$$(F + a/A^2)(A - b) = kT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

that, if A is very large, b can be neglected in comparison with A; so also the term a/A^2 can be neglected, giving the perfect-gas law. If A is smaller, but still large enough, b can be neglected to a first approximation in comparison with A, but this may not be so with a/A^2. The equation

$$(F + a/A^2)A = kT \quad \text{or} \quad FA = kT - a/A$$

is thus obtained. If the A values are not too small a/A can be put equal to aF/kT in the correcting term, and then

$$FA = kT - aF/kT \quad \text{or} \quad FA = kT - b'F \ (b' = a/kT)$$

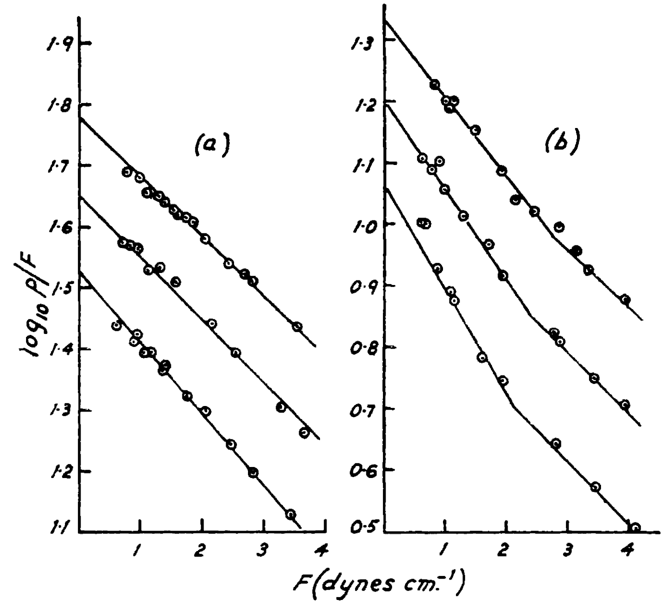


FIG. 10.
a, *n*-Hexane.
b, 2 : 2 : 4-Trimethylpentane.

At low values of F this expression holds approximately. It should be emphasised that, owing to the small values of F in our work, there were certain errors in the values for A. At small A values, A becomes almost constant and approximately equal to b, and equation (8) becomes $FA = kT + bF$. This is Volmer's equation and FA/F is linear, with slope b, and the intercept on the FA axis equal to kT. This is the equation that Kemball and Rideal (*Proc. Roy. Soc.*, 1946, *A*, **187**, 53) found to fit their results for adsorption on a mercury surface so well. In our experiments a similar linear relation holds approximately, but the slope is negative.

As was shown by Cassel and Formstecher (*loc. cit.*), if the values of A from Volmer's equation are substituted in the Gibbs equation, the relation between F and p is

$$\ln p/F = (bF/kT) + C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

This linear relation between ln p/F and F holds reasonably well at low values of F, but with a negative gradient. As F increases, the linear relation holds for the *n*-hydrocarbons, but in some other cases, a change in curvature, or even a definite break in the line, occurs (see Fig. 10). (Other instances of this behaviour will be found in Part III.)

It is noteworthy that in an equation of the Volmer form the constant b' (apart from its physical significance) could be put equal to the difference of two constants $(b - K')$, and an equation of state produced that is of the form $[F + K'F^2/(1 - K'F)](A - b) = \boldsymbol{k}T$, where K' is a cohesion constant. Substituting for A in the Gibbs expression, and integrating, we again have an expression of the same form as equation (9), $\ln p/F = DF + C$; the slope of the $\ln p/F$–F line is D $(= b/\boldsymbol{k}T - K')$ and the slope and its value depend on the relative values of b and K'; in our experiments K' is greater than $b/\boldsymbol{k}T$.

This idea of a gas film, whose molecular area can be studied as a function of F, considered as the analogue of a gas in an enclosure from which it cannot escape, whose volume can be studied as a function of P, is readily understood if the adsorbate is non-volatile and insoluble, and if it is held to the substrate by strong forces (large σ_1), and there is little tendency to form multilayers (small σ_2). The lateral attraction of the molecules in the monolayer and the co-area will affect A, which at large F values will approach that area corresponding to the compressed monolayer. This argument is not affected if the substrate is volatile or soluble or both. If a Langmuir trough technique could be applied to these vapour–water systems, avoiding in some way the adsorption of vapour on the clean-water side of the balance, the mechanical decrease in A would be accompanied by an increase in the equilibrium vapour pressure. But if, as in this work, conditions are favourable for the occurrence of multilayers well before the completion of the monolayer (small σ_1 and large σ_2), although considerable overall multilayer formation may not occur in any case, the value of A at any given value of F will depend, not only on interactions in the monolayer between molecules and groups of molecules, but also on the extent and character of the multilayer formation. Thus, the dynamic viewpoint, which is so naturally applied to these systems involving equilibria between vapours and a liquid surface, leads to the conclusion that the form of the F–p curve, the isotherm, and the F–A relationships are determined by the relative values of σ_1, σ_2, etc., which are the lives of molecules on the adsorbed surface itself, and on subsequent layers; σ_2, etc., may also be, as in Langmuir's Case IV (with different values), the lives of molecules associated with other adsorbed molecules in a monolayer. Thus in these systems, the interpretation of surface equations of condition may be very complicated.

