

THE SURFACE TENSION OF MERCURY AND THE
ADSORPTION OF SOME HYDROCARBONS ON MERCURY

by

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submitted in fulfilment of the requirements
for the Degree of

DOCTOR OF PHILOSOPHY

UNIVERSITY OF TASMANIA

HOBART

February, 1960.

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ACKNOWLEDGMENTS

I wish to thank Professor E.E.Kurth for his interest in this work; Dr. J.A.Friend, my supervisor, for his interest and encouragement; Professor V.K. La Mer of Columbia University, New York, U.S.A., for a stimulating discussion while on a visit to Hobart; Dr. R.S.Burdon of the University of Adelaide and Dr. J.R. Anderson of the University of Melbourne for advice in the construction of the glass vacuum system; Dr. M. Mulcahy, C.S.I.R.O., N.S.W., and Mr. I. Brown, C.S.I.R.O., Victoria, for a generous supply of pure hydrocarbons; Mr. M. Mason for his skilful construction of the glass measuring vessel; Mr. R.W.Harris for the optical glass window; Mrs. D. Richardson for the tedious job of typing this thesis; Mr. McMahon for the photographs of the apparatus and the reproduction of the various figures, and the Electrolytic Zinc Co. for unlimited supplies of liquid nitrogen.

Finally, I must record my heartfelt thanks to my wife for her help in innumerable ways.

PREFACE

The aim of this investigation was

- (1) To ascertain the surface tension of mercury.
- (2) To study the adsorption of the normal hydrocarbons on mercury, and hence deduce the effect of chain length on the heat of adsorption and on the orientation at the surface.
- (3) To compare the adsorption of the normal hydrocarbons on mercury and water.
- (4) To investigate the validity of the approximate form of the Gibbs adsorption equation as applied to the normal hydrocarbons and to other vapours and gases.
- (5) To clarify the work on the adsorption of water on mercury.
- (6) To review critically previous work on the adsorption of vapours on mercury.

Except for the glass measuring vessel, most of the components of the glass vacuum system were constructed and all of them were installed by the author.

ABSTRACT

The surface tension of mercury is within 0.2% of
485.4 dynes cm^{-1} at 25°C.

and

487.3 dynes cm^{-1} at 16.5°C.

These values are in agreement with the most reliable work to date (Kemball⁽³⁾). It is not necessary, as all workers have insisted, to "clean" the glass vessel in which the surface tension is measured.

The normal saturated aliphatic hydrocarbons give almost the same lowering of the surface tension at the same relative pressures of vapour, i.e. the decrease in vapour pressure on ascending the hydrocarbon series is approximately balanced by an increase in the intensity of adsorption. The results are analysed on the basis of two surface equations of state, the Volmer equation (a two dimensional analogue of Van der Waal's equation with the repulsive term predominating), and the Virial equation in two dimensions with the correction term related to the forces between the molecules. From these two viewpoints the hydrocarbon molecules appear to be relatively curled up on the surface with their electron envelopes highly distorted.

A comparison is made with the adsorption of the same hydrocarbons on a water surface. The initial thickness of the surface layer on water is almost the same as that on mercury although the much lower heat and entropy of adsorption on water indicates that the molecules are much less firmly held. The fact that Traube's Rule is not obeyed on mercury indicates that the shape of the molecules on this surface is probably rather complicated.

The adsorption of water on mercury is also studied. Unfortunately the anomalous results of other workers remain unresolved, however the reasons recently advanced for these discrepancies by Bering and Ioileva⁽²⁴⁾ are shown to be untenable.

The approximate form of the Gibbs adsorption isotherm is shown to be valid under medium temperatures and pressures.

The literature on the adsorption of vapour on mercury is reviewed.

"REVIEW OF LITERATURE ON ADSORPTION OF
VAPOURS ON MERCURY."

Many workers have studied the adsorption of insoluble vapours on liquid surfaces. Adsorption on a liquid surface is a simpler phenomenon than that occurring at the surface of a solid adsorbent. Solid adsorbents usually have irregular surfaces and often the presence of fine pores favours capillary condensation at pressures of the vapour approaching saturation. Even a perfect crystal will adsorb differently on faces of different indices because of the different arrangement of atoms corresponding to differing surface energies⁽²¹⁾.

Direct determination of the amount of vapour adsorbed is usually of low accuracy. Most investigators have determined this quantity from the lowering of the surface tension of the liquid followed by calculation from the Gibbs adsorption isotherm

$$\Gamma = \frac{1}{RT} \left(\frac{d\pi}{d \ln a} \right)_T \quad \dots (1)$$

where Γ = excess surface concentration of vapour,

π = lowering of surface tension,

a = activity of vapour,

T = temperature of surface.

The assumptions which have been made in using this equation are that the vapour behaves as an ideal gas and the excess surface concentration is equal to surface concentration. Both assumptions appear reasonable at low vapour pressures; whether they are tenable at pressures approaching saturation will be considered later.

Mercury, because of its high surface energy, is an ideal surface for following the adsorption of vapours. Surface pressures are high, and accurate determinations of amounts adsorbed are possible. This high surface energy, however, makes it very difficult to obtain a clean surface.

The objection levelled at most work on the adsorption of vapours on mercury is that the mercury surface may have been contaminated. Iredale⁽¹⁶⁾, using the drop weight and sessile drop method to measure the tension, carried out a series of investigations on the adsorption of vapours on mercury. The bulk of the measurements were made using the sessile drop method. Calculation of the surface tension by this method depends on an equation due to Worthington⁽⁹⁾

$$\gamma = \frac{1}{2} \rho g h^2 \frac{1.641R}{1.641R + h} \quad \dots (2)$$

for $R > 2 \text{ cms.}$

where γ = surface tension,

ρ = difference in density between liquid
and surroundings,

g = acceleration due to gravity,

h = distance from plane of maximum dia-
meter of liquid pool to its vertex,

R = maximum radius of liquid pool.

However, the drop used by Iredale was too small

($R \approx 0.75$ cms.) to justify the use of this equation
and he found the simple equation proposed by Quineke⁽⁸⁾

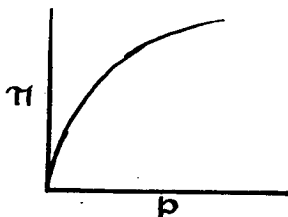
$$\gamma = \frac{1}{2} \rho g h^2 \quad \dots (3)$$

gave a surface tension close to that obtained by drop
weight method. He did not realise the reason for this⁽²²⁾
at the time, but it has since been shown that when

$R \approx 0.75$ cms. the simple formula gives very nearly the
correct surface tension. The surface tension was also
low, $472 \text{ dynes cm}^{-1}$ at approximately 20°C . and therefore
his results have only a qualitative significance. Never-
the less, he established that in general only a mono-
molecular layer is formed, and that the area occupied by
the molecule is in agreement with data from other sources.

He found that for the vapours he studied - benzene,
ethyl alcohol, propyl chloride and ethyl bromide - the
surface tension of the mercury could be restored to close
to its original value by immersing the vapour source in

liquid air, i.e. the vapours were physically adsorbed, the molecules being held by Van der Waals' forces. Methyl iodide was the only vapour to show irreversible behaviour and it is known that mercury forms a definite chemical compound with this substance. In all instances the isotherms of surface pressure (π) against vapour pressure (p) were convex to the surface pressure axis.

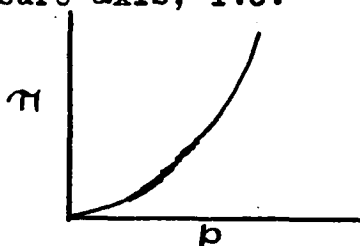


It is possible to show that such curves represent a departure from an ideal 2 dimensional gas due to a preponderance of repulsive forces between the adsorbed molecules^(1,25).

Micheli⁽¹⁷⁾, applying the drop weight method, studied the adsorption of pentane, hexane, heptane and octane. Curves of surface pressure against vapour pressure were convex. The surface tension, however, was low ($471 \text{ dynes cm}^{-1}$), and measurements were made at only high pressures of vapour. His results will be considered along with those obtained in this investigation.

Cassel⁽¹⁸⁾ and Cassel and Salditt⁽¹⁹⁾ were the first workers to carry out an extensive systematic study of the adsorption of vapours on mercury. They used the polar compounds water, isoamyl alcohol, methyl alcohol,

ethyl alcohol, n-butyl alcohol, n-propyl alcohol, allyl alcohol and nitromethane and non-polar compounds n-hexane, cyclohexane and benzene. For the lower alcohols, the initial part of the adsorption isotherm was concave to the surface pressure axis, i.e.



indicating a preponderance of attractive forces in the adsorbed layer⁽¹⁾. From their results they concluded that the polarizability of the molecule was more important for adsorption than the permanent dipole moment. Unfortunately, the initial surface tension was only 459 dynes cm⁻¹ at 50°C., and Kemball⁽²³⁾ criticized their findings because of this.

Bosworth⁽²⁰⁾ adsorbed the lower fatty acids on mercury following the adsorption by surface tension lowering, and also by dropping mercury through a vapour of known pressure and collecting the acid liberated when the drops coalesced under water. Unfortunately, the association of the fatty acid molecules in the vapour phase was neglected in the subsequent calculations.

Kemball⁽²³⁾, it seems, was the first investigator to use mercury whose surface tension was correct. However, the value he found - 484.0 dynes cm⁻¹ at 25°C. - was

in error by $1.1 \text{ dynes cm}^{-1}$ due to approximations made in the derivation of the Worthington equation ⁽⁵⁾. This should be taken into account as he claimed an accuracy of $\pm 1.5 \text{ dynes cm}^{-1}$. As the result of careful measurements, he found that for both the polar (water, acetone and the normal alcohols from methyl to hexyl) and non-polar compounds (benzene, n-heptane and toluene), convex adsorption isotherms were obtained, indicating in all cases a predominance of repulsive forces in the adsorbed layer. The layers were found to be gaseous and obeyed the Volmer equation

$$\pi(A - b) = kT \quad \dots (4)$$

where π = surface pressure,
 A = area per molecule,
 b = co-area,
 k = Boltzman's constant,
 T = absolute temperature.

By defining a standard state for the surface phase' the free energy, total energy, and entropy of adsorption were calculated. The monolayers formed by the non-polar compounds were found to be stable up to pressures approaching saturation. No conclusive evidence of two-dimensional condensation or for the formation of a second adsorbed layer was produced for the non-polar compounds. In the case of the polar compounds, all but water produced gaseous films at low surface pressures. Methyl and ethyl

alcohols showed the adsorption of a second layer at higher pressures. Acetone produced a double layer and finally a triple layer. Multilayer formation was considered on the basis of these results to be the property of small polar molecules. n-Butyl, n-amyl and n-hexyl alcohols showed two-dimensional condensation to liquid films. No connection between dipole moment or polarizability and adsorption was found.

In all cases the surface tension of the mercury was restored to its original value by withdrawal of the vapour by the application of liquid air to the vapour source, indicating that the molecules were held by only Van der Waals' forces. Herein lies the strength of the sessile drop method which Kemball employed. Other methods following adsorption, e.g. the drop weight and maximum pressure in a drop methods, are not suitable for detecting irreversibility.

B.P.Bering and K.A.Ioileva^(6,2,4) are the most recent to study the adsorption of vapours on mercury. They repeated the determinations of Kemball for n-heptane, acetone, water and methyl alcohol, and also included some results obtained previously (1940) by one of them for ethyl alcohol and n-butyl alcohol. Diethyl ether was also studied. Employing the method of the maximum pressure in a drop, the surface tension was found to be 484.5 and 485.8 dynes cm^{-1} at 25°C. for two different

capillaries, both results in close agreement with Kenball's value. Adsorption isotherms for n-heptane and acetone were in agreement with Kenball. However, those for water, methyl alcohol, ethyl alcohol and n-butyl alcohol were concave to the surface pressure axis in agreement with Cassol and Salditt. They concluded that only their results for water and the lower alcohols referred to physical adsorption and that the much higher surface pressures found by Kenball were the result of either impurities being displaced from the glass vessel or "activated" adsorption which would become evident in the sessile drop method where the drop is in contact with the vapours for the whole series of readings.

In support of their claim they quote the work of Karpartchev, Smirnov and Vorlichenkova⁽⁴⁾ on the adsorption of water vapour on mercury. Since these workers used the sessile drop method and, with an initial surface tension close to that of Kenball, obtained a convex isotherm far from coincident with his, they claim that neither of these curves has any relation to the physical adsorption of water vapour on mercury. However, the sessile drop method used by those workers was not employed as a static method as it was by Kenball. After each adsorption measurement liquid air was applied

to the vapour source; the mercury was distilled and a fresh surface was provided for the next measurement. Therefore, unless individual measurements took longer than a few minutes, the sessile drop method as used by these workers was dynamic in the same sense as the maximum pressure method. Consequently, although the adsorption isotherm obtained by Karpartchev et al. is not coincident with Kemball's, it does not support the views of Bering and Ioileva unless individual measurements occupied a long time. Figure 1 shows the isotherms obtained by Kemball(1), Bering and Ioileva(2), and Karpartchev, Smirnov and Vorlchenkova(3). Some weight is lent to their argument by the work of Stage(7). Stage(7) employing the pendant drop method, where a fresh surface is provided for each measurement, studied the adsorption of the vapours of ethyl alcohol and n-heptane and the mixed vapour of the two compounds. She found that the adsorption of n-heptane was in agreement with that found by Kemball, but that the adsorption of ethyl alcohol was very much less, the adsorption isotherm was nevertheless convex. Kemball's criticism of Cassel and Salditt's results on the basis of a low value for the surface tension (459 dynes cm^{-1} at $50^{\circ}\text{C}.$) is also applicable here as the surface tension was only 461 dynes cm^{-1} at $30^{\circ}\text{C}.$

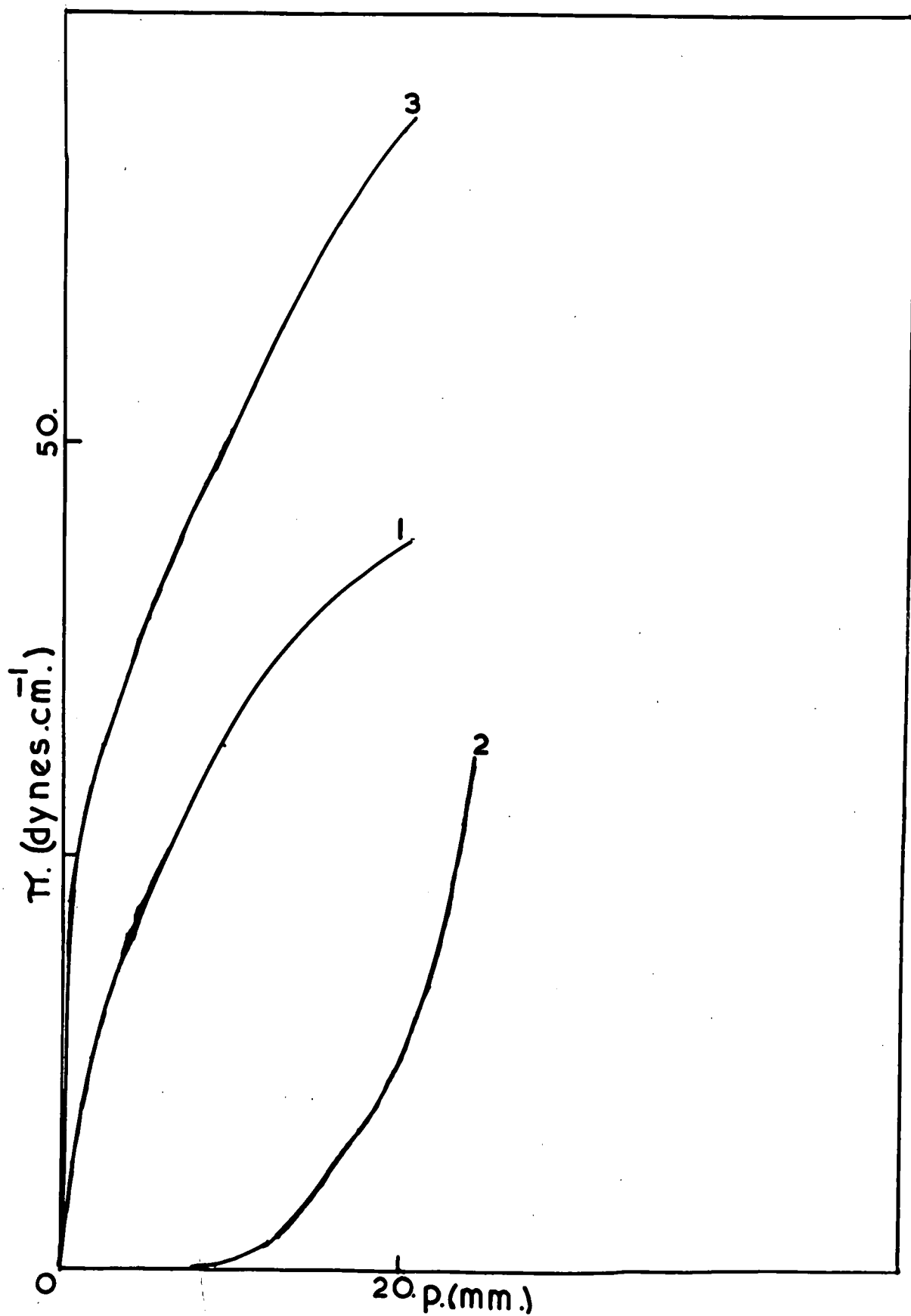


FIG.1

Bering and Ioileva found water and the lower alcohols underwent two-dimensional condensation, although in their first communication two years earlier this phenomenon went undetected.

Summary.

Summarising the literature on the adsorption of vapours on mercury, it is clear that only in the work of Kemball and Bering and Ioileva was the surface tension probably correct. All other workers reported much lower values.

Two broad types of isotherms have been observed, the initial part of the isotherm being either convex or concave to the surface pressure axis. This behaviour can be shown to correspond to either repulsion or attraction between the adsorbed molecules^(1,25).

Most workers have treated the adsorbed layer as a real two dimensional gas and applied equations of state analagous to those for three dimensional gases.

Kemball extended this treatment by defining the thickness of the surface layer and calculated the thermodynamic quantities standard free energy, entropy and total energy for the adsorption. Bering and Ioileva have adopted a refreshingly new approach by considering an equation of state based on the molecules behaving as nonlocalized,

identically oriented dipoles. This was applied to those substances whose isotherms indicated initially a predominance of repulsive forces in the adsorbed layer.

One puzzling feature of the equation is that it fits the convex isotherm reported by Kemball for methyl alcohol which Bering and Ioileva criticized. In fact B.P. Bering and V.V.Serpinsky⁽²⁶⁾ in an earlier paper employed Kemball's results for methyl alcohol in support of this equation of state.

SECTION I. SURFACE TENSION OF MERCURY.

INTRODUCTION.

The aim of this investigation was to study the effect of increasing the chain length of the saturated hydrocarbon molecule on the heat of adsorption and orientation of the molecule at a liquid mercury surface.

Surface tension measurements were used to follow the course of adsorption by calculation from the Gibbs adsorption isotherm. Naturally the first consideration was to ascertain the surface tension of pure mercury. Adam⁽¹⁾, Burdon⁽²⁾, and more recently, Kemball⁽³⁾ have summarised the large list of surface tensions obtained by different workers for mercury. Some values refer to the surface tension obtained in vacuo, others to the surface tension in air. In many cases the purity of the mercury is suspect, and often the method used to evaluate the tension was improperly understood. Adam⁽¹⁾ from the large mass of data suggested a value of 485 ± 5 dynes cm^{-1} at 20°C . Burdon⁽²⁾ placed the surface tension between 480 and 500 dynes cm^{-1} at ordinary temperatures. Kemball⁽³⁾ in his excellent work obtained a value of 484.0 dynes cm^{-1} at 25°C . with a claimed accuracy of $1/4\%$. For the

temperature coefficient of the surface tension he obtained a value of $0.20 \text{ dynes cm}^{-1}\text{deg}^{-1}$. He chose the "sessile drop" method to measure the surface tension.

Since 1946 several determinations of the surface tension of mercury have been reported, half of them agreeing with Kemball's value. S.V.Karpartchev, M.V.Smirov and Z.C.Vorlchenhova⁴, using the sessile drop method, obtained $477.4 \text{ dynes cm}^{-1}$ at 30°C . and the temperature coefficient averaged $\sim 0.4 \text{ dynes cm}^{-1}\text{deg}^{-1}$. M.Ziesing⁵ reported $483.6 \text{ dynes cm}^{-1}$, temperature coefficient $0.20 \text{ dynes cm}^{-1}\text{deg}^{-1}$. This value is that calculated from the Worthington equation for "sessile drops" (used by Kemball). However, as noted by the author independently of Ziesing, the error involved in the approximations made in deriving the equation is of the same order as the error in measurement. Ziesing calculated the former error and gave a corrected value of $484.9 \text{ dynes cm}^{-1}$ at 25°C . B.P.Bering and K.A.Ioileva⁶, using the method of the maximum pressure in drops, obtained $484.4 \text{ dynes cm}^{-1}$ and $485.8 \text{ dynes cm}^{-1}$ for different capillaries. The temperature coefficient was $0.20 \text{ dynes cm}^{-1}\text{deg}^{-1}$. Doris Stage⁷, applying the pendant drop method, reported a value of only $461 \text{ dynes cm}^{-1}$ at 30°C . No temperature coefficient is reported as measurements were made at only one temperature.

It seems likely therefore that, allowing for the error in the Worthington equation, the surface tension of mercury is close to $485 \text{ dynes cm}^{-1}$ and the temperature coefficient $0.20 \text{ dynes cm}^{-1} \text{ deg}^{-1}$. However, it is difficult to understand the lower values obtained by Karpartchev et al. and Stage. Stage cleaned the mercury by methods similar to Kemball and adopted the method introduced by Burdon of carrying out a cyclic distillation of the mercury in the apparatus before measurement. Likewise Karpartchev et al. followed this procedure; however no mention is made of their methods of purification. Kemball and Ziesing also used the method of cyclic distillation. B.P.Bering and K.A.Ioileva, however, made no mention of doing so and yet still obtained a value identical with Kemball and Ziesing.

From these considerations it appears that it is necessary to clean the mercury thoroughly before admitting it to the measuring apparatus, and it seems preferable to design the apparatus to allow the mercury to be distilled under high vacuum to remove any last traces of grease, moisture and oxide scum.

The method to be employed to measure the surface tension is fairly open. Both the sessile drop and the maximum pressure in drops method have yielded the same value. For the present investigation the "sessile drop"

method was chosen because it has a sounder theoretical basis and also avoids a contact angle, which appears desirable.

B.P.Bering and K.A.Ioileva, however, object to the sessile drop method because although it gives the correct surface tension, it has the disadvantage that the "big drop" is in contact with the vapours to be adsorbed for a long period - for the whole series of measurements - whereas the method of the maximum pressure in drops provides a fresh surface for each measurement and is in contact with the vapours for only 2-3 minutes.

Their objection is limited to the lower alcohols and water, which give convex adsorption isotherms by the sessile drop method and concave isotherms by the maximum pressure in drops method. Both n-heptane and acetone give similar results by both methods. It is, therefore, reasonable to assume that the other saturated hydrocarbons will also give similar results by both methods.

However, further work is necessary to substantiate their claim that only their results for water and the lower alcohols represent physical adsorption and that the much higher surface pressures found by Kemball are the result of the mercury being left in contact with the vapour for the whole series of measurements resulting in

either "activated" adsorption or impurities being displaced from the glass measuring vessel by the vapour. Karpartchev and his co-workers studied the adsorption of water by the sessile drop method and provided a fresh surface for each measurement. An adsorption isotherm similar (although not coincident) with Kemball's was obtained, i.e. convex. Therefore, unless individual measurements occupied more than a few minutes, the sessile drop as used by them was "dynamic" in the same sense as the maximum pressure in drops and Bering's argument is unsound.

Kemball also pointed out that the mercury during distillation acquires a high potential. Ziesing made some measure of the effect on the surface tension and found it could be lowered by over 10 dynes cm^{-1} . Perhaps Stage's low value may be partly due to this. No provision was made to earth the mercury in her apparatus.

Burdon's value of $484 \text{ dynes cm}^{-1}$, when corrected for the wedge angle of the window, suggests the surface tension was apparently unaffected by the fact that no provision was made for earthing the mercury. The only explanation is that he distilled the mercury slowly and it did not acquire an appreciable potential. The last important source of error is the wedge angle of the window through which the mercury drop is measured. For example, an

6.

angle of 0.38 degrees between the faces of a pyrex window can cause an apparent error on the high side, of 28 dynes cm^{-1} in the sessile drop method, when the diameter of the drop is 2.5 cms.

In summary it may be said that to obtain pure mercury which will give a correct measured surface tension, it is necessary

- (a) To clean the mercury thoroughly before admitting it to the measuring apparatus.
- (b) To carry out cyclic distillation of the mercury before measurement.
- (c) To make provision for earthing the mercury.
- (d) To allow for the wedge angle of the window through which the drop is measured, if the sessile drop method is used.

Further, as pointed out by Kemball, all grease taps and joints must be isolated from the measuring vessel by a liquid air trap. He showed that even high vacuum greases with very low vapour pressures lowered the surface tension.

THEORY OF SESSILE DROP METHOD

The sessile drop method for determining surface tension involves the measurement of the distance from the equator of a liquid pool to its vertex. Quincke⁽⁸⁾

originally proposed the formula

$$\gamma = 1/2 \rho g h^2 \quad \dots (1)$$

the surface tension being regarded as balancing the hydrostatic pressure of the liquid on the rectangular area of unit breadth and depth, h , (Figures 2 and 2a)

where γ = surface tension,

ρ = difference in density between liquid and surroundings,

g = acceleration due to gravity,

h = distance from equator to vertex.

