

and thus $\Gamma_2^{(1)}$ values can be obtained from the tangents to carefully drawn large-scale $\log p_2-\gamma$ or $p_2-\gamma$ curves : with experience this can be done with very fair accuracy.

In an experimental study of Antonow's rule (Carter and Jones, *Trans. Faraday Soc.*, 1934, 30, 1027), it was suggested that an explanation of the agreement of some pairs of partially miscible liquids with this rule was essentially that given by Gibbs (*op. cit.*, p. 235) in a footnote referring to the system mercury-water vapour. Here Gibbs implicitly assumed Antonow's rule. It was decided to investigate the course of the adsorption on a water-vapour surface by examining the change of γ with the partial pressures of the vapour, of some of the substances whose agreement, or otherwise, with this rule seemed fairly well established. It should then be possible to determine, within the limits of precision of the method, whether, at saturation, the adsorbed layer could be considered as of sufficient thickness to possess the bulk properties of the liquid phase (see Ottewill and Jones, *Nature*, 1950, 166, 687).

The determination of surface concentrations by this method has advantages over the analogous one where vapours are adsorbed on solid surfaces : the liquid surface can be cleaned or freshly produced, and it is reproducible ; it is unnecessary to know the area of the adsorbent, which is usually an inexact measurement for solid surfaces ; the difficult measurements necessary in experiments with small specific areas of solid surfaces, which must be used if the surfaces are to be plane, are replaced by the experimental work involved in the application of equation (2). This should be a good method for studying the occurrence, or not, of multilayers. The adsorbate vapour must not be too soluble, but the method is capable of extension in this respect.

Some earlier work on the adsorption of vapour on water surfaces has been reported by Micheli (*Phil. Mag.*, 1927, 3, 895) and by Cassel and Formstecher (*Kolloid Z.*, 1932, 61, 18). It soon became evident that our experiments led to results widely different from those of Micheli and considerably different from those of Cassel and Formstecher in the region of higher partial vapour pressure. These differences are confirmed by our experiments in which the vertical film balance is used, and which will be described in Part II.

In our experiments we bring the vapours of the adsorbate, at vapour pressures increasing up to the saturation pressure, into equilibrium with a clean surface of water, and measure the change in γ produced. It did not seem feasible to use an evacuated system, and the vapour was carried in a stream of air or nitrogen to the water surface. Sugden's adaptation of the maximum pressure in bubbles method (*J.*, 1922, 121, 858), which is independent of contact angle, was used, and also the capillary-rise method as adapted by Ferguson and Hakes (*Proc. Phys. Soc.*, 1929, 41, 414). The latter method is more accurate than Sugden's, and very convenient for our purpose, although it was necessary to show that the contact angles, with falling menisci, were sensibly zero. In either method each separate measurement was determined starting from a freshly formed bubble surface.

As expected with the adsorbates used, the adsorption process was very rapid and the results obtained by Sugden's dynamic method were in close agreement with those obtained by Ferguson and Hakes's static method.

EXPERIMENTAL

Fig. 1 illustrates the essential parts of the Ferguson and Hakes method as adapted to this work. The vessel *A*, which contained the adsorbate, was surrounded by a water-jacket whose temperature was indicated by the thermometer *T*, and was fed from a subsidiary thermostat. The water in *C* had a surface of *ca.* 6 cm. diameter, which was large in relation to the size of the capillary. It was possible to arrange the relative positions of the main thermostat and water-jacket so that, after saturating the air stream with adsorbate vapour at the chosen temperature of the jacket, the vapour stream could be passed directly to the main thermostat without being exposed to any fall of temperature, and corresponding reduction of vapour pressure. It is suggested that the much smaller surface-tension depressions usually observed by Micheli (*loc. cit.*) were due to a defect here in his experimental arrangements. Carter and Jones (*loc. cit.*) found quite erroneous results for γ for liquid water saturated with benzene, unless the vapour phase was kept saturated with benzene vapour.