Free energies of adsorption

$-\Delta G$ has been calculated from Kemball and Rideal's equation (*loc. cit.*)

$$-\Delta G = \boldsymbol{R}T \ln 12{,}500 \partial F/\partial p (F \to 0) \qquad . \quad . \quad . \quad . \quad . \qquad (10)$$

Rewriting $\ln p/F = DF + C$ as $p = Fe^{(DF+C)}$, and differentiating, we have $\partial F/\partial p (F \to 0) = e^{-C}$, which in combination with (10) gives

$$-\Delta G = 2{\cdot}303\boldsymbol{R}T(4{\cdot}0969 - C)$$

so that the free energies of adsorption can be calculated from the intercept C on the graph of $\log_{10} p/F$ against F. The values so obtained are listed in Table 3.

TABLE 3.

	0·0°	75°	15·0°		0·0°	7·5°	15·0°
n-Pentane	—	2714	2649	*n*-Octane	4083	(3994)	3905
n-Hexane	3205	3134	3052				
n-Heptane	3585	3499	3420	2 : 2 : 4-Trimethylpentane	3792	3730	3661

In Fig. 11, $-\Delta G$ is plotted against the number of carbon atoms in the *n*-saturated hydrocarbons. There is a linear relation, the increase per carbon atom being *ca.* 420 cal. mole^{-1}, a quantitative statement of Traube's rule as applied to these *n*-saturated hydrocarbons themselves.

Mono- or Multi-layers.—If the overall film thickness is defined as $d = 100\Gamma/\Gamma_m$, where Γ_m is the surface excess for a monolayer calculated for a flat molecular orientation with a maximum hydrocarbon–water interface, multimolecular layers are formed in many cases. Fig. 12 shows how the percentage of monolayer varies with p/p_0 for the *n*-hydrocarbons at 15°. If d is calculated on the basis of vertically orientated molecules, approximately a monolayer, or less, is obtained in most cases at saturation. Only in the cases of *n*-pentane and 2 : 2 : 4-trimethylpentane at 0° is a second layer completed, although in some other cases it is approached. The numerical data for *d*, for these two limiting orientations, are given in Table 4.

TABLE 4.

	0·0°			7·5°			15°		
	Γ $p = p_0$	*d* flat	*d* vert.	Γ $p = p_0$	*d* flat	*d* vert.	Γ $p = p_0$	*d* flat	*d* vert.
n-Pentane	—	—	—	35·5	1016	430	18·9	547	228
n-Hexane	10·3	314	124	9·5	295	115	7·3	228	87
n-Heptane	8·2	282	99	7·7	270	94	3·6	126	43
n-Octane	3·2	124	39	—	—	—	0·7	28	—
2 : 2 : 4-Trimethylpentane	14·5	511	276	8·4	298	159	5·8	208	109

For *n*-hydrocarbons in the vertically orientated position, a cross-sectional area of 20 sq. Å has been assumed (see Muller, *Proc. Roy. Soc.*, 1932, *A*, **138**, 514). It seems probable that flat orientations would be preferred when Γ is small but that with films of this kind, weakly attached to the substrate, a variety of groupings of adsorbed molecules, with varying orientations, would be found as Γ increased. The larger hydrocarbon–hydrocarbon affinity would be satisfied, under more crowded conditions, either by multilayers which are disposed in a more or less flat orientation or by groups of molecules in a more upright one.

FIG. 11.

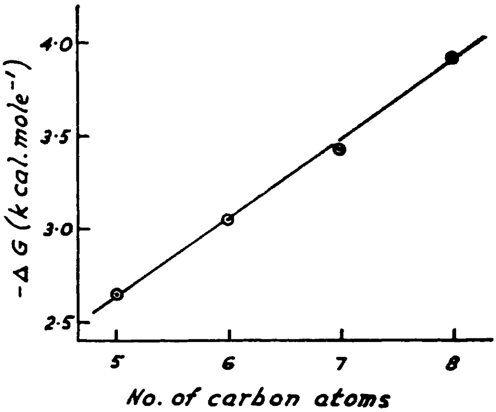
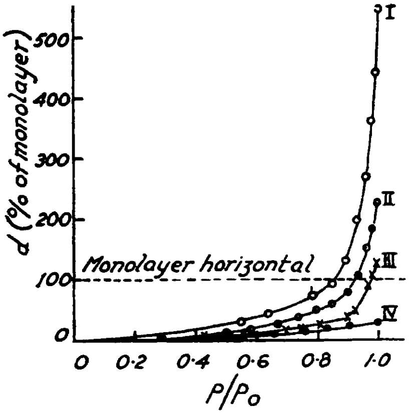


FIG. 12.



I, *n*-Pentane; II, *n*-hexane; III, *n*-heptane; IV, *n*-octane. The broken line corresponds to one horizontal monolayer.

