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THE DEPENDENCE OF VISCOSITY OF LIQUIDS ON CONSTITUTION.*

By A. H. Nissan, B.Sc., A.M.Inst. Pet., L. V. W. Clark, Ph.D., M.I.Mech.E., F. Inst. Pet. and A. W. Nash, M.Sc., M.I.Mech.E., F. Inst. Pet.

Synopsis.

In reviewing the literature the authors considered certain points to be accepted universally and took these as the basis of their work. An ultimate flowing unit of liquid was assumed to move in "jumpy" fashion and energy to be consumed in giving the ultimate unit the necessary increment to enable it to "jump." This energy was represented by Q in $\eta = Ae^{Q/RT}$. The connection between Q and the boiling point T_B was found to be more fundamental than the relationship between Q and the freezing point.

The ratio of molal latent heat of vaporization to the corresponding heat of viscosity was found to be a constant, n, characteristic of the liquid; "n" appeared to afford the key to the study of viscosity as it is affected by constitution.

The authors obtained a formula connecting the molal latent heat of vaporization and the melting point of monoatomic liquids and concluded that the three states of matter, solid, liquid, and gaseous, can be defined by a continuous series of changes with regard to the laws of viscous flow.

The relationship between viscosity and vapour pressure was studied in detail and the conclusion reached that both phenomena are functions of essentially the same variables. The value of "n" for n-paraffin was proved to be fractional, 4·13.

Trouton's rule combined with Clausius Clapeyron's equation indicated that log η plotted against T/T_B for the n-paraffins would yield a single curve. This was called the "specific viscosity curve." An artifice was used whereby the temperature scale was so changed that log η plotted against T/T_B on this constructed scale yielded a straight line. It was then proved that any liquid which yielded a straight line on these charts obeyed the same law as did the n-paraffins with regard to change of η with temperature. All the 137 liquids tested, shown to represent many hundred chemical entities, yielded straight lines. Hence it was concluded that all liquids, associated or unassociated, must possess only one formula connecting η and T.

It was found that the heat of activation of viscosity was a function of temperature even for n-paraffins. Thus the chief distinction between associated and unassociated liquids from the point of view of viscosity disappears in principle.

The liquids studied fell into three classes :—

(1) Unassociated compounds which fell in a fan-shaped manner between two limiting positions.

(2) Associated liquids, the viscosity at the boiling points of which fell in a similar manner to (1) but the "specific viscosity curve" of which deviated at a more rapid rate to the right.

(3) The elements.

In studying these liquids it was found that the chief variable which characterizes the "specific viscosity curve" was the molecular shape. Molecular shape has been discussed and postulated as the shape of the equipotential surfaces surrounding the molecule. When the molecular shape was nearly symmetrically spheroidal the "specific viscosity curve" was found to lie to the right of the curve for a liquid of which the shape of the equipotential surface was less spheroidal. Dipole moments were found to be of secondary importance. The nature of the atoms of the molecule has been shown to be immaterial; once a certain shape has been attained

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* Paper received 27th May, 1939, and presented at a meeting of the Institute in London on Thursday, 14th March, 1940.

the "specific viscosity curve" assumes a position on the chart independent of the nature of the molecule. The specific viscosity curve for CCl_4 was found to lie in the limiting position to the right.

Various liquids were discussed in view of this hypothesis, and were found to support it.

Pyridine and dibenzyl afforded additional and more definite proofs of the hypothesis, as shown from the X-ray analysis of these molecules.

Association was discussed on the same lines. It was found that association, like η, was a function of (T/T_B).

Viscosity index was studied from this point of view. A remarkable conclusion was that a liquid composed entirely of cyclic structure would yield high V.I. if the rings were all joined end-on, so that the molecule was elongated in shape.

The elements afforded important anomalies, and a study of viscosity at the boiling point of these elements showed that there was an unsuspected rise in η with rise in temperature for all liquids. Thus the chief distinction between gases and liquids with regard to viscosity disappears.

It has been shown that one formula must exist for all flowing matter with certain terms predominating, depending on the state of matter and the nature of flow; for example, the term defining fall of viscosity with rise of temperature predominates in the order: gases at low pressure, gases at high pressure, helium, metallic elements, non-metallic elements, unassociated liquids, associated liquids, non-Newtonian liquids, plastics, and crystals.

INTRODUCTION.

THE viscosity of a pure liquid is a function of many variables, the most important being the nature of the liquid, the degree of its association, and the temperature and pressure at which the viscosity is determined. In certain liquids the stress existing at the time of measurement is another important factor, whilst in all liquids specific volume appears to exert some influence. A study of the dependence of viscosity on any one variable requires that all other variables must either be eliminated or reduced to a constant datum level.

To facilitate the study of viscosity all liquids in non-Newtonian state of flow have been avoided and viscosity values at atmospheric pressure only have been used. Two variables were therefore made constant. The elimination of the effects of temperature or the maintenance of this factor at a constant value is not so easy to forecast. Thorpe and Rodger,[1] in their classical research on viscosity, assert, "It seems futile to expect that any definite stoichiometric relations should become evident by comparing observations taken at the same temperature." When comparisons were attempted at a reduced temperature of 0·6 T_C no results worthy of publication were obtained. Similarly a recent expression for a "reduced temperature" which yielded excellent results in comparing static properties of pure liquids failed with the dynamical property of vicosity.[2] On the other hand, Dunstan and Thole [3] showed that the logarithm of viscosity is additive with molecular weight and structural characteristics *at equal temperatures*. Again, the majority of viscosity–temperature equations which have proved accurate are based on the absolute-temperature scale. Nevertheless, to assume that equal temperatures should prove a fundamental basis for the comparison of viscosity of liquids boiling at various temperatures and of various critical constants appears at least an unsatisfactory foundation for this study.

To decide the correctness or otherwise of this assumption, and to understand fully the fundamental variables which were found to affect viscosity,

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a critical review of the literature on the subject was made. A list of the publications which were found useful for this purpose is given in the bibliography appended at the end of the paper.[1-53] It is felt that a brief *résumé* of the accepted concepts regarding the nature of viscous forces and the dependence of these forces on temperature would be useful here, particularly to determine the correct temperature levels for comparisons.

Various authorities have testified to the fact that the equation,

$$\eta = Ae^{B/T}$$

where η = viscosity in absolute units,
T = absolute temperature at which the viscosity measurement is affected,
A and B = constants,

holds for a large number of liquids to a remarkable degree of accuracy. Thus it has been shown that it holds for metals, paraffins, ethers, alcohols, acids, acid anhydrides, bromides, chlorides, iodides, aromatic hydrocarbons, ketones, and esters, with deviations of the general order of less than 1 per cent. (Dunn). Again, Andrade states, " It is doubtful if the experimental error is less than the very slight divergence between the calculation and experiment." Hence this formula became the basis—and the objective—of many theories attempting to explain the nature of viscosity phenomena.

Again it was found that if the constant B is multiplied by R or k, the gas or Boltzmann constant, respectively, the dimensions of the product are that of energy. Thus

$$B = Q/R$$

where Q = increment of energy of activation of viscosity.

$$\therefore \ \eta = Ae^{Q/RT}$$

Several variants of this equation have been proposed, but in view of the remarkable accuracy of the simple formula stated here, and also in view of the many statements that the improvements introduced by using the complex variants are generally negligible except in the case of such liquids as water, this formula will be used principally in this survey.

The variously accepted ideas about viscosity of liquids have some broad similarities, although there are differences in detail. Thus it is postulated that a liquid " at rest " is composed of discreet particles, each of which oscillates about a temporary point of equilibrium. Occasionally, probably due to collision with others, some particles are possessed of greater energy than the average, and when this energy is of greater value than a certain critical value, the particles possessing them take a jump in the direction of least resistance. Thus the mean position of equilibrium is transferred from one point in space to another. Since the liquid is not subjected to any external force and the distribution of the particles is at random, the direction of the jump is similarly at random. Therefore, on an average, as many particles leave a portion of space as those coming into it per unit time, and the liquid remains " at rest."

When the liquid is subjected to a pressure differential it is seen that the direction of least resistance has now been influenced. Instead of being equal in all directions, it has become increasingly difficult for a particle to jump against, and easier to jump with, the direction of the pressure differential. A greater number of particles would jump in a unit time towards the lower pressure than towards the higher one, and flow ensues. Some particles would jump in a direction across that of the main line of flow, but this point is controversial. Certain authorities maintain that the number of particles jumping from one layer to another is negligibly small. Others are equally certain that the main cause for viscous drag is due to such particles jumping from layers of slow speeds to neighbouring layers of higher speeds and *vice versa.* In the first hypothesis it will be required to impart to the particles the energy increment necessary before a sudden jerk is accomplished. With the latter hypothesis the loss of energy on collision has to be made good by an external source, and thus a viscous drag manifests itself. Of recent years the greater number of publications assume that the energy is required for particles to jump in the direction of flow.

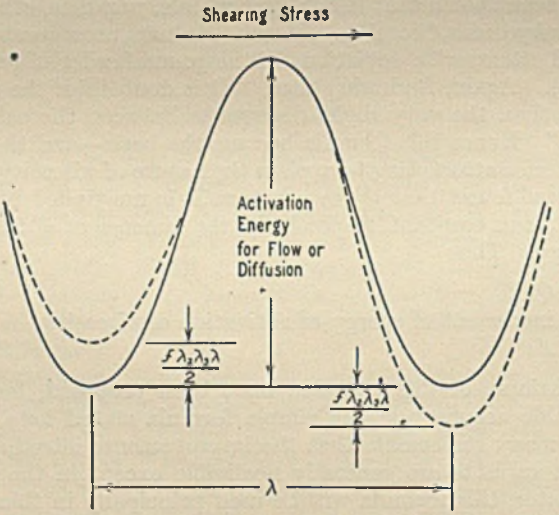


FIG. 1.

ENERGY PROFILE OF THE PATH OF A FLOWING MOLECULE.

Fig. 1 is a mathematical rendering of this physical picture (Ewell). Ordinarily a molecule, or group of molecules if necessary, can jump from right to left or *vice versa* from one mathematical minimum of energy—*i.e.*, position of equilibrium—to another, passing through an activated state represented by the maximum on the curve. When a shearing stress is imposed on the system in the direction of the arrow, the effect is to depress the mathematical minimum by a certain quantity, $f\frac{\lambda_2\lambda_3\lambda}{2}$, in the direction of the arrow and raise it by the same quantity in the opposite direction.

f = tangential force per unit area.
λ_2 and λ_3 = dimensions of the moving particle in the plane of the shearing force.
λ = distance between two points of equilibrium.

Thus flow ensues in the direction of the arrow as the system tends to attain equilibrium again.

On this basis the action is monomolecular. An equation obtained on these assumptions by Eyring and his collaborators, however, tended to show that there might be a bimolecular form of action as well. This fact is emphasized by the Andrade equation for the viscosity of molten monoatomic metals at the melting point which assumes entirely bimolecular phenomena. The manner in which two molecules take part in a viscous flow is not certain, and different workers postulated different modes of action. Fig. 2 is one example of such a mechanism (Eyring *et al.*). Andrade assumes another, nearer the formation of a temporary structure in the liquid.

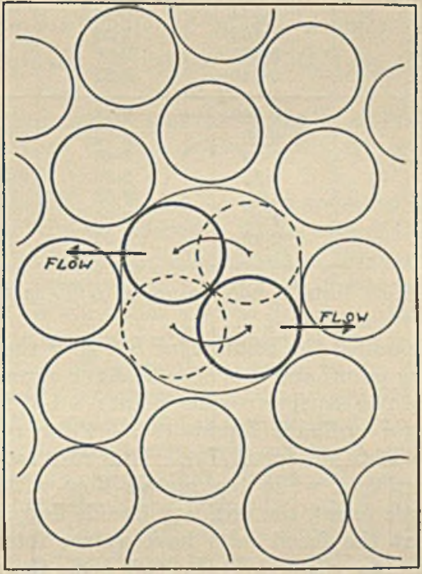


FIG. 2.

BIMOLECULAR MECHANISM OF FLOW.

Probably higher orders of actions exist, too, in viscous flow. There is evidence, however, towards the postulation that at the melting point the action is probably mainly bimolecular, whilst as the temperature rises monomolecular flow predominates. At the boiling point all flow is probably in a monomolecular form, but the fact that certain organic acids evaporate in the bimolecular form show that this generalization should not be taken too strictly. Even then, however, if the two particles forming a bimolecular complex move in the monomolecular manner, the flow is monomolecular.

Irrespective of the type of flow, it is certain that flow in ordinary liquids requires energy. This energy is represented by Q in the equation

$$\eta = Ae^{Q/RT}.$$

Attempts were made to correlate Q with the latent heat of fusion and the latent heat of vaporization. The most recent attempt to correlate it with the former is due to Bernal, who points out that the quantity B in the simple exponential formula varies irregularly, but that B/T_f, or the "viscosity entropy change of the substance" at freezing point, is, for each chemical type of liquid, relatively constant. This is substantiated by the following table.

	B.	$B/T_f \times 10^3$.	$B/T_B \times 10^3$.	
NaCl	9·10	8·44	5·40	Ionic.
NaBr	8·00	7·79	4·81	
K	7·40	7·09	4·39	
KBr	7·96	7·93	4·82	
O_2	0·406	7·41	4·49	
A	0·524	6·24	6·03	Simple.
N_2	0·468	7·39	6·35	
CO	0·463	7·00	6·46	
CH_4	0·740	8·31	6·61	
Hg	0·598	2·56	0·94	Metallic.
Na	0·96	2·59	0·95	
K	1·15	3·43	1·16	
Pb	2·32	3·86	1·33	
Cd	1·59	2·68	1·57	
Ag	4·87	3·95	2·25	
Zn	2·92	4·22	2·47	

For ionic and simple liquids the value of B/T_f is 6·2–8·4, whilst for metallic liquids the value is 2·6–4·2.

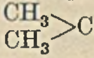
The authors have added the column for B/T_B, or the viscosity entropy change at the boiling point, and it is seen that the agreements are as good as, if not better than those for freezing point: 4·4–5·4 for ionic (7·1–8·4 for B/T_f), 6·0–6·6 for ordinary liquids (6·2–8·4 for B/T_f), and 0·94–2·5 for metallic liquids (2·6–4·2 for B/T_f). This can be explained on the assumption (Eyring) that while the metals flow without their valence electrons (*i.e.*, in ionic form), the ordinary liquids flow as molecular units. It is significant that the fused salts have values intermediate between fused metals and ordinary liquids. (On this basis the regularity of B/T_f becomes due simply to the fact that the ratio T_f/T_B is usually around 0·5). The division into ionic, simple, and metallic types is more marked with B/T_B than with B/T_f. This fact suggests a closer relationship between viscosity and boiling point (or vapour pressure) than with viscosity and freezing point.

Previously Dunn found that the ratio of the heat of vaporization to that of viscosity was a constant characteristic of the liquid and compiled the following list.

Compound.	$n = L/Q$.
Paraffins	4·0
Acetone	4·45
Ethers	4·11
Iodides	4·39
Benzene	2·75
Formic acid	2·62
Methyl alcohol	3·62
Water	2·72 at 0° C. 3·3 at 100° C. approx.

Dunn attributed the variation of n with temperature for water to the association of this liquid.

Later Eyring and Ewell again found that the equation for viscosity could be given by substituting $\frac{\Delta E_{\text{vap.}}}{n}$ for Q in the exponential term and calculated " n " for various compounds. These workers state that " n " has a value of 4 (to nearest 0·5) for liquids composed of " polar or elongated molecules " and a value of 3 for liquids composed of " spherically symmetrical molecules." A sharp separation of liquids into $n = 3$-liquids and $n = 4$-liquids is assumed as follows :—

$n = 3$ CCl_4, C_6H_6, *cyclo*Hexane, CH_4, N_2, CO, A.
$n = 4$ n-C_5H_{12}, n-C_6H_{14}, n-C_7H_{16}, CS_2, $CHCl_3$, C_6H_5–CH_3, C_2H_5–OC_2H_5,
$C_2H_5O_2C_2H_3$,  $\begin{matrix}CH_3\\CH_3\end{matrix}\!>CO$, C_2H_5I, C_2H_5Br, CH_3I, C_2H_4

No explanation is given for the fact that $C_2H_4CL_2$ and $C_2H_4Br_2$ have $n = 3\frac{1}{2}$, although the fact that O_2 also possesses $n = 3\frac{1}{2}$ is " attributed to its paramagnetic property."

The $n = 3$-liquids CH_4, CCl_4, and A have spherical fields of force about the molecules (approximate, probably, in the case of CH_4 and CCl_4), whilst N_2 and CO have probably the same shape of " potential energy shells," and the same is apparently true in the case of benzene and *cyclo*hexane. The concept is put forward that viscous flow is a form of vaporization in one degree of freedom for the $n = 3$-liquids. To explain the meaning of the last statement, reference should be made to the " theory of holes."

This theory is only an elaboration of the postulate put forward in the previous pages that a molecule or a combination of molecules require an increment of energy to move from one position of equilibrium to another. It is stated in the theory of holes that the activation energy is to be used for providing a hole into which the molecule may flow; but this may not necessarily be equal to the volume of the molecule. The energy required to transfer a molecule from liquid to vapour without leaving a hole in the liquid is $\Delta E_{\text{vap.}}$, whilst $2\Delta E_{\text{vap.}}$ is required to move the molecule and leave the hole empty in the liquid. Thus for a fraction of a hole $\frac{\Delta E_{\text{vap.}}}{n}$ is needed, where n denotes the ratio of the volume of the molecule to that of the hole —*i.e.*, $\Delta E_a = \frac{\Delta E_{\text{vap.}}}{n}$.

It appears that for spherically shaped molecules an activation energy of flow is the energy required to make a hole one-third the size of a molecule—*i.e.*, $\Delta E_{\text{vap.}}/3$—whilst for polar or elongated molecules, where certain preferred orientations are possible, a smaller fraction of the energy of vaporization is sufficient for activation $\left(i.e.,\ n \gg 3 \text{ in } Q = \Delta E_{\text{vis.}} = \frac{\Delta E_{\text{vap.}}}{n}\right)$.

When n assumes greater values than 4—as in the metals—the phenomenon is well explained by maintaining that only a small fraction of the molecular volume is being affected in each elementary process—*i.e.*, the metals are flowing without their valence electrons as ions (Ewell). This explanation receives emphasis from the fact that the ratio B/T_B for metals is a lower constant than B/T_B for ordinary liquids, whilst B/T_B for fused salts, which should consist of ionized metallic and acidic radicals, occupies an intermediate position.

A point of paramount importance arises here. In view of the close relationship of viscosity and vaporization phenomena—to be further illustrated below—should the liquid state be treated as a continuous set of changes in series with the gaseous state? Andrade believes that in studying viscosity of liquids success is possible only if the investigator starts with the solid state. In fact, the equation this worker obtained for monoatomic metals predicting the viscosity at the melting point, assuming solid vibration frequency to exist in the liquid, is remarkably accurate.

$$\eta_{\text{F.P.}} = 5{\cdot}10 \times 10^{-4} \frac{(AT_m)^{\frac{1}{2}}}{V_A{}^{2/3}}$$

where $\eta_{\text{F.P.}}$ = viscosity at the melting point,
A = atomic weight of liquid,
T_m = melting point of liquid,
V_A = volume of 1 gram atom of liquid at T_m.

The authors succeeded in correlating this equation with that of Eyring, who, unlike Andrade, did not assume that liquids are only connected with solids, but regarded viscosity as a manifestation similar to vaporization—and believe that these strict divisions are, indeed, only apparent. Eyring's equation is :—

$$\eta = 1{\cdot}09 \times 10^{-3} \frac{A^{\frac{1}{2}} T_m{}^{3/2}}{V_A{}^{2/3}} \cdot \frac{1}{\Delta E_{\text{vap.}}} e^{\frac{\Delta E_{\text{vap.}}}{nRT}}.$$

Thus for viscosity at the melting point

$$\begin{aligned}\eta_{\text{F.P.}} &= 5{\cdot}10 \times 10^{-4} \frac{(AT_m)^{\frac{1}{2}}}{V_A{}^{2/3}} \\ &= 1{\cdot}09 \times 10^{-3} \frac{(AT_m)^{\frac{1}{2}}}{(V_A)^{2/3}} \frac{T_m}{\Delta E_{\text{vap.}}} e^{\frac{\Delta E_{\text{vap.}}}{nRT_m}}.\end{aligned}$$

Eyring has shown that this expression gives a value for η twice as large as that given by experimental data in the case of anisotropic, and three times as large in the case of spherically symmetrical, molecules. Thus :—

$$\eta_{\text{F.P.}} = \eta_{\text{F.P.}} \times \tfrac{2}{3} \cdot \frac{T_m}{\Delta E_{\text{vap.}}} e^{\frac{\Delta E_{\text{vap.}}}{nRT_m}}$$

taking a spherical monoatomic molecule—*e.g.*, argon.

Hence, if these assumptions are correct

$$\tfrac{2}{3} \frac{T_m}{\Delta E_{\text{vap.}}} \times e^{\frac{\Delta E_{\text{vap.}}}{nRT_m}} \text{ should be equal to 1.}$$

For argon $T_m = 83{\cdot}9$ $\Delta E_{\text{vap.}} = 1505{\cdot}7$ and

Hence $\left(\log \tfrac{2}{3} \frac{T_m}{\Delta E_{\text{vap.}}} + \frac{\Delta E_{\text{vap.}}}{2.3nRT_m}\right) = \bar{1}{\cdot}89$, or the value for the expression is 0·78 instead of unity.

Substance.	T_m.	$\Delta E_{\text{vap.}}$.	$\left(\log \frac{2}{3} \frac{T_m}{\Delta E_{\text{vap.}}} + \frac{\Delta E_{\text{vap.}}}{13{\cdot}7\, T_m}\right)$.
Argon	83·9	1505	−0·11 instead of 0·0
Helium	0·9	23·8	0·34 ,, ,,
Krypton	104·1	2240	0·05 ,, ,,
Xenon	133·1	3200	0·18 ,, ,,

The fact that the value of n in Erying's equation is not exactly 3, his further correction of $\frac{1}{3}$ is not definite, and that Andrade is uncertain about his constants, should be considered. Further, the value of $\Delta E_{\text{vap.}}$ should be taken at T_m. Thus the rule for monoatomic spherical liquids,

$$\log\left(\frac{2}{3}\frac{T_m}{\Delta E_{\text{vap.}}}\right) + \frac{\Delta E_{\text{vap.}}}{13{\cdot}7\, T_m} = 0$$

seems to bridge the vapour, liquid, and solid states, since phenomena characteristic of each have been employed to deduce it. Since this rule was obtained from viscosity consideration, the authors believe that the three states of matter are not as sharply divided in their manner of flow as they have been maintained to be (cf. Andrade and Bernal for extremes).

This fact will be of greater significance later in this study when the laws of viscosity are investigated. To summarize these studies :—

At the melting point the elementary process appears to be mainly a bimolecular phenomenon. The exact nature of the mechanism by which momentum is transferred from one layer to another or from one molecule to another is not certain. A knowledge of such a mechanism is not essential in deriving an expression for viscosity at the melting point. All that is required is to assume a bimolecular phenomenon, and that the chief energy possessed by the molecule is due to vibration at a frequency almost identical —if not exactly so—with that existing in the solid state.

As the temperature is raised, the molecules acquire sufficient excess energy to enable them to pass over a potential energy barrier—*i.e.*, passing through an activated state—from one mean position of equilibrium to another. This denotes a monomolecular form of motion. The bimolecular system does not disappear, and evidence points to the presence of such systems, only to a smaller extent than the viscosity at the melting point indicates. Thus with increase in temperature the monomolecular system supersedes the bimolecular one. It appears reasonable to assume, therefore, that at the boiling point the monomolecular elementary process is either the sole method or at least a major one. This is corroborated by the fact that most associated liquids distil over in the monomolecular form. Acetic acid, on the other hand, boils mostly in the bimolecular form—but for the elementary process the two molecules would constitute one unit, and therefore the flow may still be considered monomolecular.

Nearly all the quantitative theories agree that loss of momentum on collision is negligible (if present)—*i.e.*, gaseous type of viscous drag is non-existent in liquids. The authors will deal with this point later in this study.[53]

The quantitative analysis of the variation of η with temperature may be given in the general equation

$$\eta = Ae^{B/T}$$

Variants of this equation containing the specific volume add slightly to its accuracy.

Different workers have had an almost equal degree of success or failure in the approximate evaluation of the factor A. The chief factors affecting it appear to be the molecular weight and the temperature.

The value of B appears to be connected with the latent heat of vaporization and to a lesser degree of certainty with that of fusion. Possibly the latter fact is due to the inter-relationship of the heats of vaporization and fusion.

B is the quotient of a latent heat of viscosity, Q, divided by the gas constant, R. Q may be found by taking a fraction of $\Delta E_{\text{vap.}}$ the latent heat of vaporization thus :—

$$Q = \frac{\Delta E_{\text{vap.}}}{n}$$

The constant "n" is characteristic of the "size and shape" of the molecule. These terms should, however, be defined more rigorously. Thus to study the relationship of viscosity with constitution n appears to provide the key. Since the elementary process changes from the freezing to the boiling points from a predominantly bimolecular action to an almost entirely monomolecular action, the ideal method is to study the liquid over its entire temperature range. If this is not possible, then the boiling point should provide the next best comparative basis, since (1) the elementary process is probably of one type, (2) the value of $\Delta E_{\text{vap.}}$ is most accurately known at T_B, the boiling point, (3) there is a minimum of disturbance due to association. It is clear that comparing liquids at equal temperatures for this purpose is futile.

An assumption has been permeating these notes that B is invariant with temperature. Ward stated that where B is invariant with temperature the mean co-ordination is also invariant; whilst the mean co-ordination will change with temperature if B is found to change. Change of B with temperature can be easily seen by plotting $\log \eta$ *vs* $1/T$, a curve resulting if B changes, whilst a straight line results otherwise. This point is to be verified, as it is considered of importance, although it is agreed that, in view of the accuracy of the simple exponential formula, any change of B with temperature appears to be of secondary importance for interpolating values of viscosity from a given set of experimental data for ordinary liquids.

Another point which has been implied throughout is the characteristic decrease of viscosity with temperature—(at least the net result is a decrease). Liquid helium was found by Keesom *et al.* to increase with temperature.

THE PRESENT WORK.

MATERIAL.

With the conclusions summarized above as the guiding principles, the following list of substances were investigated with the object of elucidating the relationship of viscosity with constitution. The data for viscosity will be found in the references indicated.[51–68]

1. Normal Paraffins,[1, 54–57].	
n-Butane to *n*-dodecane inclusive; *n*-tetradecane; *n*-hexadecane and *n*-octadecane.	
2. *iso*Paraffins [58]	15 members.
3. Acyclic Olefines [58]	7 members.
4. Cyclic Olefine [58]	*cyclo*Hexene.
5. Alkyl Halides [1]	25 members.
6. Oxygen-containing Compounds [1]	25 members.
Alcohols	11 members.
Aldehyde	Acetaldehyde.
Ketones	4 members.
Anhydrides	2 members.
Ether	Diethyl ether.
Acids	5 members.
Water.	
7. Cyclic Compounds [63–65]	30 members.
8. Elements [61, 65, 68]	12 members.
9. Inorganic Compounds [61]	10 members.

(The boiling points of these compounds were found from the literature as cited in references [1] and [54–71] taking the figures given by the investigators who gave the viscosity measurements where possible.)

Although only 137 liquids have been studied, it is thought that they represent the behaviour of a far greater number of pure liquids. More important than this is the fact that they include (1) unassociated liquids and liquids associated to various degrees, (2) ionic liquids—*i.e.*, fused salts—and metallic liquids, (3) liquids of ideal spherical symmetry such as argon and liquids of various degrees of anisotropy, (4) the principal representative organic structures and radicals, and (5) elements and compounds. Thus by comparison and contrast the effects of such factors are expected to present themselves, especially as viscosity is one of the more sensitive properties of such factors.

Exploratory and Confirmatory Work.—At the outset of this project the degree of connection between the vapour pressure (or vaporization phenomenon) and viscosity was investigated. For this preliminary work the normal paraffins were chosen, since they appeared to be least affected by secondary factors.

Thus the viscosity of the normal paraffins from *n*-pentane to *n*-decane was plotted against the corresponding vapour pressure as illustrated in Fig. 3 (For vapour-pressure data cf. [61, 69, 70].)

Certain facts became evident :—

(1) If temperatures of equal vapour pressure be accepted as corresponding temperatures, then, for normal paraffins, temperatures of equal viscosities are corresponding temperatures.

(2) Since a single curve connects vapour pressure and viscosity irrespective of molecular weight, the factors responsible for, and the laws governing, vapour pressure are identical with those affecting viscosity.

(3) In attempting to study the effects of molecular structure and molecular forces it is possible to eliminate the disturbing effect of molecular

weight. This fact is important, since but few of the liquids to be studied have an exact counterpart in molecular weight with the remainder.

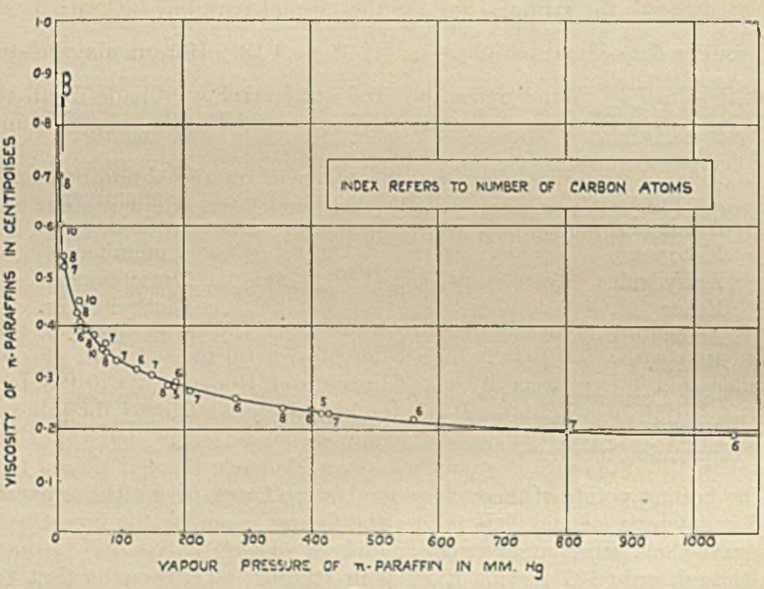


Fig. 3.

Each of the above conclusions has previously been shown indirectly, but the normal paraffins show strikingly the close connection between the two phenomena discussed. It will be remembered that plotting log. vapour pressure against log. viscosity yields a straight line for many

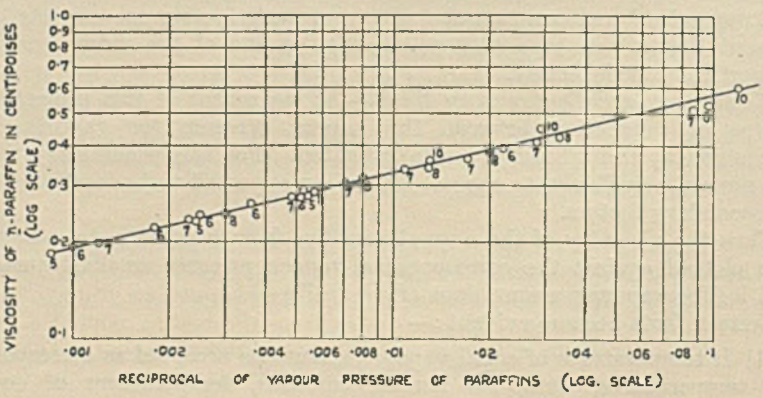


Fig. 4.

substances, the slope of which represents the ratio between the two heats of vaporization and viscosity. It is now evident that for n-paraffins above n-C_4H_{10} there will be only one line and one " n " = $\frac{\Delta E_{\text{vap.}}}{\Delta E_{\text{vis.}}}$. The authors prefer to compare log η *vs* log $1/P$ instead of log η *vs* log P.

Fig. 4 shows the straight line for the normal paraffins ($n\text{C}_5$-$n\text{C}_{10}$). The value for n for normal paraffins, or $\frac{\Delta E_{\text{vap.}}}{\Delta E_{\text{vis.}}}$, is 4·13. Here it may be stated that the authors cannot agree that the same error was made in all these data, so that 4·13 results instead of Eyring's and Ewell's integral number 4·0.

To decide definitely whether exact integers or fractional numbers exist—the importance of this point will be discussed later—the equation of the straight line was determined and found to be :—

$$\log \eta \text{ (cp.)} = 0{\cdot}242 \log (1/P_{\text{mm}}) \text{ or } \eta_{\text{cp.}} = P_{\text{mm}}^{-0{\cdot}242}$$

At the boiling point all the n-paraffins have the same viscosity. This value of viscosity is 0·194 cp. for a value of $n = 4{\cdot}0$ and 0·201 for $n = 4{\cdot}13$. Kuenen and Wisser gave 0·208. Thorpe and Rodger gave 0·198 for n-octane, 0·199 for n-heptane, 0·200 for n-pentane, and 0·204 for n-hexane. Bingham *et al.* gave 0·217 for n-hexane at 65° C. (b. pt. 69° C.). Thus, although the difference is small, whatever evidence there is points to the correctness of the fractional value of "n." (Later η_B for the n-paraffins is found to be 0·2145 ± 0·005.)

A more definite course would be the calculation of viscosity from the Clausius–Clapeyron equation for vapour pressure—*i.e.* :—

$$\log\left(\frac{P_1}{P_2}\right) = -\frac{Ml}{2 \cdot 3R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \text{ assuming } l = \text{constant,}$$

where M = molecular weight

l = latent heat in gm.-cal./gm.

$$\text{Thus } \log\left(\frac{\eta_1}{\eta_B}\right) = -\,0{\cdot}242 \log\left(\frac{P_1}{760}\right) = 0{\cdot}242\,\frac{Ml}{2.3R}\left(\frac{1}{T_1} - \frac{1}{T_B}\right)$$

where the suffix B denotes boiling point.

$$\text{or } \log \eta_1 = \frac{0{\cdot}242\,Ml}{2{\cdot}3 \times 1{\cdot}98} \cdot \frac{1}{T} - \frac{0{\cdot}242\,Ml}{2{\cdot}3 \times 1{\cdot}98} \cdot \frac{1}{T_B} - 0{\cdot}697$$

$$= A + \frac{B}{T}.$$

The extent of the error in the calculated viscosity of n-hexane justifies the conclusion that a non-integral value for n is quite accurate. As the temperature deviates to a greater extent from the boiling point the error in the calculated value of η increases (n-heptane and n-octane). That this is due to the variation of l with temperature, and not to an inaccurate evaluation of n, is proved by the fact that the more accurate formula for vapour pressure, in which the latent heat is assumed to vary with temperature, gives better results for these compounds. Throughout this discussion it should be borne in mind that Hatschek has shown that Thorpe and Rodger's figures for viscosity (mostly used here) are not reliable in the value of the third significant figure.

TABLE I.

n-Paraffin.	M.	l.	T_B.	A.	B.	Viscosity in cp. at				
						0° C.	20° C.	50° C.	80° C.	100° C.
n-Hexane	86	89·11	341·8	−1·8853	406·16			*Observed.*		
						0·398	0·319	0·2415	0·1915	(0·1675)
								Calculated.		
						0·400	0·317	0·235	0·185	0·160
								Difference.		
						0·002	0·002	0·007	0·006	0·0075
n-Heptane	100	76·3	371·5	−1·7855	404·4			*Observed.*		
						0·520	0·411	0·305	0·2335	0·1975
								Calculated.		
						0·496	0·393	0·293	0·229	0·199
								Difference.		
						0·024	0·018	0·012	0·004	0·001
n-Octane	114	70·95	398·7	−1·7720	428·67			*Observed.*		
						0·7015	0·5395	0·3845	0·2885	0·243
								Calculated.		
						0·627	0·491	0·359	0·277	0·238
								Difference.		
						0·075	0·049	0·026	0·011	0·005

Thus assuming $Ml_T = L_T = L_0 + \alpha T$

and since
$$\int d \log_e P = \int \frac{L_0 + \alpha T}{RT^2} dT$$

$$\log \eta = - 0{\cdot}242 \log P = \frac{A'}{T} - B' \log T + C'$$

where A', B', and C' may be calculated from fundamental constants and the values for $1/n = 0{\cdot}242$ and for $\eta_B = 0{\cdot}201$. This equation for the normal paraffin is

$$\log \eta = 0{\cdot}053 \frac{L_0}{T} - \frac{0{\cdot}242}{1{\cdot}98} \alpha \log T + \left[\frac{0{\cdot}242}{1{\cdot}98} \alpha \log T_B + \log 0{\cdot}201 - 0{\cdot}053 \frac{L_0}{T_B} \right]$$

To calculate the values of L_0 and α in $L_T = L_0 + \alpha T$, the data supplied by Schultz's graph for the latent heats of normal hydrocarbons at various temperatures were employed in the assumed formula for the change of this heat with temperature[71]. Table II gives the values for calculated viscosities obtained from this equation.

Table II shows that where the magnitude of the error in L_T is not serious the total error due to " n " and other sources is of the order 0·01 cp. maximum, and half this amount for the average. Thus a fractional value of n appears to satisfy the requirements without any imposed restrictions, bearing in mind the following sources of error :—

(1) Approximate nature of the equation when applied over a wide range of temperature.

(2) Assumption that α is invariant with temperature.

(3) Errors in reading and estimating the latent heats from Schultz graphs.

(3) Errors (in third place) in reported values of η.

(5) Assumption that the compounds are pure in both measurements.

TABLE II.

n-Paraffin.	L_0.	a.	T_B.	$0{\cdot}053\,L_0$ A'.	$\frac{0{\cdot}242a}{R}$ B'.	(Const.) C'.	Viscosities in cp. at				
							0° C.	20° C.	50° C.	80° C.	100° C.
									Observed.		
n-Hexane	12,502	−16·1	341·8	662·6	−1·964	−7·6122	0·398	0·319	0·2415	0·1915	(0·1675)
									Calculated.		
							0·398	0·312	0·233	0·186	0·164
									Difference.		
							0·000	0·007	0·009	0·006	0·004
									Observed.		
n-Heptane	14,077	−17·5	371·5	746·1	−2·1389	−8·2044	0·520	0·411	0·305	0·2335	0·1975
									Calculated.		
							0·548	0·415	0·297	0·228	0·198
									Difference.		
							0·028	0·004	0·008	0·006	0·000
									Observed.		
n-Octane	16,060	−20	398	851·2	2·4444	−9·1929	0·7015	0·5395	0·3845	0·2885	0·243
									Calculated.		
							0·757	0·551	0·376	0·279	0·237
									Difference.		
							0·055	0·011	0·009	0·010	0·006

It is obvious that no great value can be attached to calculations applied to higher members of the series, since uncertainties about L_T grow proportionately. Two facts are then established :—

(1) In the case of n-paraffins whatever is true with regard to vapour pressure (or its reciprocal) is automatically true with regard to viscosity when temperature is the fundamental variant.

(2) No necessity exists to round off the value of "n" to an integer.

Examining the expression

$$\log\left(\frac{P_1}{P_2}\right) = -\frac{Ml}{2\,.\,3R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

When $P_2 = 760$ mm. Hg $T_2 = T_B =$ boiling point.

$$\log\left(\frac{P_1}{760}\right) = -\frac{Ml_B}{2\,.\,3RT_B}\left(\frac{T_B}{T}-1\right)$$
$$= -\frac{K'}{2\,.\,3R}\left(\frac{T_B}{T}-1\right)$$

Since $\frac{Ml_B}{T_B} =$ const. by Trouton's rule.[72]

But taking l at T, $\log\left(\frac{760}{P_1}\right) = -\frac{Ml_T}{2\,.\,3RT}\left(\frac{T}{T_T}-1\right)$

or $\log\left(\frac{760}{P_1T_1}\right) = K''\left(\frac{T}{T_B}-1\right)$ if $\frac{Ml_T}{T} = M\delta S =$ Const.[73]

where $\delta S =$ entropy change on boiling at T.