Worthington⁹ pointed out that two important corrections are omitted in Quincke's formula. In the first instance the curvature at vertex of the pool can not be ignored. If b is the radius of curvature at the vertex, the pressure due to this curvature is $\frac{2\gamma h}{b}$ and, because the surface tension has to balance this as well as the hydrostatic pressure due to the weight of the liquid, the value of h will be less than that calculated from the simple formula.

Secondly, the curvature of the liquid pool in the horizontal plane means an added pressure inside the surface. This effect makes h larger than that calculated from the simple formula. Considering a vertical slab of liquid 1 cm. wide (Figures 2 and 2a) the surface tension exerted along each edge AE and DE¹

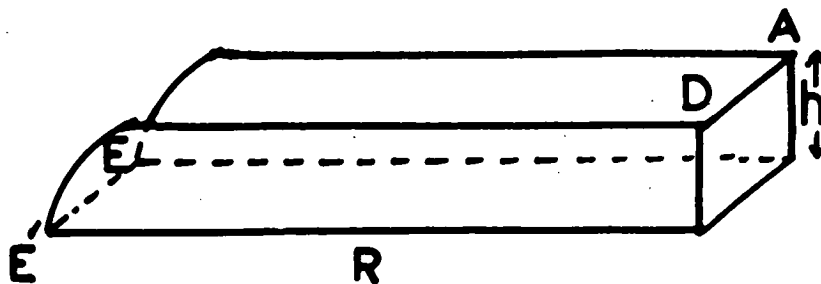


FIG.2.

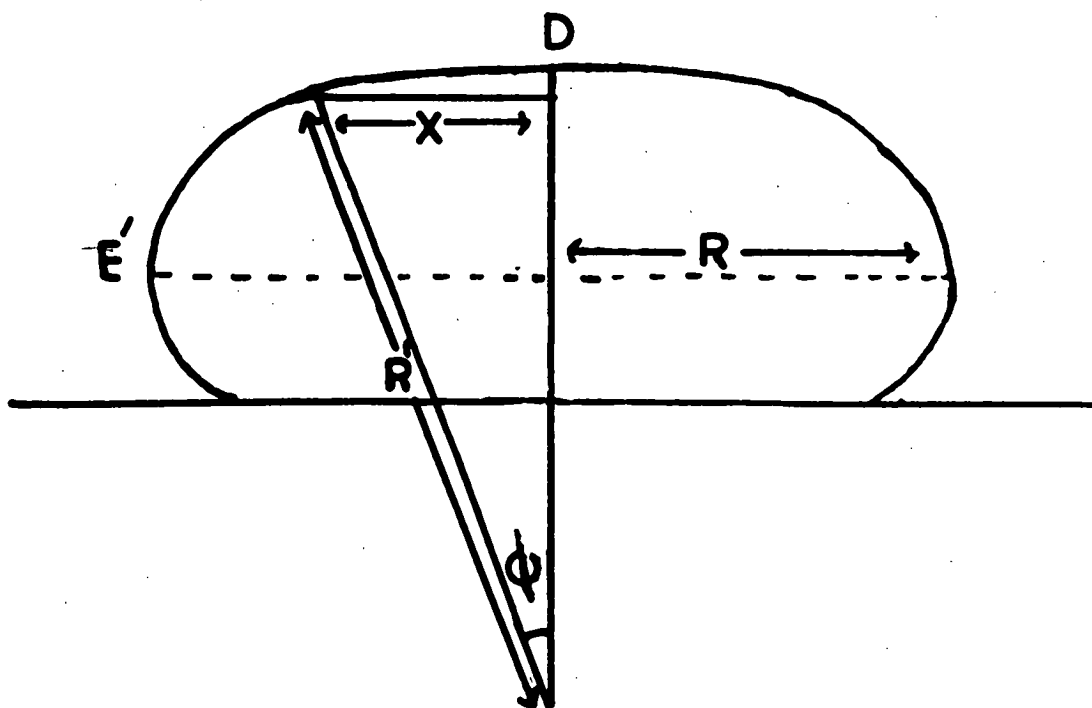


FIG.2a.

produces a pressure γ/R' on each unit area of the surface. Since the surface is one of revolution R' is length of the normal interrupted by the axis and writing ϕ for inclination of the normal to the axis measured on the side of the vertex, $1/R' = \frac{\sin \phi}{x}$ where x = horizontal radius of section. The pressure on the horizontal strip of the rectangular end of depth dz is $\frac{\gamma \sin \phi \cdot dz}{x}$. Therefore the total pressure of these forces on the area

ABCD is
$$\int_0^h \frac{\gamma \sin \phi}{x} \cdot dz.$$

Hence the corrected equation becomes

$$\gamma = 1/2 \rho g h^2 + \frac{2\gamma h}{b} - \gamma \int_0^h \frac{\sin \phi}{x} \cdot dz \quad \dots (2)$$

The value of the integral of the last term to a first approximation is shown by Laplace¹⁰ or Mathieu¹¹ to be

$$\frac{4a}{3} \cdot \frac{1 - \cos^3 \frac{\phi}{2}}{x} \quad \dots (3)$$

where $a = \sqrt{\frac{\gamma}{\rho g}}$

Worthington obtained an approximate value of a using Quincke's simple formula (Equation (1)) and he put $a = \frac{h}{\sqrt{2}}$.

When $x =$ maximum radius R , $\phi = 90^\circ$ the term reduces to

$$\gamma \cdot \frac{4a}{3R} \left(1 - \frac{1}{2\sqrt{2}}\right) = \frac{2\gamma h}{3.2817R} \quad \dots (4)$$

The corrected equation is then

$$\gamma = \frac{1}{2} \rho g h^2 + 2\gamma h \left(\frac{1}{b} - \frac{1}{3.2817R}\right) \quad \dots (5)$$

Since Worthington's time the term $2\gamma h/b$ has been neglected for drops whose radii are greater than 2 cms, and the resulting equation

$$\gamma = \frac{1}{2} \rho g h^2 \frac{1.641R}{1.641R + h} \quad \dots (6)$$

has become known as the "Worthington equation," although he gave his final equation as (5).

This equation (6) has been used by a large number of workers. Porter⁽¹²⁾ noted that the equation was reliable but estimated it was in error by 0.5% for drops over 4 cms. in diameter. However he did not make any accurate calculation of the error. Ziesing⁽⁵⁾ calculated the error accurately, and his argument is along the following lines.

Equation (6) is in error by approximately 0.2% because

of two approximations made in its derivation. The correct equation is equation (2) or in an equivalent form,

$$\gamma = \frac{1}{2} \rho g h^2 + 2\gamma h/b - \gamma \cdot \frac{4a}{3R} \left(1 - \frac{1}{2\sqrt{2}}\right) \quad \dots (7)$$

$$\text{where } a = \sqrt{\frac{\gamma}{\rho g}}$$

The first approximation was made by putting

$$a = \frac{h}{\sqrt{2}}$$

in the final term, and the second approximation was made by ignoring the term $2\gamma h/b$ where $R > 2\text{cms.}$

Both these introduce an error. For example, consider the results of Kemball⁽³⁾; he obtained $\gamma = 484.0$ dynes cm^{-1} . at 25°C. for mercury, using the "Worthington" equation. If γ is determined from equation (7) by putting $a = \sqrt{\frac{\gamma}{\rho g}}$, where γ is the value given by the Worthington equation and b is calculated according to Laplace⁽¹⁰⁾ or Mathieu⁽¹¹⁾ from

$$\frac{1}{b} = 2 \left(\sqrt{2a - \frac{3}{2}} \right) \left(\sqrt{\pi x} \right) \tan \phi/4 \exp. \left(-\frac{x}{a} - 4 \sin^{-2} \phi/4 \right)$$

which, when $x = R$ and $\phi = 90^\circ$, reduces to

$$\frac{1}{b} = (\sqrt{8\pi R/a^3}) 0.4142 \exp \left(-\frac{R}{a} + 0.5858 \right)$$

a value of 485.1 dynes cm^{-1} is obtained.

For a drop 5 cms. in diameter, which was used for the determination $\frac{1}{b} = 0.0002$, the surface tension calculated from Equation (7) is

$$\begin{aligned} \gamma &= 516.85 + 0.14 - 31.86 \\ &= 485.1 \text{ dynes cm}^{-1}. \end{aligned}$$

Therefore, using the "Worthington Equation" an absolute error of 1.1 dynes cm^{-1} is introduced, which is of the same magnitude as the accuracy claimed for the determination, 1.5 dynes cm^{-1} .

The exact correction for the size of the drop used in this investigation will be considered with the experimental results.

APPARATUS.

The apparatus was similar to Kemball's⁽³⁾ modification of Burdon's⁽¹³⁾ apparatus. Figures 3, 4 and 5 show the general layout. Figures 6 and 7 show a close-up of the measuring vessel and mercury still, between which cyclic distillation was carried out.

A mercury diffusion pump (an oil diffusion pump was avoided because of the risk of contaminating the mercury) backed by an Edwards Speedivac 2S20 rotary vacuum pump provided a vacuum of 10^{-5} mm.Hg. (McLeod gauge). A Pirani vacuum gauge was also incorporated in the system to indicate the presence of any condensable vapours. Exhaust fumes from the pump were passed outside the room.

None of the "pyrex" glass used in constructing the apparatus was "cleaned." The attitude was taken that "cleaning" methods could introduce impurities to the surface of the glass which in turn could contaminate the mercury. Mercury has such a high surface energy that it can easily be affected by impurities adsorbed on the glass surface. The central sections of the glass tubes (as they came from the factory were used and the remainder discarded. It seems the main impurity which is present is water vapour.

The measuring vessel was isolated from all grease taps and joints by a liquid nitrogen trap. Between the

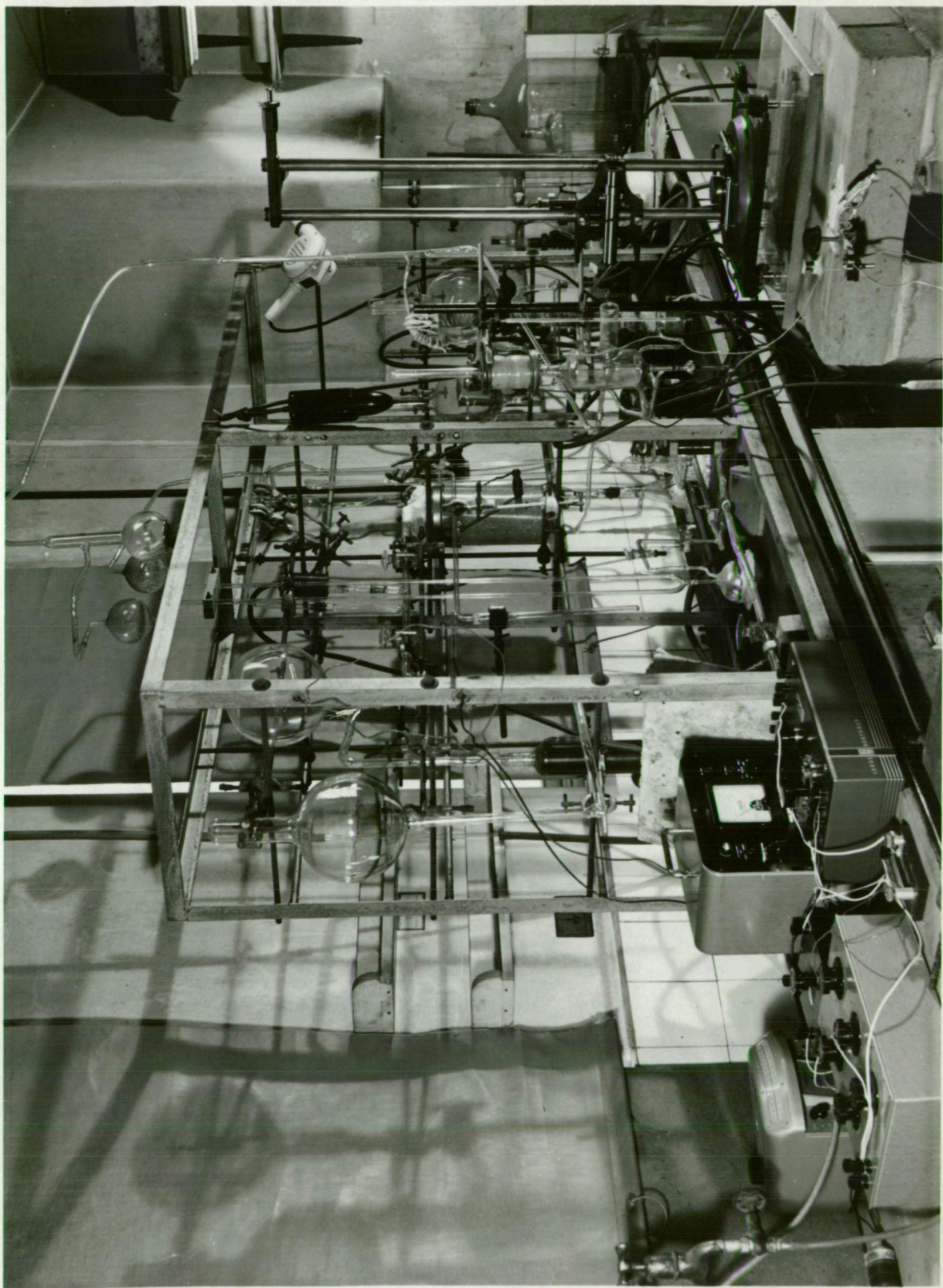


FIG.3

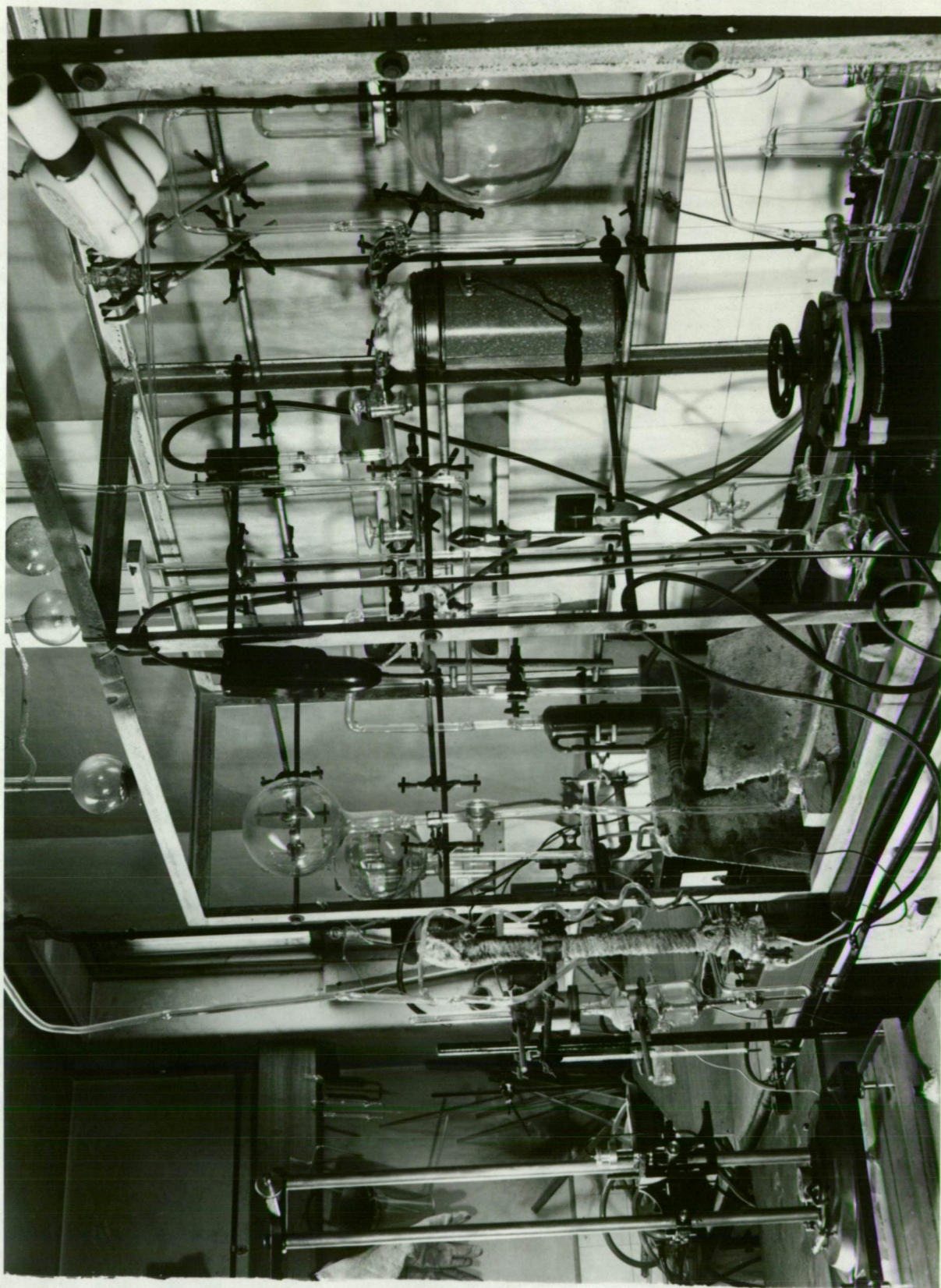


FIG.4

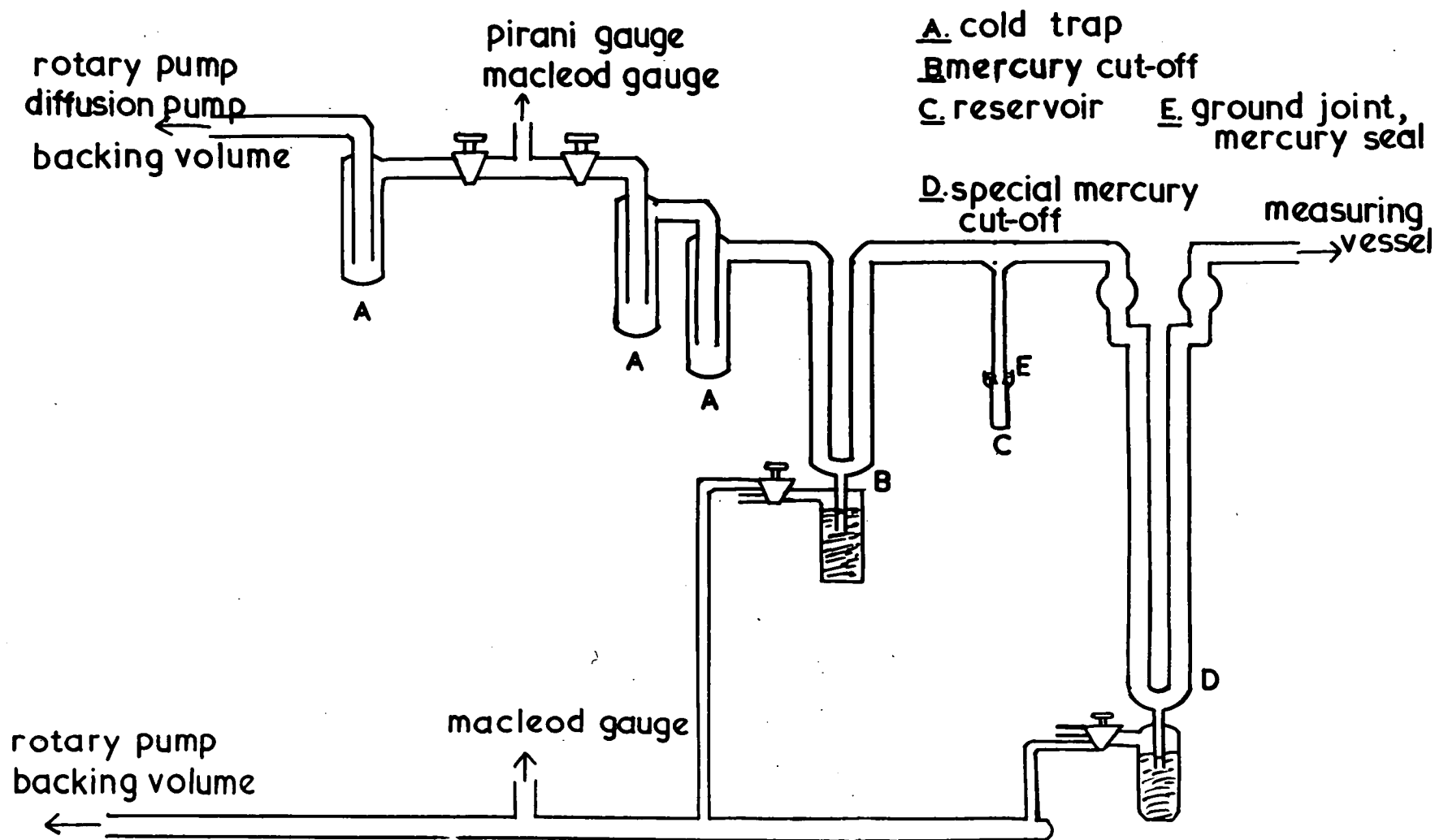


FIG. 5

liquid nitrogen trap and the measuring vessel mercury cut-offs replaced the usual grease taps.

Measuring Vessel.

Figures 6 and 7 show how the mercury was distilled from the still B up the lagged column C via the U-tube D to the cup A, which held the sessile drop. Mercury after spilling from the cup A returned to the still. To locate the vertex of the sessile drop, a tungsten pointer, embedded in a glass envelope containing a piece of soft iron and supported from the top of tube E by a tungsten spring, was operated by a solenoid F. Coincidence of the pointer and its image located the vertex. It was found necessary to darken the room and to throw a beam of light on to a white background behind and above the drop in order to obtain a clear image.

The equator was located by placing a small galvanometer light 1.7 metres from the equator of the drop and on the same level. By astigmatic reflection two images due to the different radii of curvature at the equator can be observed. The horizontal line image in front of the vertical line image gives the plane of the equator.