The capillary tube was held vertical by an especially designed clamp which gripped the

saturator *B* and was adjustable in two vertical planes at right angles. The water meniscus was forced down to the bottom of the capillary by careful adjustments to the height of a water reservoir. In order to avoid bench and floor movements, the clamp was fixed on to heavy iron wall attachments. Room draughts had to be avoided. No lubricant was used on any joints, which were mercury-sealed where necessary. The experimental application of the Ferguson and Hakes method is much simplified if the capillary is immersed to a depth h' , equal to $r/3$ where r is the inside capillary radius. The formula for γ then reduces to $1/2 \text{ } \rho r d h$, where d is the density, and h is the height in cm. of the manometric liquid necessary to force down the meniscus until it is level with the bottom of the capillary. A travelling vernier microscope was focused on a mark etched on the capillary, lowered by $r/3$, and then the capillary lowered until the mark was again on the crosswire. The area of the liquid surface in *C* was large enough to make negligible the consequent small rise in the outer liquid level. We used either water, or alcohol coloured with magenta, in the manometer, and found the latter liquid very satisfactory; it was renewed from time to time from a main supply. The manometer was held vertically in a specially constructed brass clamp attached to the wall bracket. It was immersed in the main thermostat, and the levels read by a vernier microscope with an accuracy of *ca.* ± 0.001 cm. A water-manometer was used occasionally and proved quite satisfactory; it is less sensitive,

FIG. 1.

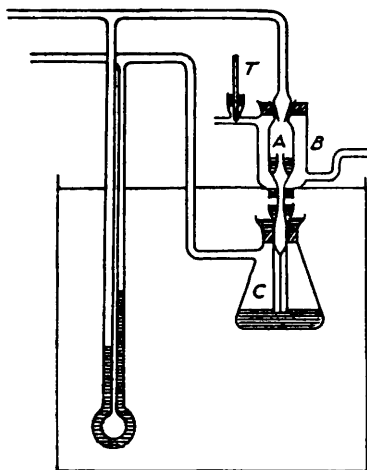
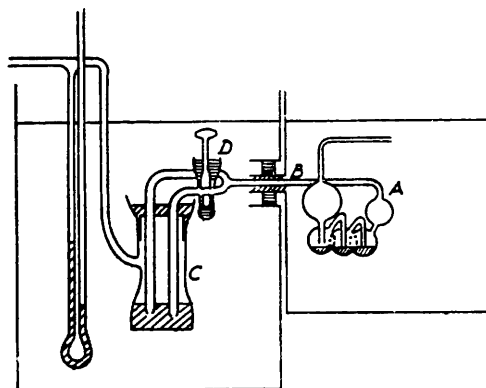


FIG. 2.



and if exposed to the London atmosphere has to be frequently renewed; it has, however, other obvious practical advantages. In this method the radius of the capillary needs only to be known at the tip, and the temperature control of the meniscus is much simplified. It was very convenient to have a static method where the adsorbing surface of the meniscus could be renewed at will by a slight increase of pressure in the apparatus.

The efficiency of the saturation was carefully tested; *e.g.*, the results were unchanged when the vapour space above the cup in the saturator *A* was packed with glass-wool soaked in the liquid adsorbate. In practice, we used a water-saturated solution of adsorbate instead of the adsorbate itself: with these sparingly soluble adsorbates, however, no difference in the results could be detected.

By appropriate adjustment of the reservoir, the surface could be merely renewed, with little vapour escaping through the liquid, or an entirely fresh supply of vapour could be drawn down from the saturator cup. If the stream of air was drawn too rapidly over the surface of the adsorbate, the temperature was lowered and the results were affected.

Fig. 2 illustrates our adaptation of Sugden's modification of Jaeger's method. The method is dynamic but the pressure increase could be controlled so as to give a very slow bubble expansion. It is also independent of contact angle and so was considered a desirable check on our other measurements. The adsorbate phase was contained in the saturator *A* in the subsidiary thermostat. Vapour was drawn through the glass connecting tube *B*, which passed through flanged openings in the sides of the tanks, to the maximum bubble pressure apparatus in the main thermostat. A plug of glass-wool separated the water in the two tanks. This provided another method of avoiding a fall of temperature between the thermostats and proved quite

satisfactory. The vessel *C*, containing the water adsorbent, had a diameter of *ca.* 4 cm., and the capillary tubes were immersed to *ca.* 1 cm. The mercury-sealed tap, *D*, on which no lubricant was used, served to cut off the vapour stream from the wider tube when measurements were being taken with the fine capillary. We followed the directions given by Mills and Robinson (*J.*, 1931, 1629) for the construction of the capillaries, including the use of quill tubing, although this proved to be rather a lengthy process. The apparatus was standardised by using both pure water and benzene.

