

LORD CADMAN OF SILVERDALE. (Died 31st May, 1941.)

THE LATE LORD CADMAN.

MEMBERS of the Institute will have learned with deep regret of the death on 31st May, 1941, of the Rt. Hon. Lord Cadman of Silverdale, G.C.M.G., D.Sc., F.R.S. Lord Cadman was twice President of the Institute, in 1916–17 and in 1935–37 respectively.

A tribute to his memory was paid by the members in London at a General Meeting held on 10th June, when the following Resolution was observed by all members standing in silence :—

"The Institute of Petroleum has sustained a serious loss by the death of Lord Cadman and we, the members of the Institute, wish to record in our Proceedings our appreciation of his many qualities.

"John Cadman was a man of wide culture and great ability, and his experience and sound judgement led him to take a broad view on all matters of policy connected with this Institute.

"It was always easy to approach Lord Cadman on any problem, for he was invariably courteous and helpful; and no trouble was too great for him in any matter which concerned the welfare of the Institute of Petroleum or its members.

"Lord Cadman reached the great position he held by his talent and ability, but with these qualities were joined a charm of manner which endeared him to those who were so fortunate as to enjoy his friendship.

"Our deepest sympathy is extended to Lady Cadman and the members of his family."

At the Memorial Service held at Westminster Abbey on 18th June the Institute was represented by the President.

It is intended to publish in a future *Journal* an account of Lord Cadman's long and brilliant career and his association with the petroleum industry and the Institute. In the meantime, the Honorary Editor has received the following tributes:

From The President, Professor A. W. Nash.

The death of Lord Cadman came as a great shock to those who knew him well and to those whom he had befriended, for he made friends easily in every walk of life, from the exalted to the most humble. Indeed, the great charm of his nature was that he was the same John Cadman to all, no matter what their station.

The writer had many opportunities of meeting Lord Cadman in widely different circumstances, and no matter whether it was amongst Government officials, scientists, colliery men, oil men, or business men, his analytical mind always showed to advantage, particularly when difficulties presented themselves.

There can be no doubt that he owed much of his success in life to that abounding energy which he displayed in anything he undertook, and the old proverb, "if you want work done, go to the man who is already fully occupied," was well exemplified by him.

John Cadman had many friends, but I cannot recall that he had a single enemy during the long period I knew him, for although he was never afraid to doubt, he always retained the disposition to believe.

Lord Cadman had a catholicity of thought and vision which showed great depth of mind and learning, and it is given to very few indeed to find success first as a Government Administrator, then as a University Professor, and finally as a leader of industry, as he did. In this latter respect he won admiration of men of science for his unceasing advocacy of the application of science to industry, and his reward was to be found in the success of the Sunbury Research Station, for the creation of which he was largely responsible.

By the old students of the Mining Department of the University of Birmingham Lord Cadman will be remembered with respect and gratitude for his kindly interest in their welfare. This was proved by the way in which they used to gather at the Annual Dinners of the University Mining Society when it was known that he would be present.

Of the many good traits in John Cadman's character, the one which most impressed itself upon the writer was the fact that he always respected the considered opinion of others even although it might clash with his own. A true sign of greatness.

A distinguished character, which held the admiration, esteem and regard of all who knew him, has passed on, but John Cadman's engaging personality will remain with us all so long as memory survives.

From Sir Thomas H. Holland, K.C.S.I., K.C.I.E., F.R.S.

Professor John Cadman was one of the group of twenty-nine, described in the original Articles of Association, dated 8th April 1914, as "the first Members of the Institution"; and in technical qualifications he was the only one among us who could be regarded in the complete sense as a "petroleum technologist". Quite appropriately therefore, he was chosen at the annual meeting in 1916 to follow the Founder as our second President. But he was far more than a technologist : on his broad technical foundation he qualified to succeed Lord Greenway as Chairman of the Anglo-Persian Oil Company, and thereafter added strength with symmetry to a great commercial industry by establishing within its structure a research organisation which has contributed substantially to the body of pure science in the related branches of chemistry, physics, geology and geophysics.

Lord Cadman's success in developing the Company was due also to his ability to look at the growing structure from outside, and so to see the parts in true perspective; to attract the best among specialist workers; to give them freedom of action and then generous appreciation of their efforts. And these measures, designed to secure the efficient health of the machine within, obtained their commercial value because of his wise "foreign" policy—his generous regard for the rights of competitors and his well-known loyalty to understandings with them. He, more than any single person, was instrumental in abolishing the "aggressive" commercial policy to which, during the earlier years of this century, some of the larger oil organisations tended, for he recognised how seriously this would lead ultimately to the disadvantage of all of them, by failure to apply technological science to their full development of the oilfield resources. With all his heavy responsibilities outside, Lord Cadman found time to lend his unusual abilities and sane judgment to the smaller affairs of the Institute, after as well as during his term of office as President. All who worked with him from our foundation, twenty-seven years ago, must feel with his death that we have lost a very valuable and trusted personal friend. Probably my contact with him goes back further than that of any other member, except Mr. Cunningham Craig; for he was specially helpful to me as a member of the Royal Commission on Navy Fuel before the last war; that was after and largely because of the warm discussion which we had had about the suitability of petroleum technology for a university degree course-a discussion in which subsequent experience showed his judgment to be the sounder of the two ! His activities were so varied that it will be difficult to summarise the many ways in which he contributed to the healthy growth of the oil industry-its bearing on education; its reaction on science and technology; its relation to other fuel industries; its national and even international value; its support of this Institute.

From Sir William Fraser, C.B.E.

I began a quarter of a century's close association with Lord Cadman in 1916. He was then about to relinquish his work in connection with gas warfare and to devote himself to petroleum. Commencing by directing the Petroleum Executive, he was to proceed to the Chairmanship of the Inter-Allied Petroleum Council, the Board of Anglo-Iranian Oil Company, the Chairmanship of that Company and the host of other activities which brought him fame. He was then Professor John Cadman, and had not yet received the many honours which subsequently rewarded his work and character. Yet, when numerous distinctions had fallen to him and he had become a figure of international repute, he remained essentially the same John Cadman that he was when I first came into close touch with him. His character was unspoiled, his charm of manner never left him, his kindliness and consideration were constant. He was not "all things to all men," but one man—and that a very human one—to all.

John Cadman entered the world of petroleum at one of its most critical and momentous periods. After the war of 1914–1918, the industry was on the threshold of tremendous developments. The mass-produced motor car, the aeroplane, the use of oil as ships' bunkers, the diesel engine on land and in ships were each to make demands on the petroleum industry. Science was to revolutionize the search for new fields, the drilling of wells and the entire technique of petroleum refining. Vast new fields were to be discovered to falsify prophecies of early exhaustion of reserves of crude. The ruthless competitive methods of pre-war days had, if the industry was to develop sanely and without waste, to be replaced by the guiding principle of co-operation.

All this, John Cadman foresaw in that wide vision which so distinguished him; and he shaped his efforts and those of the Company to further these THE

aims. He was amongst the leading exponents of two courses of action for the petroleum industry—the application of science to all its operations and the development of a co-operative spirit among all the individuals and organizations, of whatever nationality, having influence in its control.

The measure of success which, together with others of a like kind, he achieved, was amply demonstrated during the years when potential production outstripped all possible demand and when production let loose would have put an end to orderly development, to say nothing of ruining thousands of the smaller participants in the industry, as well as some of the larger, and leaving the world the poorer by the dissipation of an irreplaceable natural asset.

To John Cadman the potentialities of science were limitless. He never looked merely one or two years ahead; he was not satisfied with a small measure of progress. He had his mind always on an ideal; and although he welcomed any progress towards it, he never rested content, but regarded the completion of one stage solely as a stimulus to start on the next. He gave a great impetus to scientific development in many spheres of industrial activity in addition to petroleum. He had clear-cut views on coal and, indeed, on all types of fuel. When ships were to be constructed for the Anglo-Iranian Oil Company's fleet, he needed assurance that every scientific aid had been invoked in hull design and that the completed vessels would be the best that science and engineering skill could contrive.

It was, indeed, a well-deserved tribute that Professor John Cadman, D.Sc., became Lord Cadman, F.R.S.

From T. Dewhurst, Esq.

In the late Lord Cadman a rare and even unique personality has passed on. Even his negative qualities were remarkable, and included a complete absence of pretence and pose, freedom from turbulence and impatience and the avoidance of any but the most simple language in which to express his thoughts.