Thus log $(1/P)$ of the normal paraffins was plotted against values of T/T_B and one curve was obtained for the members n-C_5H_{12} to n-$C_{10}H_{22}$ inclusive in accordance with Trouton's rule.

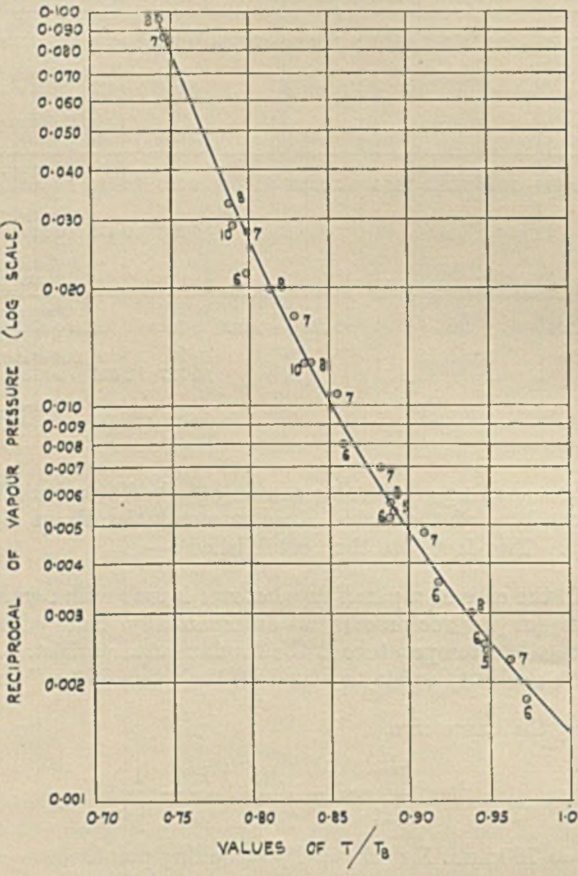


Fig. 5.

Trouton's rule was applied to viscosity for the following reasons :—

(1) A plot of log (η) against T_B/T will yield a curve representing all the members of n-paraffins for which Trouton's rule is operative and the value of $n = 4{\cdot}13$.

(2) No member of the paraffins has been studied over the entire range of the liquid state. If one curve represents all the members of the normal paraffins—excepting the first few as indicated by Ewell[46]—then this curve will represent the viscosity characteristic of these liquids from the freezing to the boiling points; since the higher members are studied near the first point, whilst the lower are studied nearer the second point. The measurement temperatures usually reported in the literature are from 0° to 100° C. The boiling point of n-butane is near 0°, whilst the freezing

point of n-octadecane is not much above it. Thus only n-C_4 to n-C_{18} are necessary and sufficient to elucidate the behaviour of the normal paraffins.

(3) Log η *vs* $1/T$ has been taken to be a straight line for unassociated liquids indicating the invariancy of B with temperature in the expression

$$\eta = Ae^{B/T}$$

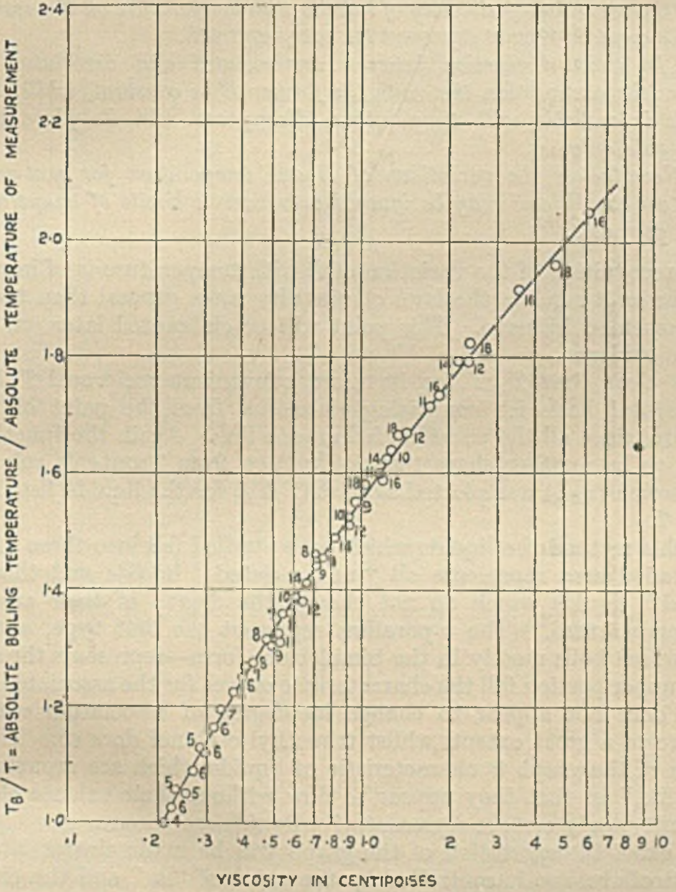


Fig. 6.

Trouton's rule applied here gives

$$\log\left(\frac{\eta}{\eta_B}\right) = \frac{Ml}{2{\cdot}3nRT_B}\left(\frac{T_B}{T} - 1\right)$$

or log η *vs* T_B/T should yield a straight line if B is invariant with temperature. Fig. 6 is a plot of log η against T_B/T for the members of n-paraffins tabulated above.

Thus it is clear that the characteristic curve, while not curving excessively, is definitely not a straight line. That various authorities obtained straight lines can only be due to the fact that the temperature range studied was not sufficiently wide to exhibit the variation of B with temperature. This variation of B with temperature for even such substances as the paraffins clearly indicates :—

(1) *All theories which attempt to explain the mechanism of liquid viscosity which assume a constant B for unassociated liquids, and all formulæ connecting the variation of viscosity of liquids with temperature on the assumption that B is constant cannot represent the complete truth.*

(2) *The strict distinction between unassociated and associated liquids, based on the assumption that with the former B is constant, whilst with the latter it is variable with temperature, disappears. In its place stands a relative rule only.*

(3) *Nevertheless the variations of B wth temperature for non-associated liquids are small, and may be ignored over narrow limits of temperature for general purposes.*

The recognition of the variation of B with temperature is of importance in so far as it renders the laws of viscosity more general than they have been presented hitherto. This point will be elaborated later on, in view of more evidence.

It is clear that T_B/T, or its more convenient reciprocal T/T_B, is a fundamental basis for comparing viscosities from the point of view of structure, since all the paraffins fall on one line. Again the function η_B/η is seen to be another characteristic function from Trouton's rule. Thus the function (η_B/η) was plotted against (T/T_B) for the liquids listed above, in Fig. 7.

By this method the liquids which were studied fell into three divisions. The shaded area represents all "unassociated" liquids and those "associated" liquids which do not change the degree of their association with temperature. (The n-paraffins represent the first type, and acetic acid—which boils mostly in the bimolecular form—represents the second.) In the upper portion fall the characteristic curves for the associated liquids. Water does not appear to change its degree of association with temperature to a great extent, whilst trimethyl carbinol does so. The lower portion of the graph is characteristic of liquids which are grouped under "metallic," in that they appear to flow without their valence electrons. For clarity, only certain representative liquids are shown.

The exact interpretation of the graph will be made clearer later; the position of the line is controlled by the value of "n" and the change of B with temperature. This fact will be better understood when further details are studied, but it may be seen directly from the formula

$$\log\left(\frac{\eta_B}{\eta}\right) = \frac{1}{n}\cdot\frac{Ml_T}{2{\cdot}3 \times 1{\cdot}98T}\left(\frac{T}{T_B} - 1\right)$$
$$= \frac{K}{n}\left(\frac{T}{T_B} - 1\right)$$

assuming that $Ml_T/T =$ constant in accordance with the generalized form of Trouton's rule. Strictly speaking, the pressure should have been varied from one atmosphere with the different measurements, but change of viscosity with pressure is negligible at low pressures and for small pressure changes.

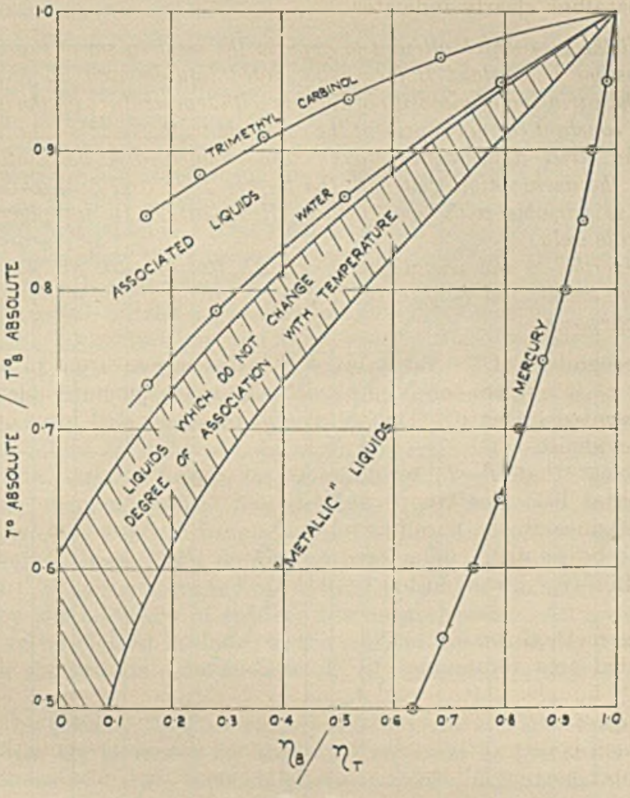


Fig. 7.

Basic Principles.

At this stage it was clear that T/T_B represented a rational, if not the only basis, for comparison, for the following reason. All the normal paraffins listed above fell on one characteristic curve; similarly there were curves representing alkyl iodides (excepting the methyl iodide), alkyl bromides and chlorides, probably the ketones and the acids above formic acid, alkylated benzene above the ethyl benzene member, and probably the alkali halides. Since these groups are mainly connected by structure, T/T_B should be the basis for investigating this phenomenon.

Similarly it appeared that it was the logarithmic function of viscosity which was of major importance—as predicted by Dunstan and Thole. Thus plots of log η *vs* T/T_B were made for all the substances under study. T/T_B was preferred to T_B/T, since with the latter the degree of curvature is small and may be obliterated by inaccuracy of experiment and plotting, whilst in the former the curve was more definite. Straight-line functions have many advantages, and therefore the following artifice was employed :—

The greater proportion of the viscosity figures reported in the literature

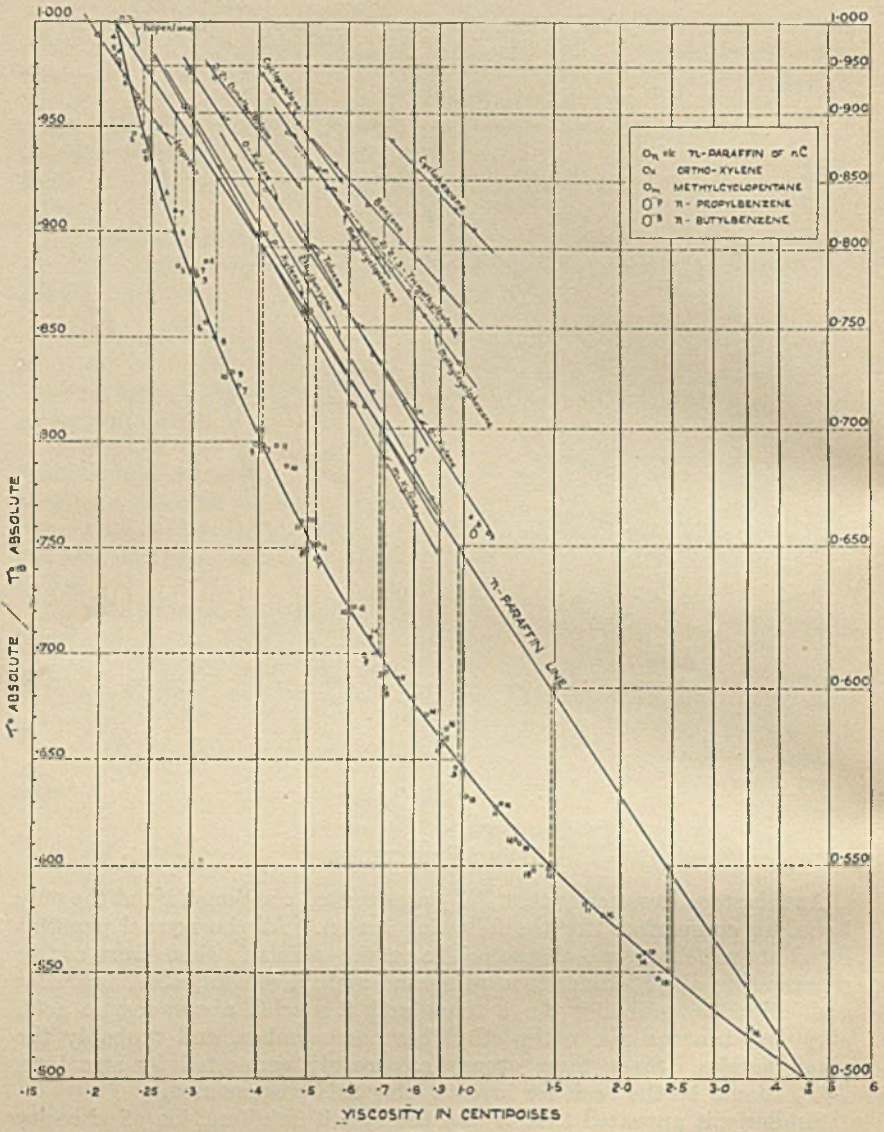


FIG. 8.

can only be relied upon to the third decimal figure. Similarly, only the third decimal in the fractional value of T/T_B can represent significant values. Thus all the graphs used below have been chosen so that 500 mm.

represent values of T/T_B from 0·500 to 1·000. Similarly the log η values have been plotted to an accuracy corresponding to the third decimal place.

In Fig. 8 the plot of log η *vs* T/T_B for the n-paraffins from n-C_4 to n-C_{18} is shown to fall on one curve.

A straight line joins the points $T/T_B = 0·500$ and $T/T_B = 1·000$. Since the curve represents the viscosity characteristic of a *species* of substances, the curve will be called " Specific Viscosity Curve " for n-paraffins. The straight line is then considered to represent the viscosity characteristic of the n-paraffins as plotted, log η *vs* a certain scale (on the right of the plot) which is $\phi(T/T_B)$. In other words, an artificial scale of T/T_B is to be constructed so as to yield a straight line for the n-paraffin " specific viscosity curve " when plotted on it. This straight line is designated n-paraffin line. The dotted lines show the construction of the scale. A value of T/T_B on the natural scale is connected by a horizontal line to the specific viscosity curve. The point on the n-paraffin line and vertically above the intersection of the horizontal line and the " specific viscosity curve " has the same value of log η as the point of intersection. Thus a vertical line is erected at the point of intersection, and the horizontal through the point on the n-paraffin line represents the value of T/T_B on the artificial scale. To read the values of T/T_B of a point on the artificial scale the reverse is employed—*i.e.*, draw a horizontal line through the point to meet the n-paraffin line, drop a vertical line through the intersection to meet the " specific viscosity curve," draw a horizontal line through the latter intersection point to read T/T_B on the natural scale. Log η is common for both scales. Thus the accuracy of plotting points on the artificial scale is governed by the accuracy of reading the natural scale. All interpolated values are to be plotted in detail in the manner described, for mere interpolation on the scale is only guess-work, as the scale varies in a complex manner.

It is to be proved that all curves which yield straight lines on this artificial scale are governed by the same equation as the one governing the basic curve—*i.e.*, the " specific viscosity curve " for normal paraffins.*

T_R = Height from base of graph representing T/T_B on natural scale
T_R' = ,, ,, ,, ,, ,, artificial scale

η_1, η_2, η_3 correspond to T_{R_1}', T_{R_2}', and T_{R_3}'

Since the n-paraffin line is a straight line,

$$\frac{T_{R_1}' - T_{R_2}'}{\log \eta_1 - \log \eta_2} = \frac{T_{R_2}' - T_{R_3}'}{\log \eta_2 - \log \eta_3}$$

By cross multiplication and cancellation

$$\log \eta_2 = T_{R_2}'\left(\frac{\log \eta_1 - \log \eta_3}{T_{R_1}' - T_{R_3}'}\right) - \frac{T_{R_3}' \log \eta_1 - T_{R_1}' \log \eta_3}{T_{R_1}' - T_{R_3}'}$$

---

* This work has been done independently from that of Irany,[14] and the two may be looked upon as confirmatory, affording proof of each other's conclusions.

The results Irany obtained with T/T_C (T_c = critical temperature), and for which no explanation was offered (*i.e.*, for the closeness of some lines and not others), can all be understood from this work, since T_B/T_c is generally $\frac{2}{3}$. In other words, T/T_B is the real " reduced temperature " and not Van der Waal's T/T_c in as far as viscosity is concerned (cf. Thorpe and Rodgers).[1]

Since T_{R_1}' may be taken as zero, T_{R_3}' as full length of scale, for n-paraffins the value of the constants A and B in the general equation,

$$\log \eta_2 = T_{R_2}' (A) + B$$

are

$$A = \frac{\log \eta_3 - \log \eta_1}{T_{R_3}'}$$

and

$$B = \log \eta_1$$

But for n-paraffins $\log \eta_2 = f(T_R)$, where $f(T_R)$ is assumed unknown

$\therefore$ $T_R' (A) + B = f(T_R)$ connecting the " specific viscosity curve " for n-paraffin and n-paraffin line.

For any line of slope A' and intercept B' the formula still remains

$$\log \eta = A'(T_R') + B'$$

$$\log \eta = \left(\frac{f(T_R) - B}{A}\right)A' + B'$$

$$= f(T_R)\frac{A'}{A} + C.$$

Thus any straight line drawn on the artificial scale will represent an equation similar to the equation governing the " specific vicosity curve " of the n-paraffin if this latter equation contains a constant which may absorb C. When all the substances listed above were plotted on this scale every substance gave a straight line showing a definite lack of curvature, excepting :—

(1) 2 : 4 : 4-Trimethylpentene-(1 and 2), which is a mixture of two substances.

(2) NaCl, the value for T_B (1686° Abs.) being an approximate value.

(3) An almost imperceptible sinusoidal curvature in pyridine indicating impurities. This substance will be studied in detail below.

It is found that the alcohols, acids, and even water, the elements, both gases and metals (cf. mercury), as well as substances behaving more normally, yield straight lines. In all the theories of the mechanism of viscosity in liquids it was admitted and accepted that water does not behave as a " normal " liquid. It exhibits no anomalies here.

These observations show that :—

There is but one law governing the change of viscosity with temperature for all the substances studied here—and probably for all liquids.

Thus the criterion of accuracy and completeness of any theory attempting to give the laws of viscosity of liquids is that such theories should yield an equation identical in form for water, alcohols, metals, and normal substances. The general equation

$$\eta = Ae^{B/T}$$

becomes only a rough approximation *as a general law,* since the errors in calculating the viscosity of water by means of this formula may amount to as much as 27 per cent.

The authors do not intend to attempt to give the general law of liquid viscosity, but the following remarks show the possibility of such a law.

It is to be remembered that Andrade proposed the equation

$$\eta = A'e^{C/(T-\theta)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (A)$$

(and later

$$\eta = A'(1 + \alpha e^{-BT})e^{b/T} \quad . \quad . \quad . \quad . \quad . \qquad (B)$$

where $(1 + \alpha e^{-BT})$ expressed decrease in association with temperature) to be used with water and other associated liquids. Prasad found that Andrade's equation (A) applied to the behaviour of lead chloride. Dunn found "n" for water to vary from 2·72 to 3·3 between 0° and 100° C. Generally it has been assumed that B is constant for a " normal " substance. It was shown in this work that B is variable with temperature even for the normal paraffins. Thus it appears that the *general equation for all liquids would contain a variable value of energy of activation*, but while the variation with unassociated liquids is negligible over narrow ranges of temperature, it is considerable with more complex substances. Since the exponential law appears to be well authenticated, a probable rendering of the general viscosity law is :—

$$\eta = (X)e^{\frac{f(T)}{T}} = (X)e^{\frac{(Ml)}{n}f(T)/RT}$$

where (X) = unknown, probably function of T.

The evaluation of $Ml/n\, f(T)$ appears to be of the same general form for all liquids, varying only in degree. It appears also that more should be known about the unit taking part in the elementary process of viscous flow before this function can be evaluated from first principles.

Ward classified liquids into those obeying one of the two equations

$$\eta = Ae^{Q/RT}$$

and

$$\eta = A(T)e^{(Q(T)/RT)}$$

where the first type represents liquids the mean co-ordination of which is invariant with temperature, to a first approximation, whilst the second represents liquids in which the mean co-ordination is variable with temperature. This classification should be taken only in an approximate manner and would disappear in principle. Ward pointed out that Andrade's equation

$$\eta v^{1/3} = Ae^{C/vT}$$

admits the variation of B with temperature in the case of normal liquids. The authors believe that since another form is necessary for water, this equation cannot represent the full facts, and should be accepted only as an excellent empirical representation.

Similarly the simple exponential formula is not to be discarded, since it does represent the variation of viscosity with temperature to a great degree of accuracy. These observations are made only in an attempt to show that there are hidden factors which have not as yet been considered and which demand investigation.

The viscosity of helium is still unique in its variation with temperature.

The graphs, Figs. 8–18, afford the following features which connect them with constitution or general molecular construction. Considering, at the moment, the compounds only, these can be divided into two groups:

(1) A group which starts with the CCl_4 line (Fig. 13) and extends to the left to slightly beyond the *n*-paraffin line. These lines show the following characteristics.

(a) *Those lines which are near the* CCl_4 *line* (*Fig.* 13) *tend to be parallel with it, whilst those near the* n-*paraffin line lie parallel to the latter.* Intermediate lines take intermediate positions. The lines will therefore satisfy the following equation:—

$$\log \eta = \frac{1}{n}\frac{Ml}{2{\cdot}3RT}\left(1 - \frac{T}{T_B}\right) + \log \eta_B$$

in which "n" for CCl_4 is 2·8 and for *n*-paraffin 4·13. Considering Ml/T to be constant, the CCl_4 line would be less steep than the *n*-paraffin line. The liquids having intermediate values of "n" will lie in an intermediate position and be in a fan shape. Here is seen why it is important to recognize the fact that "n" can have any value and not be rigidly bound to integers; if this were so, only two groups would be recognized—one parallel to the $n = 4$-liquid and the other parallel to the $n = 3$-liquid. This would introduce unnecessary difficulties—for instance, the reason for the value of $n = 3{\cdot}5$ approximately for alkyl halides.

(b) *The position of the lines does not move beyond the* CCl_4 *line.* In other words, the intercept η_B appears to have a maximum value approximating that shown for CCl_4. It is to be seen that on these lines the chief factor is "n," and as η_B is simply an ordinary viscosity coefficient, it will be affected by "n." (a) and (b) *indicate that as "n" increases in value the line moves to the left and becomes steeper.*

(c) *The effects of molecular weight are non-existent in the position of slope of a line.* Thus *n*-C_8H_{18} and *n*-$C_{18}H_{38}$ fall on the same line. Similar cases have been cited above, and it may be noted again that the alkyl halides each have characteristic lines independent of molecular weight. The first members do not fall on these lines. This is not because of a change in molecular weight, but a reason which is to be noted below—(*d*).

(*d*) While *n*-C_8H_{18} and *n*-$C_{18}H_{38}$ fall on the same line, *n*-C_8H_{18} and 2 : 2 : 4-trimethylpentane fall on definitely different lines. The position of the line is not governed by molecular weight, but by structure only. This fact renders such comparisons as *n*-$C_{18}H_{38}$ and 2 : 2 : 4-trimethylpentane possible regardless of the great difference between the two molecular weights. *Thus it is not necessary to compare isomers differing in structure only*; each line represents a "type" of liquid. This fact renders the number of liquids studied far greater than their actual number—*i.e.*, 137.

(*e*) Regularity in comparison is a remarkable fact. To mention only two of many facts to be detailed below: unsaturation *always* brings the characteristic line to the left of the saturated member, irrespective of other structures present; substitution in the cyclic compounds *always* brings the line to the left of the simple molecule. Comparison at ordinary temperature scale with these two characteristics is complicated by irregularities.

(2) The second group of compounds is characterized by few general principles.

(*a*) η_B again falls between the positon of CCl_4 and a position near that of *n*-paraffins.

(*b*) The lines are not parallel to either the *n*-paraffin line or the CCl_4-line, but are less steep—in all cases—than their position, as defined by the position of η_B, warrants.

(*c*) All these liquids are known or suspected to be associated.

The study of the elements also reveals interesting characteristics. These will be considered later.

These facts indicated to the authors, and more detailed study confirmed the supposition that the chief characteristic affecting the position and slope of the lines is the shape of the ultimate unit. The size of the unit does not appear to affect it. "Shape" of a molecule, however, is a vague term unless it is defined rigorously. Thus the following analysis appears to give the most reasonable explanation for the behaviour of the "specific viscosity curves" and their derived function the "typical lines" of liquids.

That the mean spatial co-ordinates of the centre points of the various atoms, constituting a molecule, should be the basis upon which the "shape" or structure of such molecules is built may be taken axiomatically. On the other hand, evidence in this work tends to show a "rounding off" of shapes. Thus nitrobenzene and methyl*cyclo*pentane differ greatly in spatial configuration; but they lie on one characteristic line. Similarly *cyclo*hexane cannot be made similar to carbon tetrachloride in structural configuration, yet their lines are near each other (Figs. 13 and 15). Further, alkyl benzenes above ethyl benzene change progressively with length of chain, yet yield only one "specific viscosity curve." This statement applies to *n*-paraffins, alkyl halides, isoprene and diallyl, etc.

It is evident, then, that there is an "effective shape," probably built upon the spatial configuration as a skeleton. *Once the effective shape is obtained, the nature and shape of the skeleton are immaterial, so far as specific viscosity is concerned.*

The dipole moment stands as a convenient and obvious basis. Against this should be taken the fact that both the apparent limits of the group—*i.e.*, *n*-paraffin and CCl_4 lines—and the intervening space are filled by liquids of zero moment. Polar liquids occupy spaces all along the interval. Thus dipole moments, while playing a part in the effective shape, may be considered as secondary only.

Since the "effective shape" cannot be material, the forces surrounding the molecule are considered, to give this shape. These forces have been studied in detail by London,[33] Bernal,[50a] Hudleston,[75] Glockler,[76] and others in a symposium on liquid structure (1937).

Bernal, and in general other investigators, have accepted a simplified equation for the forces surrounding a molecule in which the energy, U, is a function of two terms only, one attractive varying with the m^{th} power and the other repulsive varying with the n^{th} power of distance R :—

$$U = \frac{A_m}{R^m} - \frac{A_n}{R^n}$$

m varying between 2 and 6 and n between 10 and 20. It is interesting to find that Friend[77] calculated "m" from viscosity data, by an admittedly approximate method, and found it nearly equal to 8.

Hudleston pointed out that in the modern theory of the specific heats of solids it is conceived that at some specific distance, l, between the centres of gravity of monoatomic molecules, the resultant force between them is zero. Closer approach results in repulsion, which increases in magnitude as the distance apart decreases; greater separation results in an attractive force which, at first, increases with distance (then dies away as the sphere of influence of the molecule is reached and passed). Glockler gave a diagram of the energy variation with distance, and on it based his concept not only of Van der Waal's forces but of all chemical forces, ranging from those responsible for the holding together of atoms in a chemical compound, to intermolecular forces of association and liquid affinities (Fig. 9).

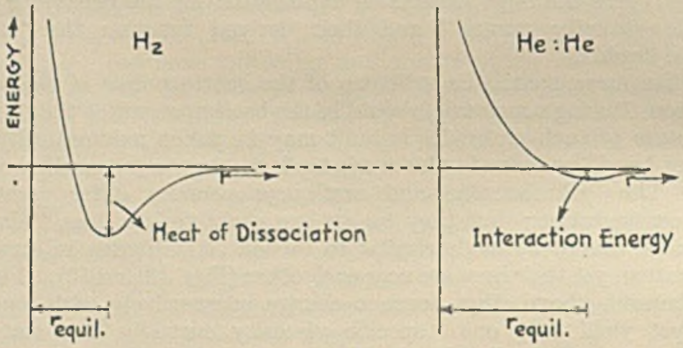


FIG. 9.

Qualitatively this concept appears to succeed where the classical valency theory appears to fail.

When molecule A is travelling towards another, B, the sequence of events is then identically the same as in the solid state, as explained by Hudleston. The molecules have two critical distances at which their effect on other molecules are nil—an outer limit and an inner zone of zero force.

Thus, in general, the tendency of two molecules is to oscillate around the inner zero point of each other. The surface which contains all the inner zero points of the molecule then constitutes the effective shape of the molecule. It is similar to a rubber sheet surrounding a multipolar magnetic skeleton; the analogy must not be taken to extremes, however. It is then seen that the effective shape will be "rounded off" and not angular; especially as the exact configuration of the atoms in the molecules and the electrons around each atom are not fixed in space, but continuously change in a complex and rapid manner.

Increase in temperature expands this enveloping surface, whilst pressure tends to contract it; mathematically, increase in temperatures lowers the energy level outside the inner zero point, whilst pressure lowers it inside the inner zero point.

In discussing the elementary process of flow from the point of view of constitution, it is the shape of the molecule as defined above which appears to be the main factor, the nature of each part of the skeleton being immaterial except in so far as it produces a hump or a depression in the "surface of equal potential" surrounding the molecule and parallel with the inner zero surface.

No attempt will be made to explain all the concepts put forward by various workers on the viscosity of liquids by these ideas; it is sufficient to point out that this picture conforms with Andrade's "holding of hands" between molecules and the sharing of momentum without collision; the concept of vibration around an equilibrium position followed by jumps in direction of flow of Dunn and Frenkel; theory of holes; Eyring's minima and energy barriers, etc. It also conforms with the general behaviour of liquids—*i.e.*, having a specific volume which expands on heating; surface tension which decreases with temperature; vapour pressure increase with temperature, and latent heat of evaporation which decreases with temperature and vanishes at T_c where the inner and outer zero surfaces appear to coincide (cf. specially Hudleston's contribution).

It is to be assumed that the molecules of a liquid at any temperature T and under their own vapour pressure (V.P.) would be touching at an average distance equal to that of the average distance of the inner zero point. At temperature T and a lower pressure than V.P. the average distance at which the molecules touch each other is greater than the average inner zero point distance, thus more molecules are liable to jump out of the sphere of influence and evaporate. At temperature T and pressure higher than V.P. the average distance between centres of gravity of two molecules would be less than the sum of the distances of their respective inner zero points—*i.e.*, the molecules are interfering with the free behaviour of each other. Let this interference be $f\frac{(P\text{ actual})}{\text{V.P.}}$. Since all viscosity values have been measured at a value of $P = 760$ mm. Hg.

$$\text{Interference} = f\frac{(760)}{\text{V.P.}}.$$

Thus if two liquids A and B are compared at equal temperatures T_1, it is seen that they are not in strictly comparable states.

Liquid.	Temp.	V.P.	Outside pressure.	Interference.
A	T_1	P_1	760	$f\left(\frac{760}{P_1}\right)$
B	T_1	P_2	760	$f\left(\frac{760}{P_2}\right)$

Calculating P_1 and P_2 by the usual formula and applying Trouton's rule, then :—

$$\log\left(\frac{P_1}{760}\right) = -\frac{M_1 l_1}{2\,.\,3RT_{B_1}}\left(\frac{T_{B_1}}{T_1} - 1\right) = K\left(\frac{T_{B_1}}{\mathrm{T}_1} - 1\right)$$

$$\log\left(\frac{P_2}{760}\right) = -\frac{M_2 l_2}{2\,.\,3RT_{B_2}}\left(\frac{T_{B_2}}{T_2} - 1\right) = K\left(\frac{T_{B_2}}{T_2} - 1\right).$$

Thus when $\frac{T_{B_1}}{T_1} = \frac{T_{B_2}}{T_2}$ then $\log\left(\frac{P_1}{760}\right) = \log\left(\frac{P_2}{760}\right)$

or at $\frac{T_1}{T_{B_1}} = \frac{T_2}{T_{B_2}}$ the interference in A = interference in B. This affords a physical reason for the comparison of viscosities or their logarithms at equal values of T/T_B—*i.e.*, comparisons at equal degrees of interference of the molecules with each other's free behaviour.

On these bases the effect of the shape of the molecule on the "specific viscosity curve" may be roughly indicated. A sphere has minimum surface for a given volume. Thus for a unit volume a sphere offers a minimum area of equilibrium around which other particles may oscillate. In other words, a larger volume has to be swept by a body travelling from one position of equilibrium to another situated on spheres than if the positions of equilibrium were on irregularly shaped or anisotropic bodies, occupying the same aggregate volumes as the spheres. Thus in a monomolecular viscous type of flow (action) the spheres would sweep relatively greater volumes, and hence require greater energies of activation, than anisotropic bodies. The case of a bimolecular reaction was shown approximately by Eyring and his collaborators to be similar (Fig. 2). Thus in both cases—higher orders of reaction are too complex to be analysed even approximately, but may be considered to follow similar lines—for two liquids, *the liquid with molecules possessing a surface of inner zero point nearer to a spherical symmetry would have a "specific viscosity curve," and consequently typical lines on the present charts, to the right of the other liquid.*

In the study of viscosity and constitution of compounds this rule is operative. Thus it is not a question of "What is the effect of CH_2, COOH, etc. on specific viscosity?" but "What is the effect on the specific viscosity of introducing CH_2, COOH, etc., into the molecules of this particular liquid?" In other words, if a radical, atom or structural characteristic increases the spheroidal symmetry of one compound and decreases it with another, the effect will be an increase in viscosity of the first and a decrease in the other when comparisons are made at equal values of T/T_B. Below is the detailed study of the substances tested; the known cases are used to establish the validity of this general law, whilst the law is used to study the unknown cases.

Normal Paraffins.—These hydrocarbons have been the basis of this study, and much has been said concerning their viscosity. A few points deserve further discussion, however.

Eyring and Ewell found that CH_4 behaved more like CCl_4 than the rest of the normal paraffins. This is acceptable on the basis of what has been stated previously. A similar case is that methyl iodide falls on a line to the right of the alkyl monoiodides, showing a nearer approach to the spheroidal shape of equipotential surfaces than the remainder.

The elementary process of the normal paraffin presents difficulties. Suggestions have been put forward that some, at least, of the *n*-paraffin molecules are "curled," and that the energy of viscosity activation has been utilized in converting the straight molecule into the curly type. These were attemps to explain the Newtonian type of flow of *n*-paraffins.

Although no definite experiment has been studied by the authors proving that the flow of *n*-paraffin is Newtonian, the following facts, at least, indicate that it is so.

(1) While various data by different authors differ, the agreement is sufficiently acceptable to prove that the value of η for any given member is independent of the type of apparatus used so long as accuracy in technique and design are maintained.

(2) The values of η collected from different sources fell on a substantially definite single curve when log η was plotted *vs* T/T_B.

(3) Again, the agreement between values of η and vapour pressure collected independently and at random from the literature give an acceptable value of the ratio of energy of activation of viscosity to that of vaporization. Thus :—

n-Paraffin.	t° C.	$1/P$.	η.	$\frac{\Delta E_{\text{vis.}}}{\Delta E_{\text{vap.}}} = \frac{(1)}{n} = \log \eta / \log (1/P)$.
n-Pentane . .	0	0·0054	0·282	0·242
n-Pentane . .	20	0·0024	0·231	0·243
n-Pentane . .	50	0·00083	0·1807	0·241
n-Heptane . .	30	0·017	0·369	0·245
n-Heptane . .	40	0·0108	0·334	0·247
n-Heptane . .	100	0·0012	0·1975	0·241
n-Decane . . .	50	0·12	0·6015	0·240
n-Decane . . .	100	0·013	0·357	0·237

Average = 0·242.

Thus it may be conceded that the *n*-paraffins behave in a Newtonian manner to a good degree of approximation. On the other hand, Pye [78] reproduces a scale model ($1·6 \times 10^7$ magnification) of $n\text{-C}_{18}\text{H}_{38}$ (Fig. 10). It is seen that it is elongated greatly in comparison with its diameter. Again the factor 4·13 for n denotes elongated flowing molecules. Thus in the ordinary type of elementary processes of viscous flow it would be expected that interlocking would take place, which, upon breaking down, should reveal lower viscosity with rate of shear.

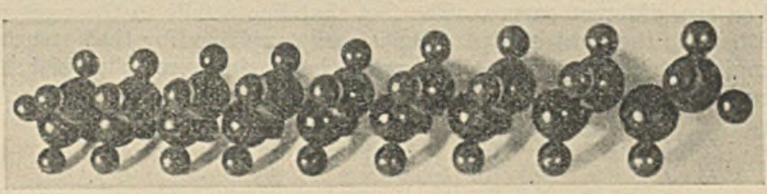


FIG. 10.

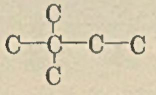
MODEL SHOWING SPECIAL RELATIONSHIP OF ATOMS IN A STRAIGHT-CHAIN PARAFFIN MOLECULE.

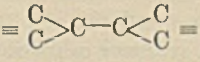
The authors believe that the jerky nature of motion of the ultimate unit and the equality of their size are sufficient to keep these units disposed in a random manner towards each other. Where the elongated bodies are much larger than the ultimate units of the medium in which they are dispersed, then orientation results and non-Newtonian flow is manifested (cf. Eyring's works, which assume that the type of flow is mainly a function of the value of the shearing stress). It is considered that the Newtonian nature of flow of such anisotropic bodies is a definite support of the theories which maintain that flow is not continuous, but of the nature of " jumps."

iso*Paraffins.*—Fig. 11 is a chart of the *iso*paraffin lines of the substances as listed on it. It should be made clear that of all the evidence, that of the *iso*paraffins is the least trustworthy in this work, since the boiling points were obtained from different authorities from those giving the viscosity. Thus only approximate generalizations are possible, and apparent anomalies are to be expected.

The *iso*paraffins represented by the first seven lines are of those compounds possessing one branch of various lengths and positions. Excepting 2-methylheptadecane and 3-ethyloctadecane, all the other five are near the n-paraffin line—the variation may be genuine or merely due to inaccuracies in the value of T_B. The authors are of the opinion that all the lines would coincide with the n-paraffin line. In other words, one branch in a paraffin has little or no effect on the " specific viscosity curve." (The points of lines 4 and 5 plot irregularly compared with the very accurate representation of a straight line by other substances, indicating either impurities in the liquid or errors in T_B.)

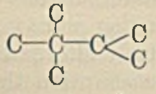
The substances studied and represented by lines 8–12 inclusive possess two branchings and present interesting support to the general theory. Both 2 : 2- and 2 : 3-dimethylbutane possess " specific viscosity curves " to the right of the n-paraffins showing greater symmetry in the equipotential surfaces of the molecules than the latter. They either fall on one curve or the small divergence between them is real. Since the boiling point has been taken from the same source as the viscosity, it appears that they fall on two different curves. The fact that line 8 falls to the right of 9 and both to the right of n-paraffins is easily explained by their structural formulae, which show a relative decrease in proximity to spheroidal shape of molecules :

line 8 =  $\mathrm{C{-}C(C)_2{-}C{-}C}$ = large spheroid with protrusion.

line 9 =  $\mathrm{(C)_2{>}C{-}C{<}(C)_2}$ = irregularly shaped ellipsoid with narrow constriction in the middle.