The stopper of vessel *C* was unlubricated and mercury sealed. A mercury aspirator provided a sensitive method of drawing the vapour through the apparatus so that a slow bubble rate (*ca.* 1 bubble every 30 sec.) could be maintained.

Contact-angle Measurements.—Contact angles against the soda-glass capillaries were measured by Bartell and Merrill's method (*J. Phys. Chem.*, 1932, 36, 1178) (see also Carter and Jones, *loc. cit.*). Photomicrographs were taken in a number of cases. In all cases the contact angle proved sensibly zero.

Thermostats.—The large thermostats were controlled to $\pm 0.03^\circ$ and were provided with plate-glass windows, of tested planarity, at back and front to allow for good illumination and observation. Accurate control of the temperature of the baths is particularly important when the measurements are being made at close to saturation, and the temperatures of the baths are very close to one another. The errors in this region are therefore greater than at other points. The thermometers were compared with an Anschütz set, standardised at the N.P.L.

Materials.—M. p.s were determined on about 15 ml. of material in a double-jacketed tube. The substance was very slowly cooled with good stirring, and the m. p. taken at the steady temperature when about half the material was solidified in the form of very fine crystals. B. p.s were determined by using the usual vapour-jacketing arrangements and corrected to 760 mm. Densities were determined in a two-limbed, Perkin type, pyknometer of about 10-ml. capacity, which was provided with ground-glass caps. The weights were calibrated, and the thermostat temperature control was $\pm 0.02^\circ$. Refractive indices were measured in a Pulfrich refractometer controlled to $\pm 0.02^\circ$.

Water. Good distilled water was redistilled from the block-tin surface of a Bousfield still, which had been in use for many years without repair or dismantling of any kind, and collected in a carefully cleaned and steamed-out storage bottle. This water gave a value of γ within ± 0.05 dyne cm.^{-1} of the accepted figures. The refractive indices for the sodium and hydrogen lines agreed closely with I.C.T. values.

Benzene. Purest material, "for molecular weight determinations," was shaken with concentrated sulphuric acid, until the acid layer only slightly darkened, was washed well with water, dried over sodium wire, and fractionally frozen to give a product of m. p. 5.45° . It was distilled through a 4-ft. Dufton column in an all-glass apparatus fitted with an electrically heated air-jacket, and the middle fraction collected. This had m. p. 5.48° , b. p. $80.10^\circ/760$ mm., d_4^{25} 0.8732, n_D^{20} 1.5012.

Toluene. Kahlbaum's purest material was chemically treated as was benzene, and twice fractionally distilled through the Dufton column. The middle fraction was used and had b. p. $110.70^\circ/760$ mm., d_4^{25} 0.8614, n_D^{25} 1.4936.

p-Xylene. Kahlbaum's "purest" material, m. p. 12.8° , was fractionally frozen until a product of m. p. 13.23° was obtained. It was redistilled and the middle fraction used: it had d_4^{25} 0.8659, n_D^{25} 1.4932.

n-Pentane. Synthetic material was washed with several amounts of 25% oleum, with dilute aqueous sodium hydroxide, and with permanganate solution, dried (KOH), and fractionally distilled through the Dufton column: it had b. p. $35.9^\circ/760$ mm., d_4^{25} 0.6210, n_D^{25} 1.3546.

n-Hexane. This was prepared from pure *n*-propyl bromide and chemically treated as for *n*-pentane. It was fractionally distilled through the Dufton column, from sodium, and distilled over completely within 0.1° : it had b. p. $68.90^\circ/760$ mm., d_4^{25} 0.6556, n_D^{25} 1.3726.

n-Heptane. A synthetic material, treated in the same way as hexane, had b. p. $98.40^\circ/760$ mm., n_D^{25} 1.3854, d_4^{25} 0.6791.