These negative traits were a mask to his positive qualities. His quiet manner concealed immense driving power, his simple language hid vast stores of knowledge and wisdom, his simplicity veiled gifts of diplomacy of a high order and his geniality and hospitality a keen appreciation of men and affairs.

His insight into human nature had an X-ray quality which gave him an instinctive knowledge of the wise course to adopt in any situation and enabled him to smooth over difficulties and remove causes of friction. In carrying out his manifold duties this quality was invaluable. For example, as chairman of a Royal Commission he would instantly and unerringly pick out the man or men who possessed the fundamental scientific and technical knowledge of the subject under reference, and such men received his complete confidence, warm friendship and generous praise.

His hospitality was princely, and enabled him to break down the barriers between various classes of men. Reference can only be made here to the remarkable gatherings at the large circular table that was made for Disraeli so that all present could be equal. Those who were fortunate enough to have been his guests will always treasure the experience. A volume would be needed to do justice to his services and achievements in various spheres of activity. In academic life, in science and technology, in the coal and oil industries and in Government service, records exist that bear the impress of his powers. The highest testimony to the value of these achievements was provided by the high positions he held, and by the honours that were showered on him by Governments, Universities, and Scientific and Technical Societies.

In his plans he showed depth of knowledge, width of outlook and length of vision. A big, simple and boldly conceived scheme of his would be regarded by some horse-shy critics as unnecessary, while others would mistake size for grandiosity. After his quiet persistence had won through, and the scheme was in being, the critics would realize their mistakes and also that wise planning such as his was one of the rarest of gifts.

Great services rendered to his country deserve a special tribute. In times of peace he served on many Government commissions and committees, and was Chairman of several of them, and the reports bear the impress of his qualities. But his services were even greater in times of war. Early in 1917 there was a serious shortage of petroleum products for the Navy, while Sir Douglas Haig had only a few days' supply. Professor Cadman was called in and became Director of the Petroleum Executive and, later, Chairman of the International Allied Petroleum Council. He was responsible to the War Cabinet through the late Lord Long, who paid the following tribute to his work. "The success which happily attended our administration is entirely due to his great ability, wonderful industry, and unsurpassed knowledge of oil questions. . . . In all the long list of services rendered by both men and women, which contributed to the ultimate victory, there is none which stands higher than the work which Sir John Cadman did." For these services he was made K.C.M.G., Officier Légion d'Honneur and Knight Commander of the Crown of Italy.

After some forty years of strenuous activity in many spheres, Lord Cadman had earned the right to peaceful sunset years, but he was to know no Indian summer, for when the Nazi war started he again placed his knowledge, experience and abilities at the disposal of the Government, and finally spent himself in the country's service.

Many men received from the late Lord Cadman more kindness and sympathetic understanding than they received from any other man. Of the many memorials to him, none will be more fitting than the thoughts and feelings of affection and gratitude in the minds and hearts of his fellows, and this memorial will endure until the last of them has passed away.

> "Our greatest yet with least pretence, Great in council and in war, A leading captain of his time, Rich in saving common-sense, And, as the greatest only are, In his simplicity sublime."

From Dr. A. E. Dunstan.

As it is proposed to publish in the *Journal* at a later date a biography of the late Lord Cadman, it is rather the intention of this short tribute to throw into relief his achievements as a man of science, and it is more than likely that it is just this aspect of his life that Lord Cadman would have wished emphasized.

After more than twenty-five years of close association with him, it is apparent that the scientific approach to industrial problems had assumed an overwhelming importance. In all the wide gamut of the petroleum industry, from the initial geophysical exploration, the geological demarcation of oil-bearing formations, the technology of drilling, the corrosion of pipe-lines and plant and ships to the chemistry of refining processes, his fluid and prehensile mind was fully occupied and extended. There was probably no one man of our epoch with the same encyclopaedic knowledge and, what is more important, the same wide and active sympathy with those who were associated with him as his scientific colleagues.

In his younger days Cadman was primarily a " coal " man. At the age of twenty-six he was appointed H.M. Inspector of Mines for East Scotland. and very shortly after was seconded to Trinidad as Government mining engineer. It was in this position that he encountered the multitudinous problems of the petroleum industry. Returning to England in 1907, he became professor of mining in the University of Birmingham, a post he held for thirteen years, during which time he founded the first school of petroleum technology to be established in the Empire, and was Professor Emeritus at the time of his death. It was in Birmingham that his close collaboration with his old friend, the late Prof. J. S. Haldane, began, and a fruitful series of investigations into various mine hazards was accomplished. In the War of 1914-18 he was intimately concerned in the problems of trench warfare and of gas protection. Ultimately he was made director of the Petroleum Executive and chairman of the Inter-Allied Petroleum Council. He co-ordinated all oil supplies both for the United Kingdom and the Allies. During these busy years, and for long afterwards, he retained his interest in the scientific and technical aspects of industry, served on innumerable commissions and committees and occupied the presidential chairs of the Institute of Petroleum, the Institute of Fuel and the Institute of Mining Engineers.

He received the medals awarded by the latter two bodies. He served on the Advisory Council of the Department of Scientific and Industrial Research of the Privy Council, the Safety in Mines Research Board, the Coal Advisory Council and the Prime Minister's Economic Advisory Council. He was a member of the Fuel Research Board from 1923 until his death, except for a short break of four years. During the time he was a member of the Board he was intensely interested in the work and took a prominent part in the discussions of the Board. Although he was so intimately associated with oil, his association with the coal industry had left him with real sympathy with the subject, and he never hesitated to use his influence to further the scientific application of coal. He continually advocated the complete gasification of coal so that cheap gas could be made accessible in large volumes in Great Britain. He also took a great interest in the production of motor spirit from coal by the hydrogenation process. The coping-stone of his scientific career was placed only last year by his election to the Fellowship of the Royal Society.

As one of his oldest colleagues, the writer wished to stress Cadman's

perpetual insistence that no industry can flourish that is not soundly based on truly scientific foundations. In the Anglo-Iranian Oil Company he fostered research. He was responsible for the creation of the largest petroleum station in the Empire, and one that will bear every comparison with corresponding organizations abroad. He was deeply sensible of the latest and best scientific advice. He supplemented the efforts of his own staff with those of highly skilled and eminent advisers. He continually visited the laboratories, and took the keenest interest in the welfare and well-being of his staff. In return he was rewarded by a constant stream of invention, discovery and development.

MOLAL VOLUME RELATIONSHIPS AMONG ALI-PHATIC HYDROCARBONS AT THEIR BOILING POINTS.*

By GUSTAV EGLOFF and ROBERT C. KUDER.

PART I. RELATIONSHIPS BETWEEN MOLAL VOLUME AND MOLECULAR STRUCTURE.

A. INTRODUCTION.

REGULARITIES in molal volume relationships among homologous series of organic liquids were first studied by Kopp.⁶ He pointed out that at the boiling point the molal volume was an additive function, its value in the case of hydrocarbons varying linearly with the number of carbon atoms in the molecule.

Other later investigators have also used the molal volume additively, calculating molal volumes of compounds from the sums of the atomic volumes of the component elements. However, as the amount of more accurate density data has grown, it has become increasingly evident that linear relationships between molal volume and molecular weight do not represent the experimental data with a sufficient degree of accuracy. Le Bas ⁷ realized the inadequacy of linear equations, and in 1915 proposed for *n*-alkanes a formula of the type :

$$V = an^2 + bn + c$$

in which V is the molal volume at the boiling point and n is the number of carbon atoms in the molecule, whilst a, b, and c are constants. Even this parabolic equation was valid for only the higher members of the series (n > 5).

Another objection to Kopp's generalizations is that isomers do not have identical molal volumes. Constitutive effects, such as branching of the carbon chain or position of the double or triple bonds, are clearly revealed in the light of present data.

In Part I of this paper, a correlation of the molal volumes of aliphatic hydrocarbons at their boiling points and the number of carbon atoms in the molecule will be made for several homologous series. The boiling point was chosen as a standard reference point, since this temperature permits comparisons to be made at approximately equal fractions of the critical temperatures.

B. SELECTION OF THE DATA.

The boiling point and density data used were the most probable values given by Egloff,⁴ except for a few changes and additions necessitated by

^{*} Presented before the Division of Physical Chemistry of the American Chemical Society Detroit Meeting, 9-13th September, 1940,

recently published data. In Table I, column 2, appear the values which differ from those of Egloff, and the reason for the change or addition.