It should be remembered that the carbon atoms are not in one plane, but arrange themselves in 3-dimensions. The case of two branches in a longer chain is represented by 2 : 7-dimethyloctane, (10), 2 : 11-dimethyldodecane (11), and 3 : 12-diethyltetradecane (12). The effect in rounding off the molecules by the branching is necessarily small in proportion as the chain is lengthened; thus 10 and 12 fall nearer to the n-paraffin line. For the same reason discussed above with regard to 4 and 5, line 11 is believed to be farther to the left than it should actually be; yet its position with regard to 10 and 12 is in accord with the theory.

On these bases the position of line 13, representing 2 : 2 : 3-trimethylbutane, being to the right of the whole, is in accordance with the probable shape of the molecular envelope as seen from the structural formula, to be imagined in three dimensions :—



$$C-\overset{C}{\underset{C}{C}}-C\begin{matrix}C\\C\end{matrix}$$

When the chain is lengthened to 2 : 2 : 4-trimethylpentane the line moves to the left again, going even beyond those of 8 and 9. This is again what is expected.

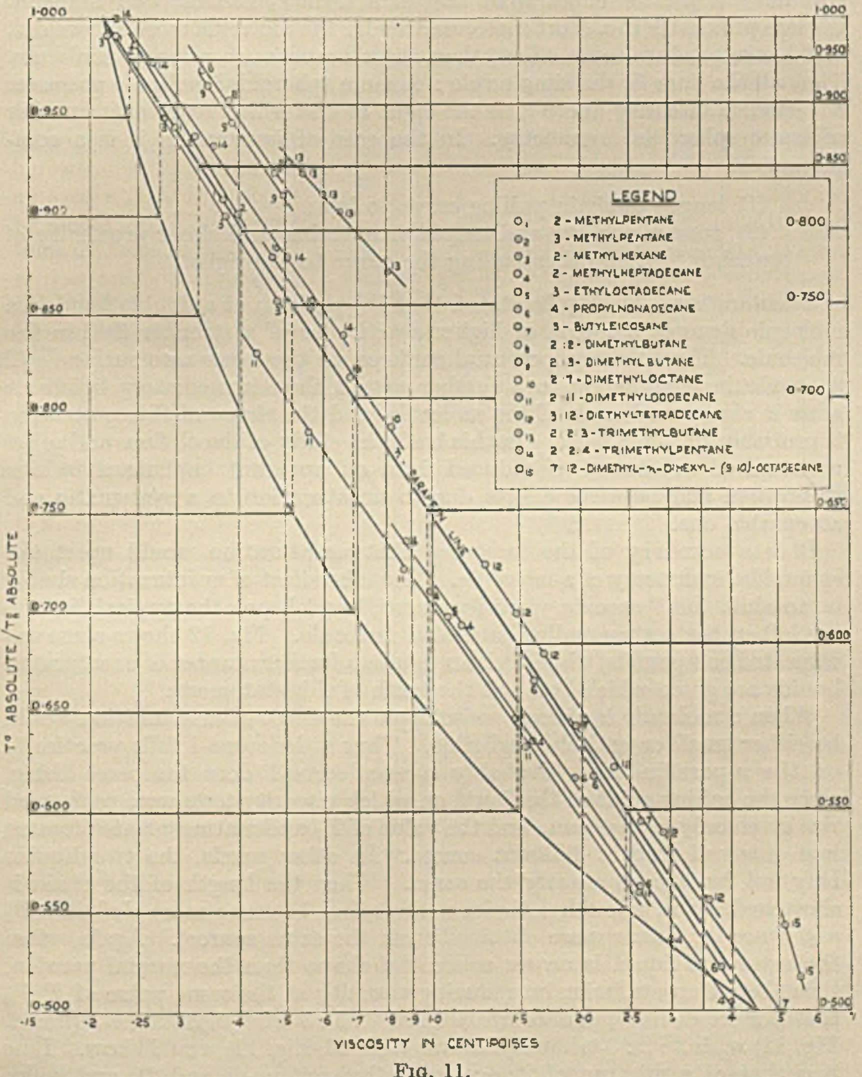


FIG. 11.

With 7 : 12-dimethyl-*n*-dihexyl-(9 : 10)-octadecane it is seen that the length of the chain tends to pull the line to the left, whilst the length of the branches tends to pull the line to the right and to give it a position of an ellipsoidal body. The boiling point is, however, most untrustworthy.

It would appear that this study affords no greater understanding of the dependence of viscosity on constitution than a comparison of viscosities at equal temperatures. Actually it brings forth the principle enunciated above that there is no general value for the effect of one or more branching but a specific effect only to be understood by taking all other factors into consideration. Thus, while three branches in a closely packed manner will have a greater effect than two in a similar manner, two branches in close proximity in a short molecular render the molecule more spheroidal, and hence produce more effect, than three branches in a longer molecule. Thus all the lines fit the simple rule: A more spheroidal molecule possesses a "specific viscosity curve" to the right of one which represents another of lesser spheroidal symmetry. In the case of *iso*paraffins it is a compromise of

(1) length of chain pulling curve to left;

(2) greater number and length of branches and closer proximity of branches to each other pulling the curve to the right.

Unsaturation.—It may be stated that the position of a double bond in a molecule denotes a region of higher activity or of a stronger field in the molecule. Thus the equipotential surfaces, or the inner zero surface, will protrude in that region to a further extent than immediately before or after it along the length of the molecule, and the shape of this protrusion is probably that of a disc. On this basis the study of the olefines and other unsaturated substances is reduced from an apparent haphazard fashion of positive and negative effects due to unsaturation to a systematic and acceptable one.

It is a corollary of the foregoing that unsaturation would upset the spheroidal symmetry of a molecule. Thus the effect of unsaturation should be to shift the "specific viscosity curve," and hence the typical line, to the left of the corresponding saturated molecule. Fig. 12 shows some unsaturated compounds, whilst in later figures a further number of unsaturated liquids are given which bear out the truth of this statement.

When a molecule is already anisotropic the effect of unsaturation would be either small or entirely negligible. Thus *n*-dodecene-1 falls practically on the *n*-paraffin line. Probably *n*-hexadecene-1 does the same thing, since the boiling point of the liquid on which viscosity tests were performed was given only at 11·5 mm., and the value of T_B under atmospheric pressure was obtained from a different source. In other words, the two liquids may not have been exactly the same. When the length of the chain is shortened, as in trimethylethylene, the effect becomes more definite (T_B and viscosity values were obtained from the same source). Again, when the saturated liquid is nearer spheroidal shape than the normal paraffin, the effect of unsaturation on reducing viscosity at the same value of T/T_B is still more definite, as a comparison of 2 : 3 : 3-trimethylbutene-3 (line 4, Fig. 12) with 2 : 2 : 3-trimethylbutane (line 13, Fig. 11) would show. Line 5 is that of a mixture of 2 : 4 : 4-trimethylpentene-(1 and 2), and hence is curved as discussed above; yet its position relative to 2 : 2 : 4-trimethylpentane bears the same evidence. Again, *cyclo*hexene, which possesses one double bond, when compared with *cyclo*hexane (Fig. 12), is definitely

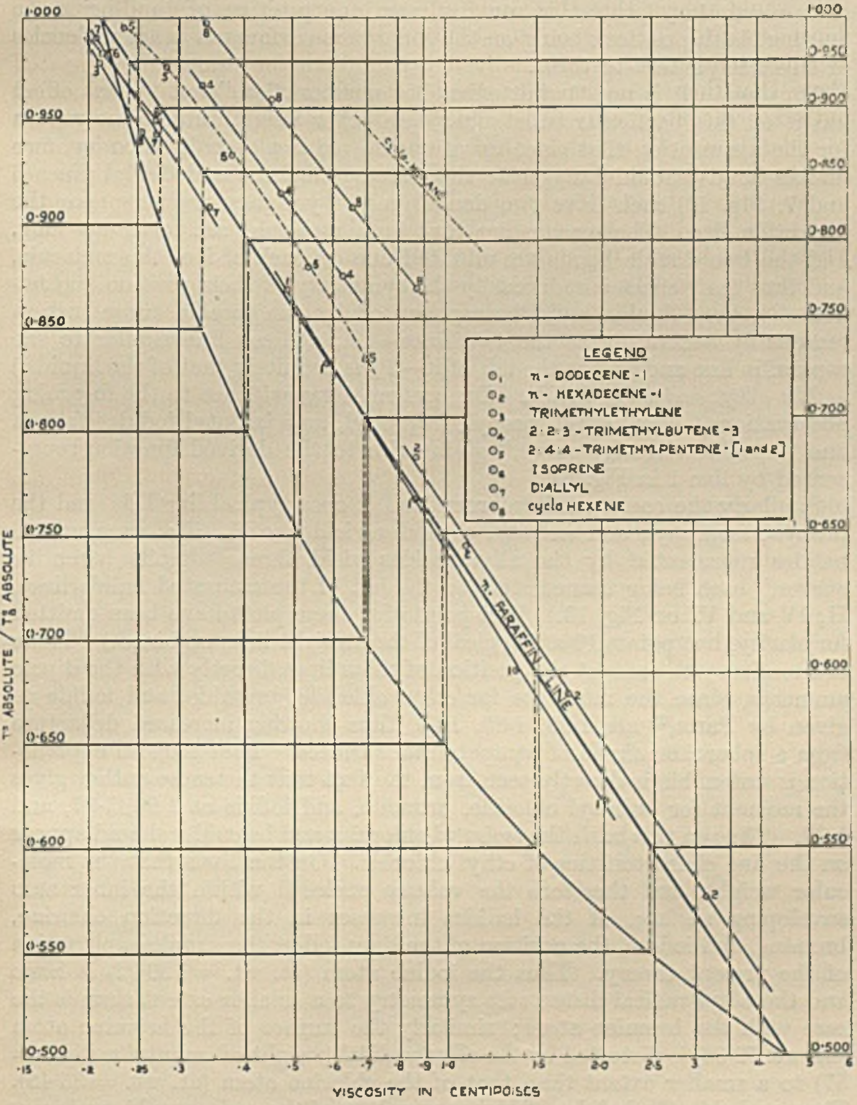


FIG. 12.

to the left. Other evidence is the position of benzene and all its homologues relative to *cyclo*hexane and its corresponding homologues (Fig. 15) and the allyl halides being always to the left of the alkyl halides. The authors

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fail to see how an increase in the activity of a molecule *reduces* the specific viscosity so persistently and generally, except on the assumption made above, that anisotropy in the shape of molecule increases the ratio of surface to volume, and thus reduces the volume swept by molecules in their elementary process of moving from one position of equilibrium to another, both positions being on the inner zero surfaces of other molecules or surfaces parallel to these.

Thus again it is not " what effect has unsaturation," but " what effect has it on this particular substance." In other words, there is no reason for the assumption that since unsaturation reduces specific viscosity, two double bonds should exaggerate the effect. Isoprene and diallyl (lines 6 and 7, Fig. 12) each have two double bonds, yet they are very near the n-paraffin line. The reasons are that both molecules are relatively long, and the two double bonds are situated one on each end of the molecule, and thus their effect is reduced by the symmetry of their position. (Incidentally, both liquids could be represented by one specific curve just as reasonably accurately as the two lines—*i.e.*, a diene line similar to the n-paraffin line and just to the left of it—T_B is definitely that of the liquids.)

The alkyl and other halides offer confirmatory evidence to the foregoing observations. Thus ethyl, propyl, *iso*propyl, and *iso*butyl iodides fall on one " specific viscosity curve," giving rise to the derived function represented by line 1 in Fig. 13.

Similarly the corresponding bromides fall on a typical line III; and the propyl-, *iso*propyl, and *iso*butyl chlorides yield line V. The unsaturated halides represented by the allyl halides yield three " specific viscosity curves," each being immediately to the left of the saturated halide lines, II, IV and VI on Fig. 13. (The points for these plots have been omitted for clarity, but points 19 are typical of the straight lines obtained.) There is a tendency to connect the position of these lines directly with the dipole moments, since the moments for ethyl chloride, bromide, and iodide as given by Parts,[79] are 1·99, 1·83, 1·66, thus showing increased departure from a spheroidal shape of equipotential surfaces. That such an explanation is untenable is directly seen from the fact that the same author gives the moment for *iso*butyl chloride, bromide, and iodide at 1·96, 1·97, and 1·87. Thus on this basis the *iso*butyl chlorides and bromides should appear on the line characteristics of ethyl chloride. On the basis that the molecular weight, and therefore the volume enclosed within the inner zero enveloping surface, of the halides increases in the direction chlorine, bromine, and iodine, the position of the lines follow the simple explanation of the present theory. Thus the iodine atom (at. wt. = 126·92) is large and the alkyl radical distorts its symmetry to a smaller extent than is the case with the bromine atom; similarly the surface of the bromine atom (at. wt. 79·96) is distorted by the alkyl radical (weight of *iso*butyl radical = 57) to a smaller extent than that of the chlorine atom (at. wt. = 35·45). Thus probably the halides of higher members of the series would gradually depart from the characteristic line as the surface of the radical changes from the minor to the major fraction of the molecular surface. Evidence towards this end is offered by methyl iodide (points 1 on Fig. 13), which shows greater degree of spheroidal symmetry than the other iodides, and thus is to the right of the others. Again, when the surface of the alkyl groups is enlarged by a double bond in the manner described above, the line drifts to the left. On this basis the monohalide of a sufficiently long chain is believed to yield a line identical with the n-paraffin line, despite the fact that the lower members tend to group around independent lines.

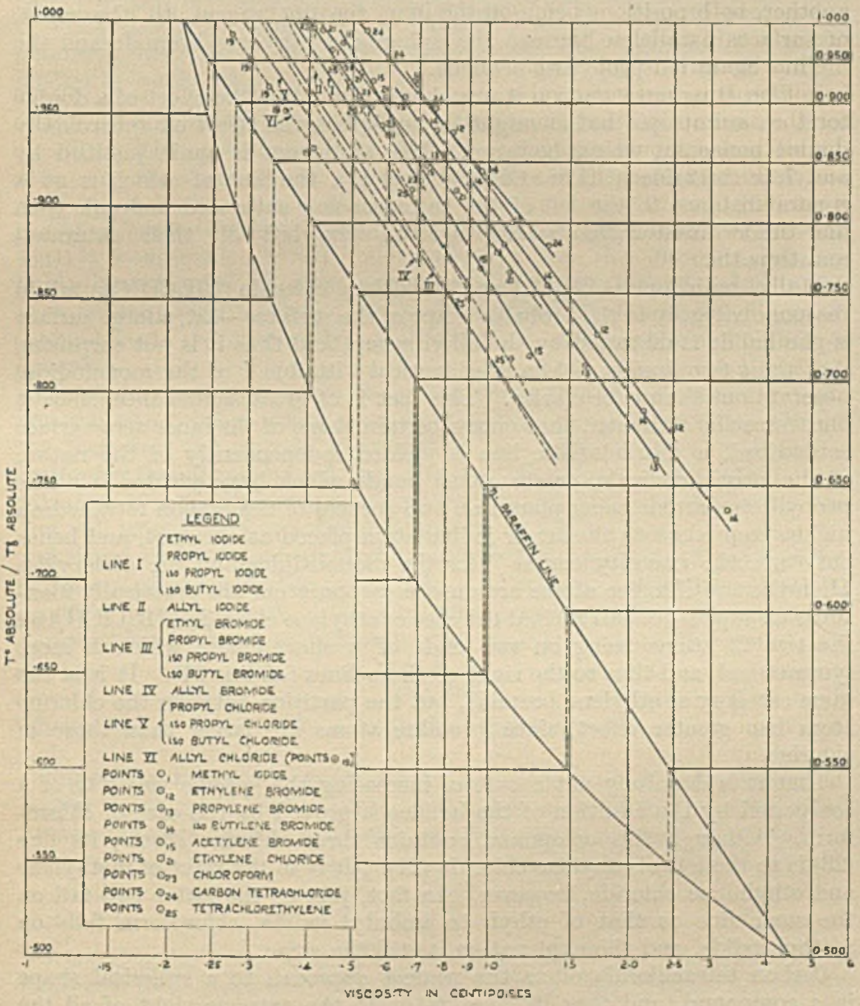
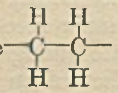


FIG. 13.

Ethylene bromide (CH_2BrCH_2Br), containing two bromine atoms in a short molecule, is naturally considered on this basis as being fundamentally characterized by the two bromine atoms, the



$$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-$$

radical, distorting but a little the general surface contours of the halides. Thus line 12 is very nearly on the carbon tetrachloride line, representing a well-balanced spheroidal surface. When the length of the chain is increased, the two bromine atoms are driven apart, and the line moves to the left as shown by propylene bromide ($CH_3CHBrCH_2Br$) (line 13). Again, when the "waisted" effect of the surface is reduced by a branch in the chain, *iso*butylene bromide ($(CH_3)_2CBrCH_2Br$), the line moves to the right, taking a mid-position between the spheroidal ethylene bromide and the slightly elongated propylene bromide.

In discussing unsaturation it was shown that while the effect of a double bond on anisotropic bodies might be negligible, the effect on spheroidally shaped molecules would be large. This statement is again justified by acetylene bromide ($CHBr : CHBr$) (line 15), the line of which is at a greater distance to the left of the corresponding saturated molecule than the other unsaturated halides are to the left of their saturated counterparts.

Methylene chloride (CH_2Cl_2) and ethylidene chloride ($CH_3CH\ Cl_2$) fall in the same category in the probable shape of the surfaces—*i.e.*, a large surface of the halide is distorted by the alkyl group, and thus it is not surprising that these two liquids yield a line identical with line 1 of the monoiodides —points not shown for clarity. This fact is of great significance, since it illustrates the statement that once a certain shape of the inner zero surface is attained, a characteristic line is yielded independently of the nature of the atoms, radicals, or structural bonds which have yielded it. The two chlorine atoms being placed on two corners of the carbon tetrahedron will be equivalent to the larger iodine atom placed at one spot, and hence the "specific viscosity curves" for the monoiodides and the dichlorides when the two chlorine atoms are on one carbon atom are practically identical. In support of this is cited the case of ethylene chloride (CH_2ClCH_2Cl), the two Cl atoms being on two ends of a short chain, which is more symmetrical, and thus to the right of these lines (cf. line 21). It is in the same category as ethylene bromide, but the partition between the chlorine atom has greater effect, since bromine atoms are larger than those of chlorine.

That it is definitely not a case of increasing the specific viscosity of a compound by the addition of the halides is proved by the case of chloroform. Although this compound contains three chlorine atoms, its line (23) is to the left of ethylene chloride (21). It is to the right of methylene and ethylidene chloride, however. In fact, just as the latter two fall on the same line as that of ethyl- to *iso*butyl iodide, chloroform falls on methyl iodide, and the explanation is still the same.

Carbon tetrachloride offers the nearest approach to a spherical shape in a compound, and thus its line (24) is to the extreme right of all the liquids yet discussed. The effect of a double bond on a usually spherical molecule is seen in the case of tetrachlorethylene ($CCl_2 : CCl_2$) to be the largest yet encountered (line 25).

Proof is thus continuously available that the shape of the equipotential surfaces or of the inner zero surface enveloping a molecule is the fundamental characteristic giving rise to the "specific viscosity curves." Or, again, that the effect of an atom, radical, or a structural characteristic may be negative, nil, or positive to a greatly varying degree, depending entirely on the relative position of the new addition in the molecule and presence or absence of other atoms, radicals, or structural bonds. Hence no useful purpose could be served in compiling a table showing the numerical or quantitative magnitude of such effects. They are special to each case, and since the lines are in a fan shape, will vary slightly with the value of T/T_B chosen for comparison. No useful purpose could be served by detailing other cases, but three charts have been prepared for further studies of special importance :—

(1) The oxygen groups for association studies
(2) The cyclic groups for viscosity index study
(3) The elements for apparent and important anomalies.

The Oxygen-Containing Groups. Many of the oxygen-containing organic compounds exhibit "association"; but this property has probably been blamed for more anomalous behaviour than those for which it is actually responsible. Thus a short consideration of the effects of "association" to be expected with regard to specific viscosity would be desirable.

Since the unit involved in the elementary process of viscous flow may perform the process either in a unimolecular or polymolecular fashion, the fact that the unit is comprised of one molecule or two associated molecules should not be evident. On the other hand, if the unit is comprised of two molecules at one temperature and only one at another, this fact will reveal itself in a definite manner, as follows :—

A liquid may be assumed, for the purpose of the analysis, to be completely unassociated at the boiling point. Then to remove one molecule from the liquid a certain energy ΔE is required, represented by the energy of vaporization. Thus for evaporating one mole the energy required is

$$\mathrm{N} \,.\, \Delta E$$

where $N =$ Avogadro's Number.

Supposing instead of vaporization the unit is made to perform the similar function of viscous flow where only a fraction of the molecular volume is swept by each molecule, then the energy required per mole is :—

$$\frac{N\Delta E}{n} = \frac{\Delta E_{\text{vap.}}}{n} = \frac{Ml}{n}$$

Assuming, however, that at a lower temperature the whole number of molecules have associated into the dimer form, they would still perform the same elementary process (if the shape is not changed greatly) and sweep the same fraction of the *new molecular volume*, which is twice the original. Thus the energy of viscous activation per mole is double the original, *i.e.* :—

$$\frac{2Ml}{n} = \frac{Ml}{\frac{n}{2}}$$

Thus n appears to decrease with decrease in temperature if on decreasing the temperature the ratio of polymers to monomers increases. Since the bases for the " specific viscosity curves " is the general equation

$$\log\left(\frac{\eta}{\eta_B}\right) = \frac{Ml}{n2{\cdot}3RT_B}\left(\frac{T_B}{T} - 1\right)$$

it is seen that as T/T_B decreases, n will decrease in value, and thus log η will increase—*i.e.*, the slope of the line will be less steep on the chart for associated liquids than for unassociated liquids. In other words, *where the degree of association decreases with rise in temperature, the characteristic line on the chart will slope away and to the right from the corresponding unassociated liquids line having the same viscosity at the boiling point as the associated.* On the other hand, *if the liquid exists throughout its range and boils in the bimolecular or trimolecular forms, then the line will be that of an " unassociated " liquid—i.e., no effects of association can be seen.* These two rules are exemplified by the alcohols representing the first case and acetic acid, which boils mostly as the dimer, representing the second, and yielding a line parallel to normal liquids occupying its position.

It is also seen that since the latent heat per mole is calculated on the basis of the mole containing N molecules, while in associated liquids the " mole " would really contain a greater number than N, Trouton's function of Ml/T would yield greater values for the associated liquids than the constant assumed in the construction of these charts. On the other hand, this does not invalidate the accuracy of the argument, since (1) the true value of the molal latent heat divided by the temperature at which the molecules evaporate *in the associated* form—hypothetical but higher than T_B, since a greater level of energy is required by the molecule—would probably yield the constant. (2) The fact that even water and trimethyl carbinol yield definitely straight lines on these charts prove that (1) is correct, and hence the basis of the argument authentic.

Thus the degree to which the characteristic line is out of parallel to the line representing a normal liquid and occupying a position on the chart at which the associated liquid loses all its association bonds is a measure of the degree of association of the liquid under consideration. The boiling point may be considered here, for simplicity, to represent a point at which all the molecules exist in their lowest isomeric form—the alcohols being assumed to be monomeric.

The Alcohols. On this basis the alcohols will be studied from two points of view :—

(1) The position of log η at $T/T_B = 1$ to indicate the degree of departure from spheroidal shape.

(2) The general slope of the line to indicate the degree of association.

To understand the shape of the alcohols it is only necessary to assume that the volume enclosed by the inner zero surface of the hydroxyl group is equivalent to the volume of the corresponding surface of an alkyl group C_nH_{2n+1}, where n is to be determined. Methyl alcohol is seen (line 1) to occupy a position at $T/T_B = 1$ midway between the CCl_4 and n-paraffin line, indicating that one surface or the other encloses greater volume. That the surface of the OH group is the larger one is seen from the fact that ethyl and propyl alcohol (lines 2 and 3, Fig. 14), move progressively to the right; *n*-butyl (line 4) however, reverses back to the left. Thus the *n*-propyl alcohol, which is the nearest of the normal alcohols to the CCl_4 line, denotes the nearest approach to spheroidal shape of the molecule amongst these substances. A nearer approximation is shown by the *iso*butyl alcohol and trimethyl carbinol. It cannot be pure coincidence that these alcohols surround the value shown by CCl_4 at $T/T_B = 1$; it is due

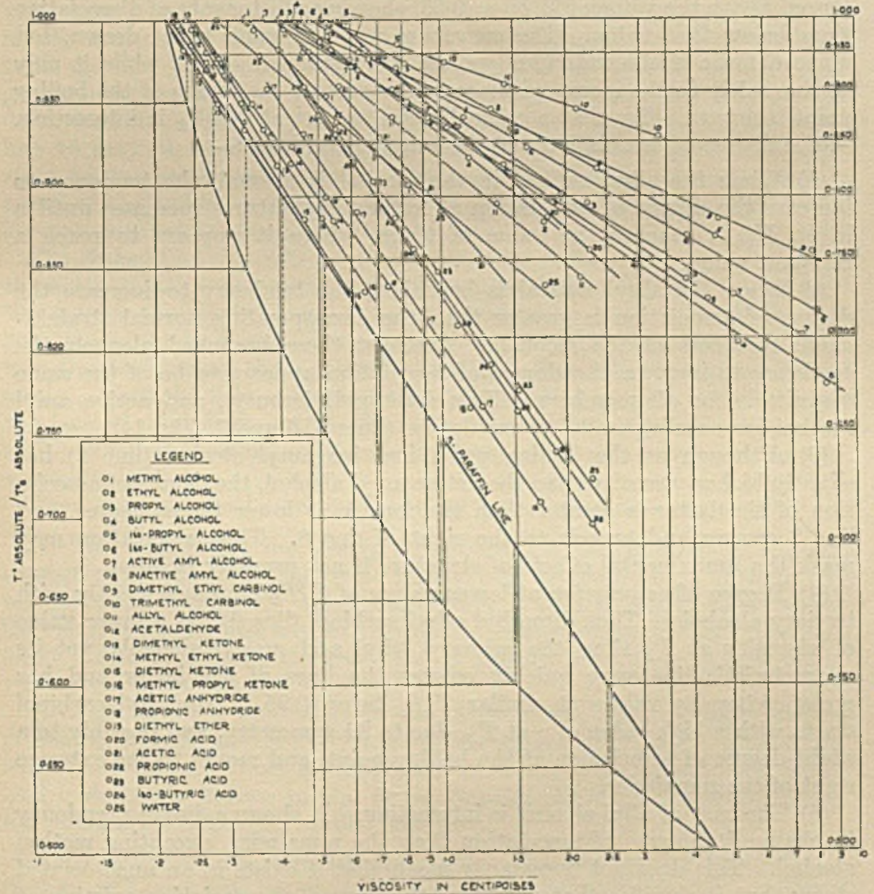


FIG. 14.

to the fact that the molecules possess balanced spheroidal effective shapes in these compounds. (It is not necessary that the moment is zero, since the centre of the spheroid is not necessarily coincident with the centre of mass.) All higher members of the alcohols show greater drift to the left, which appears to reach a constant position as shown by the two amyl alcohols (7 and 8), dimethyl ethyl carbinol (line 9), and allyl alcohol (line 11) on Fig. 14. It is to be noted that the generally accepted rule that an OH group confers large viscosity values has no basis when the effect is separated from the effect of association. This point will be again proved by the case of potassium hydroxide. In other words, any large values of viscosity in a molecule containing an hydroxyl group is due to the increased association at lower temperatures, and not to the possession of the hydroxyl group directly.

The association of the alcohols is studied from the slope of the lines. With all alcohols a slight curvature, seen on the large-scale charts, was observed above the value of $T/T_B = 0{\cdot}95$, showing a faster rate of dissociation than below that value. The curvature was too small to be drawn, but quite definite if the individual points were studied. Thus while it may be due solely to the increased inaccuracies around the region of the boiling point, the possibility that a critical region occurs at $0{\cdot}95T_B$ is interesting.

The degree of association may be summarized here :—

(1) When the alkyl radical in the alcohol is normal, the tendency to increase the degree of association at lower temperatures increases until n in $C_n\ H_{2n+1}$ reaches the value of three, where it appears to reach a constant value.

(2) When the alkyl radical is branched, the tendency to increase the degree of association is greater than the corresponding normal straight-chain members of the alcohols. Amongst these branched alcohols the tendency to increase the degree of association appears to be of the same magnitude for all members. Thus *iso*propyl, *iso*butyl, and active amyl alcohol are nearly parallel to each other (lines 5, 6 and 7, Fig. 14).

(3) Although at the boiling point inactive amyl alcohol (line 8) has slightly higher viscosity than the active amyl alcohol, the degree of association of the latter is greater than the former at lower temperatures, and line 7 crosses and travels to the right of line 8. Thus association may mask the fundamental effects of structure if not properly isolated.

(4) Degree of association at lower values of T/T_B increases greatly with tertiary alcohols. Thus dimethyl ethyl carbinol (line 9) has a lower value of viscosity at T_B than the primary ethyl and propyl alcohols, yet its characteristic line very quickly crosses the lines of the latter and has greater viscosity values at similar T/T_B below 0·95. Trimethyl carbinol starts with a high value of η at T_B, due to its symmetry, and possibly to a slight degree of association at the boiling point, and moves to the extreme right of the remainder.

(5) The case of allyl alcohol is interesting. It shows a smaller tendency to change its degree of association than the remainder, excepting methyl alcohol. This does not necessarily mean that it exists in an unassociated state; but it signifies that whatever the degree of association existing at lower values of T/T_B, it boils associated to approximately the same extent.

(6) *Association is more probably a function of the ratio T/T_B than of T.* This fact is probably of greater importance than the remainder, since the present state of uncertainty in the study of "association" may be due to the fact that the fundamental ratio of T/T_B as a basis of comparison is not recognized. On the other hand, this study of association is yet in a qualitative state, and needs further development before its findings are accepted as truths and the method used as a means for investigating intermolecular forces responsible for association.

Acetaldehyde and the Ketones exhibit normal characteristics and occupy positions near the *n*-paraffin lines. The ketones exhibit greater approach to spheroidal shape than the aldehyde (line 12). It is to be pointed out that probably the purest of the ketones studied by Thorpe and Rodger and reproduced here is the methyl propyl ketone (line 16), as the least error was observed between the calculated and actual vapour density of the liquid. Thus line 16 may be taken as authentic. The next in purity as judged by this standard is dimethyl ketone (line 13), which is found very nearly on the same line, whilst methyl ethyl ketone (14) is nearly on it on the other side. Thus the three ketones may well be taken to lie on one characteristic line, the ketone line, represented by 16. The greatest degree of impurity amongst the four ketones was found with diethyl ketone, which may account for its departure to the left. Thus the line 16 may be used for giving the viscosity of the ketones in the pure state to a greater accuracy than the reported values, once the boiling point of the unknown ketone is found accurately. This fact illustrates the practical use of the chart.

The Anhydrides and Ether.—The anhydrides show greater balance than the ketones and are unassociated—or keep the same degree of association throughout the liquid range. Acetic anhydride is more balanced in the general shape of its surface than the propionic anhydride (line 18), indicating that the field around the $(CH_3CO)_2$ is stronger than that around the (O=) group. Thus the field of the latter is comparatively weak. This explains the lack of any effect on the general surface of the *n*-paraffin when the (O=) group is included in the diethyl ether (line 19, which lies on the *n*-paraffin line).

The Carboxylic Acids are again studied from two points of view :—

(1) The viscosity at the boiling point indicates that formic acid has the nearest approach to a spheroidal surface and its value of η_B is near the region of CCl_4 and other spheroidal bodies. Thus it would be expected that as R is lengthened any movement of the line will be to the left on the chart. This is actually the case, and it appears that there is a constant value from propionic acid upwards.

(2) Association is studied from the slope of the line. Formic, acetic, propionic, butyric, and *iso*butyric show invariancy of degree of association with temperature. This is supported by other observations, as acetic acid is definitely known to boil in the bimolecular form. Thus probably the other acids behave in similar manner.

Water behaves in perfect harmony with these ideas. Its value for η_B is that of a molecule which is anisotropic but which possesses a nearer approach to spheroidal shape than the oblong paraffins. Again it shows change of degree of association with decrease in T/T_B. It is interesting to note that this change of degree of association is not excessive, in view of the following theories on water. According to Walker,[80] water in the liquid state is mainly dihydrol, with some trihydrol near the freezing point and some monohydrol near the boiling point. Kendall,[81] however, appears to agree with Langmuir "that the whole ocean consists of one loose molecule and that the removal of a fish therefrom is a dissociation process." The change shown by line 25 in the degree of association is in support of

Walker's view, unless in Langmuir's theory the "loose molecule" is made to be bound by bonds which are relatively stronger with decrease in temperature.

The most remarkable fact emerging from Fig. 14 is that all these complex compounds yield definite straight lines, thus confirming previous conclusions and proving the two facts :—

(1) *Change of degree of association with temperature is shown by such charts.**

(2) *Study of association should be made on the basis of T/T_B and not T when comparing liquids.*

Cyclic Structures.—The thirty compounds containing a cyclic structure confirm the observations made with regard to spheroidal and anisotropic shapes of the enveloping surfaces, and how the specific viscosity is affected by branching, unsaturation, etc. These will be left to be studied from Fig. 15 with only a few remarks as below.

(1) Comparison of the independent ring with its methyl and ethyl substituted homologue at equal temperatures gives a familiar anomalous behaviour, as is the case with many other substances, such as the unsaturated compounds, acids, etc.

Compound.	Viscosity at				
	0° C.	20° C.	50° C.	80° C.	100° C.
Benzene . . .	0·9015	0·6515	0·4365	0·317	0·2655
Toluene . . .	0·764	0·5835	0·417	0·3135	0·2665
Ethylbenzene . .	0·877	0·668	0·4785	0·3595	0·305
*cyclo*Pentane . .	0·556	0·4375	0·3245	(0·2525)	(0·2190)
Methyl*cyclo*pentane .	0·647	0·501	0·3615	0·274	0·2345
Ethyl*cyclo*pentane .	0·7415	0·569	0·411	0·3125	0·2685
*cyclo*Hexane . .	1·455	0·9865	0·6095	0·413	0·332
Methyl*cyclo*hexane .	0·991	0·728	0·4945	0·3665	0·3095
Ethyl*cyclo*hexane . .	1·161	0·8375	0·5715	0·417	0·350

It is also apparent that while *cyclo*pentane is less viscous than benzene, *cyclo*hexane is more so. These erratic characteristics disappear when comparing on a T/T_B basis. It is seen that :—

(*a*) Recognizing a slight degree of association in the benzene molecule, the *cyclo*hexane series is always to the right of the *cyclo*pentane series, and the latter to the right of the aromatic members. It will be remembered that in these graphs molecular weight is not a factor, and thus C_6H_{12} is comparable with C_5H_{10} and C_6H_6.

(*b*) In the three series the substitution of a methyl group in the ring

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* Numerical comparisons of the increase in association with decrease in temperature for different liquids may be obtained in this manner : Assume the degree of association to be unity at the boiling point. A line is then drawn through the intersection of the typical line with $T/T_B = 1$ and made to be parallel with the line which would represent a normal liquid having the same value for η_B, the viscosity at the boiling point. Then for any value of T/T_B chosen for comparison—say, $T/T_B = 0{\cdot}75$—the ratio of the value of $\log \eta$ at $T/T_B = 0{\cdot}75$, as given by the actual line, to that of $\log \eta$ on an hypothetically normal line at the same value of $T/T_B = 0{\cdot}75$ is a measure of the increase in degree of association over that existing at the boiling point.

shifts the line to the left, as the symmetry of the enveloping surfaces is necessarily affected.

(*c*) Lengthening the chain still brings the position of the lines nearer the *n*-paraffin, reaching a constant position with ethylbenzene and higher homologues of the aromatics, and with *n*-propyl substitutes and higher members of the more spheroidally shaped naphthenes. Thus points 3, 4, 5, 6 and 7, representing ethyl- up to *n*-hexyl-benzenes, lie on one line, points 16 and 17, for *n*-propyl- and *n*-butyl-*cyclo*pentane, on another, and points 22 and 23, for the corresponding *cyclo*hexane substitutes, on a third.

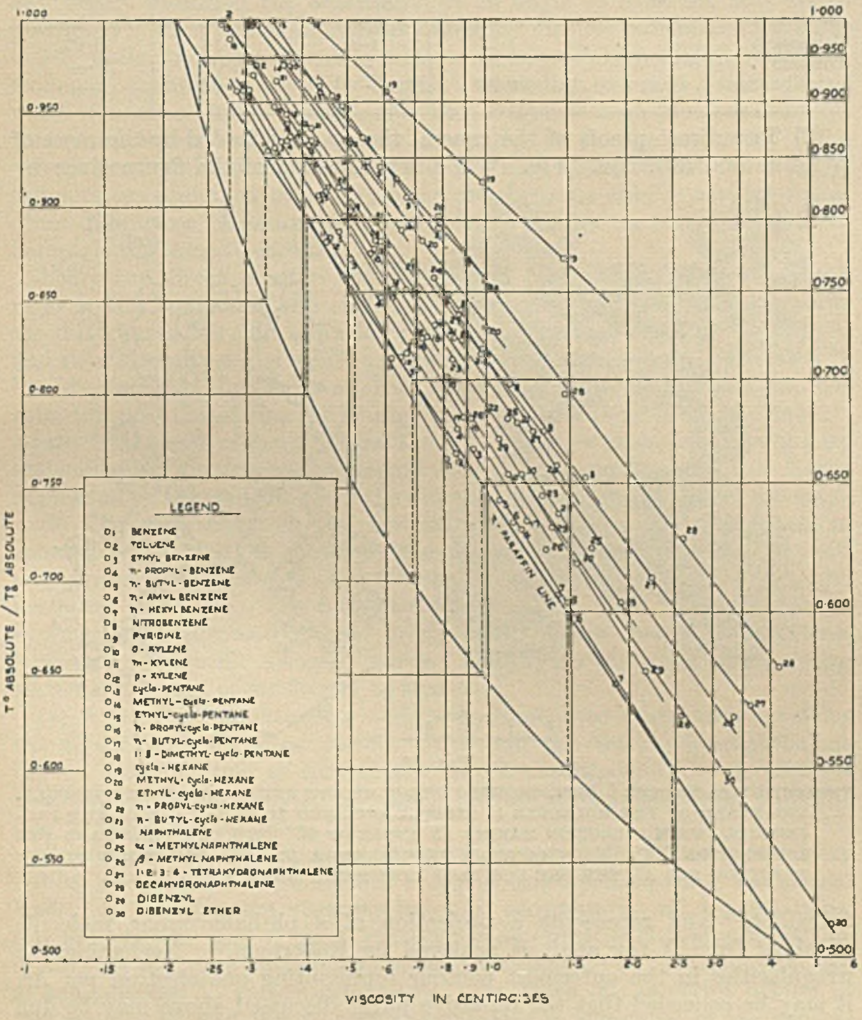

FIG. 15.

(*d*) Of these members only benzene appears to associate to a slight extent. This fact receives confirmation from the following table compiled by Hatschek,[16] which table tends to show that benzene is slightly associated.