n-Octane. An Eastman-Kodak synthetic material was similarly treated: it had b. p. $125.53^\circ/760$ mm., n_D^{25} 1.3953, d_4^{25} 0.6986.

n-Decane. A synthetic material from Malcolm Dyson was chemically treated as was hexane. It was fractionally distilled under 100 mm., then having b. p. $104.5^\circ/100$ mm., n_D^{25} 1.4102, d_4^{25} 0.7270.

n-Tetradecane. An Eastman-Kodak synthetic material was treated as for hexane and repeatedly fractionally crystallised. It was fractionally distilled under 5 mm. pressure, and the main fraction used; it had b. p. $107^\circ/5$ mm., d_4^{25} 0.7602.

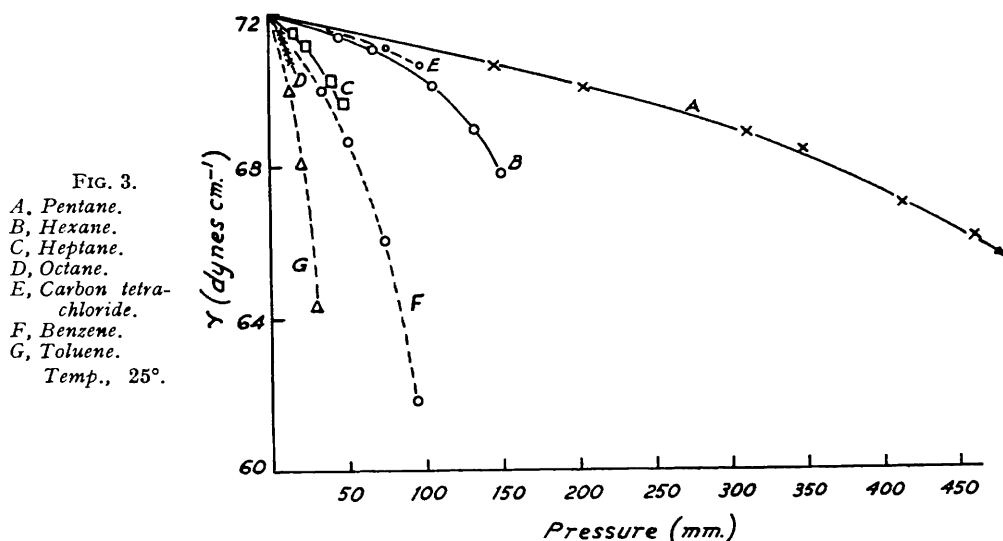
cycloHexane. A Hopkin and Williams product, purified as suggested by Jones and Amstell (*J.*, 1930, 1316), had m. p. 6.45° , d_4^{25} 0.7737, b. p. $80.93^\circ/760$ mm.

Carbon tetrachloride. "AnalaR" material was shaken with silica gel, washed with water, dried ($\text{CaCl}_2\text{-K}_2\text{CO}_3$), and fractionally distilled through a 9' column of the Clarke and Rahrs type (*J. Ind. Eng. Chem.*, 1923, 15, 349). A small middle fraction was used, having b. p. $76.71^\circ/760$ mm., n_D^{25} 1.4575, d_4^{25} 1.58442.

The physical properties of the adsorbates are in good agreement with available standard values except for *n*-hexane which has a slightly lower b. p. and density than those given by Forziati, Glasgow, Willingham, and Rossini (*J. Res. Nat. Bur. Stand.*, 1946, 36, 129).

RESULTS AND DISCUSSION

In Fig. 3 are shown the γ - p curves at 25° for the normal saturated hydrocarbons from pentane to octane (full lines) and for carbon tetrachloride, benzene, and toluene (broken lines), which are typical for all the systems investigated. At low partial pressure of the vapour, the fall of tension is almost linear. Further equal partial-pressure increments



produce continually increasing effects on the depression of the surface tension, giving curves that are concave to the γ axis: $-\text{d}\gamma/\text{d}p$ increases continuously with increase of p . In almost all binary systems previously examined the corresponding curves are convex to the γ axis. Our results for the hydrocarbons are in this respect in disagreement with those of Micheli (*loc. cit.*) but in agreement with those of Cassel and Formstecher (*loc. cit.*). The instability found by the latter authors in the neighbourhood of saturation, we did not observe, and the γ depression, and therefore the adsorption at high values of partial pressures, was often considerably greater.