Compound.	$D_{4}^{20}.$	Reason.
2 : 2-Dimethylpropane	0.613	0.613 given by Hoog, Smittenberg, and Visser: R-51-S2, II Congres Mon- dial du Petrol, Paris, June, 1937.
3:3-Dimethylhexane.	0.7095 -	0.7107 given by Marker and Oakwood, J. Amer. chem. Soc., 1938, 60, 2598.
3-Ethylheptane	0.7266	0.7272 given by Whitmore and Orem, ibid., 1938, 60, 2573.
2. Methyloctane	0.7124	0.7132, ibid.
2 · 2. Dimethylheptane	0.7105	0.7105 and 130.4 given by Marker and
a i a p intoni inc p como	(b. pt	Oakwood, loc. cit.
2 : 5.Dimethylheptane	0.7134	Conversion of S_{20}^{20} into D_4^{20} .
2:6-Dimethylheptane	0.7094	0.70949 given by White, Rose, Jr. Calingaert, and Soroos, J. Res. Nat. Bur. Standards, 1939, 22, 315.
3: 3-Dimethylheptane	0.7279	0.7254 given by Marker and Oakwood loc. cit
3:3-Dimethyloctane	0.7390 (h. pt. 161.2)	0.7390 and 161.2, ibid.
2:4-Dimethyloctane .	0.7246	Conversion of S_{40}^{20} into D_4^{20} .
Ethene	0.5676-102.4	Correction of misprint.

TABLE I.

The densities of the first four *n*-alkanes are known at their boiling points. The densities of the remaining members of the series must be extrapolated to the boiling points. For *n*-alkanes containing thirteen or more carbon atoms, density data are so few and the boiling points so high that it is impractical to extrapolate the densities to the boiling points. However, from *n*-pentane to *n*-dodecane temperature coefficients of density are valid over sufficient temperature ranges so that densities may be calculated at the boiling points with extrapolations varying from only 0.71° in the case of *n*-nonane to 18.8° in the case *n*-hexane.

Of forty-two branched-chain alkanes considered, only four have density determinations over extended temperature ranges. The densities at the boiling points of three of these (2-methylpropane, 2:2-dimethylpentane, and 2:2:4-trimethylpentane) may be interpolated accurately from the experimental data; the density at the boiling point of the other (3-ethylpentane) may be calculated from the published temperature coefficients ⁴ requiring an extrapolation of only $3\cdot3^\circ$.

For the thirty-eight remaining branched-chain alkanes, the temperature coefficients of density are either not known or are not determined over temperature ranges sufficiently wide to extrapolate the densities to the boiling points. A plot of density against temperature showed that over the ranges which have been investigated the curves for branched-chain alkanes are approximately parallel to the curves for the corresponding *n*-alkanes. Therefore the densities of the remaining branched-chain alkanes were extrapolated to their respective boiling points using the same temperature coefficients as for the corresponding straight-chain isomers. Since the extrapolations involved vary from about 40° for hexanes to nearly 150° for decanes, it is probable that the error introduced by using

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parabolic curves parallel to the straight-chain curves is not as great as that which would be introduced if straight lines determined by temperatures only $5-20^{\circ}$ apart were used.

The densities of the first three 1-alkenes have been determined over extended temperature ranges, and the densities at the boiling points are known.⁴ The density of pentene-1 and of hexene-1 at their respective boiling points were determined by graphical extrapolation. Above hexene-1 the data do not warrant extrapolation.

The densities at the respective boiling points of the first three 1-alkynes are also reported,⁴ but the density of butyne-1 at its boiling point is obviously so out of line that it was discarded from the series. The density of pentyne-1 at its boiling point was determined from the calculated temperature coefficient,⁴ and the boiling-point densities of the next three members of the series were obtained by graphical extrapolation.

It is evident from the above discussion that much more experimental data on densities near the boiling point would be very helpful in studies of this type.

C. THE EMPIRICAL EQUATION.

The boiling points of aliphatic hydrocarbons can be expressed accurately ⁵ by an equation of the type

in which the constant b' has a value of 4.4. It was considered desirable to develop an equation for V, the molal volume at the boiling point, as a function of (n + 4.4), so that a simple relationship would exist between the boiling-point equation and the molal-volume equation. Graphical analysis of the data for n-alkanes showed that a formula of the type

was required. In the logarithmic form,

 $\log (V - k) = \log a + c \log (n + 4.4)$ (3)

the constants a, c, and k were evaluated for n-alkanes by the method of least squares.* Only the first ten members of the n-alkane series were used in fitting the equation, since there are no branched-chain alkanes nor alkenes or alkynes of more than ten carbon atoms with data suitable for comparison with the n-alkanes, and since, further, the data for the higher members of the n-alkane series itself are unreliable, as pointed out above.

The constants obtained for *n*-alkanes are a = 7.9990, c = 1.32243, and k = 37.00. Table II shows the agreement between the calculated and the observed values. The agreement is good (deviations less than 0.5 ml./mol) for all members with the exception of ethane, which has a calculated value 1.11 ml. too high. The mean deviation for all ten members is 0.30 ml./mol (0.20 ml./mol, excluding ethane).

For homologous series of branched-chain alkanes the data may be represented by keeping c and k the same as for n-alkanes, whilst a is adjusted for each series. The constant a was evaluated for eleven homolo-

^{*} An approximate value of k was first chosen graphically, and the corresponding approximate values of a and c calculated. The more exact values of a, c, and k were then found by application of Taylor's expansion.

gous series of branched-chain alkanes; the calculated and observed values of the molal volumes are shown in Tables III to XIII. The mean deviation for the forty-two branched-chain alkanes considered is 0.41 ml./mol; for all fifty-two alkanes, 0.39 ml./mol.

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For alkenes and alkynes, k was kept the same as for alkanes, but a = 6.5807 and c = 1.38856 for 1-alkenes, whilst a = 5.3171 and c = 1.45121 for 1-alkynes. The calculated and observed values for the first five 1-alkenes are shown in Table XIV; the mean deviation is 0.21 ml./mol. The calculated and observed values of the first seven 1-alkynes are shown in Table XV; the mean deviation is 0.50 ml./mol.

In Table XVI is given a summary of the preceding fourteen tables. The mean deviation for all the sixty-three aliphatic hydrocarbons considered is 0.39 ml./mol. This agreement appears to be good when it is remembered that most of the "observed" molal volumes are calculated from extrapolated density values.

n.	V obs.	V cale.	$\Delta V.$
1	37.83	37.40	-0.43
2	55.03	56.14	1.11
3	75.80	75.86	0.06
4	96.59	96.46	-0.13
5	118.09	117.86	-0.23
6	140.07	140.01	-0.06
7	163.10	162.86	-0.24
8	186.64	186.37	-0.27
9	210.42	210.49	0.07
10	234.86	235.21	0.35

TABLE II.n-Alkanes.

TABLE III.

2-Methylalkanes. $V = 7.9715(n + 4.4)^{1.32243} - 37.00.$

n.	V obs.	V calc.	ΔV
5 6 7 8 9 10	$117 \cdot 81 \\ 139 \cdot 03 \\ 162 \cdot 34 \\ 185 \cdot 88 \\ 210 \cdot 07 \\ 233 \cdot 24$	117·33 139·39 162·17 185·59 209·63 234·26	$\begin{array}{c} -0.48 \\ 0.36 \\ -0.17 \\ -0.29 \\ -0.44 \\ 1.02 \end{array}$

 TABLE IV.
 3-Methylalkanes.

 $V = 7.8983(n + 4.4)^{1.32243} - 37.00.$ $V = 7.8983(n + 4.4)^{1.32243} - 37.00.$

n.	V obs.	V calc.	$\Delta V.$
6 7 8 9 10	$\begin{array}{c} 137.90 \\ 159.91 \\ 183.99 \\ 207.46 \\ 231.53 \end{array}$	$137.77 \\ 160.34 \\ 183.54 \\ 207.36 \\ 231.77$	$-0.13 \\ 0.43 \\ -0.45 \\ -0.10 \\ 0.24$

TABLE V.

3-Ethylalkanes.

 $V = 7 \cdot 8357(n + 4 \cdot 4)^{1 \cdot 32243} - 37 \cdot 00.$

n.	V obs.	V calc.	$\Delta V.$
7 8 9	$ \begin{array}{r} 158.64 \\ 182.06 \\ 205.30 \end{array} $	$158.77 \\ 181.80 \\ 205.43$	$ \begin{array}{r} 0.13 \\ -0.26 \\ 0.13 \end{array} $

TABLE VI. 2:2-Dimethylalkanes. $V = 7.9088(n + 4.4)^{1.32243} - 37.00.$

n.	V obs.	V calc.	$\Delta V.$
5	115.82	116.11	0.29
6	138.41	138.00	-0.41
7	161.14	160.60	-0.54
8	183.85	183.84	-0.01
9	207.02	207.69	0.67

TABLE VII.