Substance.	Association factor according to—			
	MacLeod.[82]	Ramsay and Shields.[83]	Bingham.[8]	Traube.[84]
Benzene	1·37	1·01	1·14	1·05
Toluene	1·08	—	1·06	—
Ethylbenzene . . .	0·91	—	1·02	—

(2) Two direct proofs of the general theory are afforded by the cases of pyridine and dibenzyl. Fig. 16 is a reproduction of the figure given by Crowfoot,[85] and represents a projection of a phthalocyanine molecule obtained from X-ray analysis achieved by Robertson.[86] Neglecting the irregularities in the outermost contour representing one electron per A^2, it may be conceded that the repulsive forces discussed above may be due to, and are generally of a contour parallel to, those of the electronic densities from two electrons per A^2 upwards.

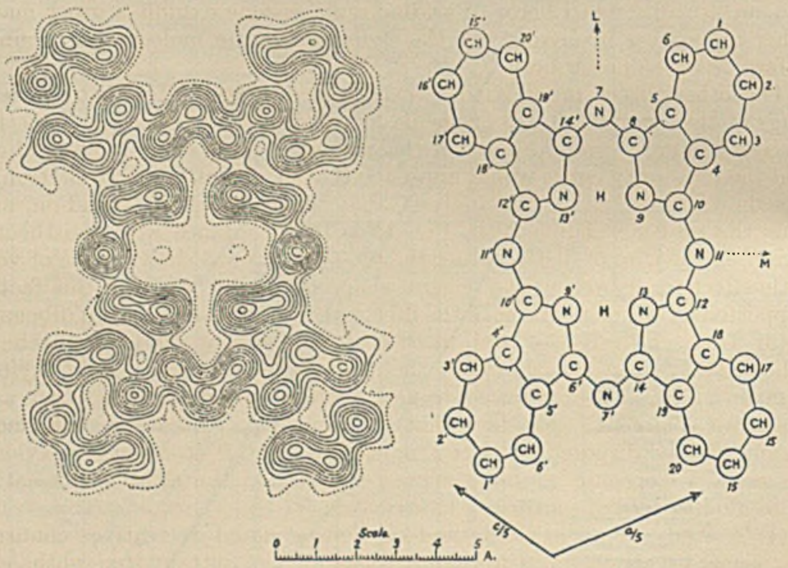

FIG. 16.

PROJECTION ALONG THE *b* AXIS, SHOWING ONE COMPLETE PHTHALOCYANINE MOLECULE. THE PLANE OF THE MOLECULE IS STEEPLY INCLINED TO THE PLANE OF THE PROJECTION, THE M DIRECTION MAKING AN ANGLE OF 46° WITH THE *b* AXIS, AND THE L DIRECTION 2·3°. EACH CONTOUR REPRESENTS A DENSITY INCREMENT OF ONE ELECTRON PER A^2, THE ONE-ELECTRON LINE BEING DOTTED.

On this basis the inner zero point would also be parallel to these, and hence the diagram deals with some property which is parallel to the surfaces being discussed here. Although the plane of the molecule is steeply inclined to that of the projection, yet in this latter plane it is seen that a nitrogen atom is surrounded by an electronic density contour almost identical with that of (CH) group in the benzene ring—taking the two-electron contour. Then, if the nitrogen atom exhibits the same characteristic in other planes, it follows that a *substitution of a nitrogen atom in the benzene ring for* (*CH*) *should not affect the* "*specific viscosity curve*" *of benzene.* In Fig. 15 the points 9 are those representing pyridine, and it is seen that line 1, which is that of benzene, represents them to a better degree than any other—including the one drawn at an angle to it as the only other possibility. This fact is significant, since the electric moment of pyridine is 2·1, whilst that of benzene is zero, or at most only negligibly different from zero as shown in detail by Smyth,[87] according to whom "the replacement of a carbon in the benzene ring by nitrogen to form pyridine destroys the symmetry of the molecule and gives rise to a large moment." The "symmetry of the molecule" discussed by this author is not the same as the surfaces discussed here. Pyridine and benzene exhibit a great many other differences in detail; but the "shape" of the molecule, as defined before, is the same for both.

The other direct proof is that seen from dibenzyl. The two benzene rings of this compound can either lie in parallel—and hence the "specific viscosity curve" would approach that of *cyclo*hexane or CCl_4—or end-on, and then viscosity curve would approach that of *n*-paraffins. Robertson[88] has shown again, by X-ray analysis, that they are definitely end-on, and thus the position of line 29 in Fig. 15 is in accordance with the theory. Again, in the case of diethyl ether the (O$=$) group was shown to be of very little effect in disturbing the general shape of the surface, and this fact is supported by the coincidence of the dibenzyl ether line with that of dibenzyl.

(3) The sensitivity of the method to anisotropy and approach to spheroidal symmetry is shown by the case of the three xylenes. *O*-xylene is given as being nearer to the toluene molecule than the other two, and needs no comment. The fact that the *p*-xylene, with its slightly more symmetrically disposed methyl groups than is the case with *m*-xylene, possesses a "specific viscosity curve" slightly to the right of the latter molecule is a sign of sensitivity to structure.

(4) A study of naphthalene and its hydrogenated derivatives confirms the remarks about unsaturation. Although the tetrahydronaphthalene lies on the same line as that of the parent naphthalene, the decahydronaphthalene is definitely to the right. Again alkyl substitution pulls the line to the left.

Viscosity Index.—The present study yields some information on viscosity indices and renders the empirical study of this function some theoretical basis. In defining the viscosity index of an unknown oil U, two other oils are chosen, one of good viscosity characteristic H and one of low quality on the same basis L, so that all three oils are of the same viscosity at temperature T_1 chosen arbitrarily. The three oils are then heated to temperature T_2 and the drop in the viscosity is compared in the general equation

$$\text{V.I.} = \frac{X - Y}{Y - Z} \times 100$$

Where X = viscosity of oil H at T_2,
Y = viscosity of oil U at T_2,
and Z = viscosity of oil L at T_2.

Thus it is a comparison of the relative drop in viscosity over the range $T_2 - T_1$ of the three oils. A similar function could be obtained if only two oils were taken, the unknown and the good-quality oil H, and a rule made that if $X - Y$ is zero, the two oils are of the same quality; if $X - Y = +ve$, the unknown is worse than H; whilst if $X - Y = -ve$, the unknown is the better oil. In Fig. 17 the two liquids A and B are assumed to yield the two lines shown on the chart. To compare the two liquids they should have the same viscosity η_1 at T_1. Thus the vertical through η_1 cuts A at a value of $T/T_B = X$ and B at value of $T/T_B = Y$. It is seen that

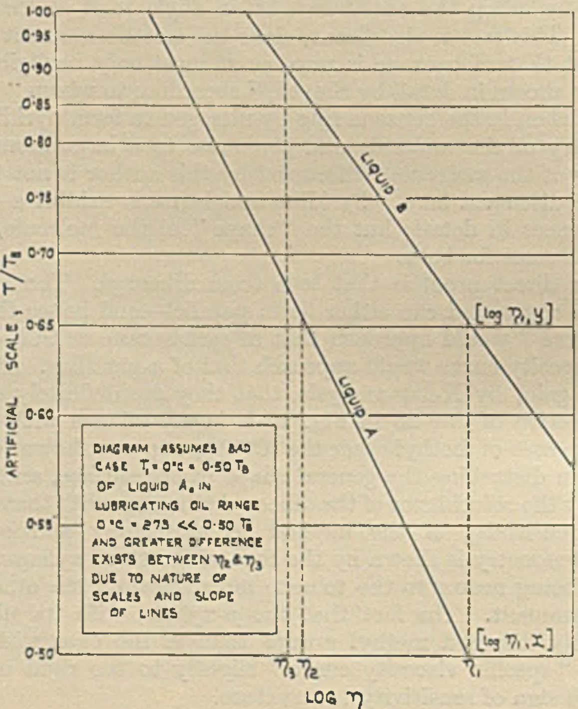

DIAGRAM ASSUMES BAD CASE $T_1 = 0°C = 0{\cdot}50\ T_B$ OF LIQUID A, IN LUBRICATING OIL RANGE $0°C = 273 \ll 0{\cdot}50\ T_B$ AND GREATER DIFFERENCE EXISTS BETWEEN η_2 & η_3 DUE TO NATURE OF SCALES AND SLOPE OF LINES

FIG. 17.

$$X \leqslant Y$$

$$\therefore \quad (T_B)_A \geqslant (T_B)_B$$

On heating the liquids to T_2 the two liquids would drop in their respective lines in viscosity in amounts proportional to

$$\frac{T_2 - T_1}{T_B} = \frac{K}{T_B}$$

Since $(T_B)_A \geqslant (T_B)_B$, the drop in viscosity for A is smaller than for B—in other words, A is of higher "viscosity index." Thus the rule is, *for two liquids, the one which yields a characteristic line on these charts to the left of the other is of higher viscosity index—i.e.*, it has a smaller proportional drop in viscosity for any constant drop in temperature. From this rule—

which is, in fact, another form of saying that of two liquids possessing equal viscosities at any one temperature the liquid with a higher boiling point is the more resistant to viscosity change with temperature—it is easy to reformulate rules already accepted in the Petroleum Industry.

(1) The paraffins possess higher V.I. values than the aromatics and naphthenic groups.

(2) Long-chain substitution in the ring increases the V.I.—“ paraflow ”-like structures.

(3) Since flat or elongated shapes are required for high V.I. values branches in the chain should be reduced to a minimum.

(4) One long chain has better effects than two small chains having the sum total length of the single chain in the case of substitution in naphthenes and naphthalene rings.

(5) Provided the chain is sufficiently long, it does not matter whether the ring is aromatic, naphthenic, or naphthalene.

(6) Dunstan and Thole’s suggestion that true lubricants consist of unsaturated compounds receives further support to their special theories, since the flat, disc-shaped surface around a region of double bond increases the V.I.

(7) The V.I. falls rapidly with increase in association, since the line travels at a faster rate to the right than the normal lines.

All these conclusions have been actually found by Mikeska[90] in 1936 and put forward in an able and interesting paper. All Mikeska’s findings receive support from these charts. A few are given here as examples of the use and accuracy of the method and to compare general principles by theoretical studies.

One important conclusion, however, is not given (as far as the authors are aware) in the literature. The idea that cyclic structures are inherently possessed of low viscosity indices is erroneous. If a molecule could be synthesized entirely of rings but the rings were joined end-on to each other (as in dibenzyl), and of sufficient length to yield viscosity values within the range of lubricating oils, such a liquid would possess a high V.I. despite the fact that it is entirely or mostly cyclic. In other words, if the shape of the molecule is elongated or disc-shaped it is immaterial whether it is cyclic or paraffinic. The most severe obstacle in the direction of such synthesis is the fact that with ring structures of the type

the C : H ratio is very high, and thus coke is formed. The difficulty lies in producing a liquid of such molecules—*i.e.*, by hydrogenation, methylation, or other means.

(An attempt to give an “ absolute viscosity index ” by comparing the liquid with the *n*-paraffin line produced downward to yield a viscous liquid of the range of the lubricating oil and utilizing the formula for the paraffin liquid

$$\log \frac{\eta_1}{0{\cdot}2} = \frac{0{\cdot}242Ml}{2{\cdot}3 \times 1{\cdot}98_{T_B}} \left(\frac{T_B}{T} - 1\right)$$

yielded a very narrow range, and thus proved impracticable).

Elements and Organic Compounds.—The alcohols presented an anomaly, in that the lines were far less steep than the shape of the molecule and the position of the line demanded. This anomaly was successfully explained by the supposition that at the value chosen for T_B a higher value for the energy of activation is required to boil the liquid in the polymolecular form, since a larger molecule is transferred to the vapour state. Another way of stating this fact is that the value chosen for T_B should be higher than that reported in the literature if the molecule evaporated in the polymolecular form—the literature reports the evaporation of the monomeride—thus the position of any point (η_T, T/T_B) would be vertically lower than that shown on the graph and the line parallel to a normal liquid. The case of acetic acid is a proof of the case, since this liquid boils mostly in the bimolecular form (cf. discussion on Trouton's rule by Friend,[73] p. 89, or any standard book on Physical Chemistry).

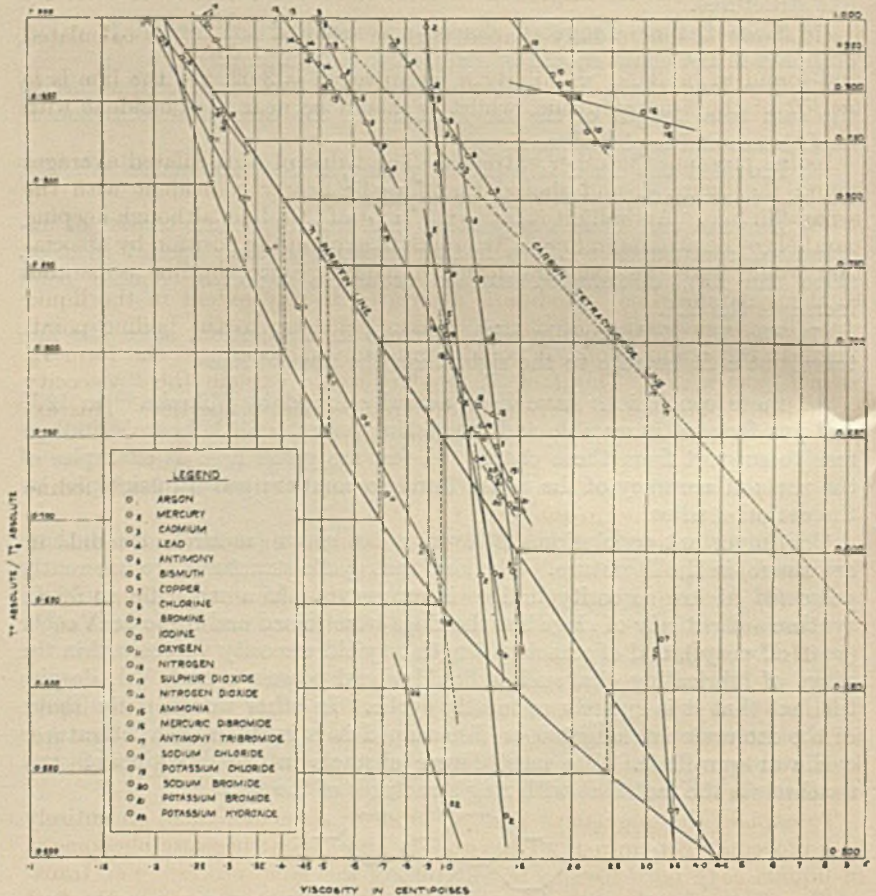

FIG. 18.

The case of the following elements present the opposite type of anomaly : Argon (point 1 on Fig. 18), Chlorine (8), Bromine (9), Iodine (10), Oxygen (11), and Nitrogen (12).

Argon and iodine will be studied in detail to illustrate these anomalies. Argon has spherically shaped equipotential surfaces.[33] The line should therefore be near that of CCl_4. Its actual place is seen nearer the *n*-paraffin line. This position cannot be explained by the supposition that the electronic orbits form an ellipsoidal surface, since the evidence of viscosity itself shows a spheroidally shaped surface when $n = \frac{\Delta E_{\text{vap.}}}{\Delta E_{\text{vis.}}}$ is calculated and found to be 3·09. Similarly n for nitrogen is 3·02, yet the line is *to the left* of the *n*-paraffin line, whilst it should be near or coincident with CCl_4.

Iodine presents the other extreme. The value of n calculated averages round the figure 4, and should therefore be nearly coincident with the *n*-paraffin line. Actually it is far to the right of CCl_4 line, although keeping parallel to the *n*-paraffin line. Attempts to explain the position by association would take the following form—and fail. Since the line is parallel to the *n*-paraffin line, if iodine is associated to any extent in the liquid state it will preserve that degree of association up to the boiling point. Then at the boiling point it could completely dissociate to the form I_2, as in $I_n \rightleftharpoons n/2I_2$. This fact, if tenable, would explain the "viscosity exaltation" of iodine, to borrow a term from optical properties. This explanation is untenable due to the following considerations :—

(1) According to data in the International Critical Tables,[91] iodine dissolves in water in the form I_2.

(2) According to Friend,[92] iodine dissolves in methylene iodide in the form I_2.

(3) According to Kendall,[21] substances dissolve in their liquid form, and not in gaseous form, as the classical theory according to Van 't Hoff postulates.

Thus it may be safely concluded that iodine exists as I_2 in the liquid form, although no actual determination is available in the literature. It is well known that over a large interval in the vapour state it is in the diatomic form.

To explain the anomalous position of these elements, then, an entirely new procedure is required. The viscosity and vapour pressure phenomena of liquids have been seen to be variants of the same process—*i.e.*, transporting molecules through a fraction of their volume of space in the first case and through their volume of space in the second. Thus the viscosity at the boiling point of these elements have been plotted as a function of the boiling point in Fig. 19.

It is seen that viscosity at the boiling point, or at a comparable state, *is a rising function of temperature.* At zero absolute the viscosity approaches zero, as is confirmed by Keesom and Macwood,[52] who give η_B for H_2 at $\leqslant 138\ \mu P$ and for He at $30\ \mu P$ and the viscosity of He at zero absolute tending towards zero (cf. also Tisza [96]).

This graph suggests the following explanation for viscosity of liquids, Up to the present it has been maintained that viscosity in liquids is essentially different from that of gases, since it always decreases with temperature in the former case, whilst it increases with the latter (cf. Andrade, Kendall, etc.). Actually, it is evident that in the elements, at least viscosity has a rising function with temperature, but superimposed upon this fact is a more important *decreasing* function. Thus it may be summarized :—

For those elements which are not ionized in their liquid state the viscosity is affected in two opposing manners when the temperature is raised. With increase in temperature the intermolecular bonds weaken, or the potential barriers to the flow of the unit from one mathematical minimum to a lower one decreases in length, thus necessitating lower values of energy of activation and resulting in a comparatively large decrease in viscosity. At the same time energy loss due to "collision" of the molecules in a similar manner to the gaseous state gets higher with temperature, resulting in a secondary increasing function of viscosity with temperature. The algebraic sum of these two effects, in those liquids where the intermolecular bonds are strong, is a decrease of viscosity with temperature—the decrease being a function of "n" and T/T_B. It is essential to note that, on this hypothesis, if the intermolecular bonds were either non-existent or extremely weak, then viscosity variation with temperature would be entirely governed by the second effect. According to Bernal,[93] liquid helium, owing to the wide amplitude of vibration, possesses "no rigidity." In other words, liquid helium would provide a test case, since its viscosity would then be entirely governed by the loss of energy on "collision." Keesom and Macwood [53] have definitely proved that the viscosity of liquid helium increases with rise in temperature, thus substantiating this hypothesis.

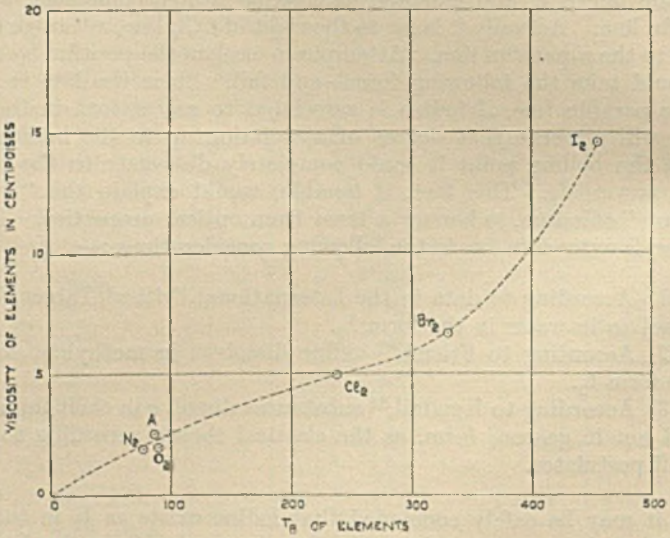

Fig. 19.

The word "collision" should be stated in more explicit terms, since in a liquid as pictured in this paper not only is there no "free space" in the meaning accepted for gases, but it has been postulated that molecules interfere with each other and have their effective boundaries within the space occupied by other molecules. Collision here simply means that when a molecule breaks contact with the zero point surface of another molecule and moves forward towards a third, it transmits part of its kinetic energy to the third in an imperfectly elastic manner—*i.e.*, with a certain loss of momentum in the form of undirected energy.

Between the two extremes, helium and the other elements mentioned here, the metals provide a medium position of varying extent. The viscosity change with rise in T/T_B is almost negligible, showing that the lowering of the potential barrier with rise in temperature is almost completely offset by the increased loss of energy on collision (of a slightly different type from that discussed above).

It was shown by Ewell that the supposition of metallic molecules flowing in the ionic form, without their valency electrons, gave an explanation for their viscous flow characteristic. Modern theory of electrical conductivity and paramagnetism of metals lends support to this view.[94] On rise of temperature, electrical resistance rises lineally with temperature, and is supposed to be due to the increased scattering of the electrons carrying the charge by the imperfection in the lattice of the metallic crystals. Similarly, in viscous flow an increase in temperature means that a smaller number of atoms is flowing without their valence electrons and greater loss of energy on collision. This cause of increase of viscosity with temperature is opposed, and slightly offset, in the opposite direction by the decrease in the energy required to move the ion across the lower potential barrier. Thus mercury (points 2 on Fig. 18), cadmium (3), lead (4), antimony (5), single point 6 for bismuth, and copper (7) all show a low value for viscosity at the lower values of T/T_B, indicating that only a small fraction of the molecular volume is involved in the elementary process. All show a very slight decrease in viscosity with temperature. To summarize the behaviour of the elements, both metals and non-metals :—

(1) Liquid helium shows only the increase effect in viscosity with temperature—possibly the decreasing effect is existing but minor in importance, as the rate of increase in the viscosity becomes less with higher temperatures in Keesom's plot of η *vs* T.

(2) Metals show an almost invariant viscosity function with temperature, thus the two tendencies tend to balance, due to the particular case of the electronic characteristics.

(3) Un-ionized elements show the decreasing effect completely counterbalancing the increasing effect. Yet even in these elements the increasing function of η with temperature is important enough to put η_B in a position opposite to what the ordinary demands of molecular shape would dictate.

A consideration of fundamental importance arises here : It was proved previously that, since all these elements and compounds yielded straight lines, they are all governed by one general law. Thus it must follow *that in all liquids rise in temperature has the two opposed effects on viscosity :* (1) *a decrease, due to lowering of potential barriers in accordance with accepted principles of liquid viscosity ;* (2) *an increase in viscosity, to a much smaller extent except in helium and metals, due to loss of energy probably in the* *manner accepted for gaseous viscosity.* The difference in the viscous behaviour of gases and liquids thus becomes a matter of degree and not of kind.*

The inorganic compounds do not show any new characteristic. Sulphur- and nitrogen dioxide are apparently in a normal state above the temperature representing $0{\cdot}9T_B$ and of the same general shape. Ammonia yields a line in accordance with the concept of the anisotropic molecule consisting of nitrogen and three hydrogen atoms being placed at the four corners of a tetrahedron and in opposition to symmetrically disposed hydrogen atoms around the nitrogen atom. Mercuric bromide shows a great degree of association at lower temperatures compared with those above $0{\cdot}95T_B$; whilst antimony tribromide appears to be spheroidal, and its line is coincident with CCl_4 (the data are, however, meagre).

The alkali halides tend to group themselves around one line representing potassium chloride (19). (The curvature in the line of NaCl is most probably due to the inaccurate knowledge of its boiling point.) Probably calculation of the boiling points of these halides would be more accurate if the reverse step were taken—assume they lie on line 19 and calculate T_B from viscosity data.

The case of potassium hydroxide (22) is of interest. This compound is completely ionized in the liquid state, and hence—since K would have very low viscosity as in the case of other ionic liquids—if the (OH) group possessed large viscosity characteristics, as has been assumed, the line would indicate it. Actually the position of the line indicates that an (OH) group is possessed of similar viscosity characteristics as the metals, thus confirming the conclusion reached from the study of the alcohols at their boiling point. The high viscosity of, say, glycerol at 0° C. is due to the fact that if the correct values of energy of activation and boiling point of the liquid in the associated state were known, the value of $273/T_B$ (representing 0° C.) would be far lower than its accepted position, and the liquid would be less viscous comparatively than the paraffins, since at such low values of T/T_B the paraffins are solids, and hence of extremely high viscosities. It is due, in fact, to the incomparable states of the two liquids, and not to the possession of high viscosity values by an hydroxyl group, or even the grouping of hydroxyl radicals in a molecule—except indirectly, since association appears to be connected with the existence of such groups as (OH), etc.

Before the conclusions it should be pointed out that Kapitza[95] has suggested that the viscosity of helium is so small that even in the flow obtained between plates the distance apart of which was estimated at 0·5 μ, the Reynolds number was above that for which turbulent flow is to be expected. This fact may detract from the value of the present conclusions; but Keesom and Macwood are " quite sure that the motion of the fluid at all times was laminar." These points await confirmation.

Again, no reason was found why the elements are affected to a greater

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* During the time the paper was being printed, W. L. Nelson (*Oil Gas J.*, 13.7.39, **38** (9), 50) correlated viscosity of high-pressure gases and liquids and found: " That at high pressures the lines for gases (viscosity) at reduced temperatures 1·5, 2·0, and 4·0 show that the viscosity of such gases decreases with temperature as you would expect liquids to behave." Since the reduced temperatures were of the order of $4T_c$ there is no question of liquefaction.

This result was directly deduced in the present work.

extent by the secondary increasing effect of viscosity with temperature than compounds appear to be. The latter are chiefly governed by the shape of the molecule. This second point should prove of interest and importance.

The general law of the variation of liquid viscosity with temperature—and possibly of all flow of gases, liquids or plastic and crystalline solids—is yet unknown. All that is known about it is: (*a*) it is exponential, (*b*) the energy of activation in the exponential term is a variable, (*c*) possibly the "constant" term is a rising function of temperature.

CONCLUSIONS (cf. Note by Authors [97]).

I. *Mechanism of Viscosity.*

In the introduction the authors formulated what appeared to them to be established principles concerning the mechanism of viscosity in liquids. It was pointed out that the rule, for monoatomic spheroidally shaped liquids,

$$\log \left\{ \frac{2}{3} \frac{Tm}{\Delta E_{\text{vap.}}} \right\} + \frac{\Delta E_{\text{vap.}}}{13{\cdot}7\, Tm} = 0$$

if proved rigorously to be correct, would render the three states of matter, gas, liquid, and solid, into one continuous series of changes with no abrupt breaks of unrealizable states in so far as flow is concerned. Further in this work it has been established that one law only governs the viscous flow of all the liquids studied by the authors. The general law of viscosity in liquid is as yet unknown. It is made up of two functions:—

(1) A rising function of temperature probably in a similar manner to gaseous viscous flow.

(2) A falling exponential function of temperature.

Thus gaseous flow and liquid flow (in the viscous state) are probably connected in the following order: gases in normal state, compressed gases, helium, metals, ionic liquids, normal liquids, and finally associated liquids showing the greatest fall in viscosity with rise in T/T_B.

Ewell has pointed out that flow in liquid and crystalline matter is of an identical nature. Eyring had produced an equation connecting Newtonian and non-Newtonian types of flow. Thus it is to be concluded that *one law governs all viscous flow in all states of matter*, and that *there must be a solitary equation giving the change, with temperature, of magnitude of viscous forces in flowing matter.* Various terms in the equation would either vanish or predominate as the substance changes its state.

Thus no theory can be complete unless it gives the mechanism of viscous flow in all states. On this basis none of the existing theories can be complete.

(Of the various formulæ put forward, Eyring's equations appear to be the nearest to the general law. These formulæ contain rising and falling functions of temperature. Before they can be established as generalizations, however, they are to be applied to gaseous as well as plastic flow. Only in one case have they been tested in the latter type of flow and in that case found to hold.)

Regarding the mechanism of viscosity of liquids the conclusions derived in the first portion of this paper are fully supported in the second, but with the addition that there is a loss of momentum due to collision.

The authors consider the following as statements of established facts :—

(1) Vapour pressure and viscosity are functions of the same variables—*i.e.*, the forces taking part are identical in both cases.

(2) The ratio of heat of activation in the case of vaporization to that of viscosity is a definite constant for a substance. In the case of associated liquids this constant *appears* to vary, but actually the variation is due to the fact that the true value of heat of vaporization at that particular temperature is not known for the polymer form.

(3) The heat of activation in viscous flow is variable with temperatures even for the *n*-paraffins. Over narrow ranges it appears invariant with temperature for non-associated substances.

II. *Constitution and Viscosity.*

(1) A "specific viscosity curve" is found for various species or types of molecules by plotting log η *vs* T/T_B.

(2) The chief variable determining the position and slope of this curve appears to be $n = \frac{\Delta E_{\text{vap.}}}{\Delta E_{\text{vis.}}}$.

(3) For normal liquids the curves arrange themselves in a fan-shaped manner in a narrow space. The position of the curve is entirely governed by the degree of spheroidal symmetry possessed by the inner zero point surfaces of the molecules as defined above. Thus it is not a generalization of the effects of such groups as (CH_2), (OH), etc., that appears to be possible to predict, but only specific cases as applying to each particular molecule :—

(4) Where the addition of any atom, radical, or structural characteristic to a molecule enhances the spheroidal symmetry of the molecule the "specific viscosity curve" moves to the right—*i.e.*, higher values of η for the same value of T/T_B. Where the effect is the reverse on the shape of the molecule the same atoms, radicals, or structural bonds will produce a drift to the left in the curve. Where the effect on the shape of the molecule is negligible the curve will represent both substances equally accurately—hence "specific viscosity curves."

(5) Association reveals itself in a rapid shift of η to the right with a decrease in T/T_B. When rise in temperature does not affect the degree of association the liquid appears normal—*i.e.*, unassociated.

(6) Effects of association can mask the effects of structures, and should be separated by studying the liquid in its lowest degree of association.

(7) The (OH) group is devoid of any high values of viscosity. The high viscosity of alcohols, glycerols, etc., is due to association. At room temperature the value of T is small relative to T_B, where T_B is not the normal boiling point, but some hypothetical boiling point at which the liquid would possess energy sufficient to make the molecules evaporate in the polymolecular form in which they exist at room temperature. This value of T_B is unrealizable physically, since the bonds of association break down at such high levels of energy.

(8) Metals possess relatively low viscosity values at lower values of T/T_B.

This is believed to be due to the flow of the metal without the valence electrons. Evidence tends to show that this is true, and that with higher temperatures the metals are nearer to the state of normal liquids in their flow.

(9) Viscosity indices of various structures are predictable by the charts employed here, by the rule that, the nearer the shape of equipotential surfaces to a spheroid the lower the V.I. One conclusion is that a high V.I. will characterize an oil of entirely cyclic structure, provided the rings are joined in such a manner that the molecule is rendered elongated. Difficulties in obtaining such substances in the liquid state will be due to the high C : H ratio.

(10) The "specific viscosity curves" of the elements are governed by the rising function of viscosity with temperature to a greater extent than those of compounds which are mainly governed by the effective shape of the molecule. No reason was found for this.

(11) The function T/T_B appears to be a suitable reduced temperature for comparing dynamic properties such as viscosity and vapour pressure. Probably association should be studied at equal T/T_B values, and not equal values of T, as it appears that change of degree of association of liquids with temperature is $f(T/T_B)$.

ACKNOWLEDGMENTS.

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THE INSTITUTE OF PETROLEUM.

A MEETING of the Institute was held at the House of The Royal Society of Arts, John Adam Street, London, W.C.2, on Thursday, 14th March, 1940, at 5.30 p.m. Professor A. W. Nash, President, occupied the Chair.

The following paper was presented by Mr. A. H. Nissan :—

"The Dependence of Viscosity of Liquids on Constitution." By A. H. Nissan, B.Sc., A.M.Inst.Pet., L. V. W. Clark, Ph.D., M.I.Mech.E., F.Inst.Pet. and A. W. Nash, M.Sc., M.I.Mech.E., F.Inst.Pet. (see p. 155).

DISCUSSION.

DR. A. E. DUNSTAN said it gave him the greatest pleasure to propose a vote of thanks to the authors for their important and interesting paper. He spoke with a certain amount of feeling, because it was just thirty-six years ago that he began his own studies on the subject of viscosity, and he thought that the members present that evening had taken very many steps forward in their appreciation of what was, to his mind, a vitally important phenomenon.

When he began his own work, which perhaps Mr. Nissan remembered, viscosity was contemplated as a highly constitutive property, a property that was particularly applicable in fathoming molecular structure, a particulate and specialized property, but a little later on it was found that certain mathematical derivatives of the viscosity constant were not quite so particulate, but perhaps were even general. Of those, there were two that emerged. One was discovered by E. C. Bingham in America, who used the reciprocal of viscosity, which he called fluidity, and that proved to be specifically additive, and not particularly constitutive. About the same time his colleague Thole and he investigated the derivative function log. viscosity, and log. viscosity proved to be definitely additive and by no means constitutive (Dunstan and Thole, *J. chem. Soc.*, 1913, **103**, 127; 1914, **105**, 782; 1915, **107**, 667). He would be interested to hear if Mr. Nissan could say why it was that viscosity itself was profoundly constitutive, whereas the reciprocal and the log. were definitely additive.

His colleague Thole and himself had plotted log. viscosity against molecular weight for a long range of many homologous series. Taking the fatty acids from C_1 up to C_{18}, at a temperature of 25° C., for example, log. viscosity against molecular weight worked out into a fairly linear relationship, *i.e.*, $\log. \eta = a + b \times \text{m.wt.}$ Leaving out the first two members, which were always out of the picture, the relationship was given by a straight line which curved at higher values of molecular weight. If one took the same materials at a higher temperature—for example, 80°, 90° or 100° C.—then the relationship became much more closely linear.

They imagined at the time that the departure from linearity at the high-molecular-weight end was due to the fact that some kind of molecular aggregation, or association or colloidal condition occurred—for example, in the case of the fatty acids, the sodium salts formed true soap which had quite different properties from those of the sodium salts of the acids farther down the line. He thought now that he and his colleague might have been quite right in supposing that the departure from linearity was due to the formation of molecular aggregations. They had taken the normal paraffins as far as they could get them, and found that for these hydrocarbons log. $CH_2 \times 10^5$ was 0·109; for a range of iodides as far as they were available log. $CH_2 \times 10^5$ was 0·102, for a sequence of ethers log. $CH_2 \times 10^5$ was 0·108, for a group of esters log. $CH_2 \times 10^5$ was 0·107, and for a range of ketones log. $CH_2 \times 10^5$ was 0·106. The alcohols were a little off the picture; they gave a CH_2 difference of 0·116, and the sulphides gave

0·091. The average, as could be seen, was fairly good, and, by taking the log. CH_2 from the hydrocarbons, one could obtain the log viscosities for hydrogen.

As a proof of the definitely additive relationship of log. viscosity, they took the substance *iso*butyl ethyl ether and built up a viscosity value from the log. viscosity value of the component atomic grouping, and the built-up figure thus calculated was 0·0378. The most authoritative determination of the viscosity of this ether was due to the late Professor Thorpe, who gave the figure as 0·0376—a remarkable illustration of the additivity of log. viscosity in non-aggregated substances.

The vote of thanks was accorded with acclamation.

PROF. A. W. NASH said, I am sure we are all indebted to Mr. Nissan for the able way in which he has explained the use of the various charts which have been put before us and the thought has occurred to me that there might be other ways in which these charts could be employed.

One point has already been discussed in the paper—that of calculating the boiling point of a liquid from viscosity data where actual determination of this criterion is difficult. For instance, in the case of sodium chloride, if the line for alkali halides be taken to apply to all, then from the viscosity of sodium chloride at one or more temperatures the boiling point could be calculated. The case of the ketones is discussed in detail in the paper.

Suppose now we look on these charts as giving us some idea of the approximate shape of the molecule, with a view to determining whether those liquids which can be used as fuels are likely to behave as good, bad, or indifferent fuels when used either in a spark-ignition engine or a compression-ignition engine. Might we not expect that those liquids with lines to the right of the charts would yield good spark ignition fuels, whilst those on the left side would yield good diesel fuels, as the more spherical the molecule, the more resistant it becomes to chemical reactions ?

Dealing with the spark-ignition fuels first, we find that, generally speaking, these expectations are justified in many compounds, but that there are also some glaring irregularities. Thus the alkylated benzene series are nearly on the paraffin line, and yet their blending octane numbers are, in fact, very high. *iso*-Octane itself is so near the normal paraffin line as to justify a prediction of but an indifferent fuel. *cyclo*Hexane is to the right of benzene, yet its octane number is not higher than benzene.

On the other hand, there are a number of examples which follow this rule. The alcohols, bezene, *cyclo*hexane, *cyclo*pentane, and many other fuels are to the right of the chart, as shown in Figs. 14 and 8. Again, in Fig. 11 the lines designated 9, 8, and 13 are all to the right of the *iso*-octane line 14. Their blending octane numbers are found to be 124, 101, and 116, respectively, whilst that of *iso*-octane is, of course, 100. Similarly, *cyclo*hexene on Fig. 12, which is again to the right of *iso*-octane, has blending number of 132. Many other liquids could be enumerated.

The case of the spark-ignition engine is complicated by the extraneous influence of a spark with its thermal, and probably electrical and catalytic effects on the course of the chemical reaction of oxidation. It is therefore not surprising, although perhaps disconcerting, that certain compounds should constitute a refutation of these arguments.

In the case of diesel-fuel combustion the reaction is spontaneous to a greater extent than in the former type, so that, if this rule should be followed, it would have a greater chance of regularity in this type of engine. We see that the alkyl benzenes support these postulates and the paraffins themselves offer a good proof. Other examples will be found on detailed study. Certain irregularities occur also, for the course of the combustion takes place in stages, and is not a single chemical reaction defined by simple principles. Changes in any stage (delay action, etc.) may alter the whole course of the successive oxidations.

But this does not affect the point I have in mind.

At the Birmingham Meeting last year, Gann Shen, Wood, and Garner (*J. Inst. Petrol.*, 1939, **25**, 695) showed that by joining a long chain to benzene a good-quality diesel fuel was produced. The chain, however, had to be of a certain minimum length.

From the charts put forward by Mr. Nissan we see that dibenzyl, although composed mainly of two benzene rings, lies well to the left of benzene.

It occurred to us that it would be interesting to compare their spontaneous ignition temperatures. The literature gives the S.I.T. of benzene, as determined by Moore's apparatus and using oxygen, as 639° C. From a test carried out on dibenzyl under similar conditions, we found the temperature to be 435° C., or 204° C. lower than benzene. It would appear, therefore, as if dibenzyl should prove a better starting point for alkylation for diesel fuel purposes, as the probable effect of a chain of a certain length would be greater with dibenzyl than with benzene, as we are starting with an advantage in our raw material.

I do not wish to infer, however, that these charts provide anything in the nature of a method of rating fuels. As I have already remarked, many irregularities do exist: combustion conditions of fuel under high pressures and temperatures in the presence of all kinds of unpredictable external influences cannot be a function of molecular shape alone. Greater percentages of hydrogen appear to affect the S.I.T. to a great extent. Thus, *cyclo*hexane, located almost on the extreme right of the chart, has an S.I.T. of 296° C., as compared with that of 639° of benzene. It should, of course, if the S.I.T. were a function of molecular shape only, have a higher S.I.T. than benzene. Still, it is worthy of note that not only has dibenzyl a lower S.I.T., but diphenylmethane which from a spot test was shown to have a viscosity line almost identical with dibenzyl, has an S.I.T. of 408° C. This fact supports our supposition that, starting with an elongated molecule, even though the radicles are benzene rings, good diesel fuels should be obtained. This point cannot be proved, however, except by experiment on alkylated products of dibenzyl. Should such experiments be attempted, the evidence of these charts, meagre as it is, is that the paraffin chain should be attached to the free end of the benzene ring—that is, in the *para* position—and not to the mid-carbon atoms joining the two benzene nuclei together.