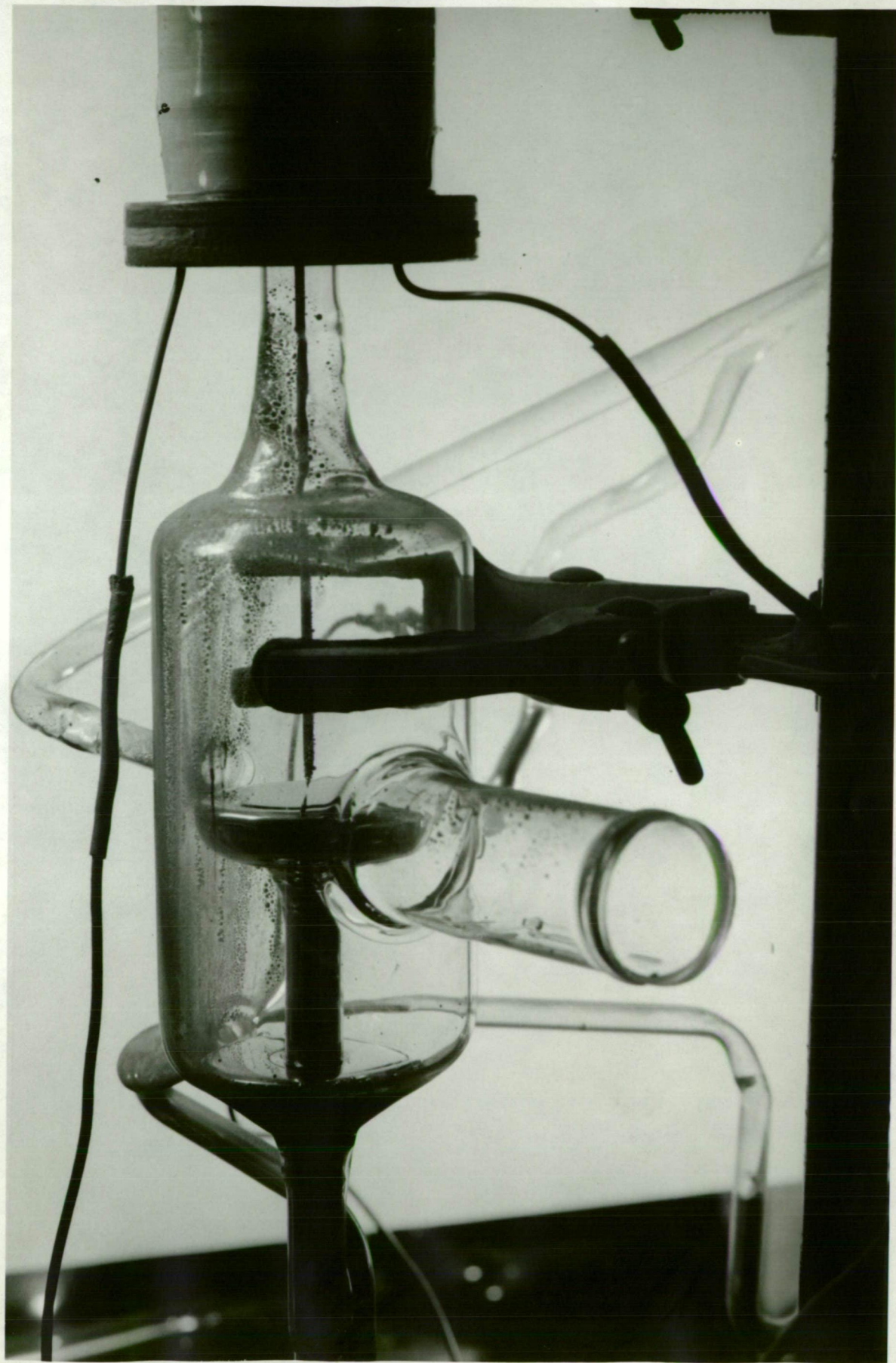


FIG. 6

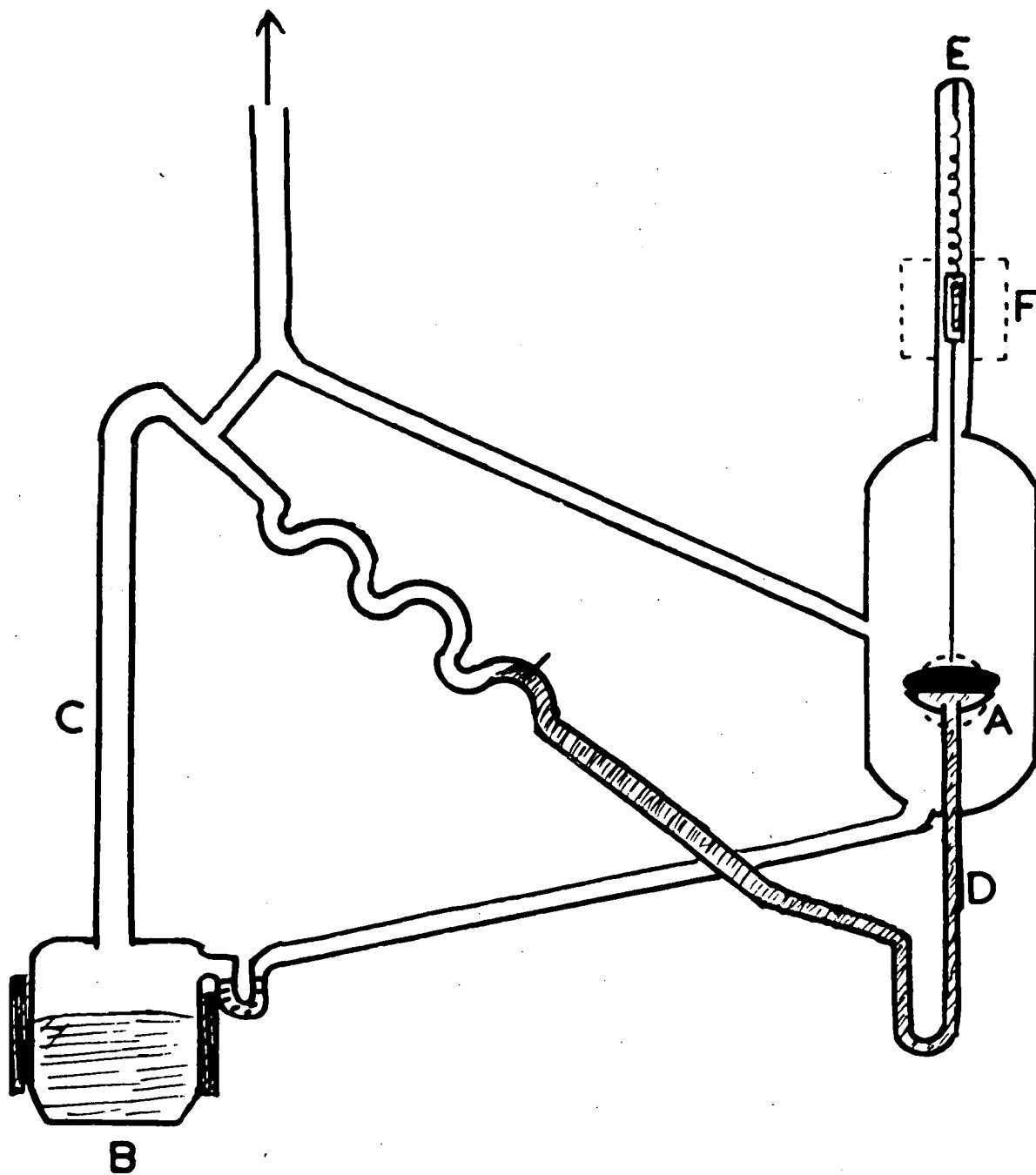


FIG. 7.

firm stand attached to a concrete block pillar cemented to the concrete floor. A level surface along which to move the cathetometer was provided by a 15"x 15"x $\frac{3}{4}$ " glass plate of requisite flatness. Three $1\frac{1}{4}$ " x $\frac{1}{2}$ " bolts were cemented to the top of the pillar and allowed to set overnight. The nuts were then placed on the bolts and adjusted to level the glass plate. A slow setting plaster was then smeared around the bolts, nuts and glass plate. With the cathetometer on top the plate was levelled over a period of 1 hour and then the plaster was allowed to set. A Watts 8" Precision square block level was used to check the plate level. The level could be read to within $\frac{1}{4000}$ " in 10", i.e. there was an uncertainty of 0.0004 cm. in 15 cm.

Glass Window.

The main difficulty in construction of the "pyrex" apparatus was the attaching of the glass window to the vessel in which the sessile drop was formed. An attempt was made to affix the window by means of a rubber ring seal. Several glass plates with circular grooves of rectangular cross-section were prepared by a local optical firm. "Edwards" "O" section rubber cord was the sealing ring. Seals of this type are meant to allow the surfaces to meet and the rubber ring under compression then provides a vacuum seal. After many trials it was found impossible

to obtain a high vacuum. A closer look at the literature revealed that rectangular grooves do not allow sufficient compression of the "O" section ring where the surfaces are mating. Trapezium section grooves are usually recommended for high vacuum work. Unfortunately, a tool capable of cutting such a groove to the required tolerance was not available and this approach had to be abandoned.

Some workers have used waxes to seal on the window. There is, however, always the danger of contamination from such substances. Silver chloride was tried because there appears little chance of contamination with an inorganic substance. While these tests were going on a "pyrex" window was successfully fused on to the apparatus. No pyrex plate was available and the window was cut from a commercial "Pyrex" baking dish. It was found to be free from strain. The faces were ground optically flat with an angle between them of less than 10 secs. The window was 30 mm. in diameter and 6.5 mm. thick. After the window was fused on the faces were found to be optically flat over the central 9 mm. and the wedge angle was 15 secs. as measured with a Hilger-Watts Auto-Collimator.

A tube packed with calcium chloride, soda-lime and cotton wool was connected to the air inlet tap near the rotary vacuum pump. This insured that reasonably pure air was admitted to the apparatus. A special mercury

cut-off capable of withstanding a pressure difference of an atmosphere between the two sides and designed by Kemball³ was placed between the measuring vessel and the remainder of the system in order that no air would be admitted to the mercury once it had been purified by cyclic distillation.

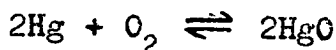
In the possible event of a serious variation in the water pressure, a safety switch was incorporated which turned off both the mercury diffusion pump and the mercury still at very low water pressures. It was necessary to turn the mercury still off because any increase in oxygen pressure above approximately 10^{-4} mm. favours the formation of oxide on boiling mercury¹⁵.

PURIFICATION OF MERCURY.

The mercury was freed from readily oxidisable metals and other impurities by sucking air through it in the presence of concentrated sulphuric acid and ferrous sulphate. After several hours of this treatment, it was washed with water, dried, and then filtered to remove any oxide scum. Two R.B. "Pyrex" flasks were fused via an air condenser to each other and then to the mercury still. With the mercury in the end flask and the system evacuated to 10^{-5} mm., distillation was begun. Most of the mercury was distilled into the middle flask and then in turn to the mercury still. When the vessels were cool the mercury was sealed off in the latter vessel.

Continuous cyclic distillation for several weeks removed the last traces of grease and oxide. The possibility of oxide forming on the mercury surface needs attention. On the assumption that the bulk phase and surface phase of mercury behave in an identical manner, it is possible from the data of Taylor and Hulett⁽¹⁵⁾ to calculate the critical pressure of oxygen at various temperatures required for the formation of mercuric oxide.

These workers studied the equilibrium between mercury, oxygen and mercuric oxide at high temperatures and determined the heat of reaction



From this quantity they calculated the dissociation pressure of mercuric oxide at other temperatures. The table below shows their calculations for the range of temperature encountered under the present experimental conditions. From their results and the vapour pressure of mercury the critical pressure of oxygen was determined from the relation

$$p_{O_2} \cdot p_{Hg}^2 = K_p$$

Temp. °C.	Dissociation pressure of mercuric oxide K_p (mm)	Vapour pressure of mercury (mm)	Critical pressure of oxygen for oxide formation (mm)
25	1.9×10^{-8}	4.14×10^{-3}	1.11×10^{-3}
200	0.1	17.3	3.34×10^{-4}
400	231	1574	9.34×10^{-5}

Since the mercury in the still boiled at approximately 200°C., a partial pressure of oxygen of less than 10^{-4} mm. would favour the decomposition of any oxide.

Also it can be seen that at 25°C. a partial pressure of oxygen less than 10^{-3} is necessary to prevent any oxide formation; of course the rate of formation at room temperature is very much less than that at the boiling point.

The vacuum attained in the system was of the order

The vacuum attained in the system was of the order of 10^{-5} mm. Therefore, providing the surface behaves as the bulk, all oxide would be decomposed at the temperature of boiling mercury. When the still was not operating the special mercury cut-off was raised with a vacuum of 10^{-5} mm. in the measuring vessel and the air admitted to the remainder of the glass apparatus. Even if subsequently the partial pressure of oxygen increased above 10^{-3} mm., the rate of formation of oxide would be very slow at the lower temperature. No surface scum was ever observed on the mercury once it had been purified by cyclic distillation.

To prevent condensation of mercury on the glass window, a heater was placed under it while distillation was carried out. A tungsten wire was sealed under the apparatus to earth the mercury. In earlier experiments no earthing was provided. Lower surface tensions were observed when the mercury was not earthed.

The lowering of the surface tension was found to depend on the rate at which the mercury was distilled. Brilliant flashes of green light were observed in the dark while the mercury was being distilled which indicated that the mercury attained a high potential on distillation, sufficient to ionise the mercury vapour. A "Pye" cathetometer was the measuring instrument with divisions to

0.0005 cms. It was checked over a small range of 0.8 mm. by comparison with a "John Bull" 4" dial gauge with divisions of 0.0002 mm. Dial gauges are very accurate over a small range, but cannot be used over the distance of approximately 3 mm. necessary in this investigation. The cathetometer was found to be reliable to 0.0002 mm. over 0.8 mm. Over larger distances the dial gauge read up to 0.0008 mm. too low, e.g. with the screw reading 0.2800 cms. the dial gauge showed 0.2792 cms. Since the screw was in perfect order, readings could most probably be relied upon to 0.0002 mm. over the length of the screw.

The telescope accompanying the cathetometer had a working distance of 4 cms. This presented serious working difficulties with the necessity of sealing the thick glass window directly on to the measuring vessel. Fortunately it was possible to obtain another eyepiece lens which gave the telescope a working distance of 14 cms., allowing the window to be fused on to a glass tube and then on to the vessel.

EXPERIMENTAL RESULTS.Size of Drop.

To ascertain the surface tension it is necessary to know the diameter of the mercury pool and the distance from the equator to the vertex. Since the surface tension depends only slightly on the diameter, it is not necessary to know it very accurately. The diameter of the mercury formed by the cup, 4.49 ± 0.01 cms., was measured before the cup was sealed into the apparatus.

Correction for Wedge Angle of Window.

The angle between the faces of the window was 15 secs., and this angle produced a slight increase in the quantity, h , the distance from vertex to equator when viewed through the window. Kemball⁽³⁾ was the first to consider this source of error. It must be remembered that the vertex and equator do not lie in a plane parallel to the window. The distance between them is the radius of the pool. For two points lying in a plane approximately parallel to the window there is negligible change in the distance between them when viewed through a window of small wedge angle. However, the distance between two points not in the same plane appears appreciably greater.

In Figure 8 the displacement of the point O when viewed through the wedge of small angle θ radians is considered. Let the refractive index of the glass be μ .

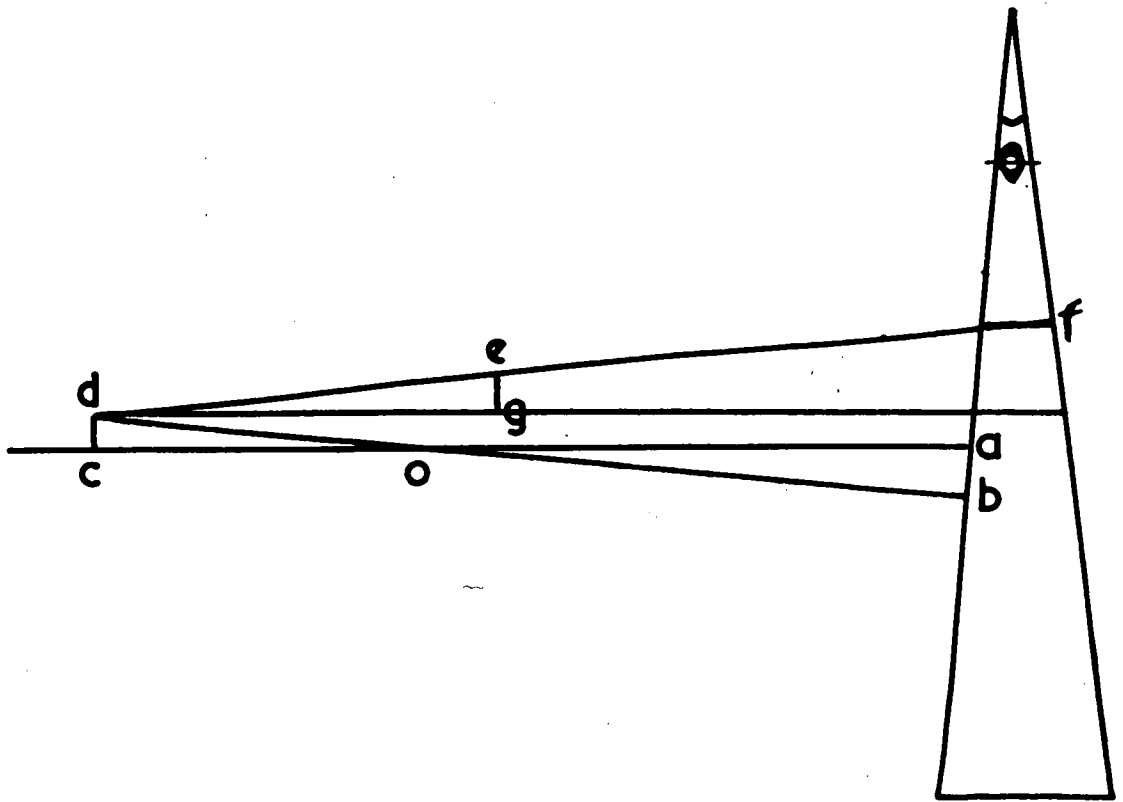


FIG. 8.

For refraction at a plane surface, the equation

$$\mu_2/v - \mu_1/u = 0 \quad \dots (1)$$

relates the distances of the object, u , with the distance of the image, v , and the refractive indices of the two media μ_1 and μ_2 . The image will lie on the line through the object perpendicular to the surface of the refracting medium.

In Figure 8 let $OA = d$.

After refraction at the first surface of the wedge, O will form an image at D where DOB is perpendicular to the front surface of the wedge.

$$\text{Now } \hat{BOA} = \frac{\theta}{2}$$

$$\text{and } \mu/DB = \frac{1}{OB}$$

$$\therefore \frac{OD}{OB} = \frac{\mu - 1}{1} = \frac{CO}{OA}$$

$$\therefore DC = OC \tan \frac{\theta}{2} = (\mu - 1) \cdot \frac{d\theta}{2}$$

Similarly after refraction at the second surface, D will give an image at E on the line DEF perpendicular to the second surface.

Let thickness of wedge at F be t_1 cms.,

$$\text{then } EG = (\mu - 1)(d + t_1) \cdot \frac{\theta}{2}$$

and total vertical displacement = $CD + EG = \mu(\mu - 1)(d + t_1/2)$

Similarly the vertical displacement of an object at a distance $d + S$ will be

$$\theta(\mu - 1)(d + S + t_2/2)$$

where t_2 is the thickness of the wedge at the appropriate point.

\therefore the apparent vertical distance between the two images is

$$\theta(\mu - 1)\left(S + \frac{t_2 - t_1}{2}\right)$$

For the wedge angle and size of drop encountered here,

$$t_2 - t_1 \ll S$$

\therefore error in h is $(\mu - 1) \theta R$

where R is the radius of the drop.

This height must be subtracted from the observed height to give true height. The theory of this correction was checked by Kemball and found to be sound.

In the present instance the distance moved by the cathetometer was not exactly the radius of the drop. The distance between readings which is S in the above argument was 2.55 cms. (which meant the pointer was 3 mm. off-centre) therefore the quantity to be subtracted from the observed height is

$$\begin{aligned} & \theta(\mu - 1) S \\ &= \frac{(0.25)(\pi)}{(60)(180)} (1.473 - 1) 2.55 \\ &= 0.0001 \text{ cms.} \end{aligned}$$

where θ is expressed in radians.

Level of Glass Plate.

It was mentioned previously that the level of the glass plate could be determined to within 0.0004 cms. over 15 cms. After the plaster had set it was found that the glass plate was slightly off level from front to back but level from side to side. This meant a correction had to be made to the observed height, h . The front of the plate was higher than the rear; the error in its level being 0.0011 cms. over 15 cms., which meant that when the cathetometer was shifted between readings 2.55 cms. it moved a vertical distance of 0.0002 cms. This quantity must, therefore, be added to the observed reading of h .

Position of Pointer.

Since the diameter of the mercury pool was 4.49 ± 0.01 cms. and the distance between the readings i.e. from the equator to the position of the pointer, was 2.55 cms., the pointer was 3 mm. off centre. However, it can be shown that there is no significant difference in height between the vertex and a point 3 mm. from it. Along with Kemball³ the difference in height has been considered as due to the sum of the two quantities

(a) the curvature of the drop at its vertex,

(b) the changing curvature of the drop from a minimum at the vertex to a maximum at the equator.

The effect of (a) and (b) is to lower a point 3 mm. from

the vertex by less than 10^{-5} cms. Since it was not possible to measure less than 10^{-4} cms. with the cathetometer screw, the correction may be ignored.

Temperature Control.

The design of the apparatus made it difficult to build a constant temperature oven around it. Fortunately the position of the room in the basement of the building made it relatively easy to maintain the room temperature within 0.2°C . of 25.0°C . during the summer using the existing heaters in the room, and when necessary a fan with a heating coil in front of it. At the lower temperature 16.5°C . measurements were made at night in the winter using the fan and heating coil. Again temperature control of the room was excellent, variations never exceeding 0.2°C .

Maintaining the room at temperature made it unnecessary to warm the remainder of the apparatus when making adsorption measurements at temperatures above day temperature. Other workers have wound the glass apparatus not in the constant temperature oven with a heating wire in order to prevent condensation of vapour near the saturation point.

Earlier views^{3,5} that mercury acquires on distillation a considerable potential, which lowers the surface tension, were confirmed. For example, with the rate of distillation used throughout the investigation, the effect was:

Temperature 25°C.	h (uncorrected)	h (corrected)	Surface tension (from Worthington Equation)
Unearthed drop	0.2786	0.2787	478.9
Earthed drop	0.2800	0.2801	483.8

Readings of the height, h , are the average of upward of four measurements.

Surface Tension of Mercury.

In Tables 1 and 2 the measurements of the surface tension of mercury at 25°C. and 16.5°C. are given. The observed height, h , is subject to two corrections, the wedge angle of window (-0.0001 cms.) and the error in the level of the glass plate (+0.0002 cms.); a total positive correction of +0.0001 cms. The uncorrected surface tension is that calculated from the Worthington equation, the corrected surface tension allows for the error in this equation. For the density of mercury at 25°C. the value given by Kemball⁽³⁾ has been used, at 16.5°C. that given by Karparchev et al⁽⁴⁾. The value of the gravitational constant, z , 980.45 cms. sec.⁻² is that determined for Hobart by the Geology Department of this University. Each value of h is the mean of at least four readings.

Temperature $25 \pm 0.2^{\circ}\text{C}$. $g = 980.45 \text{ cms. sec}^{-2}$ $R = 2.25 \pm 0.01 \text{ cms.}$ $\rho = 13.534 \text{ g. cm}^{-3}$

Date	h (uncorrected) cms.	h (corrected) cms.	γ (Worthington Equation dynes cm^{-1})
<u>1958</u>			
24th Sept.	0.2800	0.2801	483.8
21st Oct.	0.2800	0.2801	483.8
22nd "	0.2798	0.2799	483.1
28th "	0.2802	0.2803	484.5
29th "	0.2800	0.2801	483.8
7th Nov.	0.2802	0.2803	484.5
18th Nov.	0.2803	0.2804	484.8
27th Nov.	0.2802	0.2803	484.5
28th "	0.2798	0.2799	483.1
4th Dec.	0.2799	0.2800	483.5
10th "	0.2802	0.2803	484.5
<u>1959.</u>			
17th Feb.	0.2800	0.2801	483.8
24th "	0.2800	0.2801	483.8
6th Mar.	0.2799	0.2800	483.5
13th "	0.2798	0.2799	483.1
14th April	0.2800	0.2801	483.8
22nd "	0.2799	0.2800	483.5
29th "	0.2800	0.2801	483.8
19th June	0.2799	0.2800	483.5

 γ (Worthington Equation) = 483.8 ± 0.4 (mean deviation) dynes cm^{-1} . γ (corrected) = 485.4 ± 0.4 dynes cm^{-1} .

Temperature $16.5 \pm 0.2^{\circ}\text{C}.$

$R = 2.25 \pm 0.01\text{cm}.$

$g = 980.45 \text{ cms. se}^{-1}$

$\rho = 13.560 \text{ gms.cm}^{-3}$

Date 1959	h (uncorrected) cms.	h (corrected) cms.	γ Worthington Equation
5th May	0.2804	0.2805	485.8
12th May	0.2804	0.2805	485.8
26th May	0.2803	0.2804	485.5
29th May	0.2802	0.2803	485.2
5th June	0.2803	0.2804	485.5

γ (Worthington Equation) = $485.6 \pm 0.2 \text{ dynes cm}^{-1}$.(mean deviation)

γ (corrected) = $487.3 \pm 0.2 \text{ dynes cm}^{-1}$.

The corrected surface tensions were determined as follows:

The value of $\frac{1}{b}$ is 0.00050 and the value of $a = \sqrt{\frac{\gamma}{\rho g}}$ is 0.19100 at 25°C. and 0.19112 at 16.5°C.

Substituting these figures in the correct equation

$$\gamma = \frac{1}{2} \rho g h^2 + \frac{2\gamma h}{b} - \frac{\gamma 4a}{3R} \left(1 - \frac{1}{2\sqrt{2}}\right)$$

at 25°C.

$$\begin{aligned}\gamma &= 520.7 + 0.1 - 35.4 \\ &= 485.4 \text{ dynes cm}^{-1}.\end{aligned}$$

And at 16.5°C.,

$$\begin{aligned}\gamma &= 522.7 + 0.1 - 35.5 \\ &= 487.3 \text{ dynes cm}^{-1}.\end{aligned}$$

Both the surface tension values are also subject to uncertainties in the radius of the drop ± 0.01 cm., in the reading of the level of the glass plate 0.0004 cm. over 15 cms. and the setting of the lamp used to define the equator of the drop. These are summarised in the following Table.

Uncertainty in:	Magnitude	Error in h cms.	Error in γ dynes cm ⁻¹
Setting lamp to define equation	0.25 cm.	0.0001	0.3
Reading level of glass plate	0.0004 cm. in 15 cms.	0.0001	0.3
Measuring radius of drop	0.01 cms.		0.2
Reading h, (mean deviation)			0.4 (25°C.)
			0.2 (16.5°C.)

$$\text{Total error} = \frac{1.2 \text{ dynes cm}^{-1} (25^{\circ}\text{C.})}{1.0 \text{ dynes cm}^{-1} (16.5^{\circ}\text{C.})}$$

Therefore the corrected surface tensions are

$$\text{at } 25^{\circ}\text{C.} \quad \gamma = 485.4 \pm 1.2 \text{ dynes cm}^{-1}.$$

$$\text{at } 16.5^{\circ}\text{C.} \quad \gamma = 487.3 \pm 1.0 \text{ dynes cm}^{-1}.$$

The temperature coefficient is 0.22 ± 0.05 dynes cm⁻¹deg⁻¹. This value is of somewhat limited accuracy because of the small range of temperature; however, it is in agreement with the generally accepted value of 0.20 dynes cm⁻¹deg⁻¹. In the following table the surface tension determinations of Kemball⁽³⁾, Ziesing⁽⁵⁾ and Bering and Ioileva⁽⁶⁾ are given for comparison. The results of Kemball have been corrected for the error in the Worthington equation.

	Method for determining γ .	Nature of apparatus.	γ at 25°C. dynes cm ⁻¹ .
Kemball ⁽³⁾	Sessile drop	Borosilicate glass	485.1 \pm 1.5
Ziesing ⁽⁵⁾	Sessile drop	Silica	484.9 \pm 1.8
Bering and Ioileva ⁽⁶⁾	Maximum pressure in drops	Glass, type not stated	484.4 \pm 0.8 485.8 \pm 0.8
Roberts	Sessile drop	Borosilicate glass	485.4 \pm 1.2

The similarity of results in borosilicate glass and silica suggest that Burdon's⁽¹³⁾ fear that alkali from the former might contaminate the mercury was unfounded.

SECTION II. THE ADSORPTION OF SOME HYDROCARBONS
ON MERCURY.

THEORY.