The group of curves for the saturated hydrocarbons show that, as the series is ascended, (1) at the same value of partial pressure the depression of tension *increases* rapidly, but that (2) at the final points on the curves, when $p = p_0$ (approx.), the depression of γ *decreases* markedly: (2) can be ascribed to the corresponding marked decrease of p_0 as the series is ascended. These trends continue with the still higher homologues, for qualitative experiments in the neighbourhood of saturation of *n*-decane gave a much smaller depression of γ than that for *n*-octane, and for water in contact with the saturated vapour of *n*-tetradecane, no change in γ could be detected. These results were confirmed by a direct determination of γ for the aqueous layer saturated with these hydrocarbons at 25° .

The curves for benzene and toluene, lying one on each side of the octane curve, show the much larger effects produced by these aromatic hydrocarbons, especially in the lowering

of γ at the final values of p (approx. p_0), toluene, as expected, having a smaller effect than benzene. The carbon tetrachloride curve, although the depressions are small, has the same typical concavity to the γ axis.

In Fig. 4 is shown an example of $\log p$ - γ curves for toluene vapour at three temperatures of the adsorbing surface. Graphs of this kind, drawn carefully on a large scale, were used to determine the $\Gamma_2^{(1)}$ - p curves such as are exemplified for the case of toluene in Fig. 5. These curves are typical of the considerable number that have been investigated, and in Fig. 5 can be seen the relationships of the isotherms to one another as the temperature of the substrate surface increases. Compared at the same values of vapour pressure, the adsorption clearly increases with decrease of temperature, although the final $\Gamma_2^{(1)}$ values at the end points of the curve, approximately at p_0 , are fairly similar. The calculations of the heats of adsorption for these systems will be given in a later paper.

In Fig. 6 are shown the adsorption isotherms for these saturated hydrocarbons on a water surface at 25° as calculated from the values shown in Fig. 3. All the isotherms are, throughout their *realisable* course, convex to the p -axis: $d\Gamma/dp$ continually increases with increase of p or of Γ . They do not approach a limiting value of Γ asymptotically as in the models of Langmuir for Case I and for restricted adsorption in the B.E.T. theory:

FIG. 4.

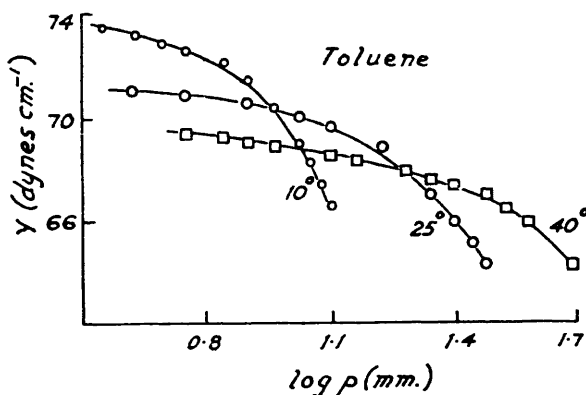
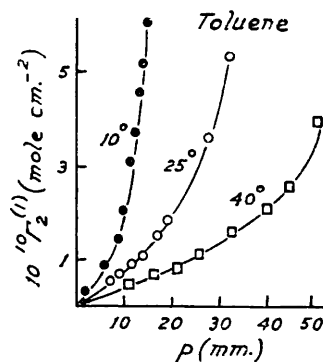


FIG. 5.



the isotherm equations are not asymptotic to a value of $p = p_0$ as in the case of unrestricted B.E.T. theory, *e.g.*, Type III, but they are, however, asymptotic to a value of $p > p_0$ in every case investigated. There is no evidence therefore, either from the experimentally determined points on the isotherm or from extrapolation of the empirical equations to the curves, that a limiting value of adsorption is being approached, even when the surface concentration is so extensive that, whatever molecular orientation is assumed, multilayers must be present.