Prof. J. D. Bernal, F.R.S., said that, as one who had taken a certain interest in the subject of viscosity, it had given him great pleasure to listen to the paper, which was a valuable contribution to the theoretical aspects of viscosity. It seemed to him to be an admirable example of what he would call extensive research. He thought that the theoreticians of viscosity, working on a rather narrow range of intensive studies of a few substances, definitely missed some quite important points that came out merely from studying a very large number of substances.

He wished, however, to suggest a certain caution in the interpretation of the extensive phenomena under discussion, in that many different properties of substances were generally functions of the same variables: *i.e.*, if one added in a series another CH_2 group, it would influence all the properties of the series—boiling points, viscosities, and everything else—and if one established a correlation between the effects on one property and on another, one might be dealing with something that was very much more fundamental than either of them. That was why he thought the most valuable feature of the paper was that it laid the stress on the shape of the molecule, which was very fundamental.

It was clearly indicated in the paper that the shape of the molecule affected viscosity, but there was one point that he wished to raise in that connection. If a round molecule and a long molecule were compared, it was found that the round molecule apparently had a higher viscosity than the long molecule, if they were examined at a corresponding temperature with regard to the boiling point. It might be, however, that the round molecule had a higher boiling point as a function of its molecular weight, and that the viscosity should be compared at a different temperature. The ideal comparative temperature had not yet been found. In liquids such as paraffin or dibenzyl it was extremely difficult to make good fits between the molecules. Owing to their shape in the liquid state being oriented in different directions, they made rather bad fits, and that led to considerable increases in volume, which tended to lower the effective boiling points of the molecules as compared with the round molecules. That would need to be gone into by bringing in another variable—*i.e.*, the pressure and volume relations. If the experiments were carried out at comparative internal pressures, very interesting relationships might be obtained.

In producing the tables given in the paper, the authors had in a very ingenious way reduced all viscosity temperature variations to two somewhat arbitrary variables: the position of the line and the slope of the line. It would be a very interesting addition to the paper if those two were treated as constants and, instead of plotting lines, Mr. Nissan took the lines as straight, and merely plotted any two parameters, such as the slope and the position, or any other two variables which he chose to characterize the lines. That might show a grouping of points which would possibly be more easy to grasp than the grouping of lines which Mr. Nissan had shown.

There were a few other remarks that he would like to make. One had reference to a detailed point that he thought required further investigation. An enormous amount of work had recently been published on liquid helium, and it would seem very dangerous to draw any conclusions from liquid helium at the moment, because of the anomalous λ point of helium and the superfluidity of helium, which obeyed quite different laws from those obeyed by normal liquids.

With regard to associated liquids, he thought the essential point which Mr. Nissan had made was absolutely correct—*i.e.*, that one was really dealing with two kinds of associated liquids in regard to their viscosity : the kind which had double molecules, and the kind in which the association extended throughout the structure in a more thorough way. It was rather interesting to notice that in Mr. Nissan's chart the liquids showing the greatest variation in slope were those where there was only one hydroxyl group in the molecule and the rest of the molecule was rather large and awkwardly placed, such as trimethylcarbinol, for instance. In that case it was clear that the association would diminish with temperature. He suggested that it was no longer very suitable to talk about association numbers in a liquid like water, because the association number was really the average number of molecules attached to any given molecule, and there was no separate associated group in a continuous liquid like water, whereas there was, of course, in a liquid like acetic acid or trimethylcarbinol. It was for that reason that the viscosity line for water fell between those of trimethylcarbinol and acetic acid.

The final point he wished to make was on the subject of the charts for the simple substances, particularly for the halogens themselves. In treating a large number of substances, one thought at first sight that one had covered all variables, but when one came to consider the matter from the point of view of molecular structure, one found that practically all the compounds except the halogen derivative compounds had what might be called neon-like molecule coverings. In neon itself, or in aromatic CH or CH_2 or NH_2, the outer electronic structure, which was what really determined the approach of the nearest other molecule, was almost the same. Therefore in the case of most of the liquids concerned one was dealing with what might be called normal neon-like liquids. The moment one introduced a derivative, a chlorine, bromine, or iodine, one produced a different kind of field. The essential thing was that the kind of potential field which Mr. Nissan had reproduced in one of his figures which controlled the distance of closest approach in a liquid would be practically exactly the same for all neon-like substances, except where they contained unbalanced electronic structures, and therefore local poles, as, for instance, in water. When one introduced chlorine, bromine, or iodine, one got a curve with a deeper potential minimum, because of the greater polarisability of the particular bromine or chlorine or iodine group. He felt rather strongly that that was the reason why, as one went in the direction towards the higher polarizabilities one also went towards the left on Mr. Nissan's curve. It was not a shape effect. The interesting suggestion that it was a temperature effect was, he thought, a cross-correlation; that was, there were reasons why the halogen derivatives had different boiling points and viscosities, and therefore one could correlate with the increase of temperature, but it was a correlation which depended on the form of the molecular field.

He thought the paper showed a real breaking into the field of viscosity of first approach by a quantitative extensive study, and he hoped it would lead to a renewed interest in the subject on the part of the theorists.

Mr. S. de Waele said he recognized that the paper should make a very great impression on the physicists interested in the subject of viscosity, and he could only reiterate the remarks of previous speakers that the paper represented one of the most important advances on viscosity and its theories that had appeared for several years. The paper was especially interesting in view of the fact that two or three years ago Irany had published before the American Chemical Society a method of obtaining linearity in the relationship between temperature and viscosity by employment of an arbitrary ("ϕ") scale based originally on the curvilinear log. viscosity–temperature relationship. His own experience, however, with this suggested treatment had been none too successful, but he was inclined to attribute his poor results to the difficulty of determining viscosity accurately at elevated temperatures. Mr. Nissan's application of the ϕ function of Irany had, however, yielded very valuable results when the reduced temperatures T/T_B were used and especial care taken to ensure experimental accuracy of the viscosity data.

Mr. Nissan had rather emphasized the significance of the high viscosity conferred by the presence of a hydroxy-group in a compound. Whilst the speaker was aware of the high viscosities of such hydroxyl compounds as castor oil and glycerin, he did not think that it was necessarily bound up specifically with the presence of hydroxyl. Thus, the higher unsaturated alcohols, such as oleyl alcohol, show normally low viscosities in conformity with their molecular weights. Now, whilst the hydroxyl group in castor oil is situated at about the middle of the chain, it is terminal in the higher unsaturated alcohols.

He did not know how far others present at the meeting would agree with him, but he felt that the position of the normal paraffins at the extreme left of the chart did not seem to have been the subject of sufficient comment in the paper. One visualized the normal paraffins as forming long-extended chains, yet, so far as adsorption and polarity were concerned, it would seem wiser to imagine the chains curled up into balls. If they did thus curl up, would not they form what Mr. Nissan referred to as spherical molecules?

He welcomed the method which had been given by Mr. Nissan to those workers interested in the connection between viscosity and constitution, and personally would be very curious to see the results of its application to a problem in which he was specially interested. Whilst the treatment in the present paper had been applied to viscosities, there was, he thought, material for interesting research in correlating the related constant of mobility with vapour pressure. Thus, whilst viscosity, or its reciprocal fluidity cannot be applied to heterogeneous systems in which such factor is not constant with the rate of shear, the mobility which is defined as the differential coefficient of the rate of shear and the stress assumes constancy at all but low shearing stresses. Such constancy, by the way, only applies when *true* velocity gradients as distinct from rates of efflux in capillary shear are calculated from the latter. Then, with increasing degree of heterogeneity by progressive introduction of disperse phase, decreasing mobility is recorded, and certain somewhat rough observations had indicated that the vapour pressure correspondingly decreased. An accurate correlation of mobility and vapour pressure, expressed on the basis of Mr. Nissan's work would, he expected, prove to be extremely interesting and open up a new field for research on a subject which had not received the attention it deserved both from a purely scientific and a technical standpoint.

Dr. E. B. Evans said he was sure that anyone interested in viscosity would be stimulated by Mr. Nissan's very interesting paper. The insistence on the fundamental conceptions of viscosity was very important, because particularly those who were organic chemists were apt to lose sight to some extent of that aspect. The discussion on the relationship between vaporization phenomena and viscosity was also of particular importance, and was of very great interest, especially as developed in this paper.

The method of plotting used, involving T/T_B against log. η, was very ingenious, but there was a disadvantage in plotting the function T/T_B. That disadvantage consisted very largely in the fact that T_B was difficult to obtain in the case even of compounds of comparatively low molecular weight. Taking the case of hexadecene-1, that was not a compound with a particularly high molecular weight or boiling point, but there was considerable difficulty in obtaining a boiling point with accuracy at normal pressure. There were two or three quite good figures at pressures of about 11 mm. or 15 mm., but they were not very useful in this connection. Hexadecene gave a line on the right-hand side instead of the left-hand side of the normal paraffin line in Fig. 12. The general effect of unsaturation was to lower the viscosity when one compared viscosities at equal temperatures. That held good in the case of α, β, γ, and δ olefines. In the case of the acetylenes the triple bond had the reverse effect and raised the viscosity. There were other exceptions to the general rule stated in the paper that unsaturation moved the line to the left; for instance, in the case of propylene bromide the line was well to the right of that for propyl bromide (Fig. 13). He would be interested to hear an explanation of that difference.

Finally, he would like to know whether this method of plotting had been tried out using kinematic viscosities, and, if so, what the result had been. There was reason to consider "kinematic viscosity" a more fundamental basis for plotting than "absolute viscosity."

The basic equation appears to be of the type given by Andrade, and on page 177 as

$$\eta v^{1/3} = Ae^{c/vt}.$$

In the speaker's opinion this should have been derived as

$$\eta v = Ae^{c/vt}$$

(Evans, Second World Petroleum Congress, 1937, p. 948), and, since $\eta v = U$ = kinematic viscosity, it would seem to be better to use functions of U rather than of η for plotting. Most of the viscosity–temperature charts in use employ functions of kinematic viscosity.

Dr. F. H. Garner said that the equation $\eta = Ae^{B/T}$ was not an entirely satisfactory expression of the relationship between viscosity and temperature, although the divergence from experimental results was only slight. The A.S.T.M. viscosity charts based on log. log. $\eta + 0{\cdot}8$ against log. T gave a straight line for practically all petroleum products, which indicated that $\eta + 0{\cdot}8 = Ae^{B/T}$ would be an improvement over the simpler equation. It was, however, difficult to attach any physical meaning to the value of 0·8 added on to a viscosity, and the authors later in the paper had pointed out that B in their equation might vary with temperature. At a still later point in the paper they reviewed various suggestions which had been put forward to obtain a comprehensive equation relating viscosity and temperature, and with the more accurate data recently available on the viscosity of hydrocarbons it might be possible to develop a more precise form of the general equation $\eta = Ae^{fT/T}$. Such an equation would, however, probably not be so suitable in practice for plotting viscosity against temperature as that adopted in the A.S.T.M. curves. Dr. Barr has suggested the use of the formula $\eta + a = 10^f$ where $f = (A + b/T)^c$ which in the logarithmic form becomes $[\log_{10} (\eta + a)]^{0.3} = A + b/T$ which is, however, purely empirical. Proceedings of General Discussion on Lubrication and Lubricants (Institution of Mechanical Engineers), 1937, 2, 220.

The President had raised the question of applying the valuable general relationship between constitution and viscosity shown in the paper to other fields, such as cetane number investigations; he felt that viscosity was influenced by such factors as the shape of molecules and possibly association in a way peculiar to this physical property, and that there were difficulties in applying the results obtained in the paper to physical properties dependent more specifically in chemical composition.

Dr. N. L. Anfilogoff said he would like to congratulate the authors on one of the best papers that the Institute had had on viscosity for a number of years. He thought that when the theorists had read the paper they might be able to correlate the results given therein with the fundamental theory of the viscosity of gases. He had always felt that Sutherland's constant, or, perhaps, more likely, one of the constants such as Reinganum's constant, would eventually be found to be involved in the fundamental theory of the viscosity of liquids. It would be remembered that Reinganum's relation reduced to Sutherland's if the exponential arising from Boltzmann's law were expanded in terms of temperature and neglecting all terms in T after the first. It might be for liquids that these neglected terms required consideration. Taking argon and hydrogen chloride, for example, if one considered these two gases from the point of view of their electron constitution, based on the Lewis–Langmuir theory, argon had a complete ring of eight electrons and hydrogen chloride had the same complete ring with the proton outside. If one investigated the viscosity change with temperature of those two gases, as he had done some years ago, it was found that, based on Sutherland's relation, the effect of the proton on the collision area calculated from viscosity–temperature changes was comparatively small. The so-called "target" areas he found to be 1 : 1·01 for the two gases on the Sutherland model basis, which difference was almost within that of experimental error. If, however, consideration were given to another model type, which was in the case he examined, the Lennard–Jones model, the proton was found to have quite an appreciable effect. The Sutherland model differed from the Lennard–Jones simply from fundamental theoretical considerations, in that the Sutherland model considered only attractive forces, whereas the Lennard–Jones model brought into consideration attractive forces superimposed upon repulsive forces between the molecules, and it was probable that when the fundamental effects of molecular force on viscous flow were established, both attractive and repulsive forces would be found to be involved. Indeed, he was able to fit the experimental results of the variation of viscosity with temperature for these two gases over a very wide range of temperature quite accurately on to the theoretical curve evolved from fundamental considerations by Lennard–Jones. It would be remembered that Hasse and Cook pointed out that this theoretical curve could be considered as of three portions—two linear portions corresponding to the extreme cases where the viscosity was determined mainly by the attractive force and the repulsive force respectively, and a curved portion where neither played a dominating rôle. In a sense they felt that the three portions corresponded to low, moderate, and high temperatures. It was possible that, in the method which Mr. Nissan had evolved in plotting the viscosities of the liquids against a paraffin series, he had by division eliminated some of the constants, and so produced a straight line. When theoreticians started to work on the subject, they might perhaps find that they would be able to develop some of the fundamental equations for viscosity–temperature changes which were missing in so far as liquids were concerned. Considering the present position as based on the theory point of view, gases which were above the critical temperature followed a fairly well defined relation, such as Sutherland's law, probably up to temperatures of 600° C. or 700° C. Above that temperature something seemed to happen to them. Going down the scale, as soon as one arrived at the vapour state (paraffin hydrocarbon vapours were investigated a number of years ago) the variation of viscosity with temperature was no longer in conformity with Sutherland's law. Mr. Nissan had now brought the subject back to the useful straight line again, and it might now prove possible to find some theoretical fundamental relations, so that a satisfactory fundamental viscosity–temperature relationship for liquids could be evolved from first principles. He felt that the authors would appear definitely to have made an advance towards that which, up to now, had been missing.

Dr. A. V. Brancker said there was no doubt as to the excellence of the paper, but he thought it should be borne in mind that the equation of the standard curve was still missing. The mathematical physicists may develop this fundamental equation, and he believed that Mr. Nissan, with whom he had been associated for some years, himself had difficulty in finding the equation. It was therefore definitely an artifice which had been employed, from which straight lines resulted, but that did *not* detract from the value of the paper.

Reference had been made to the question of molecular structure, and there were one or two minor points in that connection which required elucidation. Mention had already been made of the fact that so-called long-chain hydrocarbons were not necessarily elongated, but could have a zig-zag, spheroidal, or ellipsoidal shape, and it was thought that insufficient is known about molecular structure to attempt to draw, at present, conclusions relating viscosity and molecular structure as such. In addition, there was another point—namely, the effect of methyl groups on the alcohols. He thought he was correct in saying that the effect of a methyl group was to make the alcohol approach the position on Mr. Nissan's chart occupied by carbon tetrachloride. Having attained that position, the further addition of methyl groups outweighed the effect of hydroxyl to such an extent that the alcohol now retraced its steps away from the position of the carbon tetrachloride. If this were the case, then the methylated alcohol must eventually occupy a position on the chart previously held by a less heavily methylated alcohol. This would mean that two different compounds of different molecular structure fell in the same position on the chart, which, on Mr. Nissan's theory, was difficult to understand.

The President said the very kindly way in which the paper had been received was very gratifying to him. Owing to a fact which perhaps he ought to have stated at the beginning of the meeting, but he had not done so because he wanted to see what kind of discussion the paper would provoke, he would now state that the credit for the work described in the paper was due to Mr. Nisson entirely.

Mr. A. H. Nissan, replying on behalf of the authors, wrote as follows :

The authors wish to express their gratitude to Dr. Dunstan and the whole assembly for the kind way they have received this paper.

To find out the reason why log η should prove additive, the following analysis may be found useful. The analysis will be based on the simple exponential formula, as any refinement in it only complicates the analysis without affecting its value. This is because although B in

$$\eta = Ae^{B/T}$$

changes with temperature it does so only to a slight degree in the case of unassociated liquids. A will be eliminated.

It is shown in the text that

$$\log. (\eta/\eta_B) = K'(T_B/T - 1)$$

and that for an homologous series like the normal paraffins only one line is obtained for all the members when log. η is plotted against values of T/T_B.

It will be noticed that of the series which gave a constant value for Δ log. η on increasing the molecular weight by a CH_2 radicle, the normal paraffins, the iodides, and the ketones are characterized by such lines. The others fall practically on the normal paraffins. Probably the esters will have one line too. This means that for each series (log. η_B)is a constant for all the members, and as T is a constant for all, then the difference in log. η for 2 members is given by

$$\log. \eta_1 - \log. \eta_2 = K(T_{B_1} - T_{B2}),$$
$$\text{or} \qquad \Delta \log. \eta = K\Delta T_B.$$

In other words, the increment in log. η is a measure of the increment required to raise the energy level so that the larger molecule of the two will accomplish a " hole " into which it would flow in a similar manner to the smaller molecule. It has been postulated that the energy required in viscous flow is that for making a hole $\frac{1}{3}$ to $\frac{1}{4}$ the volume of the molecule. As we are dealing with homologous series, then, on the addition of a CH_2 to a molecule, the volume is increased by a certain quantity, and therefore the energy required is that for making a hole a fraction of the volume of CH_2 in size bigger than the hole required for the smaller molecule. For the series mentioned here the addition of a CH_2 will increase the volume by a constant, as none of them is associated, whilst the fraction $1/n$ varies from a $\frac{1}{4}$ to 1/3·5. This means that the increment Δ log. η will be roughly regular, when compared over wide limits, and fairly regular over the range of few members.

It would be expected, from this, that Δ log. η will be larger when association takes place, as the addition of a CH_2 group really means increasing the volume of the molecule by that of CH_2 multiplied by a factor greater than unity. The alcohols substantiate this hypothesis. The case of the sulphides presents difficulties—unless one assumes the reverse is taking place—*i.e.*, dissociation.

In a note to *Nature* (Nissan, *Nature*, **144**, 383, 1939) this law was derived in a little greater detail, and its limitations were set down. It is found on detailed analysis that even for the n-paraffins

$$\log. \eta = a \log. M + b$$

expresses the relationship to a higher degree of accuracy than the original,

$$\log. \eta = aM + b,$$

when the value of M is taken over a wide range—say from C_5–C_{18}. For a smaller range the latter is quite accurate, as shown by Dunstan and Thole.

On this basis the departure from linearity does indicate that some form of fundamental change in the flowing unit is taking place, and, as Dunstan and Thole surmised, may be due to the formation of aggregates.

It is not so easy to see why $1/\eta$ should prove additive. It may be that this is so to a limited extent only.

When Δ_2 is considered, it is seen that not only B, but A comes in the expression as

$$\eta_1 - \eta_2 = A_1e^{B/T} - A_2e^{B/T}$$

A is probably a constitutive property, and hence η itself will be partly additive due to B (the energy required to make a hole will increase additively on increase in molecular volume by the addition of a CH_2) and constitutive due to A. On the other hand, Δ log. η is a measure of the energy level required to cause the unit to flow, and is therefore more additive.

This is a very rough analysis, but it is hoped that it answers in part why log. η is additive while η is mostly constitutive.

Professor Bernal's contribution to the discussion was complete by itself, and we feel there is need for little comment to be made, except of appreciation. We agree particularly with his suggestions on how to continue the work—*i.e.*, comparisons at comparative internal pressures and simplifying the charts by plotting only two parameters for each liquid, etc. Of course, the latter suggestion can only be made after setting down the lines so that their linearity may be critically examined.

Probably the explanation given for the motion of the halogen derivatives to the left with increasing polarizability is nearer the truth than a simple shape effect. This point, we believe, should prove interesting under rigorous study.

The remarks about liquid helium should be borne in mind until more definite results about this liquid are obtained. We attempted to raise the same degree of doubt in the readers' mind about this liquid in one or two parts in the text.

In replying to Mr. De Waele's comments we would like to thank him for the suggested lines of research to be carried out, and hope that others might also think of carrying out investigations into these interesting and most important fields of physical chemistry. In connection with his last suggestion of correlating viscosity rise and corresponding diminution of the vapour pressure, one may add that it should prove interesting also to do the opposite on pure components—*i.e.*, investigate the possibility of obtaining one line for an homologous series by plotting log. η against the ratio of P : vapour pressure, where P is a pressure higher than atmospheric but, probably, lower than some limiting value.

The line of the paraffins appears to be near the limit to the left side of the chart, but does not constitute the limit itself. Diallyl and *iso*prene are definitely to the left of the n-paraffins. Even assuming the n-paraffins to curl up, they need not be spherical, as they can form ellipsoids with major and minor axes. They do behave, however, as if they were far removed from a spheroidal form. One may say that since one specific viscosity curve characterizes all members from C_4–C_{18} then, on the molecular shape basis, these members will have similar ratios of their fundamental dimensions. This suggests some form of "curling" or doubling-back of the molecule, so that it attains some standard pattern which is repeated by all members higher than the first few. They cannot be spherical, since methane behaves as if it were more spheroidal in shape. These remarks, however, are speculative, and cannot be taken as proven. It is difficult to speak with certainty of these molecules when they are in motion; as Prof. Bernal suggested interlocking produces some complex factors hard to define.

In reply to Dr. Evans, it is pointed out that comparison at equal values of T/T_B is in reality comparison at equal ratios of T to temperatures of equal vapour pressures. T_B was chosen as, for most compounds, the temperature at which their vapour pressures equal 760 mm. is known to a higher accuracy than for other values of vapour pressures. It is believed that in the case of n-hexadecene-1 it would be more accurate to calculate T_B from its viscosity data, assuming that its line fell exactly on the n-paraffins than calculating its boiling point from values of boiling points at pressures of 11 or 15 mms. (cf. case of ketones discussed in detail in paper).

It appears from arguments put forward in the text that comparing viscosities at equal temperatures will not give consistently regular results.

In the case of "propylene bromide" the almost unforgivable sin of using archaic terminology was committed in order to render easy reference to the original paper possible. This was unfortunate, but in reporting the results of viscosity measurements on our charts we gave in all cases the names of the compounds as given by the original investigators, in the belief that no confusion could arise in the mind of anyone who would like to check our work by reference to the original as given in the bibliography. Thorpe and Rodgers called $CH_3CH\ BrCH_2Br$ "propylene bromide," and this nomenclature has consequently crept into our paper. The compound has no double bond, and the general rule that unsaturation brings the line to the left is not therefore broken by this compound. Thanks to the query raised by Dr. Evans, we put the formula next to the name in the paper to avoid further ambiguity.

The kinematic viscosity was not tried, for the following reason: There appears to be definite relationship between specific volume and viscosity. This relationship was at first thought to have been ascertained in a complete way by Batschinsky and MacLeod, until the work of Bridgman proved that in reality the relationship was more complex than appeared at first sight. The formula put forward by Andrade including specific volume was not derived from a rigorous analysis, but from the assumption that probably such a formula is correct. In fact, the exponential term was chosen on the basis that it was advisable to "choose some simple function of specific volume" and include it in the formula, which function was chosen purely arbitrarily,(32) checked experimentally and found to hold well. The inclusion of v or $v^{1/3}$ in the left-hand term—*i.e.*, ηv or $\eta v^{1/3}$—is of secondary importance. To illustrate, water has a ratio of η at 20° C. to η at 100° of 1·0015 : 0·283 or, say, a decrease of some 250 per cent. on the smaller figure. The variation in v for the same range of temperature is of the order of 0·958 : 0·998, or an increase of 4 per cent. on the smaller figure.

In view of these remarks, it was thought that to compare a function of two properties, the exact interrelationships between which were not known, against a third—*i.e.*, ηv *vs* T_B—would result in ambiguous conclusions. It could not be possible to ascertain definitely which effect was due to specific volume and which was due to absolute viscosity.

Nevertheless, we believe that *after* ascertaining the type of functions obtained by plotting η *vs* T/T_B it should prove of great interest to plot the kinematic viscosity against similar functions of temperature, particularly if a plot of specific volume against T/T_B is made simultaneously. The three charts so obtained should prove of greater value than any one of them.

We agree with Dr. Garner that the general equation, if found, will probably not be suitable in practice to the same extent as the A.S.T.M. chart. The chief use will, of course, be the knowledge derived through such a formula regarding the physicochemical significance of such a property as viscosity.

Similarly

$$\eta = Ae^{B/T}$$

was chosen as the basis of the work in preference to the more accurate formulae, because this formula was derived in a more rigorous form of analysis than all others. The refinements added to it, in most cases, were semi-empirical in nature.

We believe that molecular shape may play a greater part in chemical reaction such as combustion than has been accepted hitherto. As an analogy, the elements may be cited. The physical and chemical properties of the elements are characterized to a greater extent by the atomic number than by atomic weight. Atomic number, in turn, is a measure of the number of extra-nuclear charges in the atom, and is thus a measure of "shape" of the atom. In other words, atomic shape influences the properties of the elements more than the atomic weight. It is believed that this rule still holds in the molecules of compounds. This, however, is only a hypothesis, and its verification will present great difficulties.

As Dr. Garner suggested, the application of such a hypothesis will present still greater difficulties.

Dr. Anfilogoff's contribution to the discussion has shed further light on the probability of the existence of a general law governing the change of viscosity with temperature applicable to all states of matter. The theory that attractive and repulsive forces played interdependent parts in the viscosity of gases is a strong support of the existence of such a law. The fact cited in a footnote in the text, that gases under high pressures possess a decreasing function of viscosity with temperature, further enhances the probabilities.

Dr. Brancker raised the question of finding the general equation which governed all the liquids studied in the paper. An attempt was made on the following line:—

For every straight line drawn on the chart an equation could be written in the form

$$\log. \eta = Af(T/T_B) + B$$

where $f(T/T_B)$ expressed the equation of the artificial scale used in terms of the natural scale T/T_B.

An attempt was made, therefore, to find the equation which governed the following relationship:

T/T_B = 0·500	0·550	0·600	0·650	0·700	0·750	0·800	0·850	0·900	0·950	1·000
fT/T_B = 0·500	0·600	0·684	0·753	0·808	0·856	0·894	0·927	0·958	0·979	1·000

All that can be said is that it has been proved that neither the simple exponential formula nor

$$\log.\ \eta = A/T + B \log.\ T + C$$

expressed the relationship completely over a wide range. Even if an empirical equation could be found, it was considered of no great value, as there were so many already. The equation, in so far as the generality of the law is concerned, should not only give the variation of viscosity of liquids with temperature, but also that of gases.

Perhaps it is not out of place to put a warning here. Even without an equation the list of $f(T/T_B)$ in terms of T/T_B given here would appear to be suitable for calculating the change of viscosity with temperature. There is, however, a source of error. The case of water will illustrate what we mean.

$$\log.\ \eta = Af(T/T_B) + B$$

For water,

T.	T_B.	T/T_B.	$f(T/T_B)$.	η.	log. η.
293	373	0·786	0·884	1·0050	0·002166
353	373	0·947	0·977	0·3565	$\bar{1}$·552060

To calculate A and B, we have to obtain the difference between two simultaneous equations, thus :—

$$\begin{array}{r} -\ 0{\cdot}447940 = 0{\cdot}977A + B \\ 0{\cdot}002166 = 0{\cdot}884A + B \\ \hline -\ 0{\cdot}450106 = 0{\cdot}093A \end{array} \qquad \text{or } A = -\ 4{\cdot}8398$$

This is where the error is introduced. $f(T/T_B)$ can be interpolated to the third decimal place. Hence it is of a fair accuracy even assuming it is accurate only to 2 in the third place. There is a possibility of an error of 4 in 93, however, on subtraction, hence the calculations can be as much as 4·5 per cent. in error, purely due to taking interpolated values. Added to that are experimental errors.

In so far as the shape of the normal paraffins is concerned, we think that it is entirely a matter of opinion whether the molecules are curled up or not. So long as one dimension is considerably greater than the other at right angle to it, the molecule satisfies the requirements of being non-spheroidal.

The case of the alcohols illustrates the fact, so heavily stressed in the paper, that it does not matter what is the skeleton or the material structure of the molecule; so long as the external shape, as defined, of two molecules look alike, they will behave similarly on these charts. In fact, that is an essential part of the theory—many examples are given in the text of similar cases. It is postulated that molecular shape affects the position and the slope of the viscosity lines because the ratios of surface area to volume of molecules differ. Spheroidal molecules offer the least area for other molecules to use as equilibrium positions, and hence molecules make larger proportional holes in their fundamental motion in viscous flow. Anisotropic bodies offer greater areas per volume than spheroidal ones. These larger ratios may be obtained in different ways, and hence our line may represent two substances if both possess the same ratios of surface area to molecular volume.

OBITUARY

EUGENE COSTE

Eugene Coste was born in Essex County, Ontario, and educated in France, first at Grenoble, then in Paris. He graduated as a Mining Engineer from the École Nationale Superieure des Mines de Paris in 1883.

On his return to Canada in 1883 he became a member of the Geological Survey for Canada and Mining Engineer of the Geological Survey in 1887; in 1888 he located and directed the drilling of a well in Essex County which brought in the Kingsville–Leamington Field (this was the first commercial gas well drilled in Canada).

In 1889 he resigned from the Geological Survey to enter private practice as a mining engineer, and in the same year located the discovery well of the Welland County Field; the gas from this field supplied Buffalo, N.Y., for eighteen years, and it is interesting to note that the original Company is still supplying gas to Niagara Falls, Welland, Fort Erie, etc., and maintaining its unbroken dividend record since 1891.

In 1900 Mr. Coste attracted considerable attention in mining circles by advocating the inorganic theory of the origin of petroleums in a paper entitled "Natural Gas in Ontario," which he read before the Canadian Mining Institute. This was followed in 1903 by "The Volcanic Origin of Natural Gas and Petroleum," which also was read before the Institute; during the same year Mr. Coste was elected President of the Canadian Mining Institute, and was re-elected in 1904. In February of that year he presented a paper entitled "The Volcanic Origin of Oil" to a joint session of the American Institute of Mining Engineers and the Mining and Metallurgical section of the Franklin Institute. This paper aroused intense interest.

In 1906 he formed the Volcanic Oil and Gas Company and drilled for gas in Kent County, Ontario. In 1909 acting as Consulting Engineer and Geologist for the Canadian Pacific Railway, he discovered the Bow Island Gas-field in Southern Alberta. He purchased this field from the Canadian Pacific Railway and, forming a Company, in 1912 piped the gas almost 200 miles to Lethbridge, Calgary, and intermediate towns which it now serves; this line was at that time one of the longest natural gas pipe-lines in existence.

In 1911 Mr. Coste read a paper entitled "Fallacies in the Theory of the Organic Origin of Petroleums" before the Institution of Mining and Metallurgy in London, England; this paper caused international discussion.

In 1913 he formed a Syndicate which drilled for gas in the Viking district of Alberta, a Company being later formed which piped the gas to Edmonton. The Viking Field, now proved to be both extensive and prolific, will undoubtedly continue to supply Edmonton and other towns for many years.

In 1916 he advised the Union Gas Company to drill in Dover Township, Ontario, which resulted in the Dover Field.

Since 1911 Mr. Eugene Coste had been assisted by his son, E. F. Coste, first in Alberta with the Calgary and Edmonton Gas Companies, then, after the war, they together formed the firm of Eugene Coste and Co. Petroleum Engineers and Geologists. Eugene Coste was an active partner in this firm up to the time of his death.

Mr. Coste had been a Member of the Institute of Petroleum since 1917.

ABSTRACTS.

AUTHOR INDEX.

The numbers refer to the Abstract Number.

The original paper referred to in the abstracts marked with an asterisk may be borrowed by Members from the Institute Library.

Geology.

603.* New Interpretation of the Structure and the Oil Occurrences of the Horst–Wipshausen Area, N. of Peine, Hanover. L. Riedel. *Oel u. Kohle*, 1.2.40, 36 (5), 39–44.—The occurrence of oil in the Horst–Wipshausen area has been known since the 1880's, and from then until 1924 a number of wells were drilled, almost all of which gave small quantities of oil, but none a reasonable production. The idea that good oil deposits could be found at shallow depths was finally discounted by the two Greiser wells, drilled in 1934.

The Diluvium in this area is about 30 m. thick, and rests on the Senonian. The Senonian itself is transgressive, the lowest horizon being the *Mucronata* zone. Below this is found the Albian. Stoller considered, on the basis of the depths to the top of the Lower Cretaceous, that a gentle but narrow arching of the strata occurs immediately to the west of Horst and strikes approximately north to south. Unfortunately, the old well logs are not exact, and since, in addition, the Lower Cretaceous was not zoned, it is impossible to get a correct picture of the structure. Between Rietze and Dedenhausen there are a number of step-faults which probably strike north-north-east to south-south-west. It appears probable that still more step-faulting has taken place in the Horst–Wipshausen district itself. In addition to the faulting there has been a certain amount of folding, but the axis of this more likely trends east-north-east than north, as Stoller suggested. Torsion balance data support this view.

The oil is associated with clay-ironstone in the Lower Albian. This clay-ironstone is not in the usual form of nodules, but occurs as fragments which are full of cracks filled with oil. The reservoir is composed of lenses of clay-ironstone which are water-bearing, the oil collecting on the top of the water. If this oil is removed, more gradually collects to take its place, and after a few months, production can be resumed. The origin of the oil is doubtful: it may come from deeper horizons in the Lower Cretaceous, or it may have migrated up fissures from great depths, possibly from the Zechstein. S. E. C.

604.* Western Oklahoma Receiving Increased Exploration. B. Altman. *Oil Wkly*, 12.2.40, 96 (10), 20, 22, 26.—7 ml. south of Elk City a well entered the Pennsylvanian at 6577 ft. and was still in it at 14,582 ft. Thick sand bodies were present, and gas was found at 10,896–920 ft.

In the Western Oklahoma basin 10,000 ft. of Pennsylvanian beds were deposited in some areas, and the older beds dip steeply.

A test in Kingfisher County was completed for 12 brl. of high-gravity distillate and 2,500,000 cu. ft. of gas from a dolomitic limestone at 7357–60 ft. In Caddo County a Binger producer found the pay at 9900–83 ft. in the Pennsylvanian. Near Carnegie a thinning of the upper beds brings the Pennsylvanian, Mississippian, Devonian, Silurian, and Ordovician nearer the surface than elsewhere, and numerous shows of dead black oil were found on the north slope of the truncated Wichita uplift. The Wilcox was found at 9184–88 ft.

Structures have been mapped seismically on the top of the Mississippian, and Pennsylvanian reflections are easily obtainable. G. D. H.

605.* Oil Possibilities in the "Last Wilderness." W. C. Lehman. *Oil Wkly*, 19.2.40, 96 (11), 18–19.—Oil-seeps have long been known in the Olympic Peninsula of Washington. A well drilled in 1939 gave gas with 2½ gal. of gasoline/1000 cu. ft. In 1932 a little oil was found at a depth of 700 ft. 2 ml. north of the mouth of the River Hoh. A second well showed the fold in question to be so strongly faulted that there had been a serious loss of pressure. A 6000-ft. test 15 ml. north-east of the mouth of the Hoh was abandoned in 1937, although electrical cores had shown favourable signs.

The west side of the peninsula is a remnant of a large Tertiary basin. The main formation (Hoh) consists of Oligocene–Miocene marine beds, up to 30,000 ft. in thickness, and containing interbedded lenses of material of terrestrial origin. This formation is highly organic in the shale parts and there are coarse sandstones. There is complicated folding and faulting. G. D. H.

606.* Partition of Poland's Oil Industry. D. E. Morgenstern. *World Petrol.*, November 1939, **10** (11), 32–39.—In 1938 Poland produced 3,801,000 brl. of oil, and its thirty-seven refineries had a capacity of 8,700,000 brl./yr. The area annexed by Germany gives 35% of the oil and consumes about 80%, whilst the total consumption was 90% of the production.

Polish drilling practice is not very progressive, and in 1938 41% of the total footage was drilled by the Canadian system. Of the 3740 wells, only 20 flow; 903 are bailed and swabbed; the rest are pumped. Air-lift and water-flooding are almost unknown.

The oil-fields lie in four zones: (1) Magura, (2) Median, (3) Marginal, (4) Deep Marginal. The Magura zone is the least important as regards production. The structures are complex. At Mecina Wielka oil is found in the Cretaceous Ropienka beds, whilst at Sekowa–Ropica Ruska it is in the Upper Cretaceous Inoceramus beds.

In the Median zone the Gorlice–Sanak region is on a great anticline which involves Cretaceous–Oligocene beds. The oil horizons are the Oligocene Krosno beds and the Menelitic shales; the Eocene Ciezkowice sandstone and red and green shales, and the Cretaceous sandstones. In the Marginal and Deep Marginal zones oil is recovered from the Jamna sandstones (Cretaceous), the Menslite shales, Polanica formation and Dobrotow sandstone (Upper Eocene), the Boryslow sandstone and Middle and Lower Eocene horizons.

The structure, producing horizons, extent, and production of the various fields are briefly described. G. D. H.

Drilling.

607.* Largest Submersible Drilling Barge Combines Best Features of Marine Design. H. L. Flood. *Petrol. Engr*, February 1940, **11** (5), 31.—The paper describes a recently completed drilling barge which is believed to be the prototype of current barge design. It is one of the largest vessels which have yet been constructed for deep-drilling purposes. It is equipped to be operated by steam, supplied by boilers mounted on smaller companion barges.

The complete barge follows the conventional pattern of most submersible drilling barges, in that it comprises two identical hulls joined by transverse trusses to provide a slot or space between the hulls as a means of moving-off the site after the well is completed. The connecting-trusses are bolted to the hulls. The drilling-derrick has to be dismantled during the move.

The derrick floor and principal working level of the barge is 15 ft. above the deck of the hulls, supported by massive steel members constituting the superstructure of the barge proper.

The rest of the barge deck is occupied principally by the reserve mud storage units, each of which is built directly on the deck-plates as a base. Decked-over, the top surfaces of these tanks serve as pipe-racks upon which drill-pipe and casing may be stored.

Details are given of the mud system, draw-works, rotary-table, and other features of the drilling-barge under separate sections.

It is not necessary to dredge or otherwise prepare a platform to provide a level resting-place for the barge. This is partly because most lakes and bayous have fairly level bottoms, and partly because the weight of the barges displaces the mud usually present and automatically prepares its own bed.

In calculating stability the most severe conditions pictured as a design basis includes 12,000 ft. of $9\frac{5}{8}$-in. casing suspended in the hole and 14,000 of $4\frac{1}{2}$-in. drill-pipe standing in the derrick. Wind load was assumed at 70-mi/hr. A. H. N.