$\begin{aligned} 2: 2'\text{-Dimethylalkanes.} \\ V &= 7.9345(n + 4.4)^{1.32243} - 37.00. \end{aligned}$

п.	V obs.	V calc.	$\Delta V.$
7 8 9 10	$ \begin{array}{r} 161.77 \\ 184.65 \\ 208.43 \\ 232.44 \end{array} $	$ \begin{array}{r} 161 \cdot 24 \\ 184 \cdot 56 \\ 208 \cdot 49 \\ 233 \cdot 00 \end{array} $	$-0.53 \\ -0.09 \\ 0.06 \\ 0.56$

TABLE VIII.2:3-Dimethylalkanes.

 $V = 7 \cdot 8358(n + 4 \cdot 4)^{1 \cdot 32243} - 37 \cdot 00.$

n.	V obs.	V calc.	$\Delta V.$
6 7 8 9	$ \begin{array}{r} 137 \cdot 30 \\ 158 \cdot 32 \\ 181 \cdot 19 \\ 205 \cdot 59 \end{array} $	$ \begin{array}{r} 136 \cdot 39 \\ 158 \cdot 78 \\ 181 \cdot 80 \\ 205 \cdot 43 \end{array} $	$- \frac{0.91}{0.46} \\ 0.61 \\ - 0.16$

TABLE IX.

2: 3'-Dimethylalkanes.

$V = 7.8937(n + 4.4)^{1.32243} - 37.00.$

n.	V obs.	V calc.	$\Delta V.$
8 9 10	183·26 207·16 231·83	$\frac{183 \cdot 41}{207 \cdot 22} \\ 231 \cdot 61$	$0.15 \\ 0.06 \\ -0.22$

TABLE X.

2:4- and 2:5-Dimethylalkanes. $V = 7.8524(n + 4.4)^{1.32243} - 37.00.$

n.	Compound.	V obs.	V calc.	ΔV
9	2:4-	205·99	205-94	$-0.05 \\ -0.61 \\ 0.66$
10	2:4-	230·82	230-21	
10	2:5-	229·55	230-21	

TABLE XI.

3: 3-Dimethylalkanes.

$V = 7.7815(n + 4.4)^{1.32243} - 37.00.$

n.	V obs.	V calc.	ΔV .
7 8 9 10	$ \begin{array}{r} 157 \cdot 79 \\ 180 \cdot 82 \\ 203 \cdot 22 \\ 227 \cdot 42 \end{array} $	$ \begin{array}{r} 157 \cdot 42 \\ 180 \cdot 28 \\ 203 \cdot 75 \\ 227 \cdot 80 \end{array} $	$-0.37 \\ -0.54 \\ 0.53 \\ 0.38$

TABLE XII.

2:2:3-Trimethylalkanes. $V = 7.7516(n + 4.4)^{1.32243} - 37.00.$

n.	V obs.	V calc.	ΔV
7	157·37	156·67	-0.70
8	178·75	179·45	0.70

TABLE XIII.

2:2:2'-Trimethylalkanes. $V = 7.8665(n + 4.4)^{1.32243} - 37.00$

n.	V obs.	V calc.	$\Delta V.$
8	183-88	182-66	$-1.22 \\ 0.12 \\ 1.10$
9	206-26	206-38	
10	229-59	230-69	

TABLE XIV.

1-Alkenes.

V = 6.5807	$(n + 4 \cdot 4)$)1.38856	37.00.
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n.	V obs.	V calc.	$\Delta V.$
2	49.42	49.64	0.22
3	68.93	68.99	0.06
4	89.69	89.38	-0.31
5	110.95	110.75	-0.20
6	132.76	133.01	0.25

TABLE XV. 1-Alkunes.

 $V = 5 \cdot 3171(n + 4 \cdot 4)^{1} \cdot 4^{5121} - 37 \cdot 00.$

n.	V obs.	V calc.	$\Delta V.$
2 3 4 5 6 7 8	$ \begin{array}{r} 41.91\\59.67\\\\101.39\\122.73\\144.92\\167.85\end{array} $	$\begin{array}{r} 41.64\\ 60.08\\ 79.68\\ 100.37\\ 122.08\\ 144.75\\ 168.34 \end{array}$	$ \begin{array}{r} -0.27 \\ 0.41 \\ -1.02 \\ -0.65 \\ -0.17 \\ 0.49 \end{array} $

TABLE XVI. Values of a and c for Aliphatic Hydrocarbons.

Series.		a.	с.	Mean deviation.
n-Alkanes		7.9990	1.32243	0.30
2-Methylalkanes		7.9715	>>	0.46
3-Methylalkanes		7.8983	27	0.27
3-Ethylalkanes .		7.8357	, , ,	0.17
2:2-Dimethylalkanes .		7.9088	22	0.38
2:2'-Dimethylalkanes		7.9345	,,	0.31
2:3-Dimethylalkanes		7.8358	22	0.54
2:3'-Dimethylalkanes .		7.8937		0.14
2:4-2:5- Dimethylalkanes.	•	7.8524	"	0-44
3: 3-Dimethylalkanes .		7.7815		0.46
2:2:3-Trimethylalkanes		7.7516		0.70
2:2:2'-Trimethylalkanes		7.8665	17	0.81
l-Alkenes		6.5807	1.38856	0.21
l-Alkynes		5.1371	1.45121	0.50

D. THE EFFECT OF MOLECULAR STRUCTURE ON MOLAL VOLUME.

If the various homologous series of alkanes are arranged in order according to the magnitude of the constant a, equation (2), some interesting relationships are evident (see Table XVII).

Among isomeric alkanes a straight-chain compound always has a larger molal volume at the boiling point than any branched-chain compound. The sole exception to this generalization is 2-methylpropane (not included in Table III), which has a molal volume of 97.44 ml., whilst *n*-butane has a molal volume of 96.59 ml. The difference in molal volume between a straight-chain alkane and any isomer is not constant within each series, but increases as the molecular weight increases, although not always regularly if calculated from the observed values. If V_1 denotes the calculated volume of a given *n*-alkane, and V_2 the calculated volume of an isomer, then, from equation (2),

$$V_1 - V_2 = (a_1 - a_2) (n + 4 \cdot 4)^c$$

where a_1 and a_2 are, respectively, the values of a for n-alkanes and for the homologous series of which the isomer is a member.

TABLE XVII.

Alkanes.					
а.	Type of substitution.	Carbon skeleton.			
7.9990	Normal	C(C)_zC			
7.9715	2-Me-	C—C—(C) _x —C			
7.9345	2 : 2-Me ₂ -	CC-(C)z-C			
7.9088	2 : 2′-Me₂-	$C - C - (C)_x - C - C \qquad (x > 0)$			
7.8983	3-Ме-	$C - C - C - (C)_x - C \qquad (x > 0)$			
7.8937	2 : 3'-Me ₂ -	$\begin{array}{c} C - C - (C)_{x} - C - C - C (x > 0) \\ \downarrow \\ C C \end{array}$			
		ç			
7.8665	2:2:2'-Me ₃ -	$C - C - (C)_x - C - C \qquad (x > 0)$			
7.8524	2:4-Me ₂ -	$C - C - C - C - (C)_x - C (x >)$			
7-8524	2 : 5-Me ₂ -	$C - C - C - C - C - (C)_x - C (x > 1)$			
7.8358	2:3-Me ₂ -	CCC(C)_xC			
7.8357	3-Et-	$C - C - C - (C)_x - C \qquad (x > 0)$			
7.7815	3 : 3-Me ₂ -	$C - C - C - C - (C)_x - C \qquad (x > 0)$			
7.7516	2 : 2 : 3-Me ₃ -	$C = C = C = (C)_{x} = C$			

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The effects of branching at the boiling point are in marked contrast with the effects at 20°, which have been pointed out previously.^{1. 2. 3} At 20° substitution in the 2-position always increases the molal volume over that of the normal isomer, unless the adjacent 3-position is also substituted.