Both the approach of Bering and Ioileva⁽²⁴⁾ and Kemball⁽²³⁾ will be used to analyse the results of this investigation.

Kemball⁽²³⁾ defined a standard state on the surface by considering the surface phase at such a concentration that the molecules could be assumed an ideal two dimensional gas. The surface layer was assumed to have a thickness of 6.0 Å and the two dimensional surface pressure was then converted to a three dimensional pressure and the standard state taken as one atmosphere^x. The standard free energy change on adsorption is then given by

$$\Delta F = -RT \ln \frac{p_0}{p}$$

where p refers to bulk phase and is the pressure of vapour molecules in equilibrium with surface molecules in standard state, and p_0 refers to the surface molecules

^x Harter Ryder and Williamson⁽²⁷⁾ have proposed another definition for the standard state on the surface.

with an equivalent three dimensional pressure of 1 atmosphere.

This relationship when combined with the Gibbs equation

$$\Gamma = \frac{1}{RT} \left(\frac{d\pi}{d \ln p} \right)_T \quad \dots (2)$$

where π = surface pressure,

Γ = excess surface concentration,

leads to

$$\Delta F = -RT \ln 12,500 \left(\frac{d\pi}{dp} \right)_T \quad \dots (3)$$

with p measured in mm. of mercury, the surface thickness as 6 \AA and Γ in the appropriate units.

This equation holds when adsorbed molecules behave as an ideal gas and therefore the initial value of

$\left(\frac{d\pi}{dp} \right)_T$ is required.

The method of introducing an arbitrary surface thickness is equivalent to defining the standard state on the surface as a given area per molecule dependent only on the temperature. This is similar in definition to the standard state of an ideal gas, 1 atmosphere, where all molecules are assumed to occupy the same volume dependent only on the temperature, e.g. at 0°C . 1 g. molecule occupies 22.4 litres, or for an ideal gas at $T^\circ\text{K}$ the

the volume occupied by a molecule is

$$v = 135.2 \text{ \AA}^3.$$

For an ideal gas in two dimensions with a thickness of 6 \AA the area per molecule is

$$A = 22.53 \text{ \AA}^2.$$

At such concentrations the ideal relation

$$\pi A = kT \quad \dots (4)$$

holds, and therefore the standard surface pressure is

$$\pi = 0.06084 \text{ dyne cm}^{-1}.$$

This means of defining the standard state is independent of temperature in the same manner as the standard pressure of 1 atmosphere is independent of temperature.

Since the isotherms are not linear even at the lowest surface pressures and because at these low pressures the relative error in measuring π is greatest, a graphical method of estimating initial slope would be only approximate. A method based on estimating $d\pi/dp$ from the curve as a whole is possible by combining the Gibbs equation (2) with an equation of state for the adsorbed molecules.

The total energy of adsorption can be determined from the Gibbs Helmholtz equation

$$\Delta F = \Delta H + T \left(\frac{d \Delta F}{dT} \right)_p \quad \dots (5)$$

and the entropy change on adsorption from the relation

$$\Delta F = \Delta H - T\Delta S \quad \dots (6)$$

It should be emphasised that the free energy and entropy of adsorption depend on the value assumed for thickness of the surface layer, since Equation (3) is of the form

$$\Delta F = -RT \ln \frac{B}{\delta} \left(\frac{d\pi}{dp} \right)_T \quad \dots (7)$$

where δ is the thickness of the surface layer,

and B is a constant,

whereas the total energy of adsorption is independent of δ because from Equations (7) and (9)

$$\Delta H = RT^2 \left(\frac{d \ln(d\pi/dp)_T}{dT} \right)_p \quad \dots (8)$$

Kemball found that the Volmer equation expressed the behaviour of the surface molecules over a wide range of surface pressures.

$$\pi(A - b) = kT \quad \dots (9)$$

where A is the area per molecule,

b is a co-area (assumed to be the actual area of a molecule, not twice the area as predicted by the simple theory).

This equation is analagous to that for a real gas where repulsive force between the molecules is far more important than the force of attraction.

Combination of Equation (9) with the Gibbs Equation (2) gives

$$\ln p = \ln \pi + \frac{b\pi}{kT} + c \quad \dots (10)$$

where b and c are constants.

Writing (12) in the form

$$p = \pi \cdot e^{(b\pi/kT) + c}$$

$$\left(\frac{dp}{d\pi}\right)_T = \left(\frac{b\pi}{kT} + 1\right) \cdot e^{(b\pi/kT) + c}$$

therefore

$$\left(\frac{db}{d\pi}\right)_T = e^c$$

$\pi \rightarrow 0$

or

$$\left(\frac{d\pi}{dp}\right)_T = e^{-c} \quad \dots (11)$$

$\pi \rightarrow 0$

The constant c is some measure of the free energy of adsorption.

Equation (10) may be tested by plotting $\log p/\pi$ against π and should give a straight line of slope $b/2.303 kT$ and an intercept c .

Equation (3) may now be rewritten

$$\begin{aligned} \Delta F &= -RT \ln 12500 \left(\frac{d\pi}{dp}\right)_T \\ &= 2.303 RT \log 12500 \times 10^{-c} \\ &= 2.303 RT(4.0969 - c) \quad \dots (12) \end{aligned}$$

Also Equation (8) may be transformed

$$\begin{aligned}\Delta H &= RT^2 \left(\frac{d \ln(d\pi/dp)_T}{dT} \right)_p \\ &= 2.303 RT^2 \left(\frac{dc}{dt} \right)_p \quad \dots (13)\end{aligned}$$

The entropy change may be determined from the relation (6).

The equation of state used by Bering and Ioileva⁽²⁴⁾ was derived by Bering and Serpinsky⁽²⁶⁾. It was applied to isotherms whose initial part was convex, indicating that repulsion was the important force between the molecules.

In this approach the adsorbed molecules are considered to behave as similarly oriented dipoles and the virial equation of state is applied to a network of such dipoles. For a two-dimensional adsorbed layer, the virial equation for a non-localised layer is

$$\pi = k T \rho + 0.5 \rho^2 \sum r f(r) \quad \dots (14)$$

where $f(r)$ is the interaction force between two molecules found at a distance r from one another and the summation is carried out for all pairs of molecules.

In the case of isotherms which indicate a repulsion between the molecules, it is reasonable to consider the repulsion as due to the molecules behaving as similarly oriented dipoles. Forces of this type decrease with distance significantly more slowly than other molecular forces, and moreover, when the surface is only partially covered it is possible as a first approximation to limit one's consideration to such forces.

Therefore the function $f(r)$ may be written

$$f(r) = 2\bar{\mu}_e^2 / r^4$$

where $\bar{\mu}_e$ is the effective dipole moment of a molecule

oriented normally to the adsorbed surface and is the sum of the permanent and induced dipole moments in the direction of the field. Topping⁽²⁸⁾ has calculated the virial term $0.5 \int \sum r f(r)$ for a network of dipoles in various modes of packing, and shown that in each case it is equal to

$$4.5 \mu_e^2 \Gamma^{5/2}$$

and therefore the equation of state assumes the form

$$\pi = kT\Gamma + 4.5 \mu_e^2 \Gamma^{5/2} \quad \dots (15)$$

Combination of this equation and the Gibbs Equation (2) leads to the following equation for the adsorption isotherm

$$\ln \Gamma/p = \ln H - \frac{7.5}{kT} \mu_e^2 \Gamma^{3/2} \quad \dots (16)$$

where H is the integration constant.

The equation for the surface-pressure isotherm corresponding to Equation (15) cannot be obtained analytically in an explicit form. (Compare the combination of the Volmer equation and the Gibbs equation in Kemball's approach to give the equation for the adsorption isotherm as

$$\ln p = \ln \pi + \frac{b\pi}{kT} + c$$

where b and c are constants which may be tested by plotting $\log p/\pi$ against π .)

If Equation (15) is written

$$\log \beta = \log (\pi - kT\bar{v}) = \log 4.5\mu_e^2 + \frac{5}{2} \log \bar{v}$$

where β represents the departure from the equation for an ideal two dimensional gas, then by plotting $\log \beta$ against $\log \bar{v}$ a straight line should be obtained with a slope of $\frac{5}{2}$ and the intercept on the $\log \bar{v}$ axis should give the value of μ_e .

There is similarity of form in the two equations of state for if the Volmer equation used by Kemball,

$$\pi (A - b) = kT$$

$$\text{where } A = \frac{1}{\bar{v}},$$

is presented in the form

$$\pi = kT\bar{v} + kTb \left(\frac{\bar{v}^2}{1 - b\bar{v}} \right)$$

and compared with the virial equation of Bering and Serpinsky,

$$\pi = kT\bar{v} + 4.5\mu_e^2 \bar{v}^{5/2},$$

it is seen that whenever the former equation is obeyed, the latter must also be obeyed.

APPARATUS AND MATERIALS.

The reservoir for the various hydrocarbons was connected to the apparatus by a ground glass joint sealed by mercury. In order to take a series of adsorption measurements, the special mercury cut off was raised to isolate the mercury in the measuring vessel with a pressure of 10^{-5} mm. in the system; air was then admitted via the calcium chloride-soda lime tube to the remainder of the apparatus after removing the liquid nitrogen trap. The liquid hydrocarbon was placed in the reservoir and the apparatus evacuated while immersing the reservoir in liquid nitrogen. Under vacuum the hydrocarbon was allowed to melt and dissolved air came out of solution; the process of freezing and melting was repeated until no more air bubbles were visible. Appreciable quantities of air appeared to be soluble in the hydrocarbons.

The temperature of the reservoir was controlled by a large vacuum flask (dimensions 9 x 21 cms.) containing commercial butanol. Liquid nitrogen was added to the alcohol until a temperature of approximately -75°C. was reached. (M.P. pure butanol = -79.9°C.) The reservoir was then immersed in the bath, a thermo-

couple was placed close to the end of the reservoir and a glass tube connected to a source of compressed air was placed well down in the liquid. Cotton wool was packed around the opening of the flask. To obtain higher temperatures, small quantities of warm butanol were added and the mixture thoroughly stirred by bubbling a vigorous stream of compressed air through the bath liquid. The temperature control was good at all temperatures. At the very low temperatures the temperature was constant within $0.2 - 0.3^{\circ}\text{C}$. for the time necessary to make a measurement, i.e. 10-15 minutes), at higher temperatures to within 0.1°C . Above 0°C . the bath liquid was changed to water, as the higher vapour pressures of butanol made the laboratory air very unpleasant.

Each reading took about 2 minutes and each surface tension measurement was the result of at least four readings.

Calibration of Thermocouple.

The thermocouple was chromel-alumel and the points used to calibrate it were

Melting Point	Water	0°C .
Melting Point	Mercury ⁽³¹⁾	-38.5°C .
Boiling Point (760 mm.)	Nitrous Oxide	-88.5°C .
Melting Point	Nitrous Oxide	-90.8°C .

Above 0°C . a mercury thermometer calibrated to 0.1°C . was used for calibration. The mercury was purified in the same manner as described previously. Nitrous oxide was a Commonwealth Industrial Gases¹-product "For Medical Use," and was used without further purification. The calibration of the thermocouple was checked after six months with identical results.

Indicator Junction ($^{\circ}\text{C}$.)	E.M.F.(mv)	Atmos.Pressure mm.Hg.
Water Bath at 25 ± 0.05 (Mercury thermometer graduated in 0.1°C .)	0.995	
H_2O (solid/liquid) 0°	< 0.002	
Hg (solid/liquid) -38.9	1.441 (16.10.58) 1.443 (8. 4.59)	
N_2O (liquid vapour) -88.7	3.087 (16.10.58)	752.0
-88.5	3.070 (8 . 4.59)	761.0
N_2O (solid/liquid) -90.8	3.165 (16.10.58) 3.162 (8. 4.59)	

On looking up the melting and boiling points for nitrous oxide in Kaye and Laby⁽²⁹⁾, conflicting values for the boiling point were noticed (page 117, M.P. $-102.4^{\circ}\text{C}.$, B.P. $-89.5^{\circ}\text{C}.$, and page 131, B.P. $-88.7^{\circ}\text{C}.$). This led to a closer look at the literature on the subject. It appears Blue and Gianque⁽³⁰⁾ are the most recent to study nitrous oxide. Their values are

Melting point N_2O $-90.84^{\circ}\text{C}.$

Boiling point N_2O (760 mm.) $-88.51^{\circ}\text{C}.$

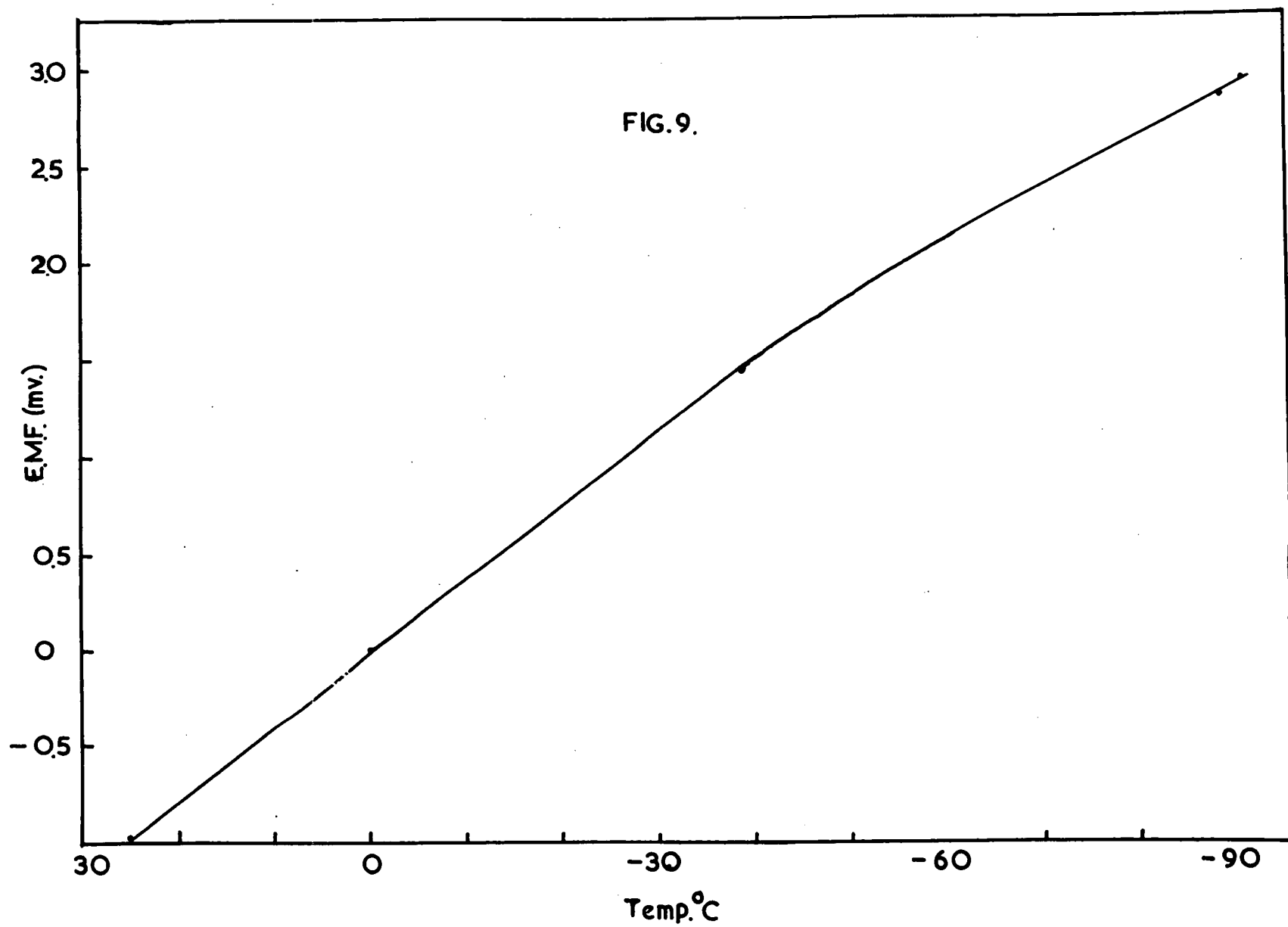
Latent heat of vaporisation $3958 \text{ cal mole}^{-1}$

Figure 9 shows calibration graph. Allowance has been made for the effect of the difference between standard atmospheric pressure and the pressure at time of measurement on the boiling point. All readings were remarkably steady, within 0.001 mv.

Materials.

The hydrocarbons selected to test the effect of chain length on the heat of adsorption and orientation at a mercury surface were n-pentane to n-octane; a branched chain hydrocarbon, iso-octane (2,2,4 trimethyl pentane), was also included in the study. The choice was limited to these hydrocarbons firstly because n-pentane is the first liquid member of the saturated series and the apparatus was designed to handle only

FIG. 9.



liquids (n-butane is also a possibility, B.P. -0.5°C.), and secondly the hydrocarbons higher than octane are very difficult to purify or extremely expensive to buy in a state of high purity. The n-hexane, n-heptane and iso-octane were donated by Mr. I. Brown of C.S.I.R.O., Industrial Chemistry Division, Victoria; their purity was approximately 99.8 mole per cent. Dr. M.F. Mulcahy, Coal Research Section, C.S.I.R.O., New South Wales, supplied the n-pentane, a Phillips product of 99 mole per cent purity. Synthetic n-octane (B.D.H.) was purified according to the method of Jones and Ottewill⁽³²⁾, the refractive index indicating a pure product, $n_{\text{D}}^{20} = 1.3974$ (n_{D}^{20} National Bureau of Standards = 1.39743).

EXPERIMENTAL RESULTS.

The following tables show the surface pressure, vapour pressure relationships for the various hydrocarbons at 25.0°C. and 16.5°C. Most of the isotherms were repeated on different days. Each value of h is the mean of at least four readings. All isotherms were completely reversible, the surface tension of mercury was restored to its original value by immersing the vapour source in liquid nitrogen. The measured initial surface tension varied slightly at the same temperature on different days (see pages 26, 27) and all surface pressures are referred to the mean corrected value for γ at 16.5°C. or 25°C., which was

$$\gamma \text{ at } 25^{\circ}\text{C.} = 485.4 \text{ dynes cm}^{-1},$$

$$\gamma \text{ at } 16.5^{\circ}\text{C.} = 487.3 \text{ dynes cm}^{-1}.$$

Surface pressures are considered reliable to within less than a dyne.

Vapour pressure measurements reported for the saturated hydrocarbons at low temperatures are rather meagre. The International Critical Tables give a selection for n-pentane to n-octane; the vapour pressures are determined by the equation

$$\log_{10} p_{\text{mm}} = \frac{-0.05223}{T} A + B$$

where

	A	B	Normal B.P.
<u>n-pentane</u> ⁽³³⁾			
-20 to +50°C.	27691	7.558	36.1
<u>n-hexane</u> ^(34,35,36,33)			
-83 to -50°C.	36702	8.782	68.95
-50 to -10°C.	35162	8.399	
-10 to +90°C.	31679	7.724	
<u>n-heptane</u> ^(34,33)			
-63 to -40°C.	37358	8.2585	98.42
	p(mm.Hg.)		
and at 0°C.	11.45		
10°C.	20.5		
20°C.	35.5		
30°C.	58.35		
<u>n-octane</u> ^(34,36,33)			
	p(mm.Hg.)		
-35°C.	0.17		
-30	0.28		
-20	0.64		
-10	1.39		
0	2.94		
+10	5.62		
20	10.45		
30	18.40		

All vapour pressures were calculated from these values by plotting $\log p$ against $1/T$ and reading off the required value by interpolation or extrapolation. For n-pentane and n-octane there is a long extrapolation to calculate the vapour pressures at the very low temperatures. Plotting the results for n-heptane obtained by Young⁽³³⁾ and Mündel⁽³⁴⁾ as $\log p$ against $1/T$ gave two lines parallel to each other, a line intermediate between the two was used to calculate the vapour pressures. It is worth noting here that the normal boiling point recorded by Mündel was $+97.5^{\circ}\text{C}$. as against the accepted value of 98.4 . The results of Stull⁽³⁷⁾ were used to calculate the vapour pressure of iso-octane from the temperature.

Recently Sondak and Thodos⁽³⁸⁾ fitted the Frost and Kalkwarf equation⁽³⁹⁾

$$\log p = A + B/T + C \log T + D (p/T^2)$$

to the data on the vapour pressures of many hydrocarbons from the triple point to the critical point. However, it was found that vapour pressures calculated from this equation for low temperatures were not in agreement with the directly determined values reported in the International Critical Tables. The absolute zero of temperature was taken as -273.1°C .

The graphs of surface pressure against relative pressure, p^s/p , where p = saturation pressure, are shown in Figures 10-14. Since the 16.5°C . and 25.0°C . isotherms are so close together, only that for 16.5°C . is shown.

B-18.

n-PENTANE

Temperature $25 \pm 0.2^{\circ}\text{C}$.

$\gamma^{\circ} = 485.4 \pm 1.2$ dynes cm^{-1} .

$p = 508.2$ mm.Hg.

Temperature of pentane $^{\circ}\text{K}$.	p^{I} mm.Hg.	$(p^{\text{I}}/p) \times 10^2$	$\pi(\gamma^{\circ}-\gamma)$ dynes cm^{-1} .
199.0	1.95	0.383	9.4
210.3	4.80	0.944	15.8
220.5	9.98	1.96	21.1
230.7	19.4	3.82	28.2
234.2	24.0	4.72	28.8
240.9	35.8	7.04	33.4
248.6	53.5	10.5	37.7
250.4	60.5	11.9	38.2
254.3	74.3	14.6	41.5
260.9	103.3	20.3	42.9
261.8	107.9	21.2	44.2
269.0	152.4	30.0	48.8
273.1	182.8	35.0	53.0
278.6	232.8	45.8	57.7
281.6	264.2	52.0	60.5

B-19.

n-PENTANE

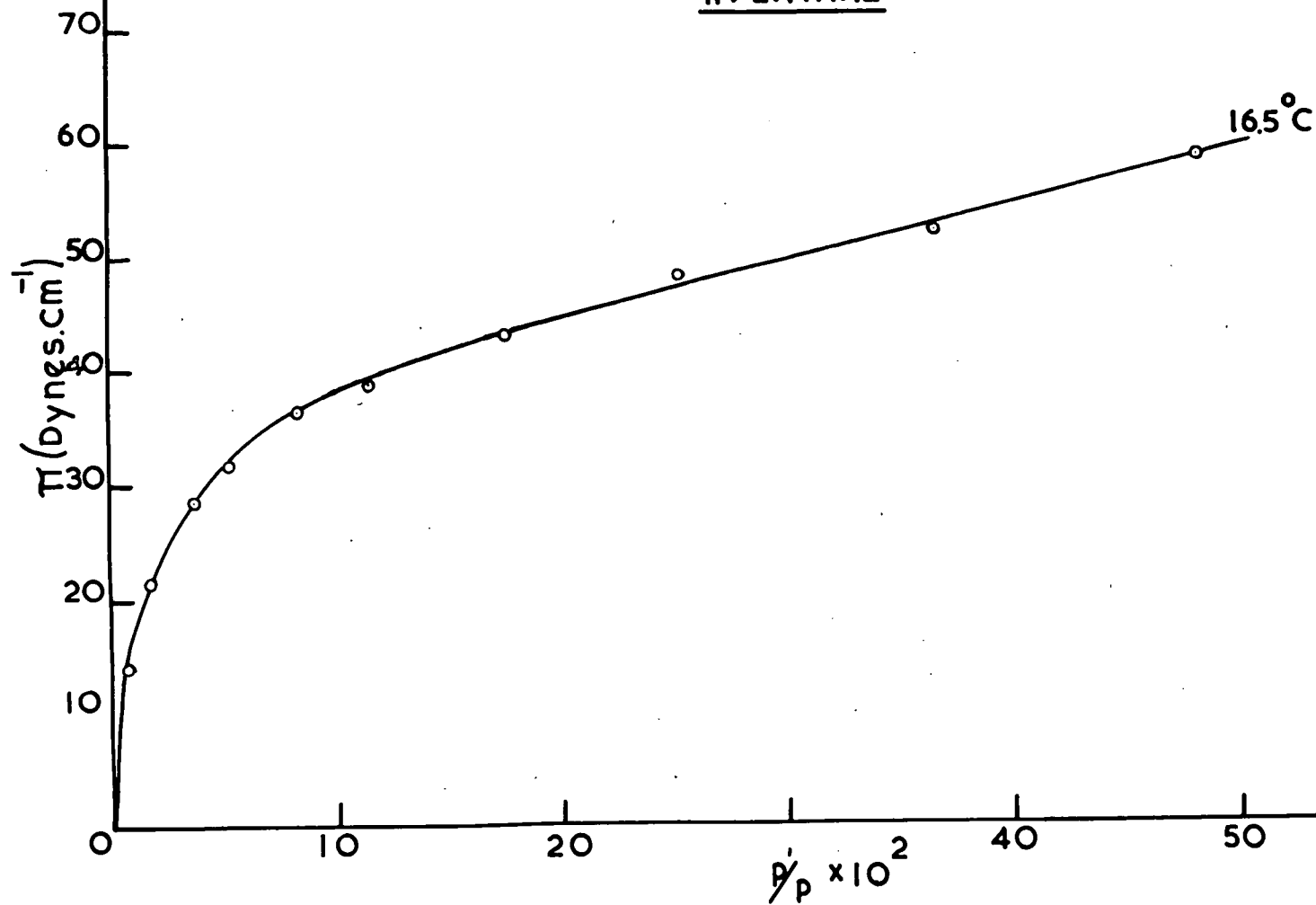
Temperature $16.5 \pm 0.2^{\circ}\text{C}$. $\gamma^{\circ} = 487.3 \pm 1.0 \text{ dynes cm}^{-1}$.