If this conclusion is correct, overall multilayer formation would seem to be occurring in all cases with the exception of *n*-octane, and the rapidly increasing Γ values, when p/p_0 exceeds about 0·85 , are due then to the large σ_2 values produced by hydrocarbon–hydrocarbon attraction.

The change of gradient in some of the $\log_{10}(p/F)$–F curves must be associated with these changes, but a consideration of this will be reserved for a later paper. It will be noticed, however, that the change of slope (Fig. 10) corresponds to a decrease in the value of the intercept *C*, and an *increase* in the value of $-\Delta G$ as the adsorption proceeds. This would be in agreement with the above views and with those expressed in Part I.

Comparison of $-\Delta H$ with the Heats of Liquefaction.—From the temperature coefficients of $-\Delta G$ shown in Table 3, and by using the Gibbs–Helmholtz equation, $\Delta G - \Delta H = T(\mathrm{d}\Delta G/\mathrm{d}T)$ values for $-\Delta H$ have been calculated which, in Table 5, are compared with the heats of liquefaction of the adsorbates : the latter are taken from the data of the National Bureau of Standards (Circular C 461, " Selected Values of Properties of Hydrocarbons "). All values are in cal. mole^{-1}; the heats of adsorption are at 7·5°. These heats of adsorption increase fairly steadily as the series is ascended, the average increase in $-\Delta H$ per carbon atom being *ca.* 720 cal. mole^{-1}; $-\Delta H$ of adsorption is in all cases less than the liquefaction heat. As is seen from the last column, these differences are considerable, and increase with the number of carbon atoms. Taking as a plausible assumption that these differences correspond approximately to the $(E_1 - E_L)$ of the B.E.T. theory, we can calculate from $c = \sigma_1/\sigma_2 = ca.\ e^{(E_1 - E_L/RT)}$, that for *n*-pentane, $c = ca.$ 0·11, and for *n*-octane, 0·001. As has been discussed in Part I, σ_1 for *n*-octane is much greater than for *n*-pentane, and the results now obtained give a degree of quantitative support to the qualitative view previously expressed, that the increase in σ_2 much outweighs the increase in σ_1 as the *n*-saturated hydrocarbon series is ascended.

TABLE 5.

	$-\Delta H$ of adsorption	$-\Delta H$ of liquefaction	$\Delta H_L - \Delta H_{Ads.}$
n-Pentane	5146	6460	1314
n-Hexane	5995	7690	1695
n-Heptane	6585	8900	2315
n-Octane	7324	10,070	2746
2 : 2 : 4-Trimethylpentane	6179	8530	2251

Entropy of Adsorption.—From the values of $-\Delta G$ and $-\Delta H$ already obtained, values of ΔS can be obtained from the equation

$$\Delta G - \Delta H = T(\mathrm{d}\Delta G/\mathrm{d}T) = -T\Delta S$$

Owing to the relatively small differences in $-\Delta G$ at the various temperatures, the values of $-\Delta S$ cannot be considered to be accurate data, but are of interest when compared with values obtained theoretically.

The translational entropy in three dimensions is given by the Sackur–Tetrode equation

$$_3S_{\text{trans.}} = 2{\cdot}303\boldsymbol{R}\log_{10}(M^{3/2}T^{5/2}) - 2{\cdot}30$$

where M is the molecular weight and the entropy is given in cal. deg.$^{-1}$ mole^{-1} for a pressure of 1 atm. The translational entropy expression for a two-dimensional gas has been given by Kemball (*Proc. Roy. Soc.*, 1946, *A*, **187**, 73) as

$$_2S_{\text{trans.}} = 2{\cdot}303\boldsymbol{R}\log_{10} MTa + 65{\cdot}80$$

where a is the area per molecule, defined in the standard state as equal to $22{\cdot}53T$ sq. Å. The values calculated from these equations are given in Table 6. From a comparison of the last two columns the entropy changes could be accounted for as being approximately equivalent to the loss in the adsorbed state of one degree of translational freedom only. This would be in accordance with the previous conclusions that the adsorbate molecules are being weakly held by relatively small forces in the field of force of the surface.

TABLE 6.

	$_3S_{\text{trans.}}$	$_2S_{\text{trans.}}$	$_2S_{\text{trans.}} - {_3S_{\text{trans.}}}$	ΔS (expt.)
n-Pentane	38·6	29·8	8·8	8·7
n-Hexane	39·1	30·1	9·0	10·2
n-Heptane	39·6	30·4	9·1	11·0
n-Octane	40·0	30·7	9·3	9·5
2 : 2 : 4-Trimethylpentane	40·0	30·7	9·3	8·7

The authors are indebted to the Royal Society and the Central Research Fund of the University of London for grants which defrayed the cost of the apparatus, and to the British Petroleum Company for gifts of hydrocarbons. One of them (R. H. O.) thanks the Department of Scientific and Industrial Research for a maintenance grant.

UNIVERSITY OF LONDON, QUEEN MARY COLLEGE, MILE END ROAD,
LONDON, E.1.
[Present Address (R. H. O.) : DEPARTMENT OF COLLOID SCIENCE,
UNIVERSITY OF CAMBRIDGE.]

[*Received, June 8th,* 1955.]