At the boiling points of monomethylalkanes the molal volume decreases the nearer the centre of the molecule the methyl group is situated—*i.e.*, 3-methylalkanes have smaller molal volumes than isomeric 2-methylalkanes. However, at 20° 2-methylalkanes are about as much larger than the corresponding *n*-alkanes as the isomeric 3-alkanes are smaller.

In dimethylalkanes at the boiling point the diminution of volume is the least when the methyl groups are in penultimate positions, either on the same carbon atom or at opposite ends of the molecule. For example, 2:2-dimethylpentane and 2:4-dimethylpentane have smaller molal volumes than 2-methylhexane, but larger than 3-methylhexane, and considerably larger than 3:3-dimethylpentane. However, at $20^{\circ} 2:2$ -dimethylalkanes are larger in volume than isomeric 2-methylalkanes, and larger yet than the isomeric *n*-alkanes. Both at the boiling point and at 20° the volumes of isomeric 2:2- and 2:2'-dimethylalkanes are nearly equal.

The contraction in volume due to adjacent dimethyl substitution which is noticed at 20° is still marked at the boiling point. 2:3-Dimethylalkanes have smaller volumes than isomeric 2:2, 2:2'-, and 2:3'-dimethylalkanes. The effectiveness of the 3-position in lowering the molal volume at the boiling point is shown by the relatively small volumes of 3-ethylalkanes and 3:3-dimethylalkanes. In dimethylalkanes in which one of the methyl groups is in the penultimate position and the other is in neither the 2- nor the 3-position at either end of the molecule, the relative position of the two methyl groups has comparatively little effect on the molal volume at the boiling point.

In trimethylalkanes the influence of penultimate and of adjacent substitution is quite noticeable. The difference in volume at the boiling point between *n*-alkanes and isomeric 2:2:3-trimethylalkanes is approximately twice as great as the difference between *n*-alkanes and isomeric trimethylalkanes in which all three methyl groups are in penultimate positions (2:2:2'-trimethylalkanes). Furthermore, the latter type of trimethyl-substitution does not cause as great a diminution in volume as do many types of dimethyl substitutions, whilst the 2:2:3-trimethylalkanes have smaller molal volumes than any other type here mentioned.

In Table XVIII are arranged several homologous series of alkanes in order of decreasing size of isomers,* summarizing the differences at the boiling point and at 20° .

The difference in order of the alkane series at the boiling point and at 20° is due chiefly not to difference in temperature coefficients of the densities, but to differences in the boiling points between *n*-alkanes and branched-chain alkanes. Since the boiling points of all branched alkanes are lower than the corresponding isomeric *n*-alkanes, the increase in molal

^{*} The arrangement at 20° is based on the plot constructed by Calingaert and IIIadky, reference 2.

ALIPHATIC HYDROCARBONS AT THEIR BOILING POINTS.

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volume between 20° and the boiling points for the branched chains is not as great as for the straight chains.

TADLE	21. 1 111.
	At 20°.
Normal 2-Me- 3-Me- 2:2-Me ₂ - 2:2'-Me ₂ - 3:3-Me ₃ - 2:2:2'-Me ₃ -	2:2:2'-Me ₂ - 2:2'-Me ₂ - 2:2-Me ₂ - 2-Me- Normal 3-Me- 3:3-Me ₂ -

The molal volumes of 1-alkenes at the boiling points are less than those of n-alkanes with the same number of carbon atoms. The 1-alkynes have still smaller molal volumes at the boiling point. These relationships among the three series also are true at 20°, and may be explained by the loss of hydrogen atoms as unsaturation increases, thus leaving smaller molecules.

While at 20° the density of members of any homologous series of aliphatic hydrocarbons increases regularly with the molecular weight, this relationship appears not to be true at the boiling point. Thus for *n*alkanes at the boiling point, the density for the first few members increases rapidly, then between hexane and heptane goes through a maximum, and for the remainder of the series decreases slowly. The branched alkanes, the 1-alkenes, and the 1-alkynes show similar maxima (see Table XIX and Fig. 1). It is possible, however, that these maxima for certain series are only the results of the extrapolations, since small changes in temperature coefficients of the densities might alter the form of the density v. number of carbon atoms curves in cases where large extrapolations have been made.

TABL	εХ	IX.

n.	n-Alkanes.		1-All	1-Alkenes.		1-Alkynes.	
	Obs.*	Calc.	Obs.	Calc.	Obs.	Calc.	
1	0.4289	0.4240					
2	0.5356	0.5464	0.5676	0.5651	0.6213	0.6253	
3	0.5813	0.5818	0.6104	0.6099	0.6714	0.6668	
4	0.6025	0.6017	0.6255	0.6277		0.6788	
5	0.6121	0.6110	0.6321	0.6332	0.6718	0.6786	
6	0.6155	0.6152	0.6339	0.6327	0.6700	0.6728	
7	0.6152	0.6143	_		0.6636	0.6644	
8	0.6129	0.6120			0.6565	0.6546	
9	0.6093	0.6095				0.0040	
10	0.6049	0.6028		_	_		

Density at the Boiling Point.

* At the boiling points obtained from equation (1); boiling point densities of all other hydrocarbons are at the boiling points given by Egloff, reference 4.

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PART II. MOLAL VOLUME-BOILING POINT RELATIONSHIPS.

Little work has been done previously on the correlation of the boiling point molal volumes with the boiling points. Schuster,⁸ in 1926, proposed an equation for *n*-alkanes, but the fit is not very good :

 $\log V = 1.3612 + 0.002287 \ T.$

By combining equations (1) and (3) of Part I, a new equation, (4), is obtained :

$$\log (V - k) = \frac{c}{a'}T + \log a - \frac{k'}{a'}c \quad . \quad . \quad (4)$$

Equation (4) may be reduced to the simple form :

in which B' =

in which V is the molal volume at the boiling point; T is the boiling point temperature on the absolute scale, and k, A, and B are constants. The value of k is the same as in equation (2), and the other constants are related thus:

$$A = \frac{c}{a'}; B = \log a - k'A$$

If the substitution $T = t + 273 \cdot 16^{\circ}$ is made, where t is the boiling point on the Centigrade scale, a more convenient equation, (6), is obtained :

Since in equation (1) only k' varies from series to series, in equation (6) A will change only with the degree of unsaturation, and B' will change for each series, whilst k remains constant for all series.

The values of A and B' were calculated for all homologous series to which both equations (1) and (2) apply. Since equation (1) does not hold for the initial members of some of the series, equation (6) is likewise not applicable to these members—namely, methane, 2-methylpropane, 2:2-dimethylpropane, ethene, ethyne, propyne, and butyne-1.

Equation (6) does not reproduce the experimental molal volume data quite as accurately as does equation (2), since there are small errors in the variable t, whereas there are none in the variable n. The mean deviation

TABLE XX.

	n-Alkanes.
	k' = -416.31, a' = 745.42.
$\log(V)$	+ 37.00 = 0.00177408t + 2.12622.

n.	t.	V obs.	V calc.	ΔV
2	-88.5	55.03	56.16	1.13
3	-42.2	75.80	75.55	-0.25
4	- 0.5	96.59	96·45	-0.14
5	36.08	118.09	117.96	-0.13
6	68.8	140.07	140.12	0.05
7	98·4	163.10	162.89	-0.21
8	125.6	186.64	186-33	-0.31
9	150.71	210.42	210.51	0.09
10	174.04	234.86	235.26	0.40

TABLE XXI.

2-Methylalkanes.

 $k' = -424 \cdot 51.$ log (V + 37.00) = 0.00177408t + 2.13926.

n.	t.	V obs.	V calc.	Δ <i>V</i> .
5 6 7 8 9 10	$\begin{array}{c} 27.95 \\ 60.20 \\ 89.7 \\ 117.2 \\ 143.0 \\ 166.8 \end{array}$	117.81 139.03 162.34 185.88 210.07 233.24	117.47 139.22 161.79 185.42 210.14 235.38	$ \begin{array}{r} -0.34 \\ 0.19 \\ -0.55 \\ -0.46 \\ 0.07 \\ 2.14 \\ \end{array} $

TABLE XXII.

3. Methylalkanes.

		k'	=	-422.88.	
log (V	+	37.00)	=	0.00177408t + 2.13237.	

n.	<i>t</i> .	V obs.	V calc.	$\Delta V.$
6	63·2	137.90	138.59	$ \begin{array}{r} 0.69\\ 0.44\\ -0.45\\ -0.03\\ 0.66 \end{array} $
7	91·8	159.91	160.35	
8	119	183.99	183.54	
9	144·18	207.46	207.43	
10	167·8	231.53	232.19	

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of the calculated from the observed molal volumes for thirty-five alkanes is 0.61 ml./mol, and for all forty-three aliphatic hydrocarbons considered, 0.62 ml./mol. The agreement of the individual hydrocarbon values is shown in Tables XX to XXVIII and summarized in Table XXIX.