From Fig. 6 it can be seen that for these four saturated hydrocarbons:

(a) When the adsorption can be compared at the same values of pressure it increases markedly as the homologous series is ascended. The small comparative differences introduced by using partial pressure values instead of collision numbers as abscissæ being neglected, this means that the life of the hydrocarbon molecules on the surface increases as the homologous series is ascended. At low surface coverages this is readily understood since the molecules would tend to lie flat on the surface. This observation is a qualitative statement of Traube's rule, applying here to molecules not possessing a water-soluble group with varying saturated hydrocarbon chains, but the varying chain itself. This effect is present, however, at all surface coverages, from conditions when only a small fraction of a monolayer is present even for octane, to conditions when the overall surface concentration is a monolayer or more, and in fact, it becomes progressively greater as the surface concentration of the compared hydrocarbons is increased.

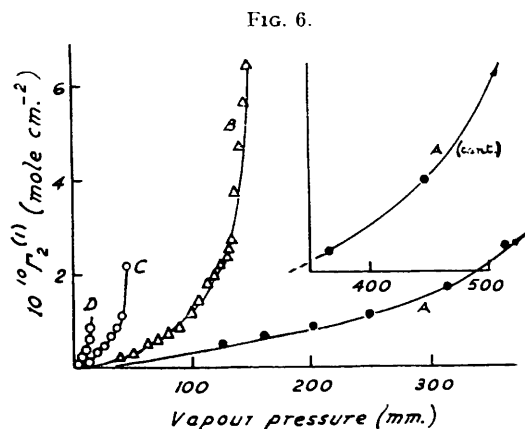
(b) The adsorption at the saturation values, indicated in Fig. 6 A, B, C, and D, decreases

markedly as the series is *descended*. This would appear to be caused by the increased life factor as the series is ascended being overpowered by the greatly increased values of the collision number, at $p = p_0$, as the series is descended (compare, *e.g.*, pentane $p_0^{25^\circ} = 507$ mm.; octane $p_0^{25^\circ} = 14$ mm.).

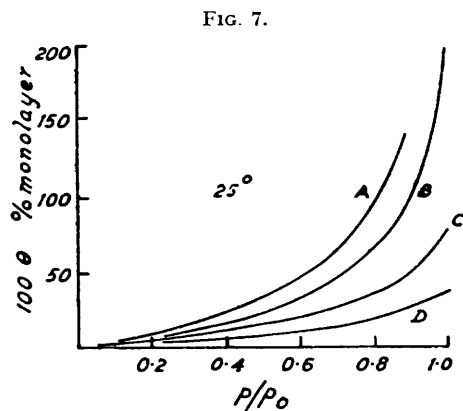
These two effects (a) and (b) above receive a ready qualitative explanation on using a simple collision mechanism for adsorption on a plane surface: effect (b) would be obscured normally when working with porous adsorbents or powders, owing to complications present in these systems at high values of p/p_0 .

We cannot, of course, deduce directly from the small and negligible values, respectively, of the lowering of the tension at the saturation vapour pressure produced by *n*-decane and *n*-tetradecane, that the adsorptions of these substances at $p = p_0$ are correspondingly reduced below that of *n*-octane, since this is determined by the value of $d\gamma/d\log p$ at $p = p_0$, but, by analogy with the results shown in Fig. 6, it would seem probable.

In Fig. 7, θ , the fraction of a monolayer, or $\Gamma_2^{(l)}/\Gamma_m$, where Γ_m is the adsorption corresponding to a completed monolayer, on the assumption of flat orientation, is plotted against p/p_0 for these hydrocarbons. As would be expected from the order of the adsorption at



A, Pentane B, Hexane. C, Heptane. D, Octane.



A, Pentane. B, Hexane. C, Heptane. D, Octane.

the saturation pressures (see Fig. 6), at all equal values of p/p_0 the values of θ are in the order pentane > hexane > heptane > octane, the explanation lying as before in the overpowering effect of the rapidly increasing values of p_0 as the series is ascended.