608.* Deepening and Completing a Well—Study in Modern Co-operative Practice. Part I. P. D. Torry and F. H. Miller. *Petrol. Engr*, February 1940, **11** (5), 155.—The paper is not a specific study of drilling, completion, or production practice, but it is rather a descriptive narration of some of the significant incidents and operations connected with one particular project. Little emphasis has been placed on theoretical considerations; detailed attention has been devoted to performance and to the many other factors that may assist in the other deep wells and the more effective production of oil and gas.

The paper is divided into five parts: (1) Geology, (2) Drilling, (3) Completion, (4) Production Tests, and (5) Considerations of Pressure Maintenance, Gasoline Recovery, and Gas Repressuring in the Shallow Producing Horizon of the Lisbon Field, Louisiana. A. H. N.

609.* Internal-Combustion Engine Used in California Deep Drilling. W. A. Sawdon. *Petrol. Engr*, February 1940, **11** (5), 173.—The drilling of a well to below 11,000 ft. with a gas-engine-powered rig has demonstrated the adaptability of internal-combustion engines to meet the requirements of deep drilling when conditions make the selection of this type of equipment advantageous.

Perhaps the most important factor in selecting the type of prime move is the availability of water or fuel, or both. Boiler troubles due to feed-water containing calcium or other deleterious substances in higher quantities than certain minima are naturally avoided whenever possible, and frequently can be eliminated only by eliminating the boiler itself. Under such conditions, and where natural gas is available for fuel, the gas-engine can be used as a prime mover.

When natural gas is not available, gas-engines in many instances are now converted to burn butane by the addition of heaters, no change in carburettors being necessary. Gasoline is seldom used for rotary drilling—the reasons are discussed in detail. Diesel engines have been used to some extent when natural gas is not available, and even when steam can be used. Fuel consumption is frequently an important item which has governed the selection of internal-combustion engine rigs for certain jobs.

A detailed description is given of the rig used to drill this particular well. The average fuel consumption for nine full months of drilling was 34,000 cu. ft./day. The greatest fuel consumption was during the deepest drilling and coring. Actual daily consumption during the deepest drilling exceeded at times the average for the maximum month.

Speed is not such an important factor in a test well when geological information and knowledge of subsurface conditions are the primary consideration. In another well the well was drilled to a depth of 7460 ft. in twenty-six drilling days, this time including the cementing of the surface- and water-strings. At one time 900 ft. of 12½-in. hole was made in 6 hr.

A new draw-works is described which has six speeds forward and two reverse.

Other gas-driven rigs are described, as well as certain diesel-driven ones. Information is given of performance and characteristics of such rigs. A. H. N.

610.* Development of a Pressure Core-Barrel. Anon. *Petrol. Times*, 2.3.40, **43** (1,103), 193.—The new core-barrel is essentially a conventional core-barrel, with the addition of special valves at either end of an inner barrel and a mechanism for closing the valves while the barrel is at the bottom of the hole.

Tests have been made in five different wells, in which seventeen cores were cut, two of which were cut and sealed at the pressure and temperature prevailing at the bottom of the drill-hole. The pressures in the test-wells ranged from approximately 1000 to 2700 lb./sq. in. Although minor changes in the design of the barrel will undoubtedly be necessary to assure satisfactory operations in every respect, the tests indicate that a core-barrel patterned after the present experimental barrel will recover cores under pressure.

The analysis of one core taken with a pressure core-barrel indicates that there was a considerable amount of contamination of the core by drilling-fluid. Although a satisfactory solution of the contamination problem does not appear impossible, the factors involved present many difficulties requiring much research before cores can be taken that will be entirely satisfactory for estimating oil reserves. A. H. N.

611.* A Portable Telescoping 84-ft. Derrick. Anon. *Petrol. Times*, 16.3.40, **43** (1,105), 240–241.—Photographs and description are given of a portable 84-ft. derrick which may be used for servicing 100 wells per unit, thus eliminating the need of erecting servicing derricks.

Since the cost of 15–20 derricks pays for the unit, a saving of at least 80 derricks out of each 100 wells will be possible. A. H. N.

612.* Drilling Activity in January 1940. L. J. Logan. *Oil. Wkly*, 12.2.40, **96** (10), 12.—A decline in drilling activity shown in January was seasonal; the field work was exceptionally brisk for an initial month. Actually, drilling activity during the first month of 1940 is around the highest level ever reached in an initial month.

Tables and graphs are presented and the data are analysed and compared with previous corresponding data. A. H. N.

613.* High Pressure Mud Stream Aids in Lowering Viscosity. Anon. *Oil. Wkly*, 12.2.40, **96** (10), 41–42.—The current trend of drilling deeper and straighter holes than previous ones increases the importance of mud viscosity control. A simple method to decrease the viscosity of the mud is described.

It consists essentially of a 10- to 20-ft. length of a large-diameter casing that is placed in the mud ditch a few feet down-stream from the outlet pipe that comes from the well. A fine stream of high-pressure mud from a small auxiliary slush-pump is forced through a small nozzle at the up-stream end of the pipe, and is directed against an irregular group of six or eight small steel baffle-plates welded to the upper part of the lower end of the pipe. The resulting sprays of the mud directed into the main stream serve to agitate the mud, and thus break down its viscosity, and aid in the escape of free gas held in suspension. For extremely critical conditions the nozzle can be swung downward to point directly into the mud, and will churn it up violently. A short piece of ⅜-in. pipe was experimentally found to be the best size for the nozzle.

The mud can be treated near the point where it leaves the hole, and so it is still moving fairly fast. Thus no gel formation is allowed to prevent the escape of occluded gas and small cuttings held in suspension. A. H. N.

614.* Degassing Drilling Fluid Prevents Blowouts. H. F. Simons. *Oil Gas J.*, 8.2.40, **38** (39), 43–44.—Blowouts are caused by the well-bore encountering a gas-bearing formation of a greater pressure than the hydrostatic head of the drilling-fluid. Two methods are available for preventing blowouts: the use of a preventer and the use of a mud having a high specific gravity.

Merely increasing the weight of the mud has, however, several disadvantages, such as a high loss of fluid in other formation, sticking of the pipe, etc. The gel strength has to be increased, with the consequence that the gas entrapped in the mud will be held more tenaciously. As the entrained gas increases, the weight of the drilling mud decreases—typical figures are given.

Several mechanical tests are now used to degas the mud. The vibrating screen removes some of the gas as well as the cuttings. Another method is to spray the mud 12–14 ft. in the air through jets, and the breaking down of the mud allows the gas to escape. This method is used to cool muds which have come in contact with hot salt-water formations.

Another method reduces the pressure on the mud. The apparatus consists of 24-in. pipe with inside baffles. A steam-jet on a small standpipe on the top of the inclined pipe reduces the pressure, and as the mud flows through, the baffles agitate it, as well as exposing a large area to the reduced pressure, and thus gas escapes. A. H. N.

615.* Metals in Drilling—Hard Facing Materials. W. L. Nelson. *Oil Gas J.*, 8.2.40, **38** (39), 50.—Although at least six types of hard-facing materials are used industrially, only the three hardest of these are used to any extent as the cutting-edge for oil well bits. These are:

Group 4.—Diamond substitutes. Fused tungsten carbides and certain metallic borides.
Group 5.—Crushed metallic carbides.
Group 6.—Black diamonds.

The properties of all six groups are compared, and it is seen that these three groups rank high in the properties of primary interest in facing oil-well drills—*i.e.*, in cold hardness, ability to scour, and roughness of deposit.

The customary materials for the main bodies of fishtail bits, drag-bits, etc., upon which the insert or facing material is laid, are tough, shock-resistant, low-manganese steels, examples of which are given in a table. These steels are normalized after forging, and again after hard-facing.

A table gives the approximate composition, percentage of carbon, tungsten, chromium, manganese, nickel, and others, as well as recommended uses of thirty-two alloys under different trade names. A list of three references is appended.

A. H. N.

616.* Rotary Rig Cathead Operator Minimizes Drilling Time. H. F. Simons. *Oil Gas J.*, 8.2.40, **38** (40), 66.—In this fairly exhaustive article the duties and responsibilities of the cathead operator with regard to the safety of the other members of the drilling crew are described in detail. Practical hints are given and certain operations are detailed with a view to helping in shortening drilling time. A. H. N.

617.* Well Logging by Radioactivity. G. H. Westby and S. A. Scherbatskoy. *Oil Gas J.*, 22.2.40, **38** (41), 62–64.—Although electrical logging has been successful, there are numerous instances in which additional information would be of great value. Furthermore, the electrical properties of formations are not particularly stable; and because their measurement is rendered impossible by the presence of the casing, the use of electrical methods also is limited to uncased holes. Thus search was made for a measurable property that would be directly and permanently associated with a given rock. Radioactivity is such a property.

Radioactivity of a rock can be considered entirely unalterable; no temperature or pressure that can exist terrestrially has the slightest effect on the radioactivity of a substance. Further, the radiations emitted by radioactive materials have the ability to penetrate through iron, a circumstance which makes it easy to log cased holes by radioactivity measurements.

Without exception all substances, either terrestrial or extra terrestrial, are radioactive. It has been found that all matter has suffered some degree of contamination by radioactive substances. Radium is distributed widely in primary rocks, and has subsequently been redistributed in secondary rocks.

From measurements made on many rock specimens by laboratory investigations, and from the gamma-ray logs of wells surveyed to date, it is apparent that there are measurable differences in the amount of radioactive material contained in sedimentary rocks. This, together with the ability of the radiations to penetrate iron, is of vital importance, since it will allow the identification of formations in cased holes in old producing fields, where in the race to reach the deep-oil sand first no adequate log was kept of the formations above.

Since the amount of radioactive material in any sedimentary rock is determined chiefly by the conditions existing at the time of deposition, the radioactivity is a characteristic which may be as widespread and as determinative as any other correlatable factor. Of the sedimentary rocks, shales are usually the most highly radioactive, whilst the sandstones and the pure limestones are the least radioactive. In wells surveyed up to date the sandstones have been, in general, less radioactive than limestones; of the shales the dark-coloured shales are the most radioactive.

Typical loggings of four wells are given and compared. Detailed study of these wells is made, and also of comparative logs taken by the radioactivity method and by the conventional electric methods. It is shown in some cases that the former is more definite, and, further, it agreed better with mechanical coring taken accurately. Certain of the radioactivity logs were made with three strings of casing in the well and compared with corresponding sections of open hole in another. The agreement appears to be good. A. H. N.

618.* Progress in Metals—Applying Hard-Facing Material to Watercourse Outlets, Catheads, and Ditcher Teeth. W. L. Nelson. *Oil Gas J.*, 22.2.40, **38** (41), 72.—Many parts of equipment used in oil-fields and refineries can be given long, maintenance-free life by hard-facing. Some equipment is furnished with parts hard-faced by the original manufacturer. Such are Christmas trees and refinery-valves for handling oil and high-temperature steam, centrifugal pumps with hard-faced shaft-sleeves, rotary bits of all types, side-tracking mills, diesel-engine valves, valve-guides, injector assemblies, and gas-engine parts. A number of additional wearing parts, however, are best hard-faced by the maintenance department or local welding-shop. Such are bit watercourse outlets, catheads, and ditching-machine teeth.

Hard-facing these machine parts results not only in long, efficient, and trouble-free service, but also when these parts are worn out they can be rehard-faced easily and at low cost.

The paper gives detailed sketches and photographs, and describes methods of hard-facing these three parts with alloys of the cobalt–chromium–tungsten type in order to obtain most favourable results. A. H. N.

619.* Drilling Time Data Reduces Costs of Drilling. H. F. Simons. *Oil Gas J.*, 29.2.40, **38** (42), 67–68.—Drilling-time information indicates to crews soft and hard streaks, proper amount of weight on the bit, correct rotary speed, best type of bit to use, and condition of the bit in the hole.

Not many drilling-rigs are equipped with instruments for recording drilling time. The method still in general use is to mark the kelly joint and log on a piece of paper the number of minutes required for each succeeding foot-mark to go through the rotary table. The logging is usually not filed, and is rarely continuous over the entire depth. It is mostly used where a change of formation is expected. Hence the method is not an ideal one.

There are two types of recorders, both of which are attached to the swivel and record its height on a time-chart. The principal difference between the two types is that one operates mechanically, the other hydraulically.

By experiment it was found that there is an optimum number of revs./min. for drilling-table to obtain the fastest drilling time. Selection of proper bit and obtaining the maximum footage out of it and other factors in economic drilling are facilitated by a study of drilling time.

A list of references is appended. A. H. N.

620. Bureau of Mines—A.P.I. Pressure Core-Barrel. (Progress Report on its Design and Development). D. B. Taliaferro and R. E. Heithecker. U.S. Bureau of Mines, Rep. of Investigations, 3481, November 1939.—Examination of core samples from subsurface formations is far more exhaustive to-day than formerly; not only is geological information sought from them, but physical characteristics and conditions are also determined and interpreted in terms of the rocks they represent; such properties include porosity, permeability, oil, and connate water contents, etc. It is pointed out that although reliable methods of studying cores have been used, such applications are more restricted when dealing with oil reservoirs at higher temperatures and pressures than normal, chiefly because core recovery from a formation under these conditions often results in loss of fluid content and a certain amount of contamination, especially by drilling-fluid. It has been rightly contended by many operators that if such obstacles could be overcome, the value of core analyses would be greatly enhanced.

With this problem in mind, the Bureau of Mines co-operating with the American Petroleum Institute have designed and constructed a pressure core-barrel to cut and seal samples of rock with their naturally inherent fluids, so that they may reach the surface intact and uncontaminated. This particular tool has now been tried out in five different oil-wells with some measure of success, although it is admitted that some minor changes in design will be necessary, especially to eliminate the drilling-fluid, apparently considered not an impossible task. Full description and illustrated details are given of this core-barrel, of the procedure to be adopted when using it, also of the method and equipment suggested for subsequent laboratory examination of the cores recovered. Reliable estimates of the quantity of available oil and gas within a reservoir leading to planning the most efficient means of their extraction are claimed to be possible with this technique, although more research and experimental work on oil-wells are foreshadowed before the pressure core-barrel is finally perfected.

H. B. M.

621. The Eykometer. A New Device for Measurement of the Yield Point of Clay Suspensions and Oil-Well Drilling Muds. A. G. Stern. U.S. Bureau of Mines, Rep. of Investigations, 3495, February 1940.—The importance of evaluating various clay suspensions by comparative tests, as, for example, with bentonitic clay and oil-well drilling mud, by appeal to the "gel" content, is emphasized, but measurement of this property presents many practical problems. It is pointed out that of the many methods in use, that of the Stormer viscometer to determine the maximum load that can be placed on the pan without causing motion of the rotor is most widely adopted, but that reproducibility of observations is poor. The eykometer is essentially an instrument for making static measurements of the "yield value" of a mud directly; it consists of a transparent tube, to one end of which is fastened a small rubber balloon; details of its specification are given.

To determine the "yield value" or solidifying strength of a mud fluid, the sample is agitated and placed in the balloon; the apparatus is then fastened into a chamber filled with water to a definite level (predetermined to compensate for difference in density between the mud and water), and pressure increased until the fluid distorts the balloon, rise of the levelling-bulb being measured on an attached centimeter scale. The yield-strength of the mud fluid is the pressure in centimetres of water-pressure at which the rise of the levelling-bulb occurs. As effects of time and characteristics of the apparatus have all been standardized, it is claimed that, subject to observation of the precautions noted in this report, an average of six or eight observations should be reproducible to within ± 5%. H. B. M.

622. Drilling Patents. G. G. Harrington. U.S.P. 2,189,029, 2,189,030, and 2,189,031. 6.2.40. Appl. 6.12.38, 14.11.38, and 14.11.38, respectively. Reamers for oil-well drilling.

M. D. Carleton. U.S.P. 2,189,032, 6.2.40. Appl. 8.12.38. Reamer construction.

H. B. Book and R. H. Hanlin. U.S.P. 2,189,033, 6.2.40. Appl. 1.4.39. Reamer construction.

G. G. Harrington. U.S.P. 2,189,034, 6.2.40. Appl. 8.12.38. Reamer.

H. L. Squires. U.S.P. 2,189,035, 6.2.40. Appl. 8.12.38. Reamer.

K. E. Jones. U.S.P. 2,189,036, 6.2.40. Appl. 16.12.38. Reamer construction.

G. G. Harrington. U.S.P. 2,189,037, 6.2.40. Appl. 8.12.38. Reamer.

K. E. Jones. U.S.P. 2,189,038, 6.2.40. Appl. 16.12.38. Reamer.

W. L. Childs. U.S.P. 2,189,039, 6.2.40. Appl. 8.12.38. Reamer construction.

K. E. Jones. U.S.P. 2,189,040, 6.2.40. Appl. 27.12.38. Reamer construction.

L. S. Copelin. U.S.P. 2,189,057, 6.2.40. Appl. 11.12.37. A rotary core-drill having means utilizing hydraulic pressure of drilling mud for retaining and supporting the core-barrel in operative position.

L. A. Gilbert. U.S.P. 2,189,244, 6.2.40. Appl. 26.8.38. A pipe-spider with slips adjustable to grip pipe and restrain motion vertically in both directions.

E. E. Miller. U.S.P. 2,189,349, 6.2.40. Appl. 21.11.38. Mud-pump piston made of a hub to fit on a rod and rubber moulded on to hub.

G. D. Steel. U.S.P. 2,189,373, 6.2.40. Appl. 5.8.38. Safety cathead.

C. R. Dale. U.S.P. 2,189,445, 6.2.40. Appl. 11.7.39. Combination plug and dump-bailer.

H. A. Raphael. U.S.P. 2,189,552, 6.2.40. Appl. 13.10.37. Weight-indicator consisting of hydraulic gauge and a secondary cable to be fastened at both ends to main load-carrying cable and provide a loop in which the gauge is held under pressure.

J. W. Culbertson. U.S.P. 2,189,560, 6.2.40. Appl. 1.11.37. Angle marker for inclination-recording apparatus.

C. C. Brown. U.S.P. 2,189,575, 6.2.40. Appl. 26.4.34. Tubing support.

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C. E. Burt. U.S.P. 2,189,702, 6.2.40. Appl. 5.3.39. Well-cementing mechanism with retainer.

D. C. Sharp and R. M. Garrison. U.S.P. 2,189,839, 13.2.40. Appl. 29.11.35. Slush-pump piston.

D. G. Hawthorn and J. E. Owen. U.S.P. 2,189,900, 13.2.40. Appl. 18.6.38. Drill-stem circuit-tester for use in a bore-hole for measuring electrical characteristics of the earth.

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O. T. Broyles. U.S.P. 2,189,937, 13.2.40. Appl. 22.8.38. Deep-well apparatus for tool-setting.

E. F. Raymond. U.S.P. 2,190,045, 13.2.40. Appl. 19.10.36. A jar for rotary drilling.

H. W. Huber. U.S.P. 2,190,235, 13.2.40. Appl. 22.5.39. Drilling apparatus fitted with a spudding action operatively connected with the drive-shaft and the drill-line.

A. C. Catland. U.S.P. 2,190,350, 13.2.40. Appl. 10.3.39. Reamer-cutter mounting-means.

H. N. Keener. U.S.P. 2,190,362, 13.2.40. Appl. 15.11.38. Well-casing made of welded bell and spigot joint.

R. W. Maxwell. U.S.P. 2,190,365, 13.2.40. Appl. 24.1.38. Cutter and bearing assembly having roller-cutters on ball bearing.

C. C. King. U.S.P. 2,190,407, 13.2.40. Appl. 19.12.38. Sand-pump.

F. L. Pivots. U.S.P. 2,190,434, 13.2.40. Appl. 20.9.37. Changeable-blade drag-bit.

C. E. Costello. U.S.P. 2,190,442, 13.2.40. Appl. 10.5.38. Tool useful for removing objects from wells using two packers to make a chamber in the well and means for gripping object and introducing fluid pressure into well to move object.

J. E. Le Bus. U.S.P. 2,190,547, 13.2.40. Appl. 7.5.37. A combination elevator and wrench for supporting pipe-sections.

F. Humphreys. U.S.P. 2,190,790, 20.2.40. Appl. 3.6.36. Bore-hole surveying-instrument, including two separate devices arranged to take up positions depending on the inclination and magnetic bearing of the axis of the lower end of the bore-hole, respectively, and recording means.

H. A. Whitlock. U.S.P. 2,190,854, 20.2.40. Appl. 23.7.38. Fibre rope-structure.

P. M. Moss. U.S.P. 2,190,880, 20.2.40. Appl. 21.1.38. Draw-works line-controller.

E. Davis Wilcox and J. Richardson. U.S.P. 2,190,901, 20.2.40. Appl. 13.9.38. Drill-hole apparatus adapted to carry ballast and move in hole by gravity.

G. Potapenko. U.S.P. 2,190,950, 20.2.40. Appl. 3.11.37. Apparatus for determining the inclination and direction of a hole by generating an elastic vibration and measuring its frequency.

I. Thomas. U.S.P. 2,191,000, 20.2.40. Appl. 3.5.37. Fishing-tool.

C. E. Van Stone and A. E. Johnson. U.S.P. 2,191,223, 20.2.40. Appl. 31.10.38. Hydrostatic bailer.

A. H. N.

Production.

623.* Bringing in a Difficult Blow-Out. Anon. *Oil Wkly*, 5.2.40, 96 (9), 15–17.—After one week of uncontrolled flow, a tricky blow-out in California field was put under control by an ingenious method. The well caught fire within a few minutes of the blow-out, and burnt down the rig.

The well was an old producing well, but at the time it started its uncontrolled flow, gas from an upper sand was being used to repressure a lower horizon. The shut-in pressure was 1450 lb./sq. in., but compressors were installed to force the gas at 3000 lb./sq. in. into the formation when the tubing failed and a blow-out ensued.

The well was making a large quantity of sharp sand and blowing an estimated 50–60 million cu. ft. of gas. Consequently, it cut away most of the surface equipment down to the ground.

The fire was extinguished without much trouble by utilizing steam to snuff it. Bringing in the well, however, demanded the design and placing in of a special packer. This packer is described in detail, and the various steps undertaken in bringing in the wild well after extinguishing the fire are outlined. A. H. N.

624.* Economics of Well Spacing. I. I. Gardescu. *Oik Wkly*, 5.2.40, 96 (9), 21.—Too heavy or too small a rate of withdrawal of oil from a field would result in waste of energy. The rate of production of individual wells would also affect the energy conservation value, as excessive rates of production would cause waste of energy in the area surrounding the well, although the rate of recovery for the field as a whole might not be excessive.

In addition to the loss of oil production through dissipation of reservoir energy, there would also be a loss of production, due to the trapping of oil, as a result of either geological conditions of the reservoir or through the by-pass of water or gas.

Although the subject of economics of well spacing was classified into separate sections, the paper discussed only those fields where the spacing of wells, within certain limits, did not affect the ultimate recovery of oil, and where operations were without restrictions of spacing and production.

A Gulf Coast field, familiar to the author, was used as a basis for computations. The data was based, as much as possible, on facts; but certain assumptions were made where data were insufficient or where the facts confused the issue or complicated the analysis.

The following basic data illustrate the type of problem tackled. The field was produced under varying conditions of competitive drilling and production. A part of the field was drilled to a density of 7·2 acres/well, another part to a density of less than 1 acre/well. The ultimate recovery of the first area was 1046 brl./acre-ft. of effective sand, and that of the latter part 1089, the difference between the two ultimate recoveries being only 4%.

The production record of the two acreas showed in both instances a primary flush stage during which time 700 brl./acre-ft. were produced, and a secondary stage of production during which the remaining 350 brl./acre-ft. were produced. The period of primary recovery was seven years for the first area (7·2 acres/well) and only two years for the second area. The period and rate of production of secondary recovery were the same for both areas.

Basing the problem on these data, and a few other detailed constants of the field and rate of production, computations were made of the present value of oil on the basis of 200 ft. of sand. Three main assumptions were made :—

(1) All wells had an equal initial production;
(2) all wells were drilled at the beginning of the producing life of the field;
(3) the decline of production during the primary stage was a constant percentage decline.

The paper showed the method of approach for solving the problem by actually solving it completely. The general attitude of many operators that fewer wells meant more profit might often be unjustified. A. H. N.

625.* Varying Well Conditions Individualize Lifting. B. Mills. *Oil Wkly*, 12.2.40, 96 (10), 15–19.—Production practices in the Rhodessa field are reviewed, and as this field is characterized by a variety of methods, the paper is of general interest. Both gas-lift and pumping are being used in the field, with the former now in the lead. As the field becomes older, however, this is likely to change.

Of the 1100 producing wells in the field, more than half are still flowing naturally, about 250 wells are on gas lift, and about 110 are on the pump. Of the gas-lift wells, about 220 use valves or intermitters of various types, and about thirty are on straight gas lift. Most of the pumping wells use conventional rods and tubing. These various production systems are described.

Particulars are given in detail of the intermittent systems used in the field. One simple system has given good results in several wells. This is a two-string installation consisting principally of a time-cycle controller and two motor valves with the necessary drips and regulators; two check valves, one for the flow line and one for the casing-head outlet; one 3-in. × 1¼-in. tubing head for the suspension of the inner string, and necessary fittings for well-head connections. The operation is described.

Troubles peculiar to this field, as well as those of general occurrence, are discussed and certain methods of overcoming them are outlined. A. H. N.

626.* Thorough Reconditioning of Old Leases Boosts Profits. F. B. Taylor. *Oil Wkly*, 12.2.40, **96** (10), 28.—No general formula exists to solve the problem whether wells should be worked over or not, and, if so, to what extent. The variables are so many that the answer is one of careful analysis rather than one formula. In all cases, however, the work, once undertaken, must be thorough.

To illustrate the type of variables affecting the problem, certain of them may be summarized here. A decision to clean out wells must be based on what increase might be expected in daily production in relation to cost. The ability of the wells to pay the cost of reconditioning plus a reasonable return on the invested capital must be determined beforehand.

In judging the applicability of clean-out methods, reserve remaining in the reservoir must be sufficient to excite an increase in flow into the hole. If the reservoir reserve is slight, it may be that flow volume is normal, despite partial blocking action of scale, etc., in which case a clean-out would be wasted effort. This is true in cases where pay sections are thin.

Remaining pressure within the formation is a major factor in the flow of oil into the hole, and relief of back pressure will proportionately increase the effective area through which the pressure may influence the migration. The older the field or well, and the less the pressure remaining, the more effective is the back pressure in retarding flow.

Down-time and length of effectiveness of reconditioning work are too highly variable for exact analysis. It is usually guesswork to predict the time for any clean-out operation.

The length of effectiveness varies not only the thoroughness of the work, but also the volume of remaining crude in the reservoir. In addition, loose material in the pay strata may quickly plug the formation about the hole and render the clean-out ineffective. A high chemical content of reservoir water, or high paraffin content of the crude, may each result in swift deposition of scale on the face of the pay, again limiting the period of effectiveness.

These principles are illustrated by quoting the production trends before and after clean-out operations were carried out on two leases in Oklahoma. The work is shown to have been thorough, and it has pulled the leases from their inferior rating.

Detailed descriptions of the clean-out operations are also presented. In brief, the operations consisted of pulling as much metal out of the hole as possible, shooting the wells, using an especially long sandpump to clean the well thoroughly of sand, allowing a few hours' standing, and using the sandpump again to take out last traces of sand, and reconditioning all the equipment both inside and outside the well.

Results prove the investment to be paying big dividends at this time, and the production graphs point to continued high production rates far above what would have been possible without reconditioning of the properties. It is believed that the thoroughness of the job is completely justified. A. H. N.

627.* Stress Peaks Relieved by Floating Rod String on Compressed Air. F. B. Taylor. *Oil Wkly*, 19.2.40, **96** (11), 14–17.—The mean effective load on rods during the upstroke is very seldom excessive, being well within stress ranges the rods are capable of handling. Instead of the ideal load curve, the mechanics of the motion produce a peak stress at some points of the cycle, which may be thousands of pounds greater than the maximum load for which the rod string was designed. Continual subjection of a string of rods to these excessive peaks of stress is a chief cause of fatigue, and hence of failure.

To relieve the rods of excessive peak stresses, engineers of one company employed the shock-absorbing power of compressed air, which is also being used successfully for this purpose on some new type pumping units that have been placed on the market. In the alleviator designed by the company the rod-string is neither directly nor rigidly connected to the beam through polish-rod and clamp. Instead, the rod-string is connected to the rod of a piston supported over compressed air, the cylinder holding the air being fixed to the end of the beam of a standard-beam pumping-rig. This leaves the rod-string mechanically independent of the beam.

A normal installation makes use of a cylinder having an inside diameter of 11 in. and an operating stroke of about 20 in. Compressed air is introduced into the cylinder below the piston, operating pressure being about 170 lb. per square inch. The energy exerted by the gas against the piston above it is sufficient to hold the piston at the upper limit of the cylinder except during periods of peak stress. The piston-rod may be said to " go through " the piston, for it extends down through the compressed air and through packing in the centre of the cylinder. The polish-rod is clamped to the piston-rod extension.

With correct pressure of air the supporting force is sufficient to keep the piston always at the top of the cylinder while the unit is not in operation. At such time the rod-string weight is less than the upward thrust of the compressed air. In operation on the down-stroke the piston remains at the top of the cylinder, but during the up-stroke the compressed air must support not only the weight of the rod-string, but also the fluid load. In this circumstance the downward pull of the rod-string, or the resistance of the rod-string plus the fluid column to be lifted, is in excess of the energy of the compressed air supporting the piston at the upper end of the cylinder. As a result, the piston is drawn down part way through the cylinder. As soon as the momentary load peak is passed, the air pressure pushes the piston back to its normal position in the top of the cylinder. Consequently the upward movement of the end of the beam is somewhat faster than the upward motion of the polish-rod during high stress phases of the stroke, this resulting in spreading out the stress peaks.

When the peak stresses of the up-swing are passed, the compressed air or gas within the cylinder is again greater than the downward pull on the polish-rod. At this point the piston is forced upward within the cylinder, exceeding the speed of the beam, increasing the stresses during this portion of the stroke in which the normal stress would be low, and completing the full stroke with the piston at the top of the cylinder. In this manner the alleviator " knocks off " the high stress peaks, distributing them into a relatively flat curve, every portion of which is within the range of stress tolerance.

Dynamometer cards indicate a reduction of as much as 28·6% of the stress range and of 10·4% in polished-rod h.p. The life of rods was longer and rod jobs markedly decreased.

Full details of the installation and its dimensions are given, together with other interesting data. A. H. N.

628.* High-Voltage Economy when Wells are Wide Spaced. W. C. Lane. *Oil Wkly*, 19.2.40, 96 (11), 20.—The wider spacing of wells as a means of reducing the cost of developing and operating oil properties has caused changes in a number of practices heretofore regarded as standard. During the 20 years electrical energy has been used for pumping oil wells, 440-volt equipment has become the standard. Under close spacing practice, used until recently, the distribution lines are short, and no difficulty has been experienced in reaching an economical number of wells without resorting to the use of excessively large cables. With wide-spacing practice this voltage may not be economical.

In more recent years another practice has come into use which presents a different problem. This is the source of power for small properties. The difficulty arises when it is impossible to locate the generating plant at the load centre, with the result that some lines are too long for economical transmission at 480 volts.

The remedy is to find a way of increasing the distribution voltage without increasing the cost of the apparatus involved. The paper discusses the economics of changing over to a higher voltage by assuming and solving certain problems.

Historically, voltage standards have gone through a number of changes. Starting with 120 volts, it was increased to the 250 range, and then settled down to the present 440 volts. It appears that the change in conditions justifies an increase to a higher voltage. A. H. N.

629.* Method of Installing Catenary Pull-rod Line. K. C. Sclater. *Petrol. Engr*, February 1940, **11** (5), 27–30.—By measuring the difference in work per stroke at the jack and at the knock-off post, it was found that the friction of the rod-line on the average installation was 20% of the rod-line weight. Roller rod-line carriers or well-constructed catenary rod-lines reduced the friction to 5% of the rod-line weight. Two adjacent leases were re-equipped with rod-lines with catenary sags, each being previously pumped from its own central bandwheel power and using conventional rod-line systems, and dynamometer charts were made of all wells before and after the new installations. A reduction in horse-power of 19·5% was obtained, despite the fact that 32% more pull-rods were used.

Formulae and eleven tables are given in detail in the paper for use in installing catenary pull-rod lines. Photographs illustrate the system.

In setting stakes for rod-line supports, a wire-line reel which attaches to the front bumper was found very convenient for field use. A. H. N.

630.* Dual-Purpose Well Salvaged for Repressuring after Blow-Out and Fire. W. A. Sawdon. *Petrol. Engr*, February 1940, **11** (5), 46.—A key-input well utilizing gas from an upper sand for repressuring a lower sand got out of control due to a blow-out which resulted in a fire. The method of snuffing off the fire and controlling the well is given.

Details are given both of the well as used normally with gas being drawn from the upper sand through the packed annular space between a casing and tubing and passing through the tubing back to the lower sand, and of the emergency manifold which was used to cap the well.

Specification and dimensions of the manifold are detailed, accompanied by a sketch. A. H. N.

631.* Acid Treatment of Sand-Well Revives Production. H. L. Flood. *Petrol. Engr*, February 1940, **11** (5), 170.—In the treatment used in the well, the Carr method was employed to pump in 1000 gal. of chemical. This process involves first filling the tubing and annular space with oil, and then displacing the oil in the tubing by the chemical by opening the casing-head and bleeding-off the oil displaced. This method provides a " cushion " of oil in the annular space that prevents the chemical from entering the annular space during the " squeeze " of the acid into the formation. After the chemical is in place ready for introduction to the formation, the casing-head is closed and the chemical pumps are used to pump water into the tubing, and thus " squeeze " the acid into the formation.

Beginning at a pressure of 500 lb./sq. in. in the tubing, the pressure was quickly increased to 1800. The pumps were shut down for 10 min., but the pressure decreased to 1500 only, indicating a tight formation. The pressure was then increased to 2200 lb./sq. in., when the acid apparently broke through, permitting the formation to take the chemical at a much faster rate than before.

The well has been watched during the few months since its treatment, and is still reported to produce substantially the same volume just subsequent to its successful treatment. A. H. N.

632.* California Well Successfully Capped and Controlled. L. P. Stockman. *Oil Gas J.*, 8.2.40, **38** (39), 36.—After running wild for 6½ days, a difficult well was put under control, after flames had been extinguished and a 6-in. pressure-operated valve using 1500 lb. pump pressure had been installed and the valve closed.

A description is given of the well equipment, the origin and extent of the damage, and of the method used to extinguish the fire and control the well.

The paper includes a detailed and dimensioned drawing of the blow-out-control manifold assembly, as well as a list of descriptions of the separate components which went into the assembly. Specifications and description of the material are also included. In principle the assembly consisted of a packer, a device to set the packer, high-pressure stuffing-box, a master gate, and accessories of pipes, etc. (Cf. abstract no. 630.) A. H. N.

633.* Arkansas' Conservation Programme Attracts Wide Commendation. Part I. A. M. Crowell. *Oil Gas J.*, 8.2.40, **38** (39), 56.—Arkansas has made great strides in the past year in the conservation of petroleum. Use of the optimum daily rate of production as a basis for determining allowables, unit operation of oil-pools by implementation, method of allocating production to wells and leases in controlled fields, operation of a commission as an engineering body, and the acceptance of the commission's policy by the public have all attracted the attention of engineers interested in conservation projects.

In this, the first of a series of three papers, the author reviews the recent production history of the State. Extensive tables are supplied for various activities of production in Arkansas.

The second article will include a field and exploratory map of the productive area, and deal with the method of regulating operations and the allocation of production for each month, and the third will continue the discussion of allocations and show the success of the method by giving the detailed production history of the State's leading fields. A. H. N.

634.* Engineering Practices Embodied in Arkansas' Conservation Act. A. M. Crowell. *Oil Gas J.*, 15.2.40, **38** (40), 48.—This article concludes the discussion started in the previous issue of the *Oil Gas J.*, and combines the second and third parts of the paper. The author describes how the Arkansas Oil & Gas Commission regulates practices of producers, determines the optimum rate of flow of wells, allocates the production for the various fields, reviews the recent production history of major fields, shows the success of modern conservation, and gives the various sections of the law under which the commission rulings are made.

Special study is made of a water-drive pool, a gas-drive pool, and a combination-drive pool. The importance of bottom-hole pressures and its maintenance are discussed.

The volumetric formula employed simply allows each well to void so much space in the reservoir, whether it be the production of oil or gas or both, in proportion to acreage assigned and pressure obtained.

It is the unanimous opinion of the Commission, after many hearings on the subject, that the methods used are reasonable and practical ones, and that they have prevented, and are preventing, reasonably avoidable drainage between producing tracts, obviating the drilling of unnecessary wells, and approaching as nearly as possible equity in production.

Over-production is being prevented in the wasteful building up of above-ground stocks of oil. Stocks on hand have been reduced by 30·5% since the discovery of the new reserves.

This long paper is liberally illustrated with tables, charts, and graphs.

A. H. N.

635.* Paraffin Problems in the East Texas Field. W. N. Little. *Oil Gas J.*, 29.2.40, **38** (42), 46, and *Oil Wkly*, 26.2.40, **96** (12), 23.—*Paper presented before American Petroleum Institute.* Physical properties of the crude oil in a reservoir, together with variable quantities of paraffin and asphaltic residues, affect the rate of underground flow, and the amount of oil that will be retained in the sand after all customary methods of recovery have been applied. Gas dissolved in an oil in a reservoir decreases the natural viscosity of the oil and allows it to flow more readily to the well bore, where the pressure has been reduced by the removal of fluid head. When the pressure decreases sufficiently, the gas comes out of solution and aids in removing the oil in the direction of the reduced pressure. The loss of vapour from the oil, the cooling effect of the expanding gas, as well as radiation of heat to the cooler upper formations, are major factors causing the precipitation of paraffin residue from the oil in the tubing, flow-lines, and stock-tanks.

Some paraffin problems can be decreased by changing production practices. It is known that low rates of production encourage paraffin deposits; however, it is beyond the scope of this paper to determine the advisability of this practice. Many of the operators of the East Texas field fear the possibility of local water coning more than paraffin accumulation.

Wells that have a high flowing pressure generally operate flowing " go-devils " very satisfactorily.

Companies operating only a few wells in the field generally prefer to use chemicals to clean paraffin deposits from troublesome wells. There is less investment necessary for proper chemical treatment than for equipment needed for mechanical scraping.

When one all-purpose unit will handle all the service work of a company, elimination of the use of tubing-board and long lubricator should result in a saving. It must be remembered, however, that the use of double-stuffing-box arrangement necessitates the use of a heavy stem in high-pressure wells.

" An ounce of prevention is worth a pound of cure," is believed to apply in removing paraffin deposits. It has proved advantageous to schedule cleaning work so as to clean the deposits from the wells before the paraffin becomes thick and hard. Light equipment can perform this work very rapidly. It is not necessary to have a derrick on the location when light equipment is used for the scraping work. The lubricator used with light equipment is usually 6 or 8 ft. long, and has a combination pulley, swivel, and oil-saver on top. Companies using light equipment for paraffin-scraping work find that fewer heavier all-purpose units are needed to take care of the heavy-duty work. A. H. N.

636.* Cutler's Rule of Well Spacing. Anon. *Petrol. Times*, 2.3.40, **43** (1103), 190–192.—This paper is a summary of the Report of Investigation No. 3479, issued recently by the U.S. Bureau of Mines, embodying a comprehensive review of Cutler's tentative rule of well spacing and a re-examination of the data considered by him as combining the essential characteristic of wells in different parts of the U.S.A. to show the difference in oil recovery that may be expected from wide and from close spacing of wells.