TABLE XXIII. 3-Ethylalkanes. $k' = -423 \cdot 01.$ $\log (V + 37 \cdot 00) = 0.00177408t + 2.12914.$

n.	t.	V obs.	V calc.	$\Delta V.$
7 8 9	93·3 118·9 143·1	$\frac{158 \cdot 64}{182 \cdot 06}$ 205 $\cdot 30$	$160.09 \\ 181.82 \\ 204.55$	$1.45 \\ -0.24 \\ -0.75$

TABLE XXIV.

2:2-Dimethylalkanes.

k' = -435.34

 $\log (V + 37.00) = 0.00177408t + 2.15505.$

n.	t.	V obs.	V cale.	$\Delta V.$
6 7 8 9	49·7 78·9 107·0 130·4	$ \begin{array}{r} 138.41 \\ 161.14 \\ 183.85 \\ 207.02 \end{array} $	$ \begin{array}{r} 138.08 \\ 160.25 \\ 184.25 \\ 206.44 \end{array} $	$-0.33 \\ -0.89 \\ 0.40 \\ -0.58$

TABLE XXV.

2: 3-Dimethylalkanes.

k' = -425.88.

 $\log (V + 37.00) = 0.00177408t + 2.13423.$

n.	t.	V obs.	V calc.	$\Delta V.$
6 7 8 9	58·0 89·7 115·7 140·6	$ \begin{array}{r} 137 \cdot 30 \\ 158 \cdot 32 \\ 181 \cdot 19 \\ 205 \cdot 59 \end{array} $	$ \begin{array}{r} 135 \cdot 64 \\ 159 \cdot 50 \\ 181 \cdot 52 \\ 204 \cdot 92 \end{array} $	$-1.66 \\ 1.18 \\ 0.33 \\ -0.67$

TABLE XXVI.

3: 3-Dimethylalkanes.

k' = -430.10.

$\log \left(V + 37.00 \right) = 0.00177408t + 2.13870.$

<i>n</i> .	t.	V obs.	V cale.	$\Delta V.$
7 8 9 10	86.0 111 137.2 161.2	$ \begin{array}{r} 157 \cdot 79 \\ 180 \cdot 82 \\ 203 \cdot 22 \\ 227 \cdot 42 \end{array} $	$ \begin{array}{r} 158 \cdot 55 \\ 179 \cdot 56 \\ 204 \cdot 04 \\ 228 \cdot 88 \end{array} $	$0.76 \\ -1.26 \\ 0.82 \\ 1.46$

TABLE XXVII.

1-Alkenes.

k' = -421.91log (V + 37.00) = 0.00186279t + 2.11304.

n.	t.	V obs.	V calc.	$\Delta V.$
3 4 5	$ \begin{array}{r} -47.7 \\ -6.47 \\ 30.1 \end{array} $	68-93 89-69 110-95	68·73 89·18 110·61	$ \begin{array}{r} -0.20 \\ -0.51 \\ -0.34 \end{array} $
6	63.5	132.76	133-35	0.29

TABLE XXVIII.

1-Alkynes.

k' = -413.81.log (V + 37.00) = 0.00194684t + 2.06310.

n.	t.	V obs.	V cale.	ΔV .
5 6 7 8	39.7 70.9 99.6 126.0	$ \begin{array}{r} 101 \cdot 39 \\ 122 \cdot 73 \\ 144 \cdot 92 \\ 167 \cdot 85 \end{array} $	$ \begin{array}{r} 101 \cdot 16 \\ 121 \cdot 90 \\ 143 \cdot 72 \\ 166 \cdot 42 \end{array} $	$-0.23 \\ -0.83 \\ -1.20 \\ -1.43$

TABLE XXIX.

Values of A and B' for Aliphatic Hydrocarbons.

Series.		$A~ imes~10^3.$	В'.	Mean deviation.
n-Alkanes		1.77408	2.12622	0.30
2-Methylalkanes .			2.13926	0.62
3-Methylalkanes .			2.13237	0.45
3-Ethylalkanes			2.12914	0.81
2:2-Dimethylalkanes		11	2.15505	0.55
2:3-Dimethylalkanes			2.13423	0.96
3:3-Dimethylalkanes		11	2.13870	1.08
1-Alkenes		1.81827	2.11304	0.41
1-Alkynes		1.94684	2.06310	0.92

SUMMARY.

By means of equations of the type

$$V = a(n + 4 \cdot 4)^c + k$$

the molal volumes of sixty-three aliphatic hydrocarbons (arranged in fourteen different homologous series) at their boiling points have been correlated with the number of carbon atoms in the molecule. The mean deviation of the calculated from observed values is 0.39 ml./mol.

By means of equations of the type

$$\log\left(V-k\right) = At + B'$$

the boiling-point molal volumes of forty-three aliphatic hydrocarbons in nine homologous series have been correlated with the boiling points, with a mean deviation of 0.62 ml./mol.

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The effect of the structure of the hydrocarbon molecule on the molal volume at the boiling point is discussed, and comparisons are made with the effect at 20° .

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Universal Oil Products Company Research Laboratories, Chicago, Illinois.

ON THE RATE OF REACTION IN THE SYSTEM MINERAL OIL-OXYGEN. A CONTRIBUTION TO THE KNOWLEDGE OF OIL STABILITY.*

By D. J. W. KREULEN, F.Inst.Pet., and D.Th. J. TER HORST.

PART I.-GENERAL INTRODUCTION.

THIS series of papers represents a study of the reaction velocities in the system mineral oil-oxygen. Previous investigations have shown that there appears to exist a certain relation between oil properties and molecular structure. Further scientific work is needed to emphasize this relation and to investigate its nature. In this connection it is pointed out that many experiments mentioned in the literature would have been more complete and of greater general importance if the average structure of the oil molecule had been given. This omission is the more regrettable since Waterman and co-workers ¹ have shown how particulars of the average constitution of the oil molecule can be obtained from a few easily determined constants. By this method the average constitution of the oil molecule can be given in percentages of aromatic rings, naphthenic rings, paraffinic side-chains, and average number of rings per molecule. Moreover, the branching of the paraffinic side-chains is established as the number of extra tertiary carbon atoms above those which agree logically with the most simple way of coupling the components to the molecule. In this statement the figure for the average number of rings per molecule is accurate if the average molecular weight is taken into account.

In order to calculate the percentages of naphthenic rings and paraffinic side-chains, a supposition is made—namely, that polycyclic 6-ring naphthenes are under consideration.

It would have been logical to have started our experiments with 100 per cent. paraffins. We did not do so for the simple reason that it is difficult to determine the constants for the higher members of the paraffinic series, as they have high melting points. Moreover, paraffins as regards their properties are so far removed from lubricating oils that we had no immediate interest in them. We chose, therefore, as the first oil, a medicinal paraffin oil, which may be considered to be a lubricating oil completely saturated with hydrogen.

This oil had the following constants: molecular weight 445; density $_{4}^{20} = 0.8833$; refractive index $D_{20} = 1.4828$; critical solution temperature (aniline point) = 109.0° C.; surface tension at 20° C. = 32.1 dyne per cm.; and specific dispersion $\frac{(N_{G'} - N_C)10^4}{d} = 158$. From these constants we derive the following figures for the "ring analysis": Aromatic rings 0 per cent.; naphthenic rings 37 per cent.; paraffinic side-chains 63 per cent.; extra tertiary carbon atoms = 5 (which corresponds to a very

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moderate branching of the paraffinic side-chains); and average number of rings per molecule = 2.8.

Two methods are available for the measurement of the rate of reaction in the system liquid-gas.

A. METHOD BASED ON THE PRINCIPLE OF A. TITOFF.²

This method is characterized by the application of a pure homogeneous medium. The gas, in this case oxygen, is dissolved in the liquid. The liquid phase is then completely separated from the gas phase and allowed to react at the desired temperature. During the reaction, samples are drawn off, and the quantity of gas still present in them is determined. It is possible to calculate the velocity K of the reaction from the alteration

of the gas concentration, according to the equation $K = \frac{1}{t}$, $\lg \frac{A}{(A - x)}$, A

being the quantity of gas in gram molecules per litre at the beginning of the experiment and (A - x) that at the time t. As the active mass of the liquid remains practically constant, the monomolecular law is followed.