$p = 366.4 \text{ mm.Hg.}$

Temperature of pentane $^{\circ}\text{K}$.	$p^l \text{ mm.Hg.}$	$(p^l/p) \times 10^2$	$\pi(\gamma^{\circ} - \gamma)$ dynes cm^{-1}
203.2	2.76	0.753	14.1
215.3	6.90	1.88	21.6
225.0	13.5	3.68	28.5
230.8	19.4	5.29	31.7
238.5	30.9	8.43	36.3
244.2	42.7	11.6	38.5
251.8	64.6	17.6	43.0
258.8	92.7	25.3	48.1
266.7	134.3	36.7	52.0
272.7	177.4	48.4	58.3

FIG. 10

n-PENTANE



B-20.

n-HEXANE.

Temperature $16.5 \pm 0.2^{\circ}\text{C}.$

$\gamma^0 = 487.3 \pm 1.0 \text{ dynes cm}^{-1}.$

$p = 102.6 \text{ mm.Hg.}$

Temperature of hexane $^{\circ}\text{K}.$	p^{I} mm.Hg.	$(p^{\text{I}}/p) \times 10^2$	$\pi(\gamma^0 - \gamma)$ dynes $\text{cm}^{-1}.$
199.8	0.161	0.157	12.1
217.0	0.861	0.839	23.6
223.5	1.50	1.46	29.5
236.5	4.22	4.11	37.5
245.5	8.13	7.92	45.0
255.6	15.9	15.5	50.7
264.1	27.0	26.3	56.0
276.5	55.0	53.6	66.4
282.8	74.8	72.9	73.0
289.6	102.6	100.0	80.9

B-21.

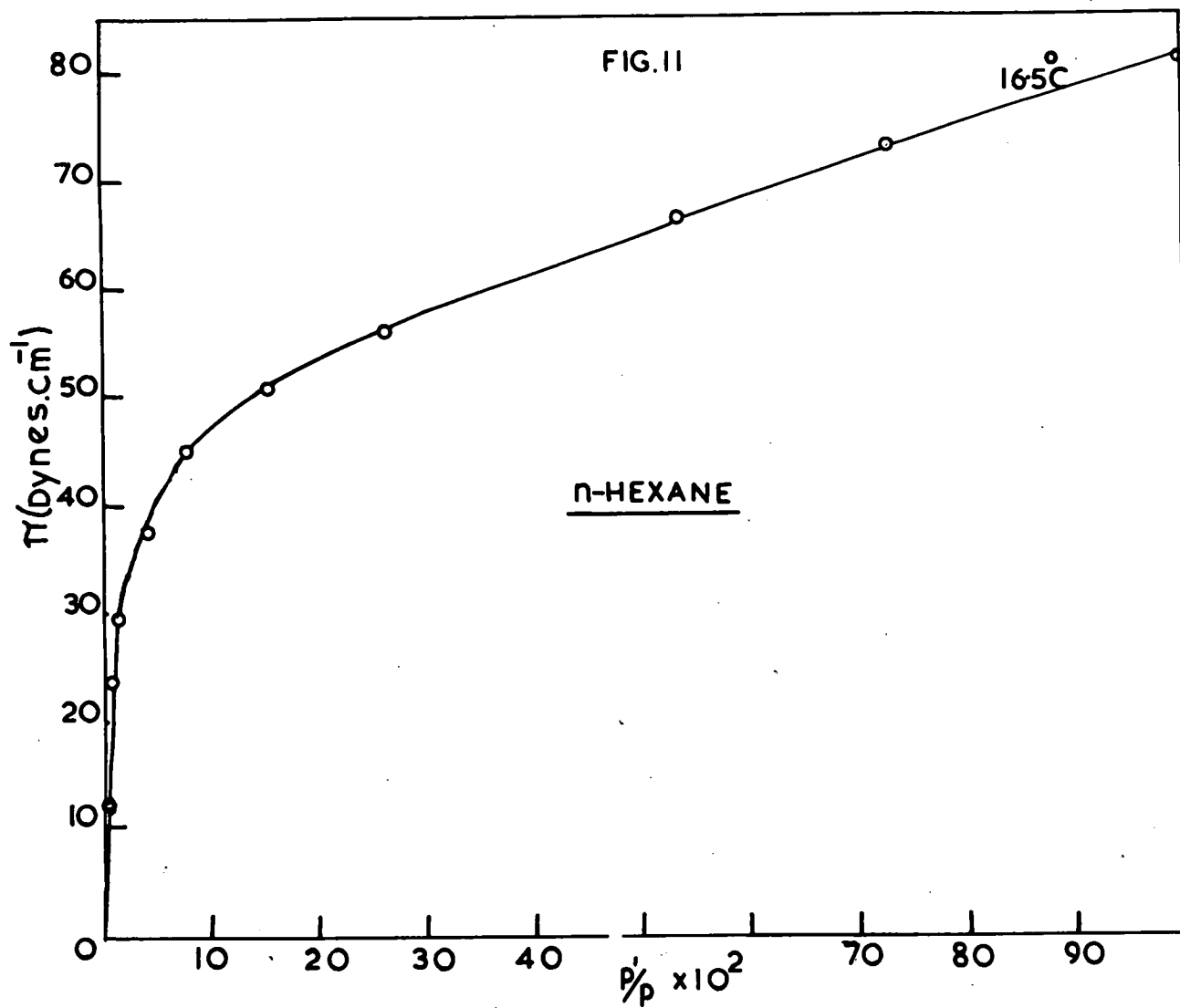
n-HEXANE.

Temperature $25 \pm 0.2^\circ\text{C}.$

$$\gamma^0 = \frac{485.4 \pm 1.2}{487.3 \pm 1.0} \text{ dynes cm}^{-1}.$$

$$p = 149.3 \text{ mm.Hg.}$$

Temperature of hexane $^{\circ}\text{K}$	p^1 mm.Hg.	$(p^1/p) \times 10^2$	$\pi(\gamma^0 - \gamma)_{-1}$ dynes cm $^{-1}$.
212.8	0.594	0.398	16.6
221.9	1.39	0.931	22.5
231.1	2.84	1.90	29.0
238.8	5.11	3.42	33.9
241.6	6.28	4.21	37.0
245.4	8.22	5.51	38.3
254.1	14.9	9.98	45.0
262.5	25.3	16.9	48.5
268.9	37.2	24.9	53.0
273.1	46.2	30.9	55.8
274.8	50.5	33.8	56.5
279.1	62.5	41.9	60.2
286.1	87.3	58.5	67.0
287.4	92.7	62.1	69.5
291.3	110.7	74.1	72.5
296.9	141.6	94.8	77.9
298.1	149.3	100.0	79.4



n-HEPTANE.Temperature $16.5 \pm 0.2^\circ\text{C}.$ $\gamma^0 = 487.3 \pm 1.0$
 ~~485.4 ± 1.2~~ dynes cm^{-1} . $p = 31.05 \text{ mm.Hg.}$

Temperature of heptane $^\circ\text{K}.$	$p^1 \text{ mm.Hg.}$	$(p^1/p) \times 10^2$	$\pi(\gamma^0 - \gamma)$ dynes cm^{-1}
194.7	0.0162	0.0522	7.5
208.6	0.0738	0.238	17.0
210.6	0.0891	0.287	17.7
218.5	0.197	0.634	24.6
228.5	0.452	1.46	31.1
235.9	0.906	2.92	36.6
238.7	1.03	3.32	37.9
245.0	1.84	5.93	43.7
253.3	3.31	10.7	47.8
253.8	3.35	10.8	49.7
261.6	5.90	19.0	54.2
264.0	6.89	22.2	56.3
270.8	10.54	33.9	61.7
280.5	18.66	60.1	68.9
289.6	31.05	100.0	81.2

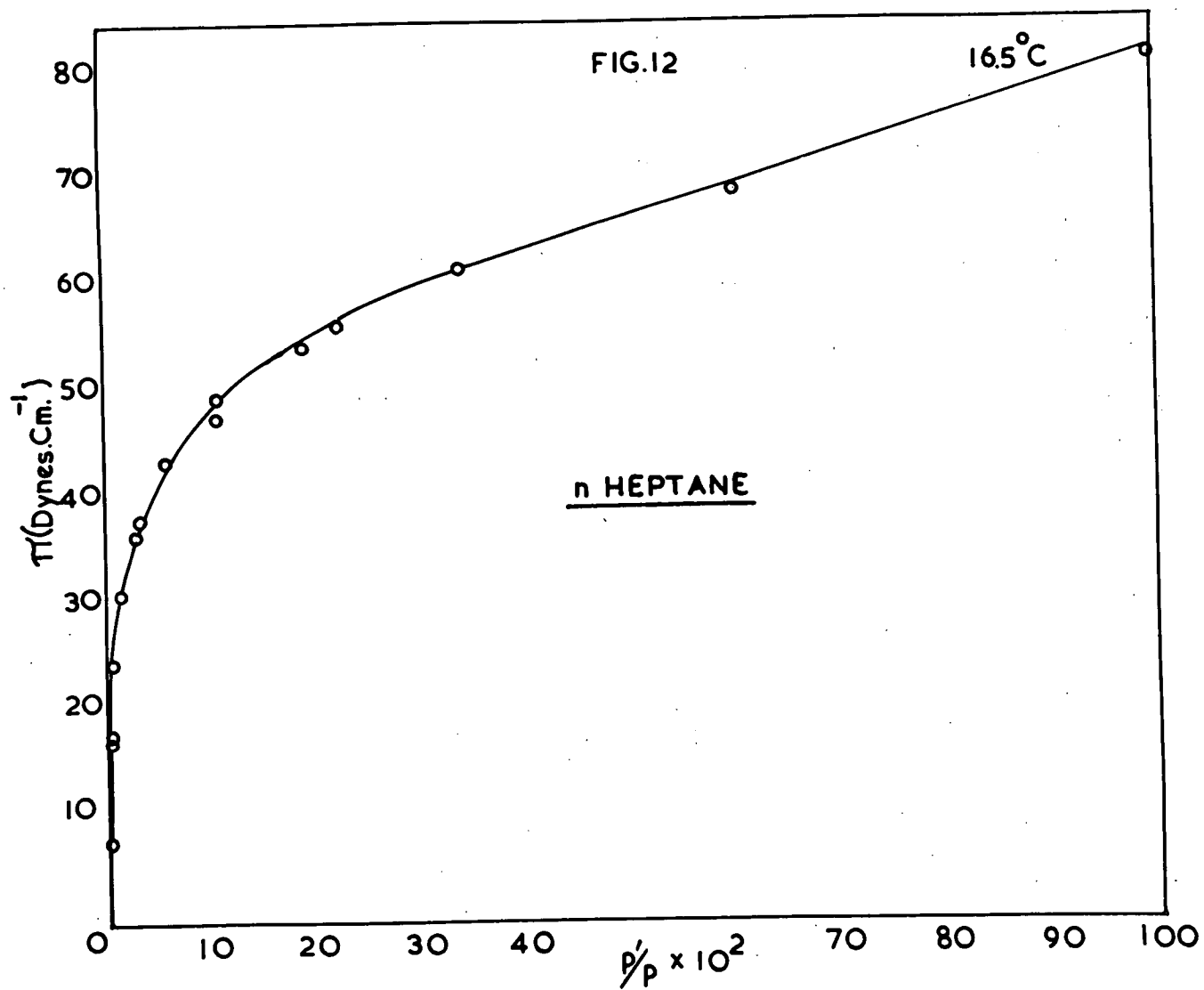
B-23.

n-HEPTANE.

Temperature $25 \pm 0.2^{\circ}\text{C.}$ $\gamma^{\circ} = 485.4 \pm 1.2 \text{ dynes cm}^{-1}.$

$p = 47.8 \text{ mm.Hg.}$

Temperature of heptane $^{\circ}\text{K.}$	$p^{\dagger} \text{ mm.Hg.}$	$(p^{\dagger}/p) \times 10^2$	$\pi(\gamma^{\circ}-\gamma)$ dynes cm^{-1}
209.5	0.0826	0.173	13.3
215.6	0.152	0.317	17.1
216.2	0.158	0.331	18.3
223.1	0.316	0.661	22.4
225.2	0.361	0.755	23.1
230.3	0.584	1.22	27.5
233.9	0.708	1.48	29.3
239.8	1.22	2.55	32.8
243.1	1.58	3.31	35.4
246.0	2.04	4.27	39.2
251.9	2.80	5.86	41.8
257.1	4.37	9.14	43.4
263.4	6.61	13.8	51.0
263.7	6.76	14.1	49.8
272.9	12.2	25.5	55.2
273.1	12.2	25.5	57.4
273.5	12.3	25.7	56.1
276.2	14.4	30.1	57.9
277.4	15.7	32.8	58.0
279.9	18.0	37.6	60.5
283.4	22.1	46.2	63.0
287.5	27.7	57.9	66.7
291.8	34.7	72.6	69.2
295.8	42.8	89.5	75.7
298.1	47.8	100.0	77.2



n-OCTANE.Temperature $16.5 \pm 0.2^{\circ}\text{C}.$ $\gamma^{\circ} = 487.3 \pm 1.0 \text{ dynes cm}^{-1}$ $p = 8.43 \text{ mm.Hg.}$

Temperature of n-octane $^{\circ}\text{K}$	$p^{\dagger} \text{ mm.Hg.}$	$(p^{\dagger}/p) \times 10^2$	$\pi(\gamma^{\circ} - \gamma)$ dynes cm^{-1}
195.6	0.00176	0.0209	4.9
205.5	0.00525	0.0622	9.5
214.7	0.0157	0.186	15.0
226.4	0.0558	0.662	23.9
232.9	0.107	1.27	29.1
242.8	0.265	3.14	35.9
250.4	0.513	6.09	43.0
258.7	1.00	11.9	47.2
269.5	2.23	26.5	55.4
281.7	5.09	60.4	66.1
287.9	7.59	90.0	72.9

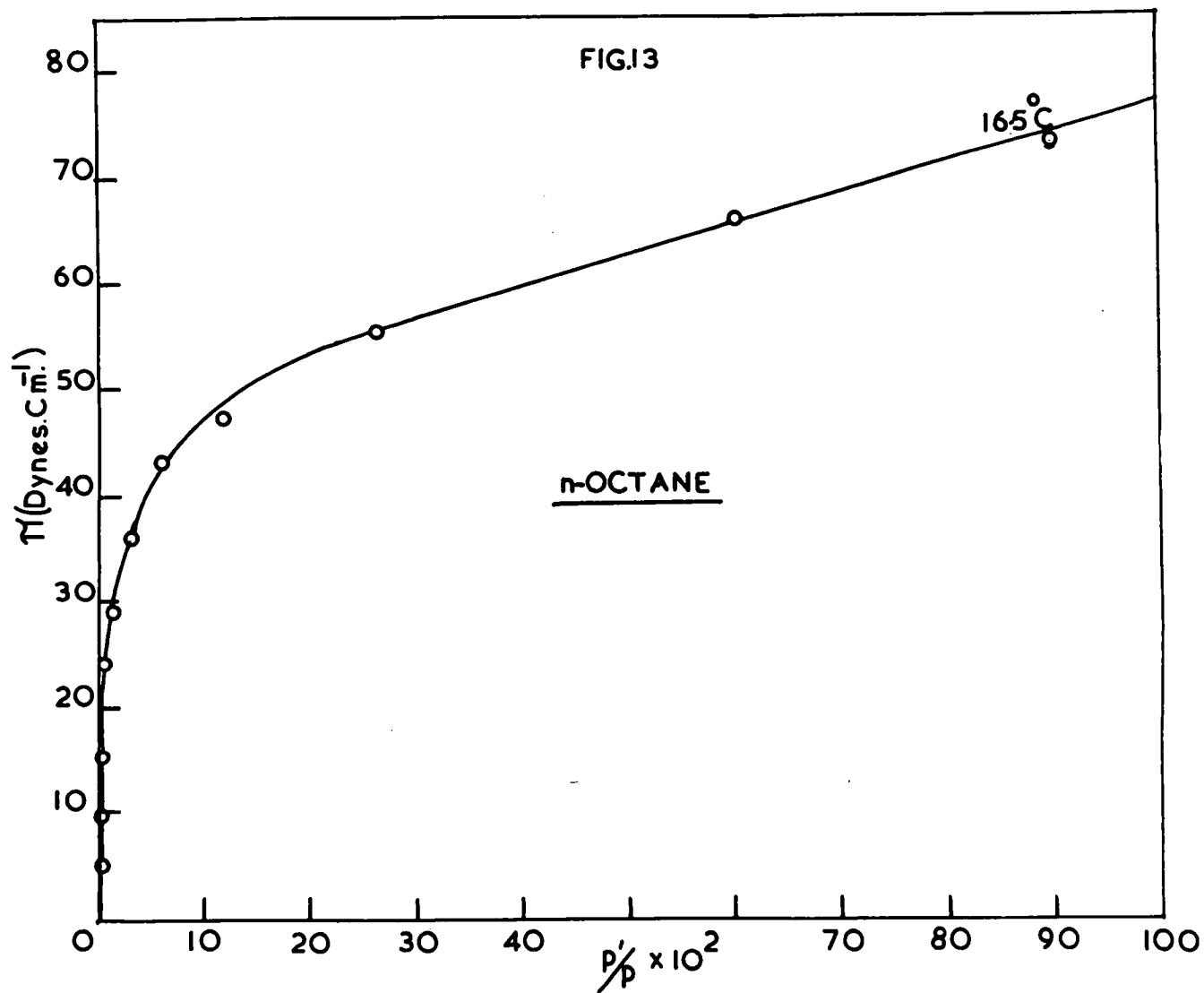
B-25.

n-OCTANE.

Temperature $25 \pm 0.2^{\circ}\text{C}.$ $\gamma^{\circ} = 485.4 \pm 1.0 \text{ dynes cm}^{-1}$

$p = 14.0 \text{ mm.Hg.}$

Temperature of n-octane $^{\circ}\text{K}.$	$p' \text{ mm.Hg.}$	$(p'/p) \times 10^2$	$\pi(\gamma^{\circ} - \gamma) \text{ dynes cm}^{-1}$
196.1	0.00151	0.0108	2.5
203.6	0.00405	0.0289	5.5
208.3	0.00745	0.0532	8.1
212.0	0.0117	0.0836	9.7
216.1	0.0185	0.132	13.7
216.4	0.0190	0.136	13.4
230.0	0.0794	0.567	23.1
233.3	0.110	0.785	26.2
235.8	0.141	1.01	27.0
244.2	0.302	2.16	33.8
251.2	0.550	3.93	38.0
258.5	0.984	7.03	43.3
265.4	1.66	11.9	49.8
273.1	2.86	20.4	52.0
275.9	3.51	25.1	55.2
282.2	5.26	37.6	61.2
289.6	8.43	60.2	67.7
292.8	10.0	71.4	70.2
296.8	13.1	93.5	76.1



B-26.

iso-OCTANE.

Temperature $16.5 \pm 0.2^{\circ}\text{C.}$ $\gamma^0 = 487.3 \pm 1.0 \text{ dynes cm}^{-1}$

$p = 32.5 \text{ mm.Hg.}$

Temperature of iso-octane $^{\circ}\text{K.}$	$p^1 \text{ mm.Hg.}$	$(p^1/p) \times 10^2$	$\pi(\gamma^0 - \gamma) \text{ dynes cm}^{-1}$
197.6	0.0202	0.0621	9.3
206.1	0.0565	0.174	14.1
213.6	0.123	0.378	20.1
225.5	0.381	1.17	30.1
231.6	0.653	2.01	33.8
233.3	0.759	2.34	35.2
244.9	1.91	5.88	42.8
252.1	3.21	9.87	48.2
258.8	5.13	15.8	52.3
266.6	8.61	26.5	58.8
275.7	15.0	46.2	63.8
273.1	12.8	39.3	61.7
278.5	17.6	54.2	67.9
280.9	20.1	61.8	68.5
284.4	24.6	75.7	74.8
289.6	32.5	100.0	80.1

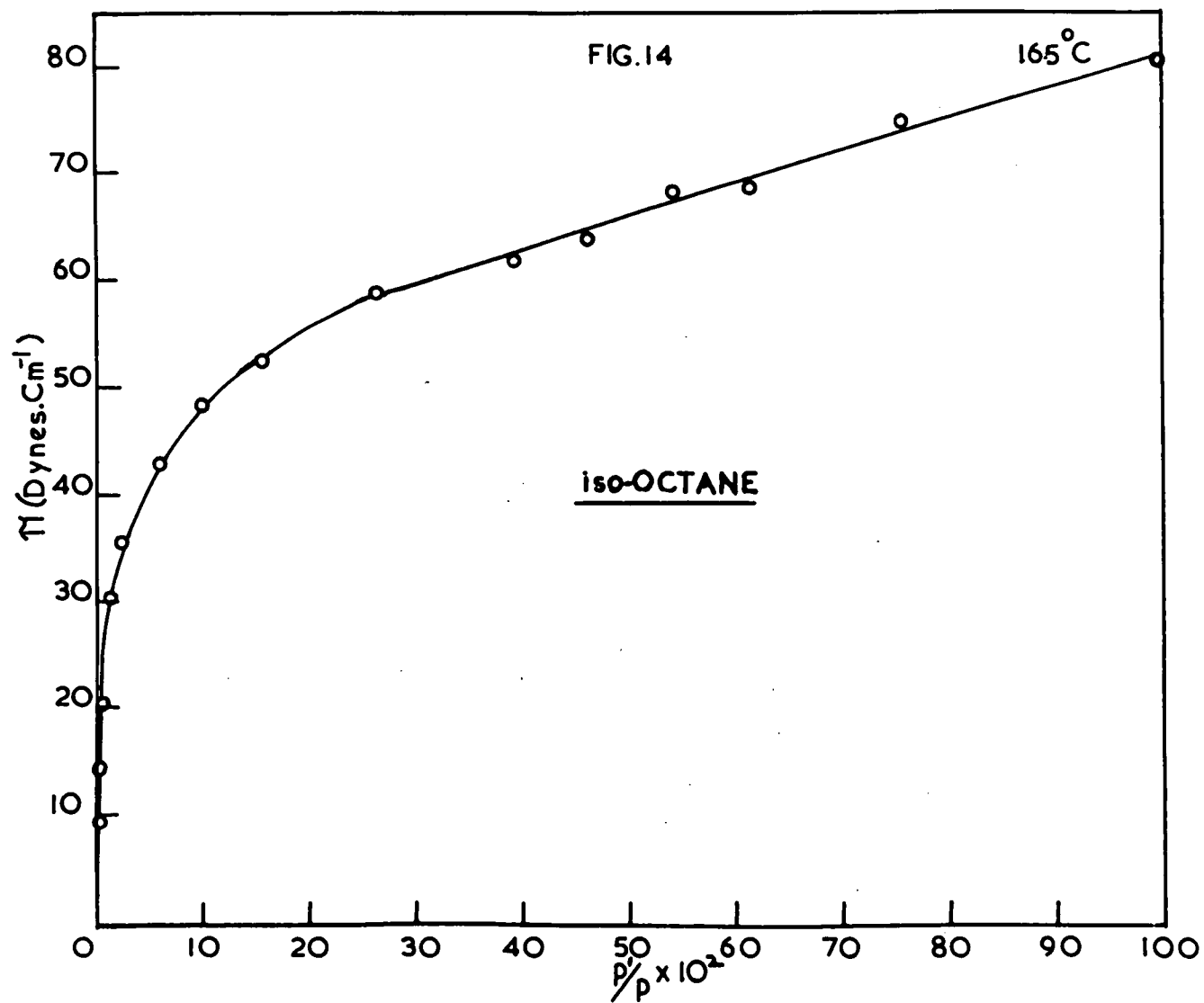
B-27.

iso-OCTANE

Temperature $25 \pm 0.2^{\circ}\text{C}$. $\gamma^0 = 485.4 \pm 1.2 \text{ dynes cm}^{-1}$

$p = 48.8 \text{ mm.Hg.}$

Temperature of iso-octane $^{\circ}\text{K}$	$p^l \text{ mm.Hg.}$	$(p^l/p) \times 10^2$	$\pi(\gamma^0 - \gamma) \text{ dynes cm}^{-1}$
203.6	0.0427	0.0875	9.5
214.6	0.136	0.279	16.7
225.3	0.380	0.779	23.1
234.2	0.813	1.67	29.6
246.4	2.14	4.39	38.9
254.7	3.89	7.97	43.5
262.6	6.61	13.5	49.2
272.6	12.5	25.6	55.2
273.4	13.2	27.0	55.2
276.9	16.1	33.0	58.9
281.9	21.6	44.3	63.3
286.5	27.9	57.2	66.8
292.2	37.8	77.5	72.6
293.9	39.8	81.6	75.4
297.0	43.6	69.3	77.3



The curves of surface pressure against relative pressure for the n-hexane, n-heptane, n-octane and iso-octane are almost identical. n-Pentane shows significantly lower surface pressures at low relative pressures but at higher relative pressures the surface pressures rapidly approach those observed with the other hydrocarbons, and at saturation all hydrocarbons give approximately the same surface tension lowering. Micheli⁽¹⁷⁾ observed the same phenomenon in the range of vapour pressures approaching saturation.

This phenomenon is basically the result of two processes (i) the rapid decrease in vapour pressure from n-pentane to n-octane at the same temperature, and (ii) the rapid increase in the surface tension lowering from n-pentane to n-octane at the same pressure. The first factor represents to a good approximation the number of collisions of the molecules on the surface, and the second, the life of the molecule on the surface. In the case of mercury it appears the increase in the life of the molecule on the surface almost exactly balances the decrease in the number of collisions on ascending the saturated hydrocarbon series.