On the basis of a Langmuir case IV or VI, the latter being the B.E.T. model, the initial slopes of the curves in Fig. 6 $d\theta/dp$ ($p \rightarrow 0$) are equal to σ_1 , the life of the various hydrocarbon molecules on the water surface, and these initial slopes are in the order octane > heptane > hexane > pentane. The initial slopes in Fig. 7, $d\theta/d(p/p_0)$ ($p/p_0 \rightarrow 0$) is equal to c or σ_1/σ_2 , where σ_2 is the life of the hydrocarbon on its own liquid surface, and this, of course, rapidly increases with the length of the carbon chain. The initial slopes in Fig. 7 are in the reverse order to those in Fig. 6, and the values are approximately those expected on this theory. This reversal indicates that σ_1 increases as the chain lengthens at a slower rate than the corresponding increase of σ_2 , or the life of an octane molecule is greater than that of a pentane molecule on a water surface, but the disparity in their lives on their own liquid surface is much greater. Undoubtedly the adsorption here is not of a localised mono- or multi-layer type, but the above explanation would apply to low adsorption coverage for a mobile film, and probably for higher surface concentrations as well.

Considering the adsorption values shown in Fig. 7, it will be seen that these experiments show conclusively that, unless some unheralded change in γ , when p is almost p_0 , occurs, at $p/p_0 = 1$, the θ values range from 0.3 of a monolayer with octane, to a monolayer with heptane, and multilayers with pentane, orientations involving maximum area of contact with the adsorbent surface being assumed. Similar diversities have been found with the

other substances experimented with: *e.g.*, carbon tetrachloride $\theta^{25} = ca. 0.7$; toluene $\theta^{25} = ca. 1.0$.

These θ values, especially for the saturated hydrocarbons, change with the orientations assumed, but it appears established for these systems that, where values of a monolayer or over are obtained, they conform approximately to Antonow's rule: the hydrocarbons pentane to heptane illustrate this. Octane is the first in the saturated hydrocarbon series to deviate somewhat from the relation, and the deviation increases considerably for *n*-decane, where θ is probably very small, and still further for *n*-tetradecane, where θ is probably

FIG. 8.

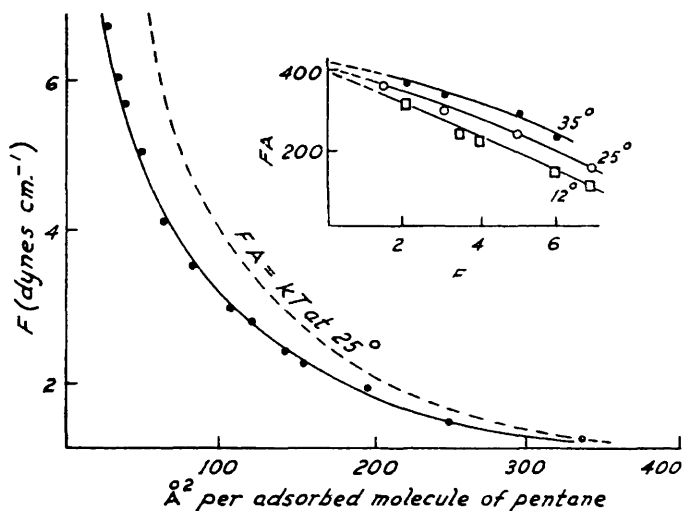
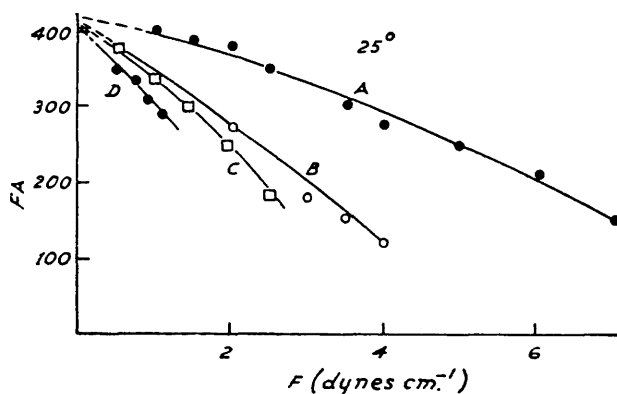


FIG. 9.
A, Pentane.
B, Hexane.
C, Heptane.
D, Octane.



negligible. Toluene conforms approximately and so does carbon tetrachloride, although θ in this case is less than a monolayer. It is possible that these gaseous films have approximately the surface properties of the bulk liquid even when the surface concentration is an incomplete monolayer (see Volmer, *Z. phys. Chem.*, 1925, **115**, 253). Further work may confirm, however, that deviation from this relation would always follow when θ , for gaseous films, becomes too small a fraction of a monolayer.