Cutler's rule is explained, as it has been misquoted and wrongly interpreted on many occasions. The rule infers that doubling the distance between wells doubles the ultimate production per well from wells having the same initial year's production, and halves the recovery of oil from the pool; or, halving the distance between them, results in halving the ultimate production per well from wells of equal size and in doubling the recovery of oil from the pool.

An example is worked out to demonstrate that the energy required per unit of time to move oil through different distances but at equal volumetric rates to wells in a homogenous formation is not proportional to the distance through which oil moves, as Cutler assumed, because such relationship between energy and distance holds true for pipe-lines and analogous conduits. The essence of the problem is that

$$\Delta P \propto \log_e \frac{r_f}{r_s}$$

and not $\Delta P \propto r_f$ as in pipe-line problems,
where ΔP = pressure drop,
r_f = distance through which oil moves,
r_s = radius of well.

Thus in the specific problem considered doubling the value of r_f from 330 to 660 ft. meant an increase in ΔP of only 10%—*i.e.*, 20 lb./sq. in., instead of 200 lb./sq. in., which a strictly linear proportionality would demand.

As energy required per unit time to move a liquid is equal to drop in pressure in lbs./sq. ft. multiplied by the volumetric rate of liquid flowing, the increase in energy required on doubling the distance for a constant rate of flow will follow the same law as the pressure drop. In the specific example increase in energy required will therefore be 10%, and not 100% more. A. H. N.

637. Résumé of Oil-Field Operations in 1937. R. D. Bush. *Summary of Operations, California Oil-fields*, 1938 (1940), 23, 3, 5.—Production of oil in the State of California in 1937 totalled 237,459,008 brl., an increase of over 24 million brl. compared with 1936. The report gives details of the several field operations during the year under review and notes the discovery of two new fields, Rio Bravo and Canal Oil-fields, Kern County, during that period. New productive areas and deeper producing zones were discovered, notably the Rancho San Francisco area of the Newhall field, the Lomita area of the Torrance field, and the western part of the Montebello field.
H. B. M.

638.* Closing a Gas Blow-Out. V. Ya Valtsev and V. P. Timchenko, *Azerb. Neft. Khoz.*, December 1938, 18 (12), 11–13.—Account is given of a successful method of closing-in a gas blow-out at a well more than 1800 m. deep in Baku field, after previous attempts had failed. Gas pressure was 60 atm. L. R.

639.* Drilling-pipe Back-Pressure Valve. L. I. Mirkin. *Azerb. Neft. Khoz.*, December 1938, 18 (12), 23–24.—Drawbacks of back-pressure valves generally used in the U.S.S.R. are: Complicated production of valve-seat and valve-stem guide, rapid erosion of seat and valve during use, and difficult repair.

An improved type of back-pressure valve has been developed by E. Kh. Mekhtiev, in which valve proper with valve-guide are placed freely into a suitable recess of the back-pressure-valve housing. The valve head carries a rubber ring on its upper face, and is pressed upwards by a coil spring against the face of the drilling-tube to which the valve housing is screwed. By means of the rubber ring a tight closing of the valve is ensured. The following advantages are claimed: simple production, easy fitting, better tight-holding, longer life, and easy repair.

Several back-pressure valves of Mekhtiev type have been tested in practice and given satisfactory results. One valve has been in use for 283 hrs. without repair.
L. R.

640.* Flow Characteristics of Gusher Wells. G. N. Gaziev. *Azerb. neft. Khoz.*, January 1939, 19 (1), 37–43.—The author indicates a method of approximately estimating the formation and casing-head pressure of a gusher well, and the rate of flow of oil through the reservoir rocks.

Equations are developed permitting to estimate:

(1) Gas pressure within the oil-string of a flowing well.

(2) Formation pressures using the indicator curve evolved by Marsh's and Robinson's empirical formulae, basing on three different rates of production obtained by varying the flow-bean diameter. The indicator curve obtained permits to calculate the reservoir pressure. An example is given.

(3) Potential flow of well—*i.e.*, that maximum rate of flow under which the formation pressure is still high enough to give the gas sufficient energy for a natural lift of the oil to the surface. This potential flow may be estimated from empirical plots of rate of flow against pressure necessary for migration of oil towards bottom-hole.

(4) Proportion of free gas to gas liberated from solution during lift.

(5) Apportioning consumption of energy of reservoir gas to individual points: reservoir rock, tubing, and flow-bean.

(6) Optimum diameter of tubing.

(7) Diameter of flow-bean. L. R.

641. Production Patents. G. A. Zeidler, Jr. U.S.P. 2,188,936, 6.2.40. Appl. 22.10.37. Method of developing wells by repeated extraction of liquid and fines from well, followed by settling the fines in the vicinity of the well, and then recharging the liquid into the formation to release all loose fines from the screen and the pay-face, and starting the cycle by liquid and fines withdrawal again.

J. F. Kohnke. U.S.P. 2,189,070, 6.2.40. Appl. 3.5.38. Pipe-joint.

H. E. Driggs and H. Rauser. U.S.P. 2,189,103, 6.2.40. Appl. 10.11.38. Testing-tool for wells consisting of tubing, packer, and inlet-valve means which can be opened by vertical movement of tubing.

C. E. Bridwell. U.S.P. 2,189,129, 6.2.40. Appl. 9.3.37. A valve mechanism adapted for being interposed in a fluid conduit and controlling the flow of fluid through the conduit.

F. Wilcom and R. D. Thompson. U.S.P. 2,189,237, 6.2.40. Appl. 21.7.37. Combination cup and plunger oil-well pump fitted with scraper and valves to remove sand from barrel into a chamber and then sand to be flushed out.

M. W. Russell and P. G. Miller. U.S.P. 2,189,272, 6.2.40. Appl. 22.8.38. Sand- and gas-trap having a tube with inside baffles.

J. L. Morris. U.S.P. 2,189,350, 6.2.40. Appl. 13.11.37. Pipe coupling.

C. E. Burt and E. Graham, Jr. U.S.P. 2,189,701, 6.2.40. Appl. 21.4.39. Production-packer and liner-hanger with hydraulically tripped slips.

C. E. Burt and E. Graham, Jr. U.S.P. 2,189,703, 6.2.40. Appl. 25.7.39. Well-production apparatus comprising a packer.

C. Irons. U.S.P. 2,189,798, 2,189,799, and 2,189,800, 13.2.40. Appl. 30.12.36. All three patents deal with treating an oil well with hydrochloric acid, wherein the acid, on admixture with oil in the formation, forms a viscous mixture hindering the penetration of the acid into the formation. Small proportions of guaiacol are used in the first, of thymol in the second, and of mono-, di-, and tri- chlorophenols in the third specifications.

J. S. Fuller. U.S.P. 2,189,893, 13.2.40. Appl. 15.7.37. Pumping apparatus with means to shift the point of application of power to obtain a maximum moment arm at the time of maximum load during the upstroke of the pump mechanism and a minimum moment arm at the time of minimum load during the downstroke. Rotating balance weights are also used.

T. V. Moore. U.S.P. 2,189,919, 13.2.40. Appl. 18.7.36. Method and apparatus for formation pressure testing which comprises shutting off communication with formation of the liquid at a point above formation, opening communication of the formation to a pressure less than the formation pressure, and recording the pressures in the hole as flow occurs.

H. A. Holzer. U.S.P. 2,190,070, 13.2.40. Appl. 14.9.38. Pumping unit.

C. T. McCoy. U.S.P. 2,190,104, 13.2.40. Appl. 14.5.38. Method and means for separating oil and gas adapted to be lowered to the lower end of a well-bore.

C. P. Walker. U.S.P. 2,190,141, 13.2.40. Appl. 29.4.39. Pressure wave velocity measuring system adapted with means to vary the frequency of wave until it resonates in the medium of a tube, and means for measuring this resonance frequency.

C. E. Braden. U.S.P. 2,190,145, 13.2.40. Appl. 27.5.39. Well-hole cleaning device with expansible brush-head mounted on a reciprocating plunger.

C. E. Blackburn. U.S.P. 2,190,250, 13.2.40. Appl. 18.10.37. Apparatus for testing oil- and gas-wells.

G. H. Ennis. U.S.P. 2,190,260, 13.2.40. Appl. 21.6.36. Apparatus for determining pressure and temperature in a well by electrical circuit which translates pressure and temperature impulses on a pressure- and temperature-responsive means at the well bottom to readings at the surface.

W. T. Robertson. U.S.P. 2,190,535, 13.2.40. Appl. 20.9.38. Pump for deep oil-wells fitted with a power-piston.

L. B. Slichter. U.S.P. 2,190,686, 20.2.40. Appl. 29.1.36. Mineral exploration in a drill-hole by creating acoustic and electro-magnetic fields and measuring them at various points.

G. L. Kothny. U.S.P. 2,190,716, 20.2.40. Appl. 16.5.39. High-pressure closure in combination with a casing subjected to high external pressures.

M. O. Johnston. U.S.P. 2,190,989, 20.2.40. Appl. 13.12.37. Method of preparing an oil-well for production.

C. J. Coberly. U.S.P. 2,191,093, 20.2.40. Appl. 6.5.38. Flow-governor for fluid-operated deep-well pumps.

C. Schlumberger and A. M. L. Doll. U.S.P. 2,191,119, 20.2.40. Appl. 11.5.35. Method of, and apparatus for, surveying the formations traversed by a bore-hole by transmitting and receiving compressional waves.

L. B. Slichter. U.S.PP. 2,191,120 and 2,191,121, 20.2.40. Appl. 2.3.35. Method of geological survey in a bore-hole by utilizing sound-vibrations.

R. L. Chenault. U.S.P. 2,191,369, 20.2.40. Appl. 20.12.38. Reciprocating-fluid motor-driven pump adapted to be positioned in a well.

R. L. Chenault. U.S.P. 2,191,370, 20.2.40. Appl. 23.3.39. Apparatus for controlling fluid flow in oil-well.

J. E. Hall. U.S.P. 2,191,380, 20.2.40. Appl. 13.1.37. Well-pump which is self-washing and self-desanding. A. H. N.

Cracking.

642.* Cracking Tars and Distillates from Coal. G. Egloff, J. C. Morrell, G. B. Zimmerman and W. E. Lemen. *Industr. Engng Chem.*, 1940, **32** (1), 39.—An investigation has been carried out in a pilot-cracking plant, using coal-tars, creosote oils, lignite tar fractions, and distillates from low-temperature carbonization of coal, with the object of evaluating such materials as cracking stocks. These charging stocks may be cracked under suitable operating conditions to produce gasoline, gas and coke or fuel oil residues. Low-boiling phenols may be simultaneously produced from higher-boiling tar acids. The finished commercial products include gasoline, cresylic acid, fuel oil, domestic coke, electrode carbon and polymer gasoline. The production of tar acids may be varied within considerable limits by changing the boiling range of the whole distillates from the cracking unit.

In comparison with petroleum cracking greater plant corrosion is encountered and lower plant capacities are obtained when cracking tars and distillates from coal. The untreated gasolines are of higher specific gravity and octane number indicating the presence of aromatic hydrocarbons. Acid treatment reduces the specific gravity and octane number to a varying degree, depending on the charging stock and the treatment given. The finished gasoline from coal tar in comparison with petroleum cracked gasoline is higher in specific gravity, octane number, and has a very high oxygen bomb stability, presumably because of naturally occurring inhibitors. Sulphur reduction and removal of gum-forming constituents are difficult with these gasolines.

The gas, although produced in greater quantity than in normal petroleum cracking, is lower in density and heating value, the difference being due to a larger proportion of hydrogen and methane. By fractionation useful concentrations of the higher olefinic constituents of the gas may be obtained for further processing to gasoline by catalytic polymerization. H. E. T.

Chemistry and Physics of Petroleum.

643.* Engineering in the Service of Chemistry. T. H. Chilton. *Industr. Engng Chem.*, 1940, **32** (1), 23.—A brief description is given of some of the many applications of engineering in chemical processes. This is followed by a discussion of the laws of fluid, mass, and heat-transfer, and the methods used by chemical engineers to correlate the available data, and to predict performance in unit processes. P. D.

644.* High-Pressure Vapour-Liquid Equilibrium. E. R. Gilliland and H. W. Scheeline. *Industr. Engng Chem.*, 1940, **32** (1), 48.—Experiments were made on the system propylene–*iso*butane at pressures up to 600 lb. per sq. in. and temperatures up to 260° F. Experiments were also made on the system H_2S–propane at pressures from

400 to 600 lb. per sq. in. and temperatures up to 200° F. The results are presented in tabular and graphical form.

The vapour–liquid equilibrium obtained is compared with that predicted by equilibrium charts based on fugacity. Reasonable agreement is obtained in the case of the hydrocarbon system at pressures up to 200 lb. per sq. in., but as the critical condition is approached considerable divergences appear.

An empirical method for deriving the equilibrium constants for binary hydrocarbon mixtures at higher pressures is suggested, based on the data for such systems given in the literature. P. D.

644*a*.* Solubility of CO_2 in Benzene at Elevated Pressures. Shen-Wu Wan and B. F. Dodge. *Industr. Engng Chem.*, 1940, **32** (1), 95.—The equilibrium phase composition were determined at temperatures of 30, 40, 50, and 60° C. over the complete range of compositions. P. D.

645.* Phase Equilibria in Hydrocarbon Systems. Propane–*n*-Butane System in the Critical Region. C. N. Nysewander, B. H. Sage, and W. N. Lacey. *Industr. Engng Chem.*, 1940, **32** (1), 118.—Volumetric and equilibrium phase compositions were determined for six mixtures at temperatures above 160° F. The experiments covered the complete two-phase system. P. D.

646.* Vapour Liquid Equilibrium of the System *iso*Propyl Ether–*iso*Propanol. H. C. Miller and H. Bliss. *Industr. Engng Chem.*, 1940, **32** (1), 123.—The solvent properties of *iso*propanol and the high octane number of the ether have recently made these materials of particular interest. Data relating the vapour–liquid equilibrium of the system have been established. These data will facilitate greatly the design of separation and purification equipment. An azeotrope having the composition 78·2 mole-% *iso*propyl ether and a boiling point of 66·15° C. is shown to be formed. J. W. H.

647.* Separation Processes : The Principle of Minimum Dilution. M. R. Randall and B. Longtin. *Industr. Engng Chem.*, 1940, **32** (1), 125.—The highest thermodynamic efficiency of a process is obtained if those streams which have to be mixed are as nearly as possible in equilibrium. Graphical methods are used to demonstrate the soundness of this principle, and consideration is given to several practical cases in which the principle is not always adhered to. P. D.

648.* Physical Properties and Chemical Constitution. IV. Methyl*cyclo*hexane and the Multiplanar Structure of Methyl*cyclo*hexane. D. M. Cowan, G. H. Jeffery, and A. I. Vogel. *J. chem. Soc.*, December 1939, 1862–1865.—These authors have presented further evidence for the existence of B and B′ forms of methyl*cyclo*hexane. The A forms (vide Part III, *J. chem. Soc.*, 1938, 1323) have been shown to be impure forms of B′, but the possibility of a third isomeride is suggested.

From the results support is claimed for the view that the methyl*cyclo*hexane ring exists in multiplanar forms. E. H. W.

649. Isolation of 2 : 2-Dimethylbutane from Natural Gas and Determination of its Physical Properties. M. M. Hicks-Bruun, J. H. Bruun, and W. B. M. Faulconer. *J. Amer. chem. Soc.*, 1939, **61**, 3099–3101.—The last isomeric hexane to be isolated from natural sources was prepared in a pure form from a West Virginia natural gas, and the specific gravity, boiling point, ref. index and f.pt. were determined. The sample was observed to freeze to transparent crystals at − 98·7° and to begin to form white crystals at − 99·7°, but no definite explanation of this is offered. Except for 2 : 3-dimethylbutane, the isomer occurs to a smaller extent than the other hexanes in natural gas (168 ml./cu. m.). R. D. S.

650. Co-Ordination Complexes of Mercuric Ion with *cyclo*Hexene. H. J. Lucas, F. R. Hepner, and S. Winstein. *J. Amer. chem. Soc.*, 1939, **61**, 3102–3106.—It is reported that two rapid reactions, viz :—(1) $C_6H_{10} + Hg^{++} \rightleftharpoons C_6H_{10}Hg^{++}$ (2) $C_6H_{10} + Hg^{++} + H_2O \rightleftharpoons C_6H_{10}HgOH^{+} + H^{+}$ occur with slower secondary reactions taking place at the same time in the distribution of *cyclo*hexene between carbon tetrachloride and aqueous solutions containing mercuric nitrate, nitric acid, and potassium nitrate of unit ionic strength. R. D. S.

651. Vapour–Liquid Equilibrium. IV. Carbon Tetrachloride-*cyclo*Hexane Mixtures. G. Scatchard, S. E. Wood, and J. M. Mochel. *J. Amer. chem. Soc.*, 1939, **61**, 3206–3210.—The authors have measured the vapour–liquid equilibrium pressure and compositions at 40° and 70° throughout the composition range of carbon–tetrachloride–*cyclo*hexane mixtures, and at 30°, 50°, and 60° for approximately equimolar mixtures. They give also their values of the densities at 25°. These results are examined from thermodynamic considerations, and the authors notice that the unexplained entropy increase on mixing is only one-thirteenth as large as for benzene–*cyclo*hexane mixtures which they have previously reported. R. D. S.

652. Structure of Vinyl Polymers. VI. Polyvinyl Halides. C. S. Marvel, J. H. Sample, and M. F. Roy. *J. Amer. chem. Soc.*, 1939, **61**, 3241–3244.—The action of zinc on a very dilute solution of polyvinyl halide in dioxane results, under the most favourable conditions, in the removal of 84–87% halide and the production of an insoluble polymeric material which does not decolorize an alkaline solution of potassium permanganate. It appears that the polyvinyl halides have the 1 : 3-dihalide structure, as neither the chloride nor the bromide liberates iodine from a peroxide-free dioxane solution of potassium iodide. This evidence is also supported by the nature of the ultra-violet absorption curves. R. D. S.

653. Structure of Vinyl Polymers. VII. Polyacrylyl Chloride. C. S. Marvel and C. L. Levesque. *J. Amer. chem. Soc.*, 1939, **61**, 3244–3246.—The results reported here show that at least part of the units of polyacrylyl chloride are arranged in a "head-to-head, tail-to-tail" formation, a behaviour which is anomalous for the vinyl halides, as these usually form "head-to-tail" polymers. The evidence is based on the production of a polymeric bromoacrylic ester by the bromination, followed by esterification of polyacrylyl chloride: when heated with potassium iodide in acetone solution, this polymer released free iodine. R. D. S.

654. Redistribution Reaction. IV. Interchange between Triethyl-lead Chloride and Radioactive Tetraethyl-lead. G. Calingaert, H. A. Beatty, and L. Hess. *J. Amer. chem. Soc.*, 1939, **61**, 3300–3301.—When trialkyl-lead halides catalyse the redistribution reaction of tetraalkyl-lead they enter directly into the reaction, and both the alkyl and halogen groups can interchange with each other. In this paper this is shown to be so when the same alkyl group (ethyl) is present in each molecule. The authors made use of radioactive lead to indicate the course of the reaction, tetraethyl-lead being made from radium D. They found that in a solution containing equimolecular proportions of radioactive tetraethyl-lead and inert triethyl-lead chloride equilibrium was attained in less than 24 hr. R. D. S.

655. Reaction between 2 : 3-Dimethyl-1 : 4-Naphthoquinone and Phenylmagnesium Bromide. II. H. M. Crawford. *J. Amer. chem. Soc.*, 1939, **61**, 3310–3314.—There are two di-addition products resulting from the 1 : 2–1 : 2 and 1 : 2–1 : 4 addition of two molecules of phenylmagnesium bromide to one molecule of the quinone. The structures and some reactions of these two compounds are given in this paper, which also shows how a parallel series of reactions results in the same product, a benzenoid hydrocarbon, formed from both compounds. In addition, structures have been assigned to various compounds formed during the reactions. R. D. S.

656. Specific Heat of Some Ethylene Halides. W. E. Railing. *J. Amer. chem. Soc.*, 1939, **61**, 3349–3353.—In this paper are values of the heats of fusion and transition and the heat capacities of 1 : 2-dibromoethane, 1 : 2-dichloroethane, and 1 : 2-bromochloroethane measured over the range 90–320° K. Inconsistent values in these properties due to the previous thermal history of the halides are discussed with reference to the restricted rotation about the carbon–carbon bond. R. D. S.

657. Reaction of Benzene with Methyl*cyclo*butene and Methylene*cyclo*butane in the Presence of Sulphuric Acid. V. N. Ipatieff and H. Pines. *J. Amer. Chem. Soc.*, 1939, **61**, 3374–3376.—A mixture composed of methyl*cyclo*butene and methylene*cyclo*butane reacts readily with benzene in the presence of 96% sulphuric acid at 0–10° to yield (*a*) 1-methyl-1-phenyl*cyclo*butane, (*b*) *p*-di-(1′-methyl*cyclo*butyl)benzene, (*c*) tri-(1′-methyl*cyclo*butyl)benzene. Hydrogenation of (*a*) gives 1-methyl-1-*cyclo*hexyl*cyclo*butane, and the *cyclo*butyl ring in the latter compound decomposes when passed over platinized alumina at 250° to form a mixture of *tert.*-amylbenzene and 2-phenylpentane by loss of hydrogen. When a phenyl group is attached to the *cyclo*butyl ring the radical becomes very stable to sulphuric acid and nitrating mixture. R. D. S.

658. Catalytic Interaction of Acetylene and Hydrogen on Platinum. A. Farkas and R. Farkas. *J. Amer. chem. Soc.*, 1939, **61**, 3396–3401.—The phenomena discussed in this paper were examined between 70 and 150 mm. pressure and over the temperature range 20–140°. Increases of pressure of the hydrogen accelerated hydrogenation, but increase of pressure of the acetylene retarded the reaction. It was noticed that when *para*-hydrogen was used for the hydrogenation, *ortho-para* conversion was much slower than it was when the acetylene was absent, and when deuterium was used, hydrogenation at 20° proceeded at only two-thirds the rate of hydrogenation by ordinary hydrogen; also deuterium was found to hydrogenate acetylene more slowly than ethylene. The mechanism of the hydrogenation of acetylene is discussed, and the authors show that acetylene proceeds to ethane by two distinct stages, the first being the formation of ethylene; the ethylene is then only further reduced to ethane after all (or nearly all) of the hydrogen has been used up: the start of the second step is manifested by a sudden increase in the rate of hydrogenation—that is to say, ethylene is hydrogenated more rapidly than it is formed. R. D. S.

659. Addition of *N*-Haloamides to Olefins. M. S. Kharasch and H. M. Priestley. *J. Amer. chem. Soc.*, 1939, **61**, 3425–3432.—The authors have formed addition products from reactions between halosulphonamides of the type R^1SO_2NBrR and various olefins. The bromine atom in the product assumed the same position as the bromine atom in the "normal" addition of hydrogen bromide. The addition of N,N-dibromosulphonamides to olefins, however, resulted in products in which the bromine atom took up the same position as the bromine atom in the "abnormal" addition of hydrogen bromide to these compounds. R. D. S.

660. Chlorinations with Sulphuryl Chloride. II. The Peroxide-Catalyzed Reaction of Sulphuryl Chloride with Ethylenic Compounds. M. S. Kharasch and H. C. Brown. *J. Amer. chem. Soc.*, 1939, **61**, 3432–3434.—Investigations into the reaction of sulphuryl chloride with olefinic compounds show that it is catalysed by organic peroxides with the same mechanism as that proceeding in the chlorination of aliphatic hydrocarbons —viz., intermediate formation of free radicals and chlorine atoms. Ethylenic compounds which, normally, are not readily responsive to the presence of traces of peroxide can be purified to a high degree so that no reaction with sulphuryl chloride will occur, whereupon the addition of a small quantity of (*e.g.*, 0·002 mole of benzoyl) peroxide will bring about a smooth chlorination. The olefins studied in this work were *cyclo*hexene, allyl chloride, dichloroethylene, tetrachloroethylene, stilbene, and tetraphenyl ethylene; in each case the product of chlorination was the corresponding dichloride. R. D. S.

661. Ketene in the Friedel–Crafts Reaction. I. Direct Acetylation of Aromatic Hydrocarbons with Ketene. J. W. Williams and J. M. Osborn. *J. Amer. chem. Soc.*, 1939, **61**, 3438–3439.—The authors show how to improve the yield of acetophenone from ketene and benzene in the Friedel–Crafts reaction by (1) use of a considerable excess of ketene, (2) use of ketene which contains minimum amounts of ethylene and carbon monoxide, (3) operation at 0°, (4) addition of aluminium chloride in small portions, with rapid stirring, (5) use of at least 1·5 moles of aluminium chloride per mole of hydrocarbon, and (6) use of an inert diluent, as carbon disulphide. Further, they show how the reaction between ketene and naphthalene may be regulated so that α-naphthyl ketone may be obtained to the practical exclusion of the β-isomer. The preparations of methyl β-tetrahydronaphthyl ketone and *p*-phenylacetophenone, using ketene, are also reported. R. D. S.

662. Density, Thermal Expansion, Vapour Pressure, and Refractive Index of Styrene, and the Density and Thermal Expansion of Polystyrene. W. Patnode and J. W. Schieber. *J. Amer. chem. Soc.*, 1939, **61**, 3449–3451.—Physical constants of styrene and polystyrene are given over various ranges, the results being shown mainly on graphs. The thermal behaviour of the polymer is discussed. R. D. S.

663. Thermal Data on Organic Compounds. XIX. Modern Combustion Data for some Non-Volatile Compounds Containing Carbon, Hydrogen, and Oxygen. J. W. Richardson and G. S. Parks. *J. Amer. chem. Soc.*, 1939, **61**, 3543–3546.—This is an account of an investigation of the heats of combustion of β-methylnaphthalene, phthalic anhydride, phthalic acid, anthracene, phenanthrene, stilbene, pyrene, *n*-hexadecane, cetyl alcohol, 1 : 3 : 5-triphenylbenzene, and a sample of poly*iso*butylene, determined in a bomb calorimeter. The original paper should be consulted for a summary of experimental and derived thermal data at 25°. R. D. S.

664. Raman Spectra of Acetylenes. II. Displacements and Depolarization Factors for Phenylacetylene and Derivatives of the Type $C_6H_5C \equiv R$. M. J. Murray and F. F. Cleveland. *J. Amer. chem. Soc.*, 1939, **61**, 3546–3549.—Raman frequencies and depolarization factors are reported for twelve disubstituted acetylenes. Two lines on the polarization film in the 2200 cm.$^{-1}$ region have been noticed, and it has been previously suggested that one line is due to a symmetrical vibration. The authors show, however, that both lines were depolarized to the same degree, thus disposing of the above theory, since symmetrical vibrations are, in general, strongly polarized and asymmetrical vibrations are strongly depolarized. R. D. S.

665. Cycli-Alkylation of Aromatic Compounds by the Friedel and Crafts Reaction. H. A. Bruson and J. W. Kroeger. *J. Amer. chem. Soc.*, 1940, **62**, 36–44.—The authors have shown that 1 : 4-ditertiary glycols will condense in the presence of aluminium chloride with phenols, phenol ethers, and aromatic hydrocarbons. Thus 2 : 5-dimethylhexane 2 : 5-diol and phenol give a tetramethyltetrahydronaphthol derivative.

This introduction of a new hydroaromatic cycle into the aromatic nucleus has been termed "cycli-alkylation."

Isomeric compounds to those given using aluminium chloride are formed if sulphuric acid or boron trifluoride is used as the condensing agent.

1 : 4-Dichlorides, 1 : 5-diolefines, and 2 : 2 : 5 : 5-tetraalkyltetrahydrofurans gave similar condensation products to the 1 : 4-ditertiary glycols. Thiophenols behaved differently from phenol and gave diaryl dithio ethers. Thiophene took up one hydroaromatic cycle, but benzene, naphthalene, and diphenylene oxide took up two hydroaromatic cycles. E. H. W.

666. Structure of Vinyl Polymers. VIII. Polystyrene and some of its Derivatives. C. S. Marvel and N. S. Moon. *J. Amer. chem. Soc.*, 1940, **62**, 45–59.—The preparation and peroxidic polymerization of *ortho*-bromostyrene are reported.

Poly *o*- and *p*-bromostyrenes were treated with sodium in boiling xylene solution. The polymers formed sodium derivatives, but there was no evidence of a Wurtz–Fittig reaction. This was said to indicate a 1 : 3 structure for the polymers.

A preparation of α-acetoxystyrene is described, but attempts to polymerize this and a variety of α- and β-substituted styrenes were unsuccessful. E. H. W.

667. Further Observations on the Use of Hydrogen Fluoride in Acylations and Cyclizations. L. F. Fieser and E. B. Hershberg. *J. Amer. chem. Soc.*, 1940, **62**, 49–53.—Perinaphthane and hydrindene were acetylated at room temperature in the presence of hydrogen fluoride. It was shown that naphthalene and phenanthrene could be acylated at slightly higher temperatures under pressure.

The cyclizing of *o*-(naphthylmethyl)benzoic acid with hydrogen fluoride was used in syntheses of 9-methyl- and 9-allyl-1 : 2-benzanthrene. An attempt to synthesize

1′ : 9-dimethyl-1 : 2-benzanthrone by cyclization of *o*-(8-methyl-2-naphthyl)benzoic acid by this method gave instead the linear isomer, which was isolated in two modifications. E. H. W.

668. Peroxide Effect in the Addition of Reagents to Unsaturated Compounds. XXIV. The Addition of Hydrogen Iodide to Propene 1-Bromopropene, Allyl Chloride, and Allyl Bromide. M. S. Kharasch, J. A. Norton, and F. R. Mayo. *J. Amer. chem. Soc.*, 1940, **62**, 881–886.—The addition of hydrogen iodide to propene, allyl chloride, and allyl bromide has been shown to give in each case only one product, thus providing strong evidence that the direction of addition of hydrogen iodide to olefines cannot be reversed.

Peroxides were shown to accelerate the action because they liberated free iodine which acts as catalyst for this addition.

Addition of hydrogen iodide to 1-bromopropene gave a mixture of one-third 1 : 1- and two-thirds 1 : 2-dihalide, these proportions being in agreement with those for hydrogen chloride and hydrogen bromide additions. E. H. W.

669. Condensations by Sodium. XV. Reactions of Disodium Compounds with Ethylidene and Methylene Chlorides. A. A. Morton and J. T. Massengale. *J. Amer. chem. Soc.*, 1940, **62**, 120–123.—Amylidene-disodium was shown to react with ethylidene chloride giving heptene-2, and with methylene chloride giving hexene-1.

With benzylidene-disodium ethylidene and methylene chlorides were shown to yield respectively methylstyrene and styrene.

Phenyl-sodium prepared from chlorobenzene was less reactive with toluene than the phenyl-sodium prepared from amyl-sodium.

The authors made unsuccessful attempts to use benzyl chloride and benzal chloride as sources of mono- and di-sodium compounds, respectively. They could discover no evidence of expected reactions between the disodium compounds and pentamethylene dibromide and benzal chloride. E. H. W.

670. Condensations by Sodium. XVI. The Formation of Decane in the Wurtz Reaction. A. A. Morton and C. M. Richardson. *J. Amer. chem. Soc.*, 1940, **62**, 123–126.—The Wurtz reaction is shown to take place in two phases : first, the formation of organosodium compounds, and secondly, their reaction with alkyl chloride, giving decane.

The presence or otherwise of free radicals is discussed. E. H. W.

671. Catalytic Hydration of Acetylene and some Alkylacetylenes. R. E. Schaad and V. N. Ipatieff. *J. Amer. chem. Soc.*, 1940, **62**, 178–180.—Acetylene and six alkylacetylenes are shown to undergo catalytic hydration when passed with steam through a heated tube containing a solid phosphoric-acid catalyst. E. H. W.

Analysis and Testing.

672.* Consideration of Methods of Testing Lubricants. G. B. Martinenghi. *Olii Minerali*, 1940, **20** (1), 1–3.—A brief consideration of the A.S.T.M. method for determination of saponifiable matter in lubricating greases is made, pointing out the inconvenience, and lack of clarity of the details of the method. The methods employed by the R. Experimental Station for Oils and Fats, Milan, are described, the method being varied according to whether the nature of the saponifiable matter is or is not known. In the former case the determination is rapidly and accurately effected volumetrically, whilst in the latter case the saponifiable material is determined by weighing the sodium soap. This method takes the possible presence of free acids into consideration. A note concerning the estimation of saponifiable matter in lubricating oil is included, and it is claimed that 0·5% of saponifiable matter can be detected. P. G.

673.* Flow Characteristics of Lime-Base Greases. J. F. T. Blott and D. L. Samuel. *Industr. Engng Chem.*, 1940, **32**, 68.—The determination of the absolute viscosities at 25° C. of several lime-base greases in a capillary viscometer under shearing stresses up to 6000 dynes/cm.^{2} has shown that the viscosity of the oil base is the main factor in controlling the viscosity of the grease at shearing stresses considerably greater than the yield value. Empirical measurements of the flow of these greases at high shear stresses (10^6 dynes/cm.^{2}) confirm this observation. Approximate determinations of the shearing stress at the yield point have been made by means of a concentric-cylinder torsion viscometer, and it appears probable that the soap content of the grease controls the magnitude of the yield value. J. W. H.

674.* Viscosity Index of Lubricating Oils. E. W. Dean, A. D. Bauer, and J. H. Berglund. *Industr. Engng Chem.*, 1940, **32**, 102.—The equations on which the Dean and Davis viscosity-index scale are founded, and the Davis, Lepeyrouse, and Dean subsequent modifications, are reviewed. The present paper extends the former work at viscosities below 50 sec. Saybolt at 210° F., by experimental determination of the relationship between L and H (the basic zero and 100 V.I. constants representing viscosities at 100° F. of hypothetical oils having the same viscosities at 210° F. as the oil under examination). At the lower viscosities the authors have considered it essential to work in terms of the kinematic unit, and the new data presented cover the range of 2·0–4·2 centistokes at 210° F. With this extension the viscosity-index scale can now be applied to all ordinary lubricating oils. This extension is admittedly arbitrary, as were the constants for the higher range, but it is demonstrated that the use of the new values permits viscosity indices to be obtained for light oils which correspond closely to those of more viscous products refined by the same processes from the same stocks. Specimens of nomograms and charts facilitating the estimation of viscosity indices are given, with the address from which complete sets of the charts and tables may be obtained. J. W. H.

675.* Researches on an Absolute System of Viscosity and Viscosity Index. M. G. Hugel and M. L. Clairlois. *Ann. Off. Combust. liq.*, March–April 1939 (2), 235.—By mathematical consideration of existing viscosity equations a system is arrived at which allows the representation of all viscosity temperature curves. It is considered that the general equation of viscosity curves is

$$\eta = Ae^{\frac{2{\cdot}303\,c}{T-b}}$$

and that Drucher's law is only a special case where $b = 0$. The application of the derived mathematical form is illustrated by examples which include naphthenic, paraffinic, and tar oils.

In the second part a mathematical definition of absolute viscosity index is given, and is illustrated in graphs comparing calculated and practical values. A general equation for this is also given. H. L. W.

676.* Comparison of Logarithmic Formulae Linking Viscosities Linearly with Temperature. G. Juge–Boirard. *Ann. Off. Combust liq.*, March–April 1939 (2), 253.—The author proposes the formula $\eta^t = k(t + c)^a$ or $\log \eta^t = \log k + a \log (t + c)$ for viscosity temperature relations. This formula is compared and contrasted mathematically with the Walther—A.S.T.M. equation. Some doubt is thrown on the value 0·8 in the latter formula, and the value given by other workers is quoted.

Values obtained experimentally with a number of liquids are compared with those calculated by the Walther and the authors' formula. Although neither of the equations is in exact agreement with the experimental values, it is shown that the formula proposed gives closer agreement than that of Walther. H. L. W.

677.* Improved Sight Gauge for A.S.T.M. Tests for Burning Quality of Kerosine Oils. F. H. N. Waite and M. M. Rhodes. *A.S.T.M. Bull.*, 1940, **102**, 19–20.—Details are given of a gauge for measurement of flame dimensions in the kerosine burning test. The gauge consists of a tapered metal box with an eyepiece at the small end, a transparent glass plate having a series of vertical and horizontal graduations at the wide end, and two vanes extending 4½ in. beyond the glass plate. The gauge is mounted on an upright metal stand, having a friction clamp to facilitate vertical adjustment, and in operation is placed in front of the lamp with the vanes on either side of the chimney, so that the vertical shadow cast by the lamp falls exactly on a vertical line on each vane. Lateral and vertical adjustments are made to bring the scale to the proper position for measuring the dimensions of the flame. A. O.

678. Amperometric (Polarometric) Titrations. 1. Amperometric Titration of Lead with Dichromate or Chromate. I. M. Kolthoff and Yu-Djai Pan. *J. Amer. chem. Soc.*, 1939, **61**, 3402–3409.—An electrometric method of titration, called "amperometric titration" by the authors, is discussed historically, and with particular reference to the determination of lead. The current which passes between two suitable electrodes at a constant e.m.f. is measured; depending on the conditions, one or both electrodes are placed in the titration medium. The end-point is found as the point of intersection of two lines giving the change of the current before and after the equivalence point. In this work the authors show that an accurate and rapid titration of lead with dichromate or chromate can be made using the dropping mercury electrode as an indicator electrode without applying an external e.m.f., a high degree of accuracy being obtained even on a 0·001-*M* solution of lead. When barium is present in large quantities, lead can be titrated amperometrically by acidifying slightly with perchloric acid. An attempt to determine both lead and barium in one titration by fractional precipitation with potassium chromate was not successful owing to co-precipitation of barium chromate with lead chromate. R. D. S.

679.* Gum Formation in Cracked Gasolines. D. L. Yabroff and E. L. Walters. *Industr. Engng Chem.*, 1940 (32) 1, 83.—The formation of gum during the induction period of cracked gasolines has been found to proceed according to an exponential law at elevated temperatures. The time required for a gasoline to attain a gum content of 10 mg. per 100 ml. (designated as the 10 mg. gum time) is affected by temperature and oxygen pressure in essentially the same manner as in the induction period.

The effect of temperature on the 10-mg. gum time may be expressed by the equation

$$t_g = Ae^{B/T}.$$

where t_g = 10-mg. gum time in hours.
T = absolute temperature, °F.
A, B = constants depending on the gasoline under test.

The 10-mg. gum time may therefore be extrapolated to storage conditions, and thus allow a prediction of the storage life of the gasoline. H. E. T.

See also Abstract No. 621.

Lubricants and Lubrication.

680.* Utilization of Mineral Oils for the Lubrication of Aeroplane Engines. E. Thomas. *Bull. Ass. franc. Tech. Petrol.*, 15.1.40 (1), 29.—Although castor oil has been largely replaced by mineral oils an account of its gumming tendency, it is still used to a limited extent on account of its excellent lubricating qualities. The instability of castor has led to researches for a "stabilized" castor, researches which have yet to reach a satisfactory conclusion. The author stresses the importance of thoroughly cleaning an engine when changing from castor to a mineral oil.

The difficulties in manufacturing a satisfactory mineral aviation oil are great, and it must not be thought that solvent extraction is a universal panacea. A typical refining process is outlined and the types of addition agents are enumerated. In describing the characteristics required of mineral oils, the French specification, including the Dixmiar, Damian oxidation test, is mentioned. Curves are given showing the increase in viscosity, Conradson carbon, and insolubles in petroleum ether found in a 40-hr. test of a 450-h.p. engine with and without changes of oil at intervals. A comparison is made with these results and those obtained in the air specification 1093 oxidation test. It is concluded that in the engine the introduction of extraneous matter appears more important, and that the acidity is far removed from the 2·2 value found in the artificial ageing test. Formation of chloroform insolubles is important in the engine, whilst in the oxidation test there are none.