In our case this method has a disadvantage, due to the slight solubility of oxygen in oil. The problem is thus to estimate relative small quantities of dissolved oxygen with sufficient accuracy, which is somewhat difficult.

The method was applied to oils by Ornstein and co-workers.³

B. METHOD ACCORDING TO R. LUTHER AND J. PLOTNIKOW.⁴

In this method also the liquid phase as well as the gas phase is present during the reaction. The gas phase is continually stirred into the liquid phase. Both form together one closed system, precautions being taken to prevent any escape of gas. Thus, at the end of the experiment the total oxidation products which are formed are obtained.

In such an experiment the relation between reaction velocity and supply velocity of the oxygen is of primary importance. The method and velocity of stirring are critical, and for this reason the method and apparatus of Luther and Plotnikow, as modified by W. Reinders and S. I. Vles,⁵ was used.

Our apparatus is shown in Fig. 1.

A hollow stirrer of special construction is used. The lower part, which has the form of a Segner's water-wheel, serves to disperse the gas into the liquid. At the top of the stirrer a couple of small openings are made, through which the gas is allowed to enter. A glass partition placed in the liquid prevents too much whirling, so that the division of the gas is increased. The division of the gas becomes more intensive with increased stirring velocity. Reaction velocities are measured only if the liquid remains continually saturated. It is therefore necessary to choose that stirring velocity at which this requirement is fulfilled. In our case we applied a stirring velocity of 1500 revs. per minute. This stirring velocity will be justified below.

In order to be sure of a constant pressure of oxygen, the experiments in this apparatus were carried out under a slight constant pressure (5 cm. Hg).

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FIG. 1.

The average reaction was followed by measurement of the mean dipole moment as a function of time.

W. N. Stoops ⁶ had already realized that the decomposition of transformer oils may be closely followed by measuring the dielectric constant of the oils as they deteriorate in service.

Ornstein and co-workers ⁷ have also studied the change in polar characteristics of transformer oils by means of laboratory tests.

An extensive and systematic research in this field has, however, not yet been carried out.

We attach great importance to the introduction of the average dipole moment to characterize the degree of oxidation reached by an oil, since if an oxygen molecule takes hold of an oil molecule, the first result will be the introduction of a polar group into the system. Moreover, the average



FIG. 2.

dipole moment includes all oxidation stages, whilst other figures—e.g., acid value, electrical conductivity, saponification number, etc.—represent only the oxidation stage. Measuring the increase of the average dipole moment per unit of time at a constant given temperature will give a quantity which is proportional to the mean reaction velocity of the system.

The dielectric constant was measured by the high-frequency method. The apparatus is sketched diagrammatically in Fig. 2.

In this figure (1) is the oscillator and (2) the receiver. The oscillator valve, a Philips E442, is so adjusted by suitable choice of the tension on the screen-grid and the plate that the plate current decreases with increasing plate tension. In this way it is possible to keep the circuit, consisting of the induction coil L and the variable air-condenser C_1 (capacity from 0 to 500 $\mu\mu$ F.) in oscillation. The adjustment of the plate tension is possible by means of the potentiometer R_1 (resistance 50.000 Ω), which is shortcircuited for high-frequency currents by the condensers C_1 and C_2 of 2 μ F. each. The control grid of the valve was connected to the cathode

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by means of a condenser of 1μ F. and a resistance of $10^6 \Omega$. The voltage necessary for plate and screen-grid were supplied by a rectifier which was stabilized by means of neon-valves. The rectifier was fed by an alternating tension of 220 V. The filament of the oscillator valve was fed directly by alternating current. The frequency of the oscillator could be varied from $3 \cdot 10^5$ to 10^6 cycles. We always worked with a frequency of about $3 \cdot 10^5$ cycles per second.

The receiver was a triode voltmeter. By suitable choice of grid-tension, a radio valve Philips E415 is so adjusted that the plate current, measured by the galvanometer G, is nearly zero. If we adjust the circuit formed by the induction L_1 and the air condenser C_1 (capacity from 0 to 500 $\mu\mu$ F.), so that this circuit is in resonance with the L.C. circuit from the oscillator, the galvanometer shows this current rectified by the radio valve. This current will reach a maximum for full resonance of the two L.C. circuits from oscillator and receiver.

The direct current for the plate of the radio valve was supplied by a second neon stabilized rectifier.

Parallel with the condenser C_1 , we could couple a second condenser, C_0 , filled with the oil to be examined. C_0 was made of Monel metal, and had a capacity of about 74 cm.

The resonance values of the condenser C_1 , when C_0 was empty or filled with oil, were estimated. Assuming that the two values of C_1 were respectively c_1 and c_2 , the dielectric constant of the oil ε , and the capacity of the empty condenser c_0 , then we have $\varepsilon = \frac{c_2 - c_1}{c_0}$. In the same way the resonance values of the condenser C_1 were determined by us, for the condition when the empty condenser was coupled to the circuit and when it was not coupled to the circuit. Assume these two values to be c_2' and c_1' .*

Now we have :

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$$\varepsilon = \frac{c_2 - c_1}{c_2' - c_1'}.$$

The condenser C_1 was compared relatively with a standard capacity.

The dipole moment was estimated as the difference between the molecular polarization P and the molecular refraction P_0 at a temperature of 20° C. Here

$$P = \frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{d}$$
$$P_0 = \frac{N^2 - 1}{N^2 + 2} \frac{M}{d}$$
$$\bar{\mu} = 0.0127 \cdot 10^{-18} \sqrt{(P - P_0)T}$$

* The capacity measured in this way is not only the capacity of that part of the condenser which can be filled with oil. The connection wires and the glass insulation of the condenser itself exert their influence. Therefore in our experiments this capacity c_0 was calculated back from measurements which were carried out before and after filling the condenser with a liquid of known dielectric constant. For this purpose we used molecular-weight benzene (Kahlbaum). We accepted 2.285 as being the most probable value for the dielectric constant c_0 . The data obtained by our experiments may be considered to be reliable to within $\frac{1}{2}$ per cent.

where $\varepsilon = \text{dielectric constant}$, M = molecular weight, d = density, N = refractive index, $\overline{\mu} = \text{mean dipole moment}$, and T = absolute temperature.

The factor 0.0127. 10⁻¹⁸ is the numerical value for $\sqrt{\frac{9K}{4\pi N}}$, where K

represents the Boltzmann constant and N the number of Avogadro. A series of observations with our oil is given in Table I. The oxidation was affected at 100° C. During the experiment a spider of electrolytic copper was attached to the stirrer. Its surface amounted to 25 cm.². A stirring velocity of 1500 revs. per minute was applied. The molecular weight was determined by the cryoscopic method using naphthaline as a solvent.⁸

Time, hrs.	Density ²⁰ .	Refractive index, D20°.	630°.	Mol. weight.	Mol. ref	Corrected.	Mol. polarization.	Mol. polarization minus mol. re- fraction.	μ̃ 10 ⁻¹ e.s.u.	Dispersion $(N_{g'} - N_e) 10^4$.	Specific dispersion $\frac{N_{\theta} - N_{\theta}}{d}$. 10 ⁴ .
0 6 13 20 27 33 40 47 52 57 62 67 72 77	$\begin{array}{c} 0.8833\\ 0.8833\\ 0.8833\\ 0.8833\\ 0.8833\\ 0.8833\\ 0.8833\\ 0.8833\\ 0.8844\\ 0.8860\\ 0.8878\\ 0.8898\\ 0.8926\\ 0.8961\\ 0.8997 \end{array}$	$\begin{array}{c} 1\cdot 4828\\ 1\cdot 4828\\ 1\cdot 4828\\ 1\cdot 4828\\ 1\cdot 4828\\ 1\cdot 4828\\ 1\cdot 4829\\ 1\cdot 4829\\ 1\cdot 4829\\ 1\cdot 4832\\ 1\cdot 4833\\ 1\cdot 4833\\ 1\cdot 4839\\ 1\cdot 4839\\ 1\cdot 4839\\ 1\cdot 4839\\ 1\cdot 4842\end{array}$	$\begin{array}{c} 2.193\\ 2.192\\ 2.190\\ 2.190\\ 2.193\\ 2.193\\ 2.191\\ 2.199\\ 2.225\\ 2.241\\ 2.279\\ 2.314\\ 2.379\\ 2.457\\ 2.536\end{array}$	445 445 445 445 445 445 445 445 445 445	$\begin{array}{c} 143\cdot82\\ 143\cdot82\\ 143\cdot82\\ 143\cdot82\\ 143\cdot82\\ 143\cdot82\\ 143\cdot82\\ 143\cdot86\\ 143\cdot69\\ 143\cdot47\\ 143\cdot47\\ 143\cdot20\\ 142\cdot89\\ 142\cdot62\\ 142\cdot04\\ 141\cdot55\\ \end{array}$	$\begin{array}{c} 143 \cdot 21 \\ 143 \cdot 25 \\ 143 \cdot 25 \\ 143 \cdot 08 \\ 142 \cdot 86 \\ 143 \cdot 59 \\ 142 \cdot 28 \\ 142 \cdot 01 \\ 141 \cdot 43 \\ 140 \cdot 94 \end{array}$	$\begin{array}{c c} 143\cdot33\\ 143\cdot28\\ 143\cdot08\\ 143\cdot08\\ 143\cdot08\\ 143\cdot33\\ 143\cdot89\\ 145\cdot87\\ 145\cdot87\\ 146\cdot96\\ 149\cdot82\\ 152\cdot33\\ 156\cdot99\\ 162\cdot34\\ 167\cdot47\\ \end{array}$	$\begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 $	0 0 0 0 0 0 17 0·36 0·44 0·58 0·69 0·84 0·99 1-12	139 139 139 139 139 139 139 139 139 139	158 158 158 158 158 158 158 157 157 157 157 157 156 156 155 155