Cutting and Jones⁽⁴⁰⁾ and Jones and Ottewill⁽³²⁾ have studied the adsorption of the same hydrocarbons on water and found that as the series is ascended at the

same pressure of vapour the adsorption increases markedly. However, the decrease in vapour pressure on ascending the series is not matched by an equivalent increase in the life of the molecule on the surface, and consequently the order of adsorption at saturation pressure of vapour is n-pentane > n-hexane > n-heptane > n-octane. It seems that mercury, because of its much higher surface energy ($\gamma_{\text{Hg}}^{25^\circ\text{C}} = 485.4 \text{ dynes cm}^{-1}$, $\gamma_{\text{H}_2\text{O}}^{25^\circ\text{C}} = 72.0 \text{ dynes cm}^{-1}$), increases the life of the hydrocarbon molecule on its surface as the inverse of the vapour pressure.

The isotherm for n-heptane may be compared with that obtained by Kemball⁽²³⁾. Surface pressures are almost exactly 4 dynes cm^{-1} higher than those recorded by Kemball at all pressures of the vapour. In this connection it is worth noting that his n-heptane was not perfectly pure as the refraction index was $n_{\text{D}}^{20} = 1.3882$ ($n_{\text{D}}^{20} \text{ N.B.S.} = 1.3876$). On the other hand, Bering and Ioileva report an isotherm identical with Kemball's employing the method of the maximum pressure in a drop to measure the surface tension. As against this, of the two values for surface tension of mercury reported in the preliminary publication two years earlier⁽⁶⁾, differing by $1.5 \text{ dynes cm}^{-1}$, the lower value $484.4 \text{ dynes cm}^{-1}$ was chosen as the correct value to place it in agreement with Kemball's $484.5 \text{ dynes cm}^{-1}$, but as mentioned earlier, Kemball's value should be increased to $485.6 \text{ dynes cm}^{-1}$ due to the error in the

Worthington equation. Consequently all surface pressures reported by Bering and Ioileva should be increased by 1.5 dynes cm^{-1} . Since the isotherm found in the present instance fits in with the isotherms of the other hydrocarbons better than either that reported by Kemball or the corrected isotherm of Bering and Ioileva, it is considered to be more likely correct.

Adsorbed layer as a real two dimensional gas.

All isotherms are convex to the surface pressure axis indicating a predominance of repulsive forces between the adsorbed molecules. The Volmer equation

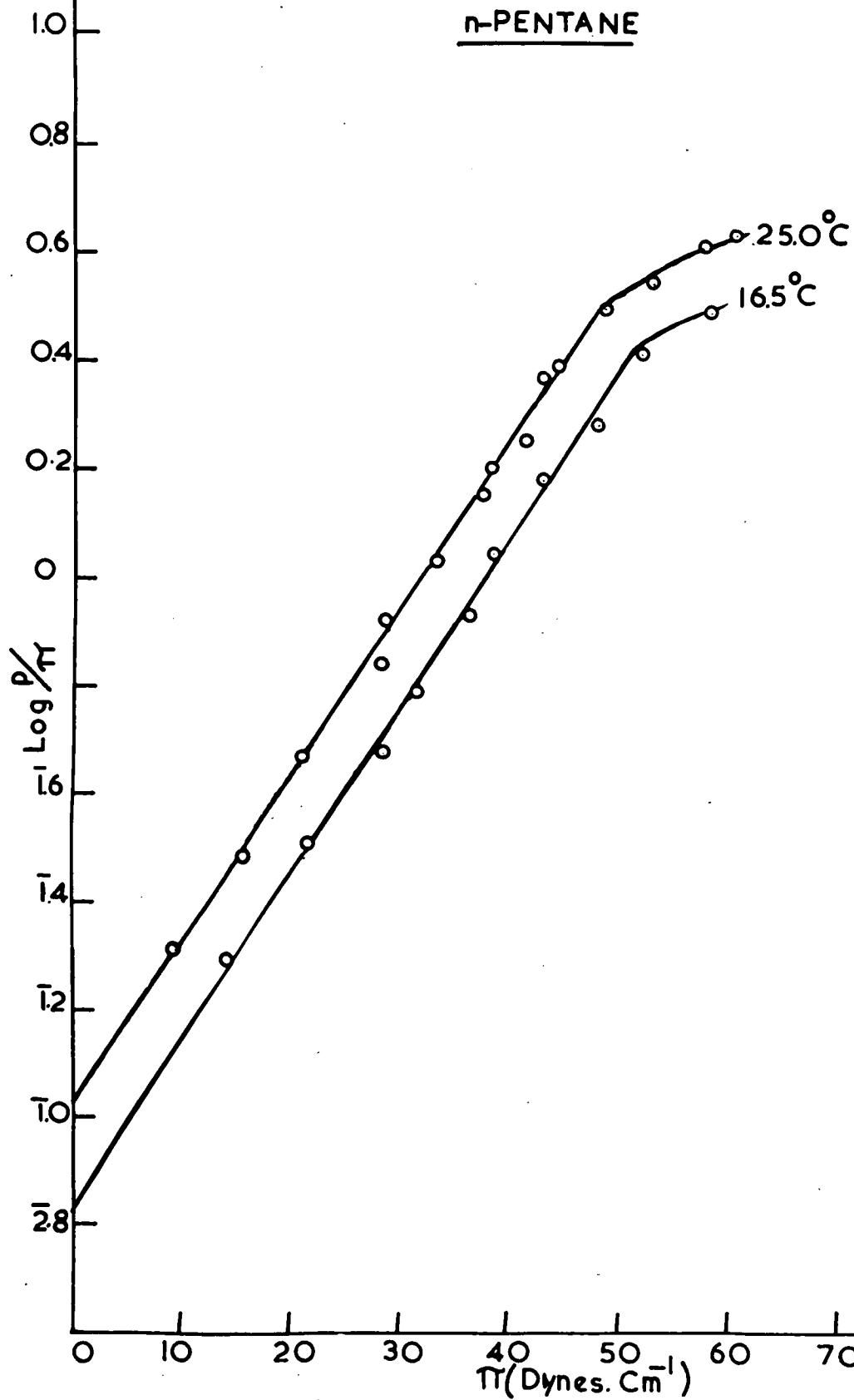
$$\pi(A - b) = kT$$

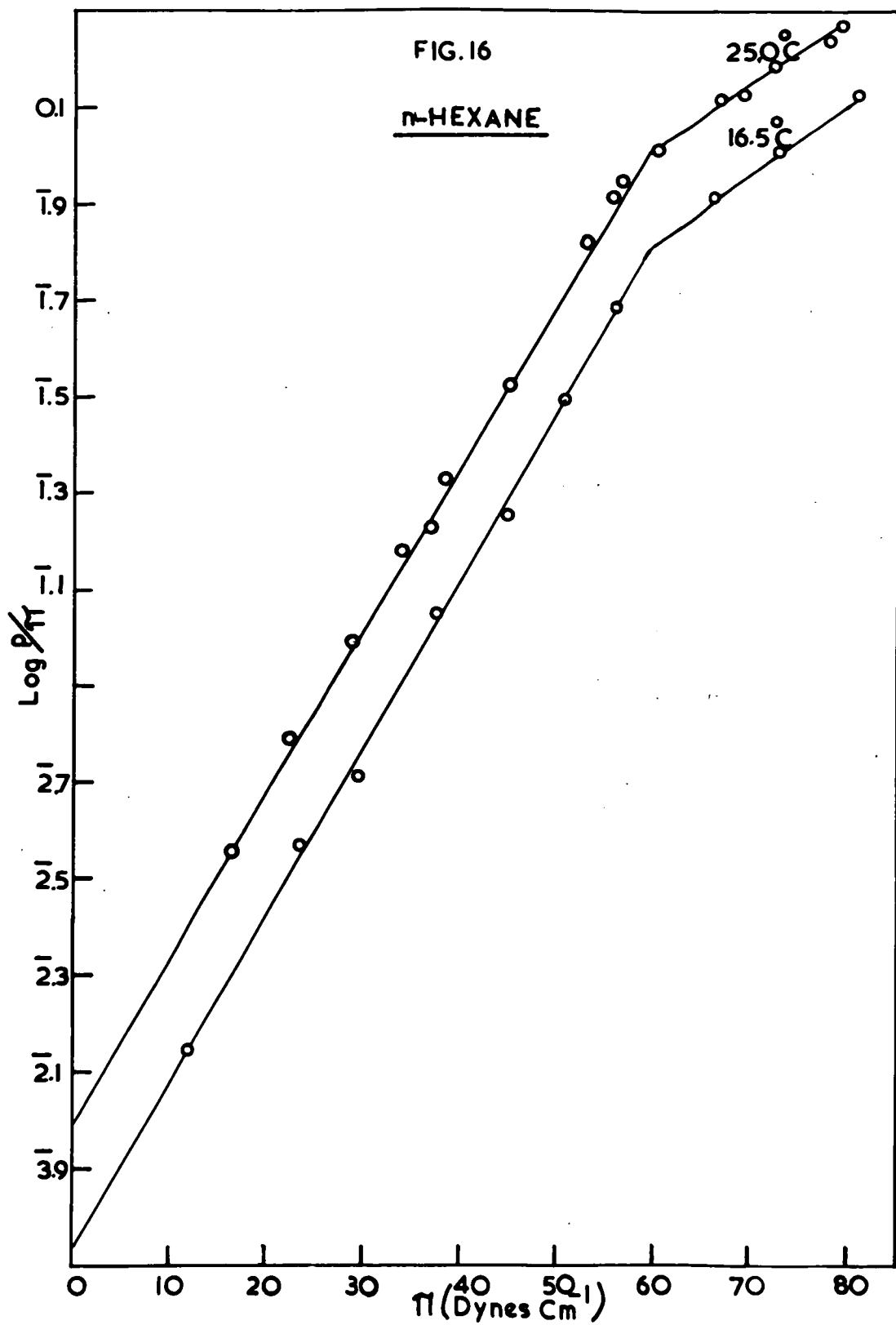
for a real two dimensional gas can be fitted to all the isotherms. The co-area, b , has been assumed equal to the actual area occupied by the molecule on the surface, not twice the area as predicted by the simple kinetic theory. If b were twice the area occupied by the molecule, infinite surface pressure would be needed to satisfy the Volmer equation when the surface was half covered. In all cases the equation is obeyed up to higher surface coverages.

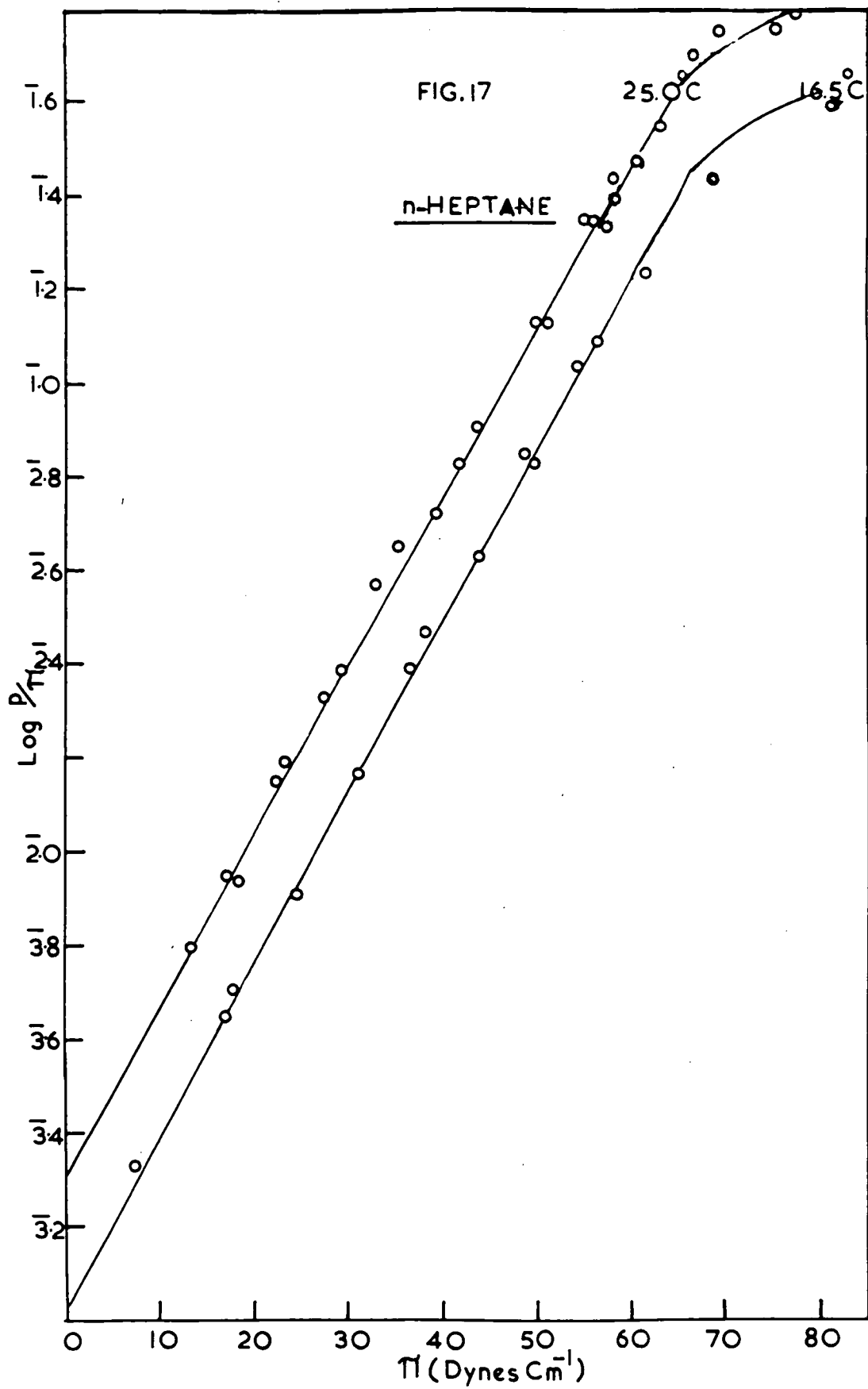
The standard free energies, entropies and total energies of adsorption, and co-areas were calculated, as outlined previously, by plotting $\log p/\pi$ against π , Figures 15-19. In all instances reasonably good straight lines are obtained for the first portion of the graph, at high surface pressures the gradient changes. For the time being, only the first portion will be considered.

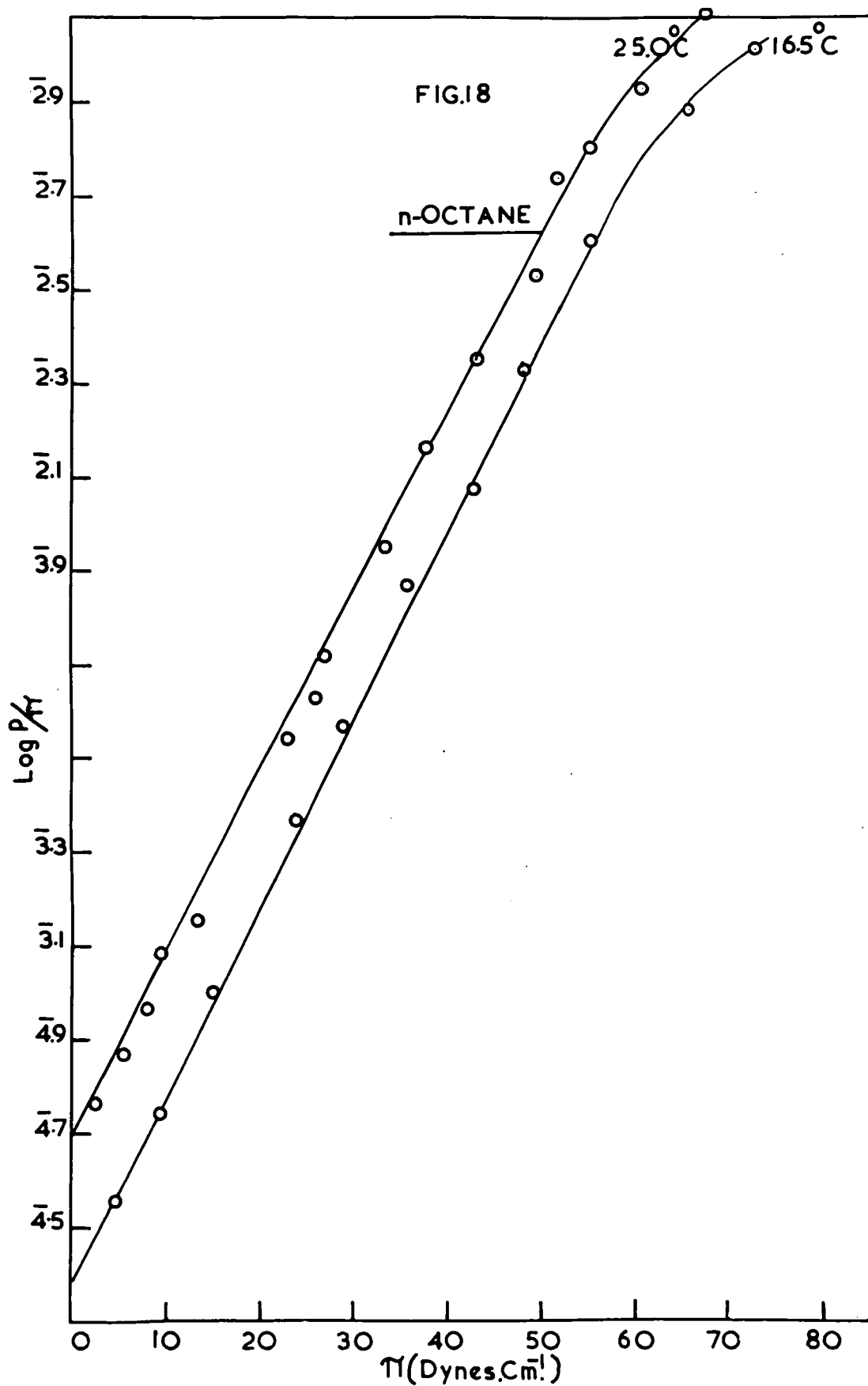
FIG. 15

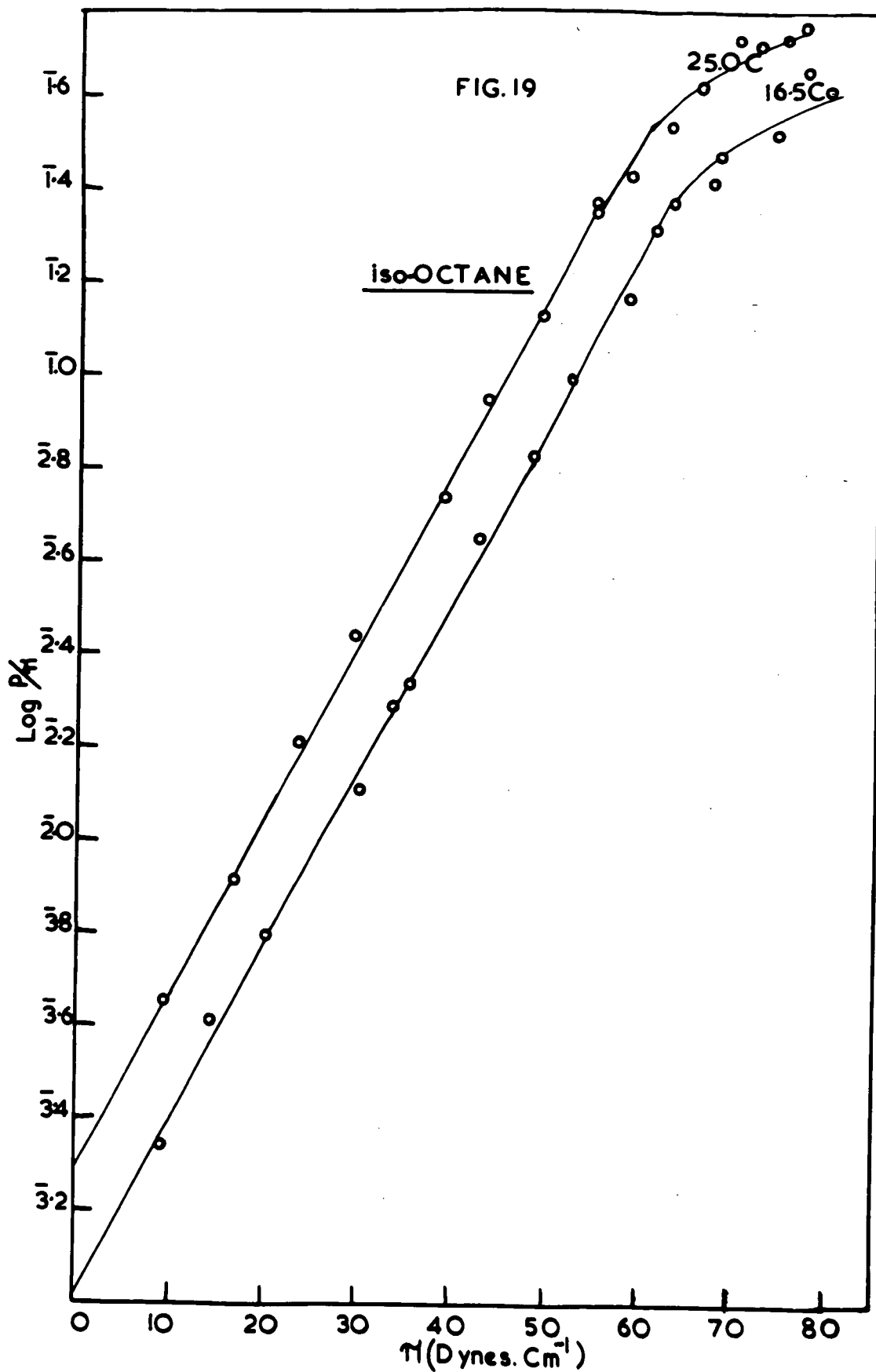
n-PENTANE











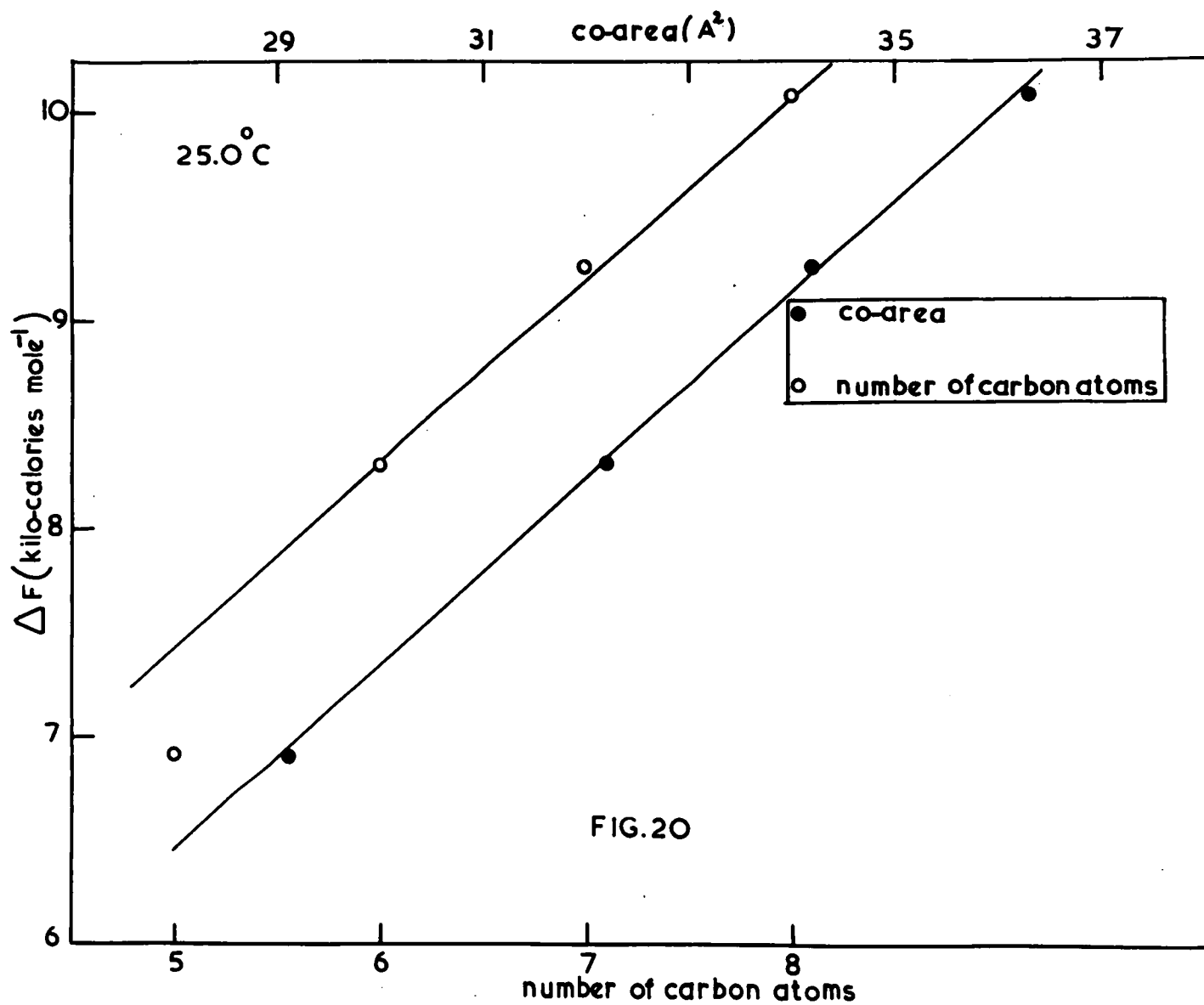
B-31.