The deposits in the engine might be formed from the burning of oil in hot places or from incomplete combustion of the fuel. These deposits are suspended in the oil and are deposited in various places; this is shown by the analyses, which are similar to those obtained from insolubles from used oils. Tests of carbonization in the absence of air by the Damian method prove that insolubles in $CHCl_3$ do not begin to form until 340° C.—the temperature at which oils begin to crack.

Bearing corrosion can be remedied by suitable choice of bearing metals, improved cooling of the oil, and the use of corrosion inhibitors. It is concluded that the task of refiners is immense: they must satisfy specifications, the tests of which are frequently quite arbitrary, as well as ensure that the oils behave well in practice. H. L. W.

681. Hypoid Lubricants for Truck Axles. Anon. *Automotive Ind.*, 15.1.40, 82 (2), 74.—It has been found that some types of hypoid lubricant are unsatisfactory at low speeds and heavy loads. Wear tests on the Almen machine differentiate between the so-called active and mild E.P. lubricants, the former giving a much higher temperature and rate of wear.

The Chrysler Corporation now uses two classifications for hypoid lubricants, truck duty, and passenger-car duty. An outline of the testing procedure used by the above Corporation is given, and it is concluded that two sets of hypoid lubricants will become general: the truck duty, a non-active (to copper) product, and the generally accepted active passenger-car lubricant. H. L. W.

682. Cutting Fluids. J. Geschelin. *Automotive Ind.*, 15.10.39, 81 (8), 424.—An Independent Research Committee on cutting fluids has been formed with the object of studying the use of cutting oils and to give reports of use to production men and users. Some simplification can be achieved by limiting the number of types used in a given shop to a minimum. An example is the Spicer Co., who use only one grade of soluble and neat cutting-oil, with the small exception of a special oil for the Gleasons. Central supply systems aid in this simplification, but where fine grinding is required, filters may be necessary.

It is safe to say that many improvements in machinery have been due to the availability of suitable cutting-fluids. An outline is given of the general requirements of cutting-fluids and of the types available. New developments—*e.g.*, sulphurized soluble oils—are mentioned; whilst an interesting example of use of neat cutting-oil with special wheels for grinding is given. The elimination of occupational diseases by keeping the cutting-fluid clean and use of suitable antiseptic is stressed.

A bibliography on cutting-fluids is given as well as the names of the chief suppliers (American) and the grades and types they market. H. L. W.

683.* Characteristics Proposed by the R. Experimental Station for Oils and Fats, Milan. Anon. *Olii Minerali*, 1939, 19 (11–12), 156–158, 168–172.—The specifications proposed by the R. Experimental Station in agreement with the Chemical Products Manufacturers' Federation, covering all petroleum products for the Italian market, are listed. P. G.

Asphalt and Bitumen.

684.* Flow Properties of Asphalts and their Measurement by the Penetrometer. C. Mack. *J. Soc. Chem. Ind.*, 1939, 58, 306–310.—Since asphalts are sols of asphaltenes in a mixture of asphaltic resins and oily constituents, this solubility determines their flow properties, which are defined by either viscous or plastic flow, thixotropy, and elasticity. After discussion of previous work on the problem, the author shows that plotting the logarithm of penetration against the logarithm of time gives a straight line, and thus the depth of penetration can be expressed as a function of time. One constant, " c," of this equation is found to be constant (0·54) for viscous flow, but not for plastic flow. By expressing the viscosity of a plastic asphalt as a function of the rate of shear, it was deduced that " c " served as a numerical value for the flow properties of these asphalts. It is very difficult to determine the yield value from the logarithm of the rate of penetration and the logarithm of penetration, since the necessary penetrations are usually outside the range of the penetrometer needle. If the asphalt has a definite yield value it will not flow from a penetration-can placed on edge. Most paving-asphalts, irrespective of their flow properties, have no yield value. The difference in the value of " c," when the penetration is taken before and after ageing, expresses the degree of thixotropy, if present. The determination of the elasticity by means of the " c " value of successive penetrations is mainly qualitative. A knowledge of the value of " c " also gives a complete picture of the flow properties, and ductility measurements then become unnecessary, and with its aid the consistency of asphalts can be expressed as the time required for a given penetration. It is pointed out that the viscosity/temperature coefficient remains fairly constant for a viscous asphalt, but for a plastic asphalt increases with decreasing temperature. H. G. W.

685.* Report of the Institution for Experimental Work on Roads of the C.T.I. and R.A.C.I. for 1939. R. Ariano. *Le Strade*, 1940, **22** (1), Ricerche Studi, 3–20.—The activities of the above laboratory during 1939 and conclusions reached therefrom are described.

Asphalts and Asphalt Emulsions.—The relationship between penetration and softening point was confirmed, and was found to be the same for asphaltic bitumen after emulsification. Ductility, on the other hand, does not show any relationship to these properties, and was found to be reduced on solution of asphaltic bitumen. Ductility was also found to be dependent on the paraffin content of the bitumen. It is suggested that some other test should replace the ductility test for natural asphalts or asphalts containing fillers.

Asphaltic bitumens recovered from emulsion were generally found to have penetrations higher than 150.

Asphalt Powder.—The determination of paraffin content of the extracted bitumen by the method at present used in Italy was not possible in many cases, owing to the high sulphur content. Adhesion of the extracted bitumen to stone was very good, and was believed to be probably better than for petroleum bitumen. Asphaltene determinations are made on the extracted bitumens, since this, together with sulphur content and granulometric examination, is a guide to the source of the rock-asphalt.

An attempt was made to reduce the time required to determine the bitumen content of asphalt powder, from 7 days to 24 hr., by using different containers for sedimentation.

Asphaltic and Tar Oils.—The distillation test, which is at present the principal test for these oils, gives comparative results only. An attempt was made to improve this test by substituting an electric heater instead of gas flame, or by employing the A.S.T.M. method, and results are compared. The necessity for replacing this test by some other more accurate method in order to obtain better reproducibility is pointed out.

Adhesion Tests.—Although recently adopted, using a device to measure the adhesion of binders to stone when undergoing a stress direct and normal to the contact surface, the test appears to give results corresponding to behaviour in actual service. Emulsifying agents increase the adhesion to stone of bitumen from emulsions, but the bitumen is more readily affected by water. Special precautions are necessary in testing the adhesion of oil–asphalt powder mixtures. P. G.

686.* Tar Emulsions. A. Di Renzo. *Le Strade*, 1940, **22** (1), 4–13.—The author briefly reviews the development and manufacture of tar emulsions and considers the properties of emulsions produced in Italy and other countries. Emulsions of tar-asphaltic bitumen mixtures, prepared with 1·3–2% of fatty acids, wool fat, fish oil, or coconut fat derivatives, are more frequently used than emulsions of tar alone. Methods of manufacture are briefly described and specifications for various grades of tar given. The specifications and methods of testing issued by the B.S.I. in the United Kingdom and by the D.I.N. in Germany are compared with those employed by the laboratory of the Milan municipality. P. G.

687.* Use of Asphalt Rock Powder in Liquid Mixtures. A. Berti. *Le Strade*, 1940, **22** (2), 53–60.—The first experimental application of liquid mixtures of asphaltic rock-dusts for surface treatments, using tar-oil and regular tar as vehicle, are described.

The experiments made to ascertain the behaviour of the compounded binders with regard to traffic and inherent road conditions were carried out on two roads of intense traffic.

The condition of the roads at the time of application, materials employed, treating temperatures, and treatments are described. The organization of the experimental work and a detailed summary of materials, labour, and costs are included.

In conclusion, it is stated that the described type of road-paving is superior to that obtained with tar-emulsions, and that it compares favourably even with asphalt pavings. P. G.

688.* Evaluation of Fillers for Tar and other Bituminous Surfacings. J. G. Mitchell and A. R. Lee. *J. Soc. chem. Ind.*, 1939, **58**, 299–306.—It is pointed out that fillers have been used for some considerable time, but specifications are still generally ambiguous, and this paper shows how the choice and use of the filler can be placed on a quantitative basis. From a review of the previous literature it was concluded that little or no quantitative use could be made of the detailed grading analysis of a filler with respect to the mechanical properties of a bituminous road mixture. It is now shown, however, that the bulk density of a filler which has been allowed to settle in benzene or other suitable liquid under standardized conditions gives a quantitative measure for proportioning it as a constituent of a bituminous surfacing. It is pointed out that differences between the properties of different fillers of the same kind may be as great as the differences between different types of fillers. To measure the bulk density, the filler is suspended in the given liquid, boiled while being stirred with a copper rod to facilitate escape of air and then allowed to settle. After 24 hr. it is gently disturbed with a wire to reduce segregation. The bulk density is a result of the wetting properties of the liquid, and the grading and geometrical properties of the filler particles, each of which is apparently surrounded by an envelope of liquid. From investigations of the colour change of tar solutions before and after contact with fillers, it was concluded that the latter adsorbed certain of the tar constituents from solution, limestone and slate being most effective. These constituents appear to be mainly resinous, and the adsorption is a second-order effect. Adding filler to tar gives an increase in viscosity, but different fillers give different results. It has been shown experimentally, however, that the addition of the same bulk volume of different fillers (measured by settling in benzene) produces the same change in the viscosity of the binder. The mechanical properties of filler-binder mixtures show that there is an optimum filler-binder ratio to give a strong ductile material for each filler, and it has been shown that this optimum ratio for a given binder is proportional to the bulk densities of the fillers. It has also been shown that for any sand-filler–binder mix which contains its optimum binder content a minimum quantity of filler must be present to give maximum resistance to deformation. This quantity is determined simply by the bulk density and voids in the sand. Full-scale road experiments have shown that this bulk density is its most significant property, and that failure may easily occur through neglect to adjust the filler–binder ratio on this basis. The general conclusion is that existing specifications should contain a clause defining the relation between the bulk density of the filler and the binder content (tars and asphaltic bitumens). H. G. W.

Detonation and Engines.

689.* Tests on a Medium-compression Two-stroke Injection Engine. R. Düll and F. Zahren. *Automobil. Zeit.*, September 10, 1939, pp. 482–484.—The engine was a two-litre, single-cylinder, crankcase scavenge pump-engine with inlet ports and two exhaust-valves. The exhaust-valves were on opposite sides of the conical combustion space, with two sparking-plugs in between them. The injection-valve was in the centre of the head, and the inlet ports were arranged tangentially to induce swirl. The stroke/bore ratio was 1·91. Tests with a compression ratio of 6·2 showed that either petrol, benzol, or heavy oil could be used. With petrol or benzol, air regulation and external ignition had to be employed for part-load running, but with heavy oil, compression ignition took place without air regulation at all loads, although idling was not satisfactory. There was no knocking if the injection timing was adjusted correctly.

Spark ignition was generally necessary for starting. Further tests were made with heavy oil using compression ratios of 7·2 and 7·8, at speeds up to 1600 r.p.m., the mean piston speed then being 2200 ft. per min. The effect of exhaust pipe-length on power and fuel consumption was considerable at certain speeds, due to vibrations of the column of exhaust gas. This could be overcome by a pipe fixed in front of the intake-valve of the scavenge-pump, which had the effect of raising the volumetric efficiency. Under these conditions the load could be increased until the m.e.p. was 85 lb./sq. in. The maximum power developed was 36 b.h.p. at 1500 r.p.m. with a full-load fuel consumption of 0·49 lb./b.h.p.-hr. at speeds over 800 r.p.m. There was no knocking, in spite of a very rapid pressure rise to a maximum pressure of 850 lb./sq. in. The injection point varied with speed between 25° and 50° before t.d.c., and must be carefully controlled. Good slow running could only be obtained with the exhaust-valve opening 100° before b.d.c. and closing at b.d.c., and a compression ratio of 9·3. Good running at 250 r.p.m. was then obtained. H. R. M.

690.* Steam Turbines for Motor Vehicles. Anon. *Automobil. Zeit.*, September 10, 1939, pp. 485–486.—The Hüttner (German) rotary boiler turbine consists of a ring of U-tubes with radial arms. One arm of each tube opens into a collecting-ring containing water, whilst the other connects to a ring-shaped steam chamber. The arms on the steam-chamber side are heated by burners, and the steam generated passes through a ring of jets and impinges on the blades of a turbine disc. The reaction drives the boiler in the opposite direction to the turbine, and the action of the centrifugal force on the water compresses the steam until equilibrium is reached. After passing through the turbine, which may have several stages, the steam is condensed and again collects in the U-tubes.

If the feed-water is used in the condenser, it is preheated in its passage through the turbine to the boiler. Tests on a small model showed that the 0·077 lb. water which it contained was evaporated 700 times an hour. When idling, the pressure was 13 lb./sq. in. and the boiler speed 2,800 r.p.m., whilst at full load the pressure was 73 lb./sq. in., the boiler speed 5000 r.p.m., and the turbine speed 17,000 r.p.m. The boiler efficiency was 80% throughout the load range. For starting, the boiler must be turned at 1/10 the full-load speed. The starting time is 10 sec. The design of a multi-stage 100-kW. turbine is shown.

The Béchard (French) boiler consists of three or six hollow discs joined by short tubes, enclosing a shaft on which are mounted a similar number of thin discs which divide the hollow discs into two spaces. The feed-water enters the space at one end through the shaft, and the whole boiler is heated by gas or oil-burners. The steam passes out of the end of the boiler opposite to the feed through a ring of jets, and its reaction against the blades of a fixed turbine disc rotates the boiler. When the boiler has been running long enough to reach equilibrium, the water is heated in the first hollow disc, evaporated in the second, and superheated in the third. The feed-water and the burner are regulated according to the load. Tests on a boiler holding 0·21 cu. ft. of water showed that with a pressure of 440 lb./sq. in 50 h.p. was developed at a speed of 1800 r.p.m.

The Besler (American) boiler consists of a single spiral tube of Inconel. Water is fed in one end by a high-pressure pump, and leaves the other end in the form of superheated steam at 400° C. and 1300 lb./sq. in. pressure. It is heated by a thermostatically controlled oil-burner which is turned out if the steam exceeds the specified temperature and pressure, and electrically ignited when the pressure falls again. Trials on a boiler, coupled to a 600-h.p., 2-cylinder compound railway engine, showed that it took 4 min. to heat up before starting. H. R. M.

691.* Water Injection in Petrol and Hot-bulb Engines. W. Riedel. *Automobil. Zeit.*, January 25, 1940, pp. 25–35.—A Mercedes 1·7-litre car was driven at 90 km./hr. with varying amounts of cold water drawn in at the carburetter venturi. With small quantities no effect was observed, but fuel consumption increased when the volume of water exceeded 25% that of the fuel. Similar results were obtained in a 1·7 Adler Trumpf engine on the bench with a consistent increase in fuel consumption and decrease in output with increasing addition of cold water.

In another test, steam was introduced between the air-cleaner and carburetter of the Adler Trumpf engine. The adverse effect of steam was considerably greater than that of cold water. The reduction in power was mainly due to the displacement of part of the intake air by steam.

In Lanz two-stroke hot-bulb tractor engines operating on heavy fuels, water is added at the orifice of the open nozzle in order to eliminate knock and deposits. With an engine of 225- and 260- mm. bore and stroke, 6·9 : 1 C.R., running at 630 r.p.m. and developing 20 b.h.p., injection of 21·7% water reduced the wall temperature of the hot-bulb from 800 to 520° C., with 15% decrease in fuel consumption. With a C.R. of 10·75, at 630 r.p.m., the power output was limited to 32 h.p., due to knock, but could be raised to 48 h.p. when water was injected. L. R.

692.* Fuel Consumption (Extracted from Year Book of German Aeronautical Research. Air Ministry translation No. 945). F. A. F. Schmidt. *Auto. Engr*, 1940, **30**, No. 393, 20–22.—(1) *Theoretical Possibilities of Improving Fuel Consumptions.*—The possibility of improving fuel consumption by increase of compression ratio depends on the nature of the fuel utilized, as the upper limit to the compression ratio is governed by the phenomena of detonation and pre-ignition. Data are given showing the theoretical consumption and MEP as a function of the compression ratio calculated from data by Kuhl. It is clear that fuel economy can only be obtained by using weak mixtures at high compression ratios.

(2) *Improvement of the Relative Efficiency of Weak Mixtures by Early Ignition and Employment of Multiple Sparks.*—Curves are given showing the effect of ignition timing on power with excess air; the effect of excess air on power and consumption; the effect of multiple sparks with one or more plugs on power and consumption at varying mixture strengths.

The principal reason for drop in relative efficiency with weak mixtures is bad distribution. Suitable carburettor installation may improve matters to some extent, and further improvements are obtained if multiple sparks are employed. A combination of two plugs, one normal, and a second provided with series sparks, gave constant specific consumption over a range of weak mixtures; minimum consumption (with no misfiring) was obtained with 20% excess air.

(3) *Increase in Performance by Valve Overlap Accompanied by Supercharging.*—Data are presented showing the relation between boost pressure on consumption and IMEP. If appreciable valve overlap exists, it is possible to increase the charge weight still further by scavenging the clearance volume, and so increase power. Curves illustrating this and the influence of valve overlap on air consumption at varying speeds are given. C. H. S.

693.* Engine Combustion and Pressure Development. G. M. Rassweiler, L. Withrow, and W. Cornelius. *J. Soc. Aut. Engrs*, 1940, **46** (1), 25–48.—In an earlier paper (see Abstract No. 1177, 1938) the authors discussed methods for determining from the pressure-card the amount of charge that is burned at any time during an engine explosion. The study has been extended to various operating conditions, utilizing high-speed motion pictures of the flames, together with pressure records of the same explosions. The photographs show that the flame envelopes were generally not spherical in shape, and were more " ragged " with weak mixtures. Shifting the ignition point from the side to the centre of the combustion space advanced the time at which combustion ended and maximum pressure occurred; the maximum pressure also was increased. At part throttle the centre of volume of the inflamed charge was frequently at some distance from the spark gap. This is attributed to mass movements of the charge.

Some quantitative relationships between the fraction of charge burned and the pressure developed at any time during the explosion have been correlated with the experimental data obtained under various operating conditions. It is shown that the fractional volume and fractional mass of charge inflamed at any time may be calculated from the pressure-cards with an accuracy comparable with that of the experimental observations. K. A.

Economics and Statistics.

694. Petroleum Refineries, Including Cracking Plants, in the United States, January 1, 1939. G. R. Hopkins and E. W. Cochrane. U.S. Bureau of Mines, Information Circular 7091, October 1939.—While the number of completed refineries in the United

States declined in 1938, crude oil capacity materially increased, the figure on January 1, 1939, being 4,508,555 brl. Daily average crude runs in 1938 were 3,192,000 brl. Capacity of cracking units increased in 1938, and on January 1, 1939, was 877,347 brl. during 1938 the daily average production of cracked gasoline was 714,000 brl.; the Texas Gulf Coast showed the largest gain in active cracked gasoline capacity.

H. B. M.

695.* Report of the Department of Petroleum and Hydrocarbons, Venezuela. Minister of the Exchequer. *Revista de Fomento de Venezuela,* Special number, January to June 1939.—It has been decided to suspend the granting of new concessions for exploiting mineral-oil deposits, whilst the Government will study the geological and geophysical character of various zones which are expected to be petroleum-bearing. The ultimate aim of these investigations is to enable the Government to secure more profitable terms from future concessionaires. At the same time a more active refinery policy is being pursued. A contract has been signed with the Standard Oil Co. of Venezuela to build immediately a refinery capable of dealing with 2385 cubic metres of crude petroleum daily. Another concern,—the Caribbean Petroleum Co.—in association with the Venezuela Oil Development Co., has completed extensions at San Lorenzo, which will add 1600 cubic metres daily to the capacity of their existing refinery. A considerable number of concessions have been invalidated for a number of different reasons, and these will be brought in under the new scheme. There is to be a tightening up of the regulations permitting duty-free importation of certain articles by the exploiting companies.

H. I. L.

696.* Economic Aspects of Exploitation of Petroleum in Colombia E. Ospina Racines, *Revista de Fomento* (*Venezuela*), October 1939, **11** (17), 108–119.—Colombia, is from the geological, economic, and political standpoints, in a very favourable position for developing its output of petroleum. It now stands seventh on the list of world producers. In 1937 production amounted to 20,298,000 brl., whilst their home consumption was only 2,453,000 brl. The bed of the Magdalena River is at present the only producing area, whilst the bed of the Catatumbo is in active development and indicates a deposit of major importance. There are three other areas susceptible of development. Income is derived from royalties on oil exported and from taxes.

H. I. L.

BOOK REVIEWS

Finding and Producing Oil. Pp. 338. Prepared by Division of Production, American Petroleum Institute, Dallas, Texas. 1939. Price $2.00.

The American Petroleum Institute has rendered a great service to the Petroleum Industry by the publication of its first edition of "Finding and Producing Oil," a well-conceived and excellently produced volume, adequately provided with diagrams and plates.

One of its main objects is to indicate the vast amount of available literature on the subject. The reader is able to select a subject, study it through the media of the literature mentioned, and then (if need be) consult the firms intimately concerned with the operations of that particular section, without the necessity for consulting any other publications. In spite of omissions, a well-balanced bibliography has resulted. The promise to augment and revise various sections is to be applauded.

The publication is divided into fifteen sections, six of which are concerned with the finding and production of oil. These cover such operations as Geological Methods of Oil Exploration; Geophysical Methods; Methods of Drilling; Sampling, Coring and Bore-hole Surveying; Production Methods; Measuring, Sampling, and Testing Oil Products. These sections are sub-divided to deal with the necessary individual operations.

The remaining sections deal with such subjects as Voluntary Co-operative Activities; Vocational and Scholastic Training; Oil and Gas Conservation Laws; Producers of Oil; Drilling Contractors, etc. A number of these sections are of interest only to operators of the United States of America, but this fact in no way detracts from the value of the publication.

Little can be said of the subject-matter of the various sub-sections except that sufficient is quoted to explain the titles. The authors have done their work well, and are to be congratulated on having condensed their subject-matter to readable proportions without loss of explicitness.

"Finding and Producing Oil" should appeal to all interested in Petroleum Technology, and can be confidently recommended. L. V. W. Clark.

De La Carbonization Aux Carburants D'Aviation. Tome II. La Cokerie et l'Usine à Gas Modernes. By Charles Berthelot. Preface by G. Claude. Pp. xx + 514, with 182 figures in text. Published by Dunod, 92 Rue Bonaparte, Paris, 1940.

This is the second volume of three by the same author on the subject of "From Carbonization to Aviation Spirits." Volume I of the series dealt with the subject of Petrol and its substitutes, and has been reviewed in the July, 1939, and March, 1940 numbers of this *Journal*.

The volume under review is devoted entirely to coke-ovens and modern gas-works, whilst Volume 3, which is in preparation, will deal with carbonization as a means of gas production and with the utilization of coke-oven gases as a source of synthetic chemical products. The book is divided into fifteen sections, each of which is sub-divided, and a useful summary and conclusion are included in each sub-section. It is only possible to mention a few of the topics discussed in the book. The author begins with a review of the methods of preparing and blending coal for carbonization at low and at high temperatures, including coal-cleaning and washing plants.

A description is given of the modern coke-ovens in operation in different countries for the production of metallurgical coke. The author states that the most up-to-date are to be found in the Ruhr, in Belgium, in Holland, and in England. A whole chapter is devoted to the development of the coke-ovens in the Ruhr in October 1938. The industrial application of coke-oven gas in Germany is described, including its use in the Fischer–Tropsch synthetic process for the production of liquid motor fuels and of soap by saponification of the fatty acids derived from the wax.

The modern coke-ovens of Germany, Holland, Belgium, and England are described in detail, including dimensions, costs and yields of coke, gas, and by-products.

Technical details are given of the heat balance of coke-ovens and the quantity of heat required for the carbonization of coal.

Other sections of the book deal with refractory materials and the many other items required in the construction of coke-ovens, including the machines for charging and discharging and the instruments for recording temperatures and gas pressures.

Since the use of gas producers enables low-quality fuels to be utilized for heating modern coke-ovens, a description is given of a number of different kinds of gas-producers used in the industry.

The recovery of tar (and of tar fog), and of numerous by-products, is treated in some detail. There is a short survey of the modern methods of tar distillation and refining for the production of pure products such as naphthalene, etc. The manufacture of sulphate of ammonia is briefly described.

In view of the increasing attention it is now receiving, about one-seventh of the whole book is devoted to modern methods of benzol recovery and its purification.

The principal methods for the recovery of elemental sulphur from coke-oven gases are described, and it is stated that in 1937 Germany obtained 120,000 tons of sulphur in this way from coke-oven gas, corresponding to about 500,000 tons of sulphuric acid.

The treatment of the effluents to render them innocuous is not overlooked.

The preparation of the coke for domestic and other markets, including the semi-coke (Carbolux) produced at les Mines de Bruay by the medium-temperature carbonization of coal, is fully described. A part of the book deals with the Woodhall-Duckham and Glover-West continuous vertical ovens and steam injection, about which the author appears to be well informed from first-hand information.

A description of the Otto horizontal chamber-type of coke-oven as used in the gas-works of Rotterdam is also included.

In a short chapter, Monsieur Berthelot discusses ways and means of eliminating the poisonous carbon monoxide from town's gas, resulting from the addition of water gas.

The book concludes with an urgent plea from the author for the modernization of the coking industries, and for more and more economy in both the construction and operation of coke-ovens—an economy which, he says, can only be acquired by the application of science and ceaseless research.

Like its predecessor, the volume under review is well printed in clear type, written in an interesting style, and is remarkably free from mistakes. There is a comprehensive table of contents at the end. The addition of an index would have enhanced the value of the book as a work of reference. W. H. CADMAN.

BOOK RECEIVED

1939 Book of A.S.T.M. Standards. Part II. Pp. xxvii + 1217. **Part III.** Pp. xx + 1175. American Society for Testing Materials, 260, South Broad Street, Philadelphia, Pa. Price $15 for any two parts.

The Book of A.S.T.M. Standards is now issued in three parts, of which Parts II and III are of particular interest to the petroleum industry, since the former includes methods of testing and specifications of bituminous road, waterproofing, and roofing materials, whilst the latter includes methods of testing petroleum products and specifications for fuel oils, gasoline, Stoddard solvent, and petroleum spirit. Methods of testing and specifications which have been adopted as standard appear in the front of each part, whilst tentative standards are at the end. A number of revisions have been made, and while many are of a minor character or of an editorial nature, the following should be noted.

In the ductility test the period of cooling of the specimen in air prior to immersion in the water-bath is now specified as 30 min. Changes have been made in connection with the ventilation of the loss on heating oven.

In the Reid vapour-pressure test it is now specified that the internal chamber of the connection between the air-chamber and the pressure-gauge and of the passage-way from the Bourdon tube, of the pressure-gauge, to atmosphere shall not be less than 3/16 in.

The use of any form of capillary-tube viscometer for determination of kinematic viscosity is now permitted, provided the apparatus is capable of measuring viscosity with an error not greater than 0·2%. Pure distilled water has been adopted as the primary viscosity standard, but oil samples obtainable from the A.P.I. or National Bureau of Standards may be used as secondary standards.

In the kerosine burning test it is now specified that any change in the dimensions of the flame at the end of the test shall be recorded. Any deposit on the chimney shall be reported as light, medium, or heavy, and the colour of the deposit described. The tensile strength of the wick fibre as determined by pulling the charred portion with the fingers shall be qualitatively expressed as uninjured, weakened, or destroyed.

The Low-Cloud and Pour-Point thermometer is now calibrated for 3-in. instead of 4½-in. immersion.

In addition to the above revisions, three new tentative methods of test are included; these are the Test for Carbon Residue by the Ramsbottom method, Test for Gum Stability of Gasoline and Test for Tetraethyl Lead in Gasoline. A. O.

INSTITUTE NOTES.

April 1940.

CANDIDATES FOR ADMISSION.

The following have applied for admission to the Institute or transfer to another grade of membership, and in accordance with the By-laws the proposals will not be considered until the lapse of at least one month subsequent to the issue of this *Journal*, during which any Fellow, Member or Associate Member may communicate by letter to the Secretary, for the confidential information of the Council, any particulars he may possess respecting the qualifications or suitability of any candidate.

The object of this information is to assist the Council in grading candidates according to the class of membership.

The names of the candidate's proposer and seconder are given in parentheses.

ALLEN, Eric Edgerton, Engineer, The Bungalow, Bodorgan, Anglesey, North Wales. (*J. Cuthill ; E. G. Thorn.*)
ALLEN, Sydney Hugh, Engineer (*Valvoline Oil Co.*), 65, Cookridge Lane, Horsforth, Leeds. (*J. M. Marshall ; W. H. Goddard.*)
DOUGLAS, Robert Tertius, Engineer (*Lobitos Oilfields Ltd.*), Highbury, Vale Road, Ellesmere Port. (*D. M. Glendinning ; J. C. Wood-Mallock.*)
DUCE, Richard George, Physicist (*Asiatic Petroleum Co. Ltd.*), 8, Philbeach Gardens, London, S.W. 5. (*J. Kewley ; W. W. Goulston.*)
HUNTER, Thomas Girvan, Lecturer (*Birmingham University*), 130, Hanging Lane, Northfield, Birmingham, 31. (*A. W. Nash ; A. E. Dunstan.*) (*Transfer to Fellow.*)
PYMAN, Lawrence Lee, R.A.F., c/o R.A.F. College, Cranwell, Lincs.
THOMSON, John Rennet, Engineer, Manchester Oil Refinery, Twining Road, Barton, Manchester. (*E. J. Dunstan ; V. M. Farrant.*)
YONGE, Dudley Arthur, Chemist (*Shell Refining & Marketing Co.*), Ince Hall, Ince, Chester. (*E. LeQ. Herbert ; J. A. Oriel.*)

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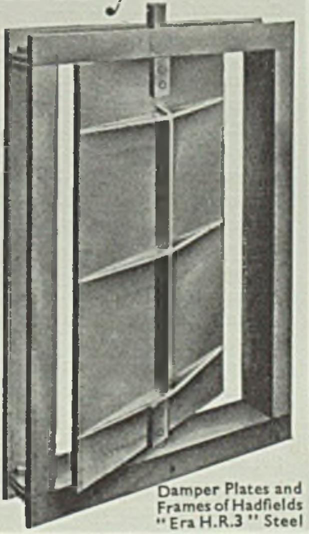

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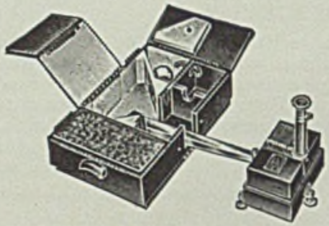

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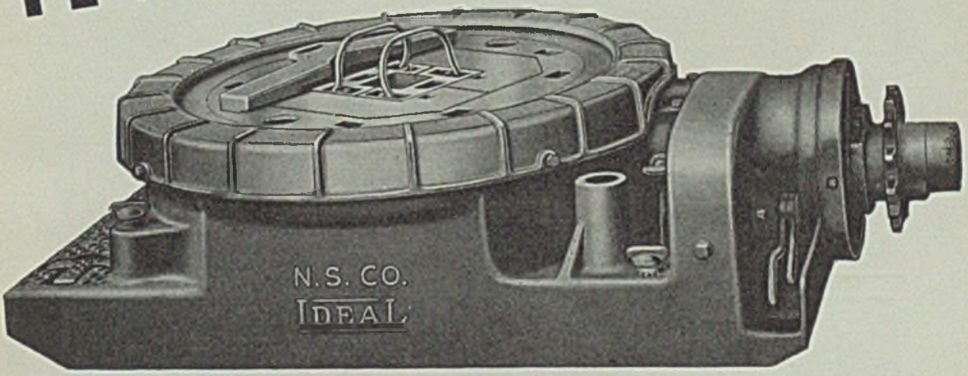

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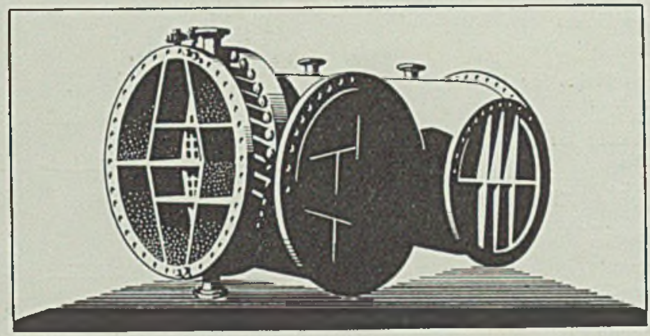

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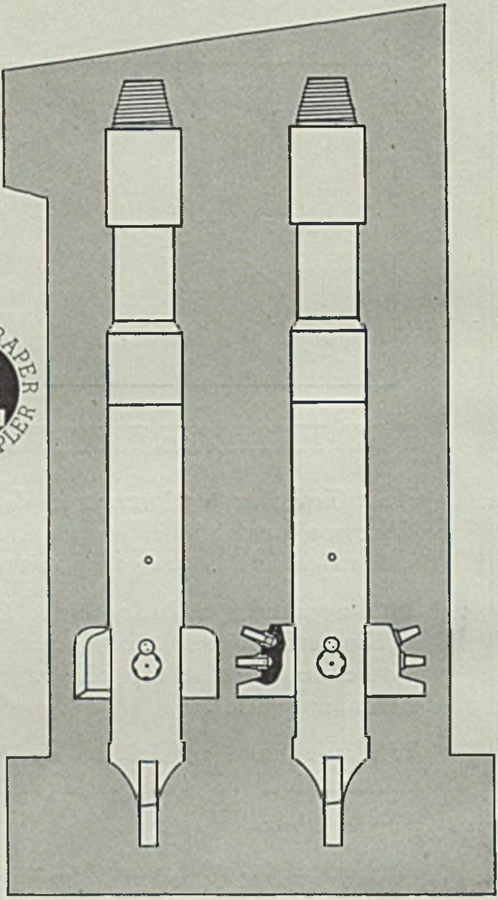

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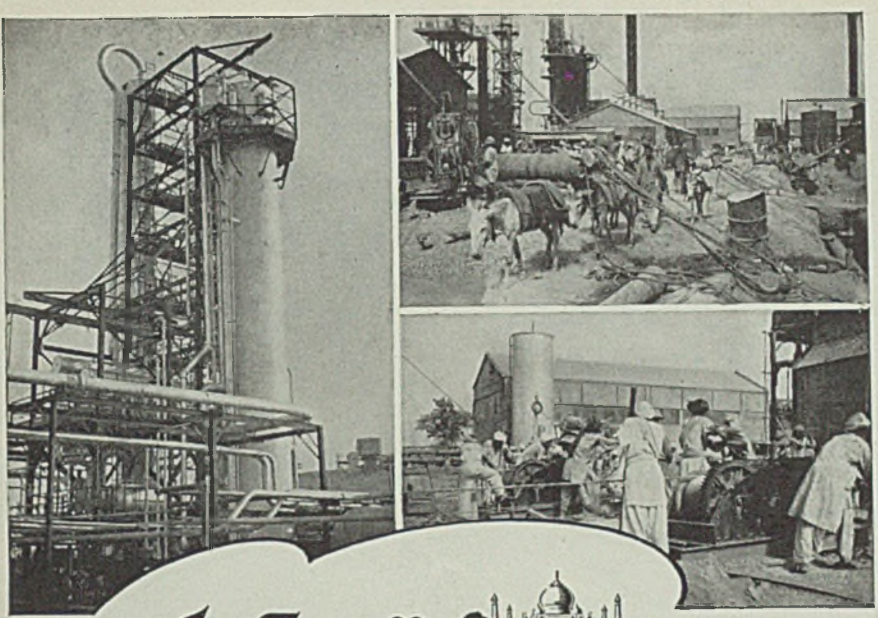

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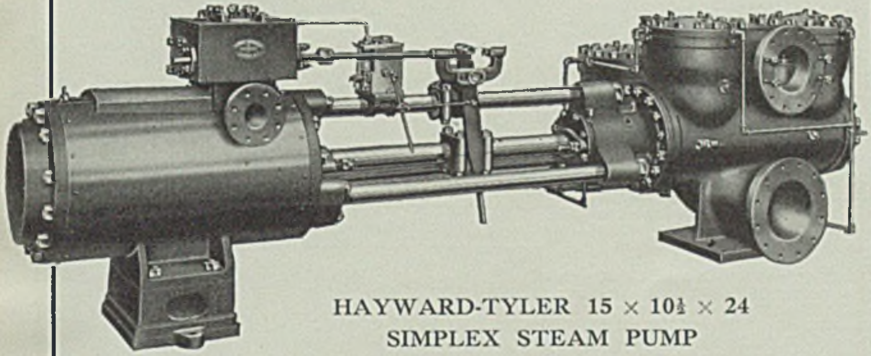

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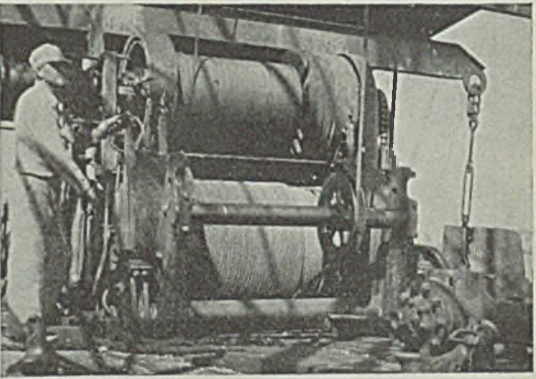

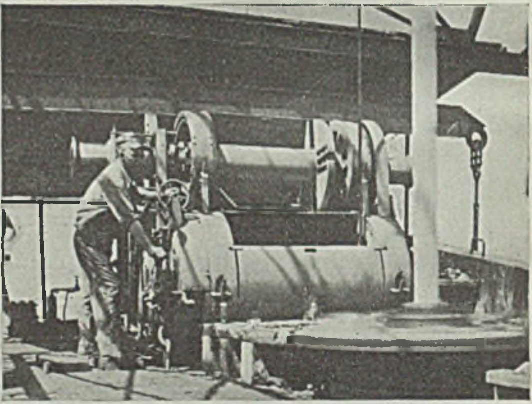

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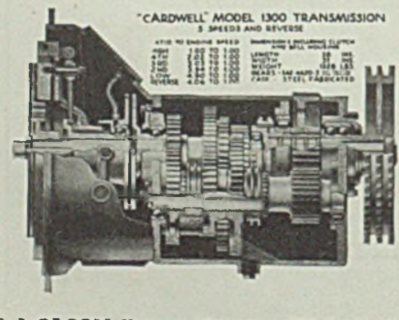

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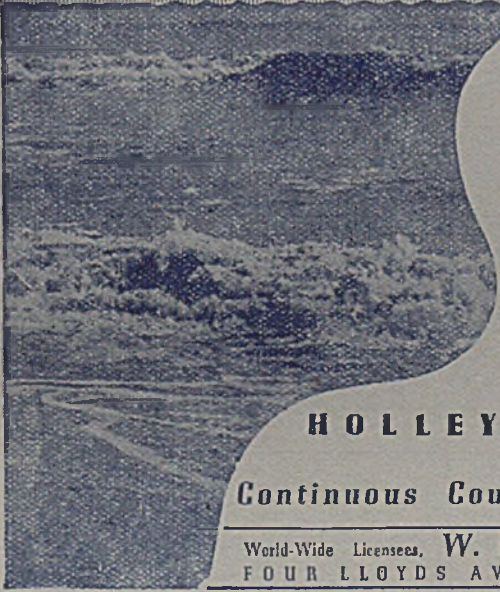

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