Fig. 8 is typical of the surface pressure-area (F/A) relations found for all the systems investigated. The curve that would be obtained at the same temperature for an ideal gaseous adsorbed film is also shown. It is seen that there is an increasing deviation from the ideal conditions which are found approximately at large A values; as A diminishes (Γ increases) for a given value of surface pressure, F , the A value found is always less than the ideal

one—the film appears more compressed—and this effect increases continuously up to the highest value found, *i.e.*, at the saturation vapour pressure, p_0 , of the adsorbate; the films therefore could be described as gaseous, with considerable corrections, the attractive correction term always predominating.

These deviations from the ideal-gas conditions are seen perhaps more clearly in Fig. 9, where, for the four saturated hydrocarbons, the FA values are seen to fall increasingly below the ideal value as F increases. With some other vapours there seems to be evidence that the initial fall in FA is followed by a flattening of the curve, but no evidence is found, in any case, of a subsequent rise, much less of an attainment of a value of FA corresponding again to an ideal state of balance between the attraction and repulsion factors in the undoubtedly gaseous films formed by the ethyl esters of certain dicarboxylic acids (Adam and Jessop, *Proc. Roy. Soc.*, 1926, *A*, 112, 376). Even when the films are so concentrated that the overall values of Γ approach or even exceed monolayers, as in many cases they do, the attractive effects remain predominant. The effect due to increasing mutual attraction of the longer hydrocarbon chains in the steeply oriented films formed on water by the higher members of the acetic acid series is familiar, but the effect is observed in our experiments with such molecules as carbon tetrachloride, heptane, and benzene. In Kemball and Rideal's experiments (*Proc. Roy. Soc.*, 1946, *A*, 187, 53) the same vapours, *e.g.*, heptane, adsorbed on to a mercury surface give isotherms of a quite different kind, *viz.*, Type II, and the films, which are gaseous, follow the Volmer equation, so that the deviation from the surface analogue to the perfect-gas equation is opposite in character to ours in that the area per molecule is always, at a given value of F , greater than that corresponding to $FA = kT$.

If we consider F as analogous to a surface osmotic pressure, the character of the deviation of a gaseous film should depend not only on the interaction of adsorbate molecules between themselves, but on the adsorbate-adsorbent interaction, so that a variation with substrate is to be expected just as the osmotic pressure of a solution depends on the solvent, although in this latter case the solvent-solvent interaction is also present and very important.

In the case of heptane vapour in contact with water it is probably the water-water interaction that accounts mainly for the very small bulk mole-fraction of heptane. The surface mole-fraction in our experiments is much greater, owing to the non-involvement of the water-water interaction, but the smallness of the heptane-water attraction compared with the heptane-heptane one accounts for the type of deviation from an ideal surface film which we found: the heptane-mercury attraction is, no doubt, much greater.

From the dynamic Langmuir-B.E.T. viewpoint the type of isotherm obtained (see Jones *et al.*, *J.*, 1951, 126, 1127, 1464) depends on (*a*) σ_1/σ_2 or c , where σ_2 could also be the life of a heptane molecule contiguous to another in the monolayer as envisaged in Langmuir's case IV, and on (*b*) layer restriction as, *e.g.*, in the films of the higher aliphatic acids on water. For our substrates the high overall $\Gamma_2^{(1)}$ values in some cases, and the isotherm shape, show that this restriction is not present. It would be erroneous to consider that this was a two-dimensional film in which ordinary heptane molecules were interacting only with each other as in the vapour phase, the water surface acting merely to "anchor" the adsorbed molecules temporarily to the surface.

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