The following table summarises the results of the calculations.

	Temp. °C.	$\Delta F(\text{cals. mole}^{-1})$	$\Delta H(\text{kilocals mole}^{-1})$	$\Delta S(\text{cals mole}^{-1} \text{deg}^{-1})$	Co-area (\AA^2)
n-pentane	16.5	7010	10.3	11.4	28.8
	25.0	6909			29.1
n-hexane	16.5	8424	12.1	12.7	31.7
	25.0	8314			32.2
n-heptane	16.5	9370	13.0	12.6	33.7
	25.0	9255			34.2
n-octane	16.5	10200	13.9	12.8	36.0
	25.0	10087			36.3
iso-octane	16.5	9378	13.0	12.5	34.6
	25.0	9269			35.1

The standard free energies of adsorption are reliable to within 10 cal.mole⁻¹, the co-areas to within 0.2 Ångstrom units², the total energies to within 0.5 kilocal mols⁻¹, and the entropies to within 1.5 calories mole⁻¹ degree⁻¹.

If the standard free energies of adsorption are plotted against the number of carbon atoms in the molecule a linear relationship is observed, except for n-pentane which has a lower free energy of adsorption than predicted from such a graph. However, a straight line is obtained if the co-areas, which are assumed to be the actual areas of the molecules on the surface, are plotted against the number of carbon atoms in the chain, indicating that the standard free energy change depends on the area covered by the molecule and not on the number of carbon atoms, Figure 20. The variation of ΔF with the number of carbon atoms is known as Traube's Rule⁴¹, and is obeyed by hydrocarbons on a water surface^{32, 40}. Langmuir⁴³ interpreted Traube's Rule as meaning that when members of a homologous series are adsorbed on a surface, initially each CH₂ group occupies a similar position on the surface, or in other words, the hydrocarbon molecule is lying stretched out on the surface.



Ward⁽⁴²⁾ has pointed out that Langmuir's interpretation is incorrect because it involves the implicit assumption that the molecules are stretched out in the bulk phase, which is unlikely for the following reason. The shape of the hydrocarbon molecule is determined by considerations of both entropy and surface energy. When surface energies are without influence, as for a hydrocarbon molecule surrounded by like molecules, the shape is determined solely by configurational probability. Treloar⁽⁴⁴⁾ has calculated distribution curves for hydrocarbon molecules from this point of view and found that the "most probable" state is approximately a spheroid, intermediate between the extreme shapes of a cylinder (stretched out) and a sphere (rolled up with a minimum surface area).

Adsorbed on a water surface the "most probable" shape for the hydrocarbon molecule is a spheroid; Ward⁽⁴²⁾ has calculated the energies of the hydrocarbon molecule on a water surface and hence deduced that a spheroid (almost a sphere) has the lowest potential energy. The observation then that the free energy of adsorption varies linearly with the number of carbon atoms is due to the fortuitous manner in which the molecular volumes vary from pentane to octane, making the areas of the corresponding spheroids (almost spheres) vary in arithmetical progression. In other

words, since the hydrocarbon molecules are in the form of spheres in the bulk phase and in the surface phase, equal increments in area and hence free energy on adsorption are obtained from pentane to octane.

The co-areas of the hydrocarbon molecules on mercury suggest that they are partially curled up on the surface. The following table shows the co-areas compared with the corresponding areas occupied by the stretched out forms. Kemball⁽²³⁾ gives the area occupied by a CH_2 group as approximately 7 \AA^2 .

25°	Co-area \AA^2	Area of stretched out form on surface \AA^2
n-pentane	29.1	35
n-hexane	32.2	42
n-heptane	34.2	49
n-octane	36.3	56

An approximate value for the initial thickness of the surface layer may be obtained by dividing the molecular volume⁴² by the area of the molecule on the surface (co-area). This value may be compared with that for water which has been deduced by Ward on the basis of the most probable length of the hydrocarbon molecule.

20°C	Molecular Volume (Å ³)	Thickness of surface layer on Mercury (Å)	Thickness of surface layer on water (Å)
n-pentane	193	6.7	7.0
n-hexane	219	6.9	7.4
n-heptane	246	7.3	7.6
n-octane	268	7.4	7.7

The agreement is remarkably good.

A further comparison may be made with the thickness assumed for the surface layer, 6Å , in the derivation of the equation for the standard free energy change on adsorption. From the accompanying table it is clear that if the thickness of the surface layer (δ) is as given above and the standard free energy change on adsorption is calculated from these values, the difference from the values already determined is not significant. The conversion is readily made if it is remembered that

$$\Delta F = -RT \ln \frac{B}{\delta} \left(\frac{d\pi}{dp} \right)_T$$

Equation (7), page B-4, where B is a constant.

$$\text{Whence putting } \left(\frac{d\pi}{dp} \right)_T = e^{-c} \quad \pi \rightarrow 0$$

Equation (11), page B-5,

where c is the intercept of the plot of $\log p/\pi$ against π ,

$$\Delta F = -RT \ln \frac{B}{\delta} \frac{d\pi}{dp} \bigg|_T$$

$$= 2.303 RT (\log \frac{B}{\delta} - c)$$

25.0°C.	δ Angström	ΔF cal.s.mole ⁻¹
n-pentane	6	6909
	6.7	6844
n-hexane	6	8314
	6.9	8232
n-heptane	6	9255
	7.3	9139
n-octane	6	10087
	7.4	9963

Significance of the Co-area, b, in the Volmer Equation.

The adsorption of iso-octane confirms the fact that the molecules are curled up on the surface. n-Heptane and iso-octane have the same free energy of adsorption, suggesting that both molecules cover the same area of surface. It is possible to show with models that in the most stretched form iso-octane (2.2.4 trimethyl pentane), because of the position of the methyl groups, can not have more than 5-6 carbon atoms in contact with a surface at any one time. Since the co-area of iso-octane 35 \AA^2 indicates that the equivalent of 5 CH_2 groups are in contact with the surface, it is most likely that the co-areas represent the actual areas occupied by the molecules on the surface.

A rigid proof that the co-area is the actual area occupied by the molecule on the surface could be obtained by studying the adsorption of the incompressible hydrocarbon isomer neo-pentane (2.2-dimethyl propane). Unfortunately, attempts to procure this hydrocarbon in Australia were unsuccessful. Another incompressible molecule is acetone. However, some assumption has to be made regarding its orientation on the surface (no such assumption is necessary with neo-pentane since it is a spherical molecule). Bering and Ioileva⁽²⁴⁾ conclude that the acetone molecule makes contact on a mercury surface

B-38a.

with the three carbon atoms and the oxygen atom. It is, therefore, possible to ascertain the area occupied by the acetone molecule.

The most recent measurements of Romers and Creutzberg⁽⁵⁴⁾ on the structure of acetone are summarised below:

	Bond length (Å)		Bond angle (deg.)
C-C	1.52	C-C-C	109.5
C=O	1.24	C-C=O	118.5
C-H	1.09		

The bond angles indicate acetone has a planar structure. Taking half the C-C bond length as the covalent radius of the carbon atom, the covalent radii of the other atoms become

	Covalent radius (Å)
Carbon	0.76
Hydrogen	0.33
Oxygen	0.48 0.68

B-38b.

From these data Figure 20(a) has been constructed. The area occupied by the acetone molecule on the surface (taken as the area enclosed by the straight lines) is 16\AA^2 which, compared with the co-area of 18.8\AA^2 (23) at 25°C . provides strong evidence that the co-area b in the Volmer equation is the actual area occupied by an adsorbed molecule on a mercury surface.

It should be remembered that Traube's Rule implicitly assumes that the entropy of the molecules on adsorption is unchanged. Strictly, the total energy of adsorption should be considered with reference to area occupied by the molecules on the surface. However, in the present instance ΔS (within the limits of experimental error) is constant for all the hydrocarbons, and because

$$\Delta F = \Delta H - T\Delta S$$

increments in the total energy change are equivalent to increments in the free energy change.

The entropy change on adsorption is also consistent with the picture of the molecules curled up on the surface.

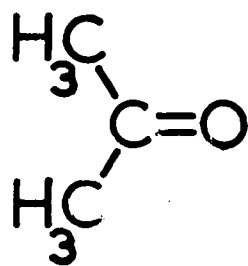
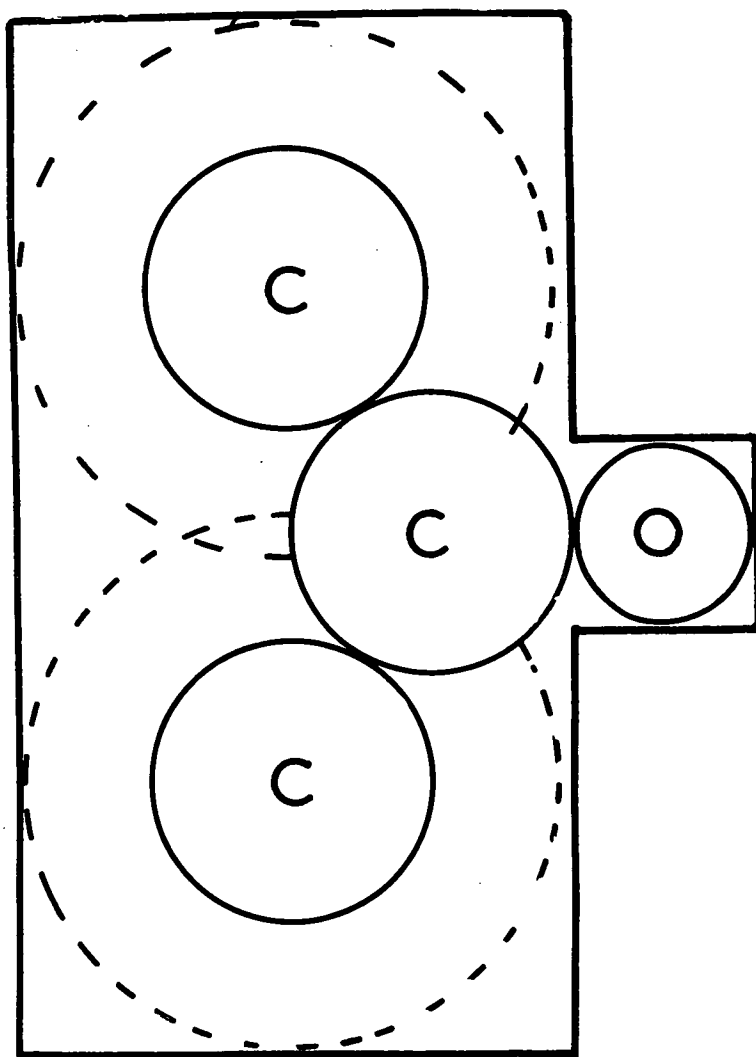


FIG. 20(a).

It can be shown that the entropy change may be considered as due to the molecules losing one degree of translational freedom and being converted from randomly linked gaseous molecules (intermediate between cylindrical and spherical form) to spherical molecules on the surface. Ward, it will be remembered, predicted spherical molecules on the surface from energy considerations.

The translational entropy in three dimensions for an ideal gas is given by the Sackur-Tetrode equation

$${}_3S_{\text{trans}} = 2.303 \log(M^{2/3} T^{5/2}) - 2.30$$

where M is the molecule weight and the entropy is given in cal.s.deg⁻¹mole⁻¹ for a pressure of 1 atmosphere. For an ideal two dimensional gas in the standard state (surface pressure 0.06084 dyne cm⁻¹, page B-3), Kemball²³ has given the translational entropy as

$${}_2S_{\text{trans}} = 2.303 \log M T a + 65.80$$

where a is the area per molecule, defined in the standard state as equal to 22.53 Å² (page B-3). In the following table the experimental entropy change, $\Delta S_{\text{exp.}}$, is compared with entropy change due to a loss of one translational degree of freedom, ${}_3-{}_2\Delta S_{\text{trans}}$.

20°C.	${}_3S_{\text{trans}}$	${}_2S_{\text{trans}}$	${}_3-{}_2\Delta S_{\text{trans}}$	$\Delta S_{\text{exp.}}$	$\Delta S_{\text{exp.}} - {}_3-{}_2\Delta S_{\text{trans}}$
n-pentane	38.6	29.9	8.7	11.4	2.7
n-hexane	39.1	30.2	8.9	12.7	3.8
n-heptane	39.6	30.5	9.1	12.6	3.5
n-octane	40.0	30.8	9.2	12.8	3.6

Huggins⁴⁶ has calculated the entropy of hydrocarbon molecules randomly linked (most probable shape in gas phase, Treloar⁴⁴) and in the spherical form (most probable shape in surface phase from energy considerations, Ward⁴²).

His equations are:-

Molecules randomly linked (gas phase)

$$S = 54 - 3k_{ir} + 9 \ln n + (1.8 + k_{ir})n$$

Molecules rolled into a sphere (surface phase)

$$S = 52 - 3k_{ir} + 8 \ln n + (1.8 + k_{ir})n$$

where k_{ir} is a constant giving the entropy of internal rotation per carbon atom and n is the number of carbon atoms in the chain.

Although the above equations are derived for large molecules, Huggins showed that smaller molecules obey them approximately. The difference between the two equations is $2 + \ln n$ and hence the decrease in entropy

associated with a molecule going from the gas to surface phase, $R \rightarrow S \Delta S$, above that due to a loss of a translational degree of freedom is

	$R \rightarrow S \Delta S$	$\Delta S_{\text{exp}} - 3 - 2 \Delta S_{\text{trans}}$
n-pentane	3.6	2.7
n-hexane	3.8	3.8
n-heptane	3.9	3.5
n-octane	4.1	3.6

The close agreement between the theoretical and experimental entropy change indicates that the picture of the hydrocarbon molecules relatively stretched out in the gas phase and rolled up into a spherical mass on the surface with a loss of one translational degree of freedom is a plausible one. This is in agreement with the work of Aston, Isserow, Szasz and Kennedy⁴⁷ who deduced from the calculation of the potential energy of the ethyl groups in n-butane that the relatively stretched out form of the hydrocarbon was favoured in the gas phase and who concluded that most of the short chain normal paraffins would be likewise.

In the accompanying table the entropy change calculated

by making allowance for the thickness of the surface layer, is compared with the theoretical entropy change. It is clear that the thickness of the surface layer has little effect on the values calculated on the basis of a standard surface thickness of 6\AA . However, it appears that previously there has been no justification in assuming a surface thickness of 6\AA on mercury.

	$R \rightarrow S \Delta S$	$(\Delta S_{\text{exp}})_{\text{corr.}} - 3-2 \Delta_{\text{trans.}}$
n-pentane	3.6	3.1
n-hexane	3.8	4.3
n-heptane	3.9	4.0
n-octane	4.1	4.1

The question of why n-pentane has such a low free energy change of adsorption remains to be answered. It was noted earlier that the standard free energy change on adsorption was almost a linear function of the co-area and not of the number of carbon atoms. Therefore it seems that n-pentane is relatively more curled up than the other hydrocarbons, as the increase in co-area along the series is:-

25°C.	Increase in co-area \AA^2
n-pentane - n-hexane	3.1
n-hexane - n-heptane	2.0
n-heptane - n-octane	2.1

This phenomenon may be due to the fact that, because of the valency angle of carbon ($109^{\circ}28'$), n-pentane can be curled up into a relatively smaller area than the other hydrocarbons. On the other hand, the observation may be due to the n-pentane not being of sufficient purity. It was 99 mole % as against 99.8 mole % for the other hydrocarbons.

The relatively low free energy of adsorption of n-pentane may be viewed from a slightly different angle. If the initial slopes of the surface-pressure (π) - vapour pressure (p) curves, $(d\pi/dp)_T$ are tabulated, it is clear that the initial slope of the n-pentane isotherm is relatively less than those for the other hydrocarbons. It was shown (page B-5) that

$$(d\pi/dp)_T = e^{-c}$$

$\pi \rightarrow 0$

where c is some measure of the free energy of

adsorption and is the intercept obtained by plotting $\log p/\pi$ against π .

25°C.	$(d\pi/dp)_{\pi \rightarrow 0}$	Ratio per CH ₂ group
n-pentane	2.64	2.80
n-hexane	7.39	1.99
n-heptane	14.72	1.84
n-octane	27.10	

Cassel and Salditt¹⁹ obtained an isotherm at 50°C. for n-hexane with an initial slope less than that calculated on the basis of the present investigation. The calculation is performed by assuming the same value of ΔH and calculating c from the equation (page B-6)

$$\Delta H = 2.303RT^2 \left(\frac{dc}{dt} \right)_p$$

and hence
$$e^c = (d\pi/dp)_{\pi \rightarrow 0}$$

This predicted value of $(d\pi/dp)_{\pi \rightarrow 0}$ may be compared with that derived from a plot of $\log p/\pi$ vs π of Cassel

and Salditt's data to obtain the intercept c and hence $(d\pi/dp)_T$ at $\pi = 0$.

50°C. n-hexane	$(d\pi/dp)_T$ $\pi \rightarrow 0$
Cassel and Salditt	2.83
Roberts	3.92

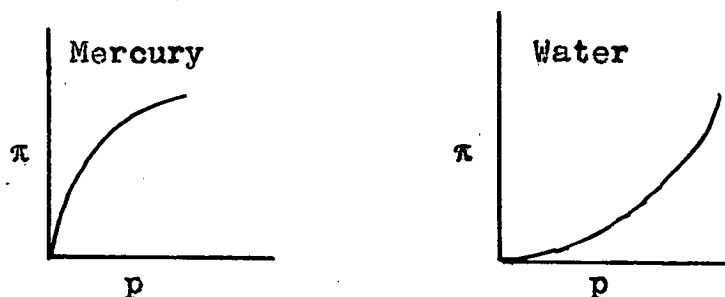
The lower value for the initial slope found by Cassel and Salditt can be readily explained, as the initial surface tension of the mercury was only 459 dynes cm^{-1} at 50°C. (assuming a temperature-coefficient of 0.2 dynes $\text{cm}^{-1}\text{deg}^{-1}$, $\gamma_{\text{Hg}}^{50^\circ\text{C.}} = 480.4 \text{ dynes cm}^{-1}$.) and hence the surface impurity in all probability prevented normal adsorption of n-hexane at low vapour pressures.

However, in the present instance the surface tension was correct and therefore the small amount of impurity in the n-pentane (~1 mole %) could only increase the initial slope if it were more strongly adsorbed or not affect it if it were not as strongly adsorbed as the n-pentane. The only mechanism by which impurity could lower the

initial slope would be to lower the vapour pressure (Raoult's law) and possibly lower dp/dT , and hence possibly give an apparently lower value of $(d\pi/dp)_T$ where p is calculated from the temperature $\pi \rightarrow 0$ (method used here) and not measured directly. Even so, 1 mole % would hardly cause such a drastic change. Consequently, the relatively low free energy of adsorption of n-pentane must arise from it being relatively more curled on the surface than the other hydrocarbons.

Comparison of the adsorption of hydrocarbons on mercury and water.

The adsorption isotherms on mercury are convex, on water concave^(32,40).



Convex isotherms represent a predominance of repulsive forces, concave isotherms a predominance of attractive forces between the adsorbed molecules. Consequently it is better to use the term "surface osmotic pressure" in place of "surface pressure" in order to emphasise the

effect of the surface in determining the forces between the adsorbed molecules.

The two-dimensional analogue of the Van der Waal's equation,

$$\left(\pi + \frac{a}{A^2}\right)(A - b) = kT$$

where a and b are constants depending on the nature of the surface and the adsorbed molecules, has been applied to adsorption on mercury and water.

The Volmer equation

$$\pi(A - b) = kT \quad \dots (1)$$

has been shown to fit the results for adsorption on mercury. This equation is simply the analogue of Van der Waal's equation with the repulsive forces predominating.

On water, the equation

$$\left(\pi + \frac{a}{A^2}\right)A = kT \quad \dots (2)$$

fits the data; here the attractive forces are the only important ones.

Both these equations in the form

$$\pi A = kT + b\pi \quad \text{for a mercury surface,}$$

$$\text{and } \pi A = kT - b'\pi \quad \text{for a water surface,}$$

$$\text{where } b' = \frac{a}{kT}$$

(since from (2) $\pi A = kT - \frac{a}{A}$ and A can be put equal to kT/π in the correction term), can be combined with the approximate form of the Gibbs equation to yield

$$\ln p/\kappa = \frac{b\kappa}{kT} + c.$$

For mercury, the plot of $\log p/\kappa$ vs κ has a positive gradient, for water a negative gradient. On the assumption of a standard surface thickness, the standard thermodynamic quantities may be determined.

It is worth noting here that with a mercury surface the surface pressures are high, and are consequently easy to measure, but of course it is very difficult to obtain a clean surface. On the other hand, with water it is easy to obtain the correct surface tension but difficult to measure the very low surface pressures.

In the accompanying table are given the standard thermodynamic quantities ΔH and ΔS for the adsorption of the hydrocarbons on water and mercury. The heat of condensation⁽⁵¹⁾ is also included.

	Surface	ΔH kilo-cal. mole ⁻¹	ΔS cal.mole ⁻¹ deg ⁻¹	ΔH kilo-cal.mole ⁻¹ condensation
n-pentane	Hg	10.3	11.4	6.46
	H ₂ O	5.1	3.7	
n-hexane	Hg	12.1	12.7	7.59
	H ₂ O	6.0	10.2	
n-heptane	Hg	13.0	12.6	8.90
	H ₂ O	6.6	11.0	
n-octane	Hg	13.9	12.8	10.07
	H ₂ O	7.3	9.5	
iso-octane	Hg	13.0	12.5	8.53
	H ₂ O	6.2	8.7	

If the heat of condensation is thought of as a heat of self adsorption, it appears that the hydrocarbon molecules are more firmly held in the liquid hydrocarbon than on the surface of water and less firmly held than on the surface of mercury. In other words, the hydrocarbon-hydrocarbon attraction is greater than the hydrocarbon-water attraction resulting in a concave isotherm, whereas the hydrocarbon-hydrocarbon attraction is less than the hydrocarbon-mercury attraction producing a convex isotherm.

The mutual repulsion of the adsorbed molecules on mercury will be dealt with quantitatively as the effect of molecules behaving as dipoles because of their electron envelopes being distorted in the field of force of the mercury surface.

The validity of the approximate form of the Gibbs equation.

Since the graph of $\log p/\pi$ against π is a test of the Gibbs equation in its approximate form

$$\Gamma = \frac{1}{RT} \left(\frac{d\pi}{d \ln p} \right)_T$$

and the surface equation of state

$$\pi(A - b) = kT \quad (\text{see page B-5}),$$

the departure from the initial linear portion of the graph at high relative pressures may be due either to the breakdown of the approximate form of the Gibbs equation or to the failure of the Volmer equation to express the state of the adsorbed molecules. All workers have accepted the two assumptions

- (i) vapour pressure = fugacity (activity) of vapour,
 - (ii) surface excess concentration = surface concentration,
- when using the Gibbs equation. As yet no-one has advanced evidence to justify the first assumption; the second assumption seems justifiable as the vapour phase would certainly have a very much lower concentration of molecules than the surface phase.

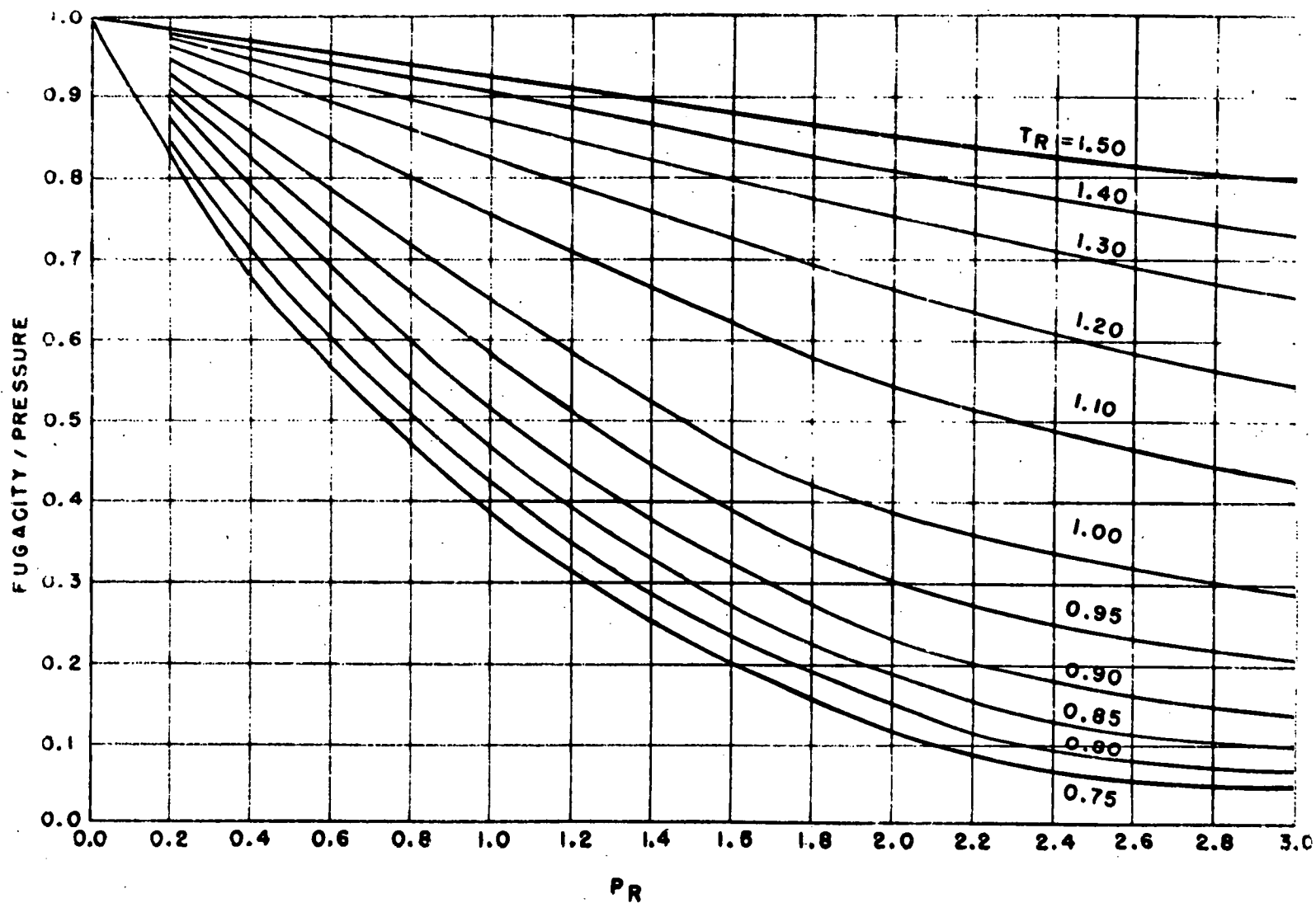


Figure 21 Fugacities of Hydrocarbons Plotted on a Reduced Basis

Newton⁽⁵⁰⁾ has shown that the ratio of the fugacity to the pressure, the "activity coefficient," is a function of the reduced temperature (ratio of the absolute temperature to the absolute critical temperature) and reduced pressure (ratio of the pressure to the critical pressure) only, for a large number of gases and vapours. It is clear from his graphs that the "activity coefficient" is almost unity over the range of temperature and pressure recorded for adsorption measurements on mercury. To give a more quantitative expression for the hydrocarbons, the following table gives the "activity coefficient" at saturation pressure at 25°C. estimated from either Newton's standard graphs or from the graph originally obtained by Kaye⁽⁴⁹⁾ and reproduced by Miller and Barley⁽⁴⁸⁾ for the normal saturated hydrocarbons, Figure 21.

25°C.	p_{sat} (atmos)	p_c (atmos)	p_r	T_c (°K)	T_r	f/p_{sat}
n-pentane	0.67	33.3	0.02	469.8	0.63	0.96
n-hexane	0.20	29.9	0.006	507.9	0.59	0.98
n-heptane	0.06	27.0	0.002	540.2	0.55	0.99
n-octane	0.018	24.6	0.0007	569.4	0.52	1.0

where p_{sat} = saturation pressure

p_c = critical pressure

p_r = reduced pressure

T_c = critical temperature

T_r = reduced temperature

f = fugacity.

The critical constants are those selected by Kobe and Lynn⁽⁵²⁾.

The error in assuming an activity coefficient of unity is not great, although n-pentane is beginning to show a significant departure from ideality and at higher temperatures the error is greater still, e.g. at 50°C.

$p = 1.59$ atmos., $p_r = 0.05$, $T_r = 0.68$ and hence the activity coefficient is 0.93.

The breaks in the $\log p/\pi$ vs π graphs must therefore be the result of the breakdown of the surface equation of state.

Changes of slope in graphs of $\log p/\pi$ vs π .

The surface pressures, at which departure from the initial linear portion of the graphs of $\log p/\pi$ vs π occurs, are shown in the accompanying table together with the corresponding areas per molecule, calculated from the Volmer equation, and the appropriate co-areas.

16.5°C.	π (dynes cm ⁻¹)	Area per molecule (Å ²)	Co-area (Å ²)
n-pentane	51	36.6	28.8
n-hexane	60	38.4	31.7
n-heptane	61	40.2	33.7
n-octane	62	42.5	36.0
iso-octane	61	41.1	34.6

An inspection of the graphs of π vs p^1/p , Figures 10-14, shows that $d\pi/dp$ increases rapidly at first and then much more slowly, and finally a further increase occurs. At surface pressures slightly greater than those quoted above $d\pi/dp$ is a minimum, indicating in all probability that a relatively stable monolayer is complete because

$$\Gamma = \frac{p}{RT} \left(\frac{d\pi}{dp} \right)_T$$

and therefore the number of molecules in the surface layer

is relatively steady, a state of affairs expected when a monolayer is formed. This observation lends further weight to the assumption that the co-areas represent the actual areas occupied by the hydrocarbon molecules on the surface.

At vapour pressures approaching saturation a rough calculation from the Gibbs equation shows that the area per molecule is approximately 20 \AA^2 . In addition, the lowering of the surface tension is very nearly the same for all the hydrocarbons at saturation. The simplest explanation of these two facts is that the hydrocarbon molecules are unrolled and adsorbed end on to the surface, the area occupied by the molecule being the cross sectional area for the hydrocarbon chain. Such a closely packed monolayer would be more stable than the less closely packed monolayer produced at lower relative pressures.

The adsorbed molecules as similarly oriented dipoles.

Bering and Serpinsky⁽²⁶⁾ starting from the virial equation of state derived the following equation of state (for the adsorbed molecules),

$$\pi = kT\Gamma + 4.5\mu_e^2\Gamma^{5/2}$$

where μ_e is the dipole moment of the molecule oriented normal to the surface.

They reasoned that the repulsive forces could be considered as due to the mutual repulsion of induced dipoles. This equation may be tested by taking logarithms

$$\log(\pi - kT) = \log \beta = \frac{5}{2} \log \Gamma + \log 4.5\mu_e^2$$

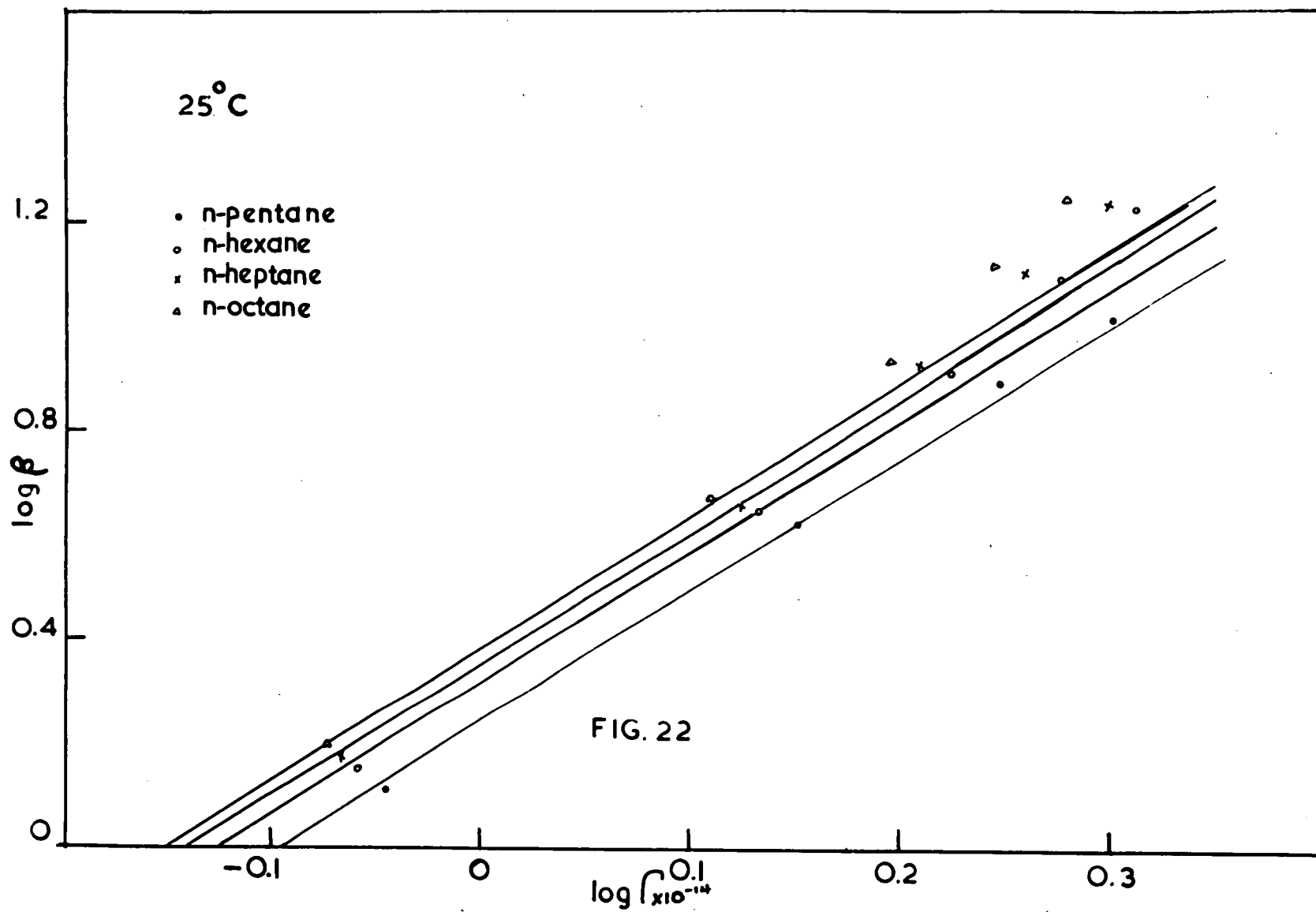
(where β is departure of the actual isotherm of state from the ideal isotherm which would be given by an ideal two dimensional gas),

and plotting $\log \beta$ against $\log \Gamma$. A straight line should be obtained with a slope of $\frac{5}{2}$ and the intercept on the $\log \Gamma$ axis should enable μ_e to be determined.

It is more convenient to calculate Γ from the Volmer equation than from the Gibbs equation. Also calculation from the Volmer equation will show the range of surface pressures over which the two equations express the state of the adsorbed molecules. The table below shows the values of Γ calculated for arbitrarily selected surface pressures over which the Volmer equation is valid; also

included are the calculated values of β , the departure from ideality, and the values of μ_e . Figure 22 shows the plot of $\log \beta$ vs $\log \Gamma$. Straight lines of the correct slope $\frac{5}{2}$ are obtained up to surface pressures of 10-15 dynes cm^{-1} . This indicates that although the virial equation of state is similar in form to the Volmer equation (page B-9), its range of applicability is more limited. The value of k was taken as 1.381×10^{-16} .

25°C.	η dynes cm ⁻¹	$\eta \times 10^{-14}$ molecules cm ⁻²	β	μ_e (Debye units)
n-pentane	5	0.901	1.3	1.9
	10	1.42	4.2	
	15	1.77	7.77	
	20	2.01	11.7	
	25	2.19	16.0	
n-hexane	5	0.874	1.4	2.1
	10	1.36	4.4	
	15	1.68	8.1	
	20	1.89	12.2	
	25	2.06	16.5	
n-heptane	5	0.859	1.5	2.2
	10	1.33	4.5	
	15	1.62	8.3	
	20	1.82	12.5	
	25	1.98	16.9	
n-octane	5	0.843	1.5	2.3
	10	1.29	4.7	
	15	1.57	8.6	
	20	1.76	12.8	
	25	1.90	17.2	
iso-octane	5	0.853	1.5	2.2
	10	1.31	4.6	
	15	1.60	8.4	
	20	1.80	12.6	
	25	1.94	17.0	



It is clear that the electron envelopes of the adsorbed molecules are greatly deformed in the field of the mercury surface and that the induced dipole moments are of the same order as the permanent dipole moments of polar molecules. These findings are in agreement with Mignolet's surface potential measurements of CH_4 , C_2H_2 , C_2H_4 and C_2H_6 on a mercury surface; these hydrocarbons showed surface potentials of +0.16 - 0.27 volts. Mignolet concluded that the molecules are strongly polarised in the field of the mercury surface. Bering and Ioileva have shown that for toluene, diethyl ether and acetone the induced dipole moments are proportional to the mean polarizability of the molecule. Using these data, it is possible to attempt an estimation of the magnitude of the electric field intensity at a mercury surface and hence deduce the freedom of movement of the molecules on the surface. The induced dipole moment (μ_e) is proportional to the electric field intensity (F) where the proportionality constant is the polarizability (α)

$$\mu_e = \alpha F$$

	μ_e (Debye units)	$\alpha \cdot 10^{25}$ (c.g.s. units)	$F \cdot 10^5$ (e.s.u. cm^{-1})
Toluene	2.2	123	1.8
Diethyl ether	1.8	88	2.0
Acetone	1.5	64	2.3

Since 1 e.s.u. of potential cm^{-1} is 300 volts cm^{-1} , the mean electric field intensity is 6×10^7 volts cm^{-1} . The maximum energy of a dipole μ (e.s.u.) in a field of strength F (e.s.u. cm^{-1}) is μF ergs. Hence the energy associated with an induced dipole of the order of 2×10^{-18} (e.s.u.) is

$$\mu F = 2 \times 10^{-18} \times 2 \times 10^5 = 4 \times 10^{-13} \text{ ergs molecule}^{-1}.$$

The mean energy of thermal agitation for ideal gas in two dimensions is kT per molecule. As a first approximation the thermal energy of the adsorbed molecules may be taken as kT ergs molecule $^{-1}$ or 4.1×10^{-14} ergs molecule $^{-1}$ at 25°C . Since the energy of the dipole is approximately 10 times the energy of thermal agitation, the molecules must be rather firmly attached to the mercury surface.

Summary.

The results have been analysed on the basis of the Volmer and Virial equations of state. The co-area in the Volmer equation has been identified with the area occupied by the adsorbed molecule. It appears that, although the co-areas and entropy of adsorption are consistent with the picture of the hydrocarbon molecule stretched out in the gas phase and rolled up in the surface phase, the relatively high heat of adsorption and the extreme distortion of the electron envelope of the adsorbed molecule indicates that the shape on the surface is rather complicated.

SECTION III. THE ADSORPTION OF WATER ON MERCURY.

The anomalous results obtained for the adsorption of water vapour on mercury have been mentioned under the "Review of Literature on Adsorption of Vapours on Mercury." Kenball⁽²⁵⁾ (1946), Karpartchev, Smirnov and Vorlichenkova⁽⁴⁾ (1953) and Bering and Ioileva⁽⁶⁾ (1953) obtained different adsorption isotherms, although the mercury used in each instance was of the correct surface tension (within the limit of experimental error). The "sessile drop" method was used by Kenball and Karpartchev et al., the "maximum pressure in a drop" method by Bering and Ioileva. The latter group of workers claimed that only their results corresponded to the physical adsorption of water vapour on mercury and that the much higher surface pressures obtained with the sessile drop method were due to either

(a) displacement of impurities from the glass measuring vessel by the water vapour, or

(b) "activated type" adsorption,

both, they claimed, were likely to occur with the sessile drop method in which a single large drop is in contact with the vapour for the whole series of measurements.

In order to test these explanations the following procedure was adopted to render the "sessile drop" method

dynamic in the same sense as the "maximum pressure in a drop" method, in that a fresh surface is provided for each measurement and the measurement is completed within 3 minutes of being in contact with the water vapour. The vapour source was held at a temperature to give a pressure of water vapour which could come to equilibrium quickly throughout the system on lowering the large mercury cut-off separating the mercury surface from the vapour source. It was found that a vapour pressure of several millimetres of mercury could reach equilibrium almost immediately on lowering the large mercury cut-off. The rate of attainment of equilibrium was judged by the pressure difference recorded between the arms of the cut-off which isolated the grease taps from the grease-free part of the apparatus. It was possible to complete a measurement of the surface tension before 3 minutes had elapsed from the time of lowering the large mercury cut-off.

In preliminary experiments it was observed that the surface tension continued to fall on allowing the mercury to remain in contact with the water vapour. However, repeating the process of admission of water vapour, withdrawal of vapour by application of liquid nitrogen followed by evacuation and distillation of the mercury, the surface tension which was recorded in the first 3 minutes remained steady (an hour was the longest period tested). The most likely explanation of this phenomenon

is that water vapour slowly displaces impurities from the glass surface of the measuring vessel which are then adsorbed on the mercury surface.

Figure 23 shows the adsorption isotherm for water obtained by Karpartchev et al. and the results of the present investigation. The agreement is good. All readings were obtained by the method outlined. It will be remembered that the procedure adopted by Karpartchev et al. was similar to that used here; however, no mention was made in their work of how soon after the admission of the water vapour the surface tension was measured.

The good agreement with Karpartchev's work does not clarify the anomalous result obtained by Kemball and Bering and Ioileva. Nevertheless it is clear that Bering and Ioileva's explanations are untenable.

C-4.

WATER

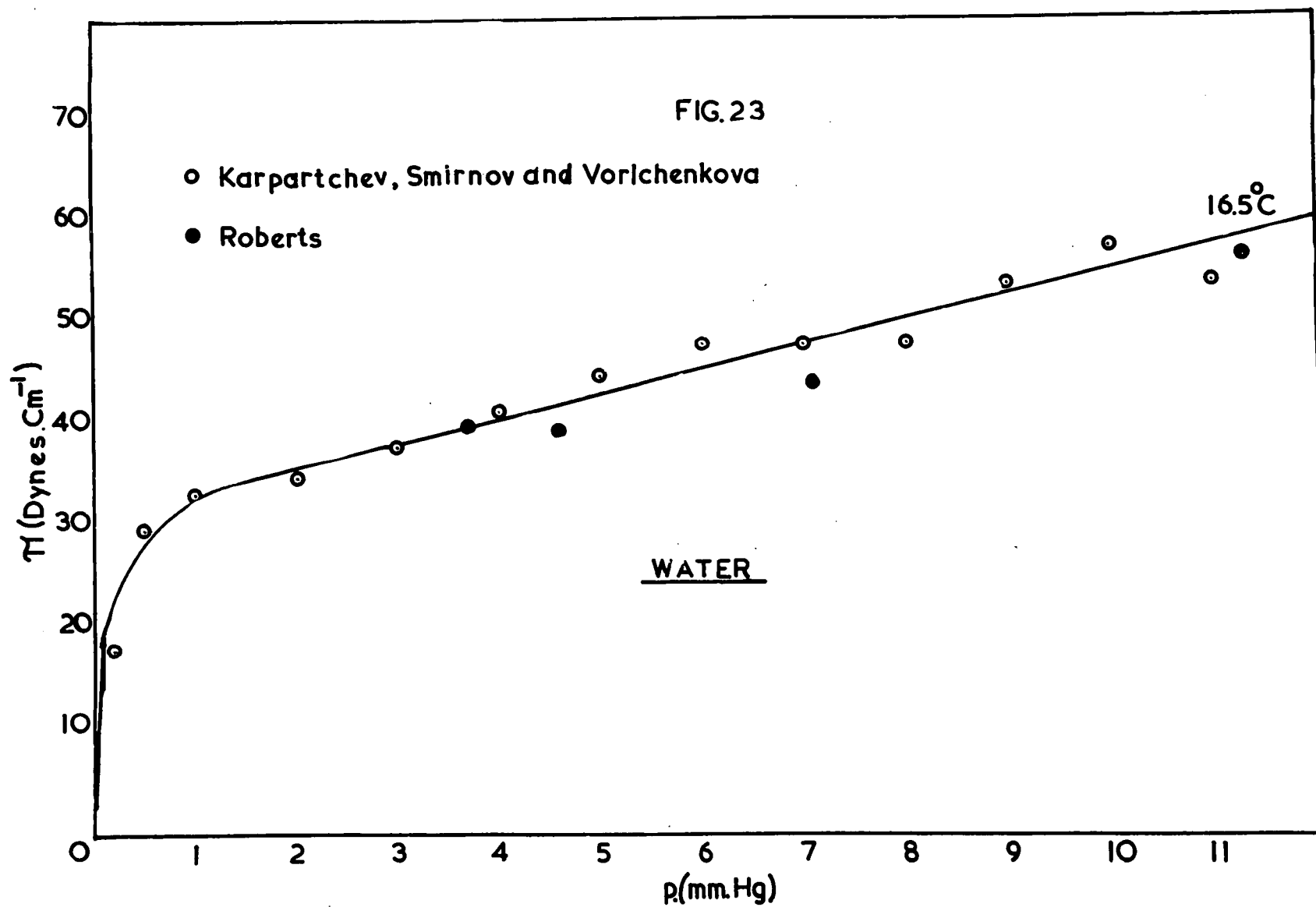
Temperature $16.5 \pm 0.2^{\circ}\text{C}.$

$\gamma^0 = 487.3 \pm 1.0 \text{ dynes cm}^{-1}$

Temperature of Water $^{\circ}\text{C}.$	p (mm.Hg) [⊗]	π (dynes cm^{-1})
- 2.5	3.7	40.0
0	4.6	39.6
+ 6.1	7.1	43.7
+13.0	11.3	56.2

⊗ Vapour pressures are taken from the

"Handbook of Physics and Chemistry (1943-4).



REFERENCES

1. ADAM, The Physics and Chemistry of Surfaces, 3rd Edition, 1941.
2. BURDON, Surface Tension and the Spreading of Liquids.
3. KEMBALL, Trans. Faraday Soc. 526 (1946).
4. KARPARTCHEV, SMIRNOV and VORLCHENKOVA, J.Phys.Chem. (U.S.S.R.), 27, 1228 (1953).
5. ZIESING, Aust. J.Physics, 86 (1953).
6. BERING and IOILEVA, Proc.Acad.Sci.(U.S.S.R.), 23, 85(1953).
7. STAGE, Iowa State College Journal of Science, 31, 33(1956).
8. QUINCKE, Phil.Mag. April (1871).
9. WORTHINGTON, Phil.Mag., 20, 51 (1885).
10. LAPLACE, Méc.Céleste, 2nd supplement to book 10, p.483.
11. MATHIEU, Theorie de la Capillarite, p.137.
12. PORTER, Phil.Mag., 15, 163 (1933).
13. BURDON, Trans.Faraday Soc., 28, 866 (1932).
14. BARTON, Vacuum, 3, 51 (1953).
15. TAYLOR and HULETT, J.Phys.Chem., 17, 565 (1913).
16. IREDALE, Phil.Mag., 45, 1088 (1923).
IREDALE, Phil.Mag., 48, 177 (1924).
IREDALE, Phil.Mag., 49, 603 (1925).
17. MICHELI, Phil.Mag., 3, 895 (1927).
18. CASSEL, Z. Elektrochem., 37, 642 (1931).
19. CASSEL and SALDITT, Z. Phys.Chem.A, 155, 321 (1931).

20. BOSWORTH, Trans.Faraday Soc., 28, 903 (1932).
BOSWORTH, Trans.Faraday Soc., 35, 1349 (1939).
21. MILLER, Adsorption of Gases on Solids, Cambridge University Press (1949).
22. GIBSON, quoted by Burdon, Trans.Far.Soc., 28, 866 (1932).
23. KEMBALL and RIDEAL, Proc.Roy.Soc., A187, 53 (1946).
KEMBALL, Proc.Roy.Soc., A187, 73 (1946).
KEMBALL, Proc.Roy.Soc., A190, 117 (1947).
KEMBALL, Proc.Roy.Soc., A201, 377 (1950).
24. BERING and IOILEVA, Bull.Acad.Sci.(U.S.S.R.), 7 (1955).
BERING and IOILEVA, " " " " 193 (1955).
25. BERING and SERPINSKY, Problems of Kinetics and Catalysis, Acad.Sci.U.S.S.R. Press.Moscow and Leningrad, 383 (1949).
26. BERING and SERPINSKY, Reports, Acad.Sci. U.S.S.R., 79, 273 (1951).
27. HARTER, RYDER and WILLIAMSON, J.Chem.Physics 23, 1966(1955)
28. TOPPING, Proc.Roy.Soc., A114, 67 (1927).
29. KAYE and LABY, Tables of Physical and Chemical Constants, 11th Edition, 1956.
30. BLUE and GIAUQUE, J.A.C.S., 57, 991 (1935).
31. International Temperature Scale (1948).
32. JONES and OTTEWILL, J.C.S., 4076 (1955).
33. YOUNG, Scientific Proceedings of Royal Dublin Society, 12, 374 (1910).
YOUNG, J.Chem.Soc., 73, 675 (1898).

34. MÜNDEL, Z.Phys.Chem., 85, 435 (1913).
35. FARADAY, Phil.Trans.Roy.Soc., 135, 155 (1845).
36. WÖRINGER, Z.Phys.Chem., 34, 257 (1900).
37. STULL, Ind. Eng.Chem., 39, 517 (1947).
38. SONDAK and THODOS, American Inst.Chem.Eng., 2, 347 (1956).
39. FROST and KALKWARF, J.Chem.Phys., 21, 264 (1953).
40. CUTTING and JONES, J.C.S., 4067 (1955).
41. TRAUBE, Liebigs Ann., 265, 27 (1891).
42. WARD, Trans.Far.Soc., 42, 399 (1946).
43. LANGMUIR, J.A.C.S., 39, 1883 (1917).
44. TRELOAR, Proc.Physic.Soc., 55, 345 (1943).
45. MARK, Physical Chemistry of High Polymeric Systems,
141 (1940).
46. HUGGINS, J.Chem.Phys., 8, 181 (1940).
47. ASTON, ISSEROW, SZASZ and KENNEDY, J.Chem.Phys., 12,
336 (1944).
48. MILLER and BARLEY, Ind.Eng.Chem., 36, 1018 (1944).
49. KAY and LEWIS, Oil Gas J., 32 No.45, 40, 114 (1934).
50. NEWTON, Ind.Eng.Chem., 27, 302 (1935).
51. National Bureau of Standards Circular C461, "Selected
Values of Properties of Hydrocarbons."
52. KOBE and LYNN, Chem.Reviews, 52, 117 (1953).
53. MIGNOLET, J.Chem.Phys., 21, 1298 (1953).
54. ROMERS and CREUTZBERG, Rec.Trav.Chim., 75, 331 (1956).