TABLE 1.	T	ABLE	1.
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In connection with the dipole moment the question arose whether an orientation of the polar molecules had taken place. This, however, appeared not to be the case.*

During the oxidation the specific dispersion remained practically constant. In each case no increase was noted. Thus cyclization certainly did not occur during our experiments.

In Fig. 3 the increase of the average dipole moment is plotted as a function of time.

From this figure it is apparent that no appreciable increase of polar compounds can be observed until an induction period, with an initial period of very slow reaction, is passed. Beyond this induction period there exists a linear relation between $\overline{\mu}$ and the time of oxidation. During our experiments we got the impression that the introduction of polar compounds into the system did not begin suddenly, but that a slight and increasing reaction exists in the latter part of the induction period.

^{*} To control this the dipole moment of the oil, after an oxidation for 77 hours, was estimated by means of the dilution method (P. Debye, "Polare Molekeln," Leipzig, 1929). As dilution solvent we used benzene. With the dilution method an average dipole moment of 1.17×10^{-18} e.s.u. was found, which is in good agreement with the figure 1.12×10^{-18} e.s.u. stated for the non-diluted oil.

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FIG. 3.



FIG. 4.

In Fig. 3, besides $\overline{\mu}$, the increase of the acid value is also drawn as a function of time. One sees that it is difficult to conclude from the latter curve where exactly the period of induction comes to an end. The superiority of $\overline{\mu}$ for the estimation of the length of the period of induction will be obvious.

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In many of the widely applied technical tests the alteration of constants is determined after a certain, standardized time of reaction. From this alteration conclusions are then reached with regard to the stability of the oil.

This, however, is incorrect if an induction period comes into play.

In Fig. 4, oil 1 is the less stable $(tg \ d_1 > tg \ d_2)$, but one would conclude the reverse if only one measurement at the time t had been taken.

As stated in the discussion of the principles of our oxidation apparatus, these tests are correct only if the solution velocity of the oxygen is large in comparison with the reaction velocity. Then real reaction velocities are measured which are not affected by diffusion velocities.

To control this the reaction velocity was determined as a function of the stirring velocity. The results which were obtained are given in Table II.

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Stirring velocity,	Reaction velocity,	
revs./min.	tg dipole-line.	
0 450 950 1500 2000	$\begin{array}{c} 0.4^{\circ},0.5^{\circ},0.3^{3}=0.4^{4}\\ 0.6^{5}\\ 1.3^{\circ}\\ 1.3^{\circ}\\ 1.2^{6} \end{array}$	

Fig. 5 shows the reaction velocity as a function of the velocity of stirring.



It is evident that the measured velocities are independent of the intensity of stirring when the latter is higher than 1000 revs. per min. To be on the safe side our experiments were made at a stirring velocity of 1500 revs. per

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min. Then the reacting system is a greyish-white liquid due to the small oxygen bubbles, which are thoroughly divided in the liquid.*

A similar curve to the one shown in Fig. 5 would be obtained if the division of oxygen in the oil reached a maximum at 1000 revs. per min. This, however, is not the case here, for, though an exact measurement of the dispersed oxygen was not carried out, one may clearly observe an increasing division of oxygen, and, in consequence of this, an increase in volume of the liquid phase, when higher stirring velocities than 1000 revs. per min. are applied. That nevertheless a constant value for the reaction velocity is reached proves that our reaction is a homogeneous one, and not a reaction at the interface liquid-gas.

During our experiments larger deviations than desirable were obtained in the second decimal place of the reaction velocity. We tried to increase the accuracy with which the dipole moment could be measured. Also the density and the refractive index are reliable to within 2 per cent.₀₀. The measurement of the temperature had an accuracy to within 1 per cent.₀. During the oxidation the average molecular weight did not change, in each case the variations which were found were well within the accuracy of the experiment.

Now, it is true that this accuracy is rather poor $(\frac{1}{2} \text{ per cent.})$, but the figure applies equally well to the molecular polarization and the molecular refraction. Thus it may be considered as a constant factor.

The experimental error is, in the first instance, dependent on the accuracy with which the dielectric constant can be measured, which is, at the best, $\frac{1}{2}$ per cent.

About fifty experiments showed that a simple relation exists between the increase of the density and the dielectric constant. The results are collected in Table III.

$\frac{\text{Density}}{\frac{2^0}{4}}.$	Density $\frac{20}{4}$.	$\underset{\overset{0}{4}}{\overset{0}{4}}$
$\begin{array}{c} 0.8833 & 2\cdot 193 \\ 0.8834 & 2\cdot 194/2\cdot 196 \\ 0.8835 & 2\cdot 198 \\ 0.8838 & 2\cdot 200 \\ 0.8839 & 2\cdot 207 \\ 0.8840 & 2\cdot 201 \\ 0.8841 & 2\cdot 208/2\cdot 210 \\ 0.8844 & 2\cdot 204/2\cdot 225 \\ 0.8847 & 2\cdot 221 \\ 0.8848 & 2\cdot 212/2\cdot 223 \\ 0.8848 & 2\cdot 212/2\cdot 223 \\ 0.8849 & 2\cdot 229 \\ 0.8851 & 2\cdot 227 \\ 0.8852 & 2\cdot 228 \\ 0.8853 & 2\cdot 233 \\ \end{array}$	$\begin{array}{c} 0.8855 & 2.233 \\ 0.8856 & 2.232 \\ 0.8860 & 2.241 \\ 0.8862 & 2.251 \\ 0.8863 & 2.244 / 2.246 \\ 0.8864 & 2.246 \\ 0.8866 & 2.245 \\ 0.8867 & 2.262 / 2.263 \\ 0.8872 & 2.264 / 2.267 \\ 0.8873 & 2.273 \\ 0.8878 & 2.273 \\ 0.8878 & 2.279 / 2.291 \\ 0.8880 & 2.275 \\ 0.8882 & 2.284 \\ 0.8883 & 2.305 \\ \end{array}$	$\begin{array}{c} 0.8885 & 2.291/2.308 \\ 0.8887 & 2.299 \\ 0.8888 & 2.298 \\ 0.8892 & 2.307 \\ 0.8898 & 2.312 \\ 0.8898 & 2.314 \\ 0.8900 & 2.324 \\ 0.8904 & 2.344 \\ 0.8904 & 2.344 \\ 0.8905 & 2.340/2.354 \\ 0.8915 & 2.356 \\ 0.8920 & 2.380 \\ 0.8961 & 2.457 \\ 0.8961 & 2.457 \\ 0.8961 & 2.457 \\ 0.8961 & 2.457 \\ 0.8961 & 2.457 \\ 0.8961 & 2.536 \\ 0.9019 & 2.594 \\ \end{array}$

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In Fig. 6 the dielectric constant is graphically plotted as a function of the density. A linear relation is obtained, deviations from the average

^{*} The stated critical stirring velocity does not increase our appreciation of technical tests in which quantities varying from 2 to 15 litres per hour are introduced into the oil.

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line lying well within the accuracy of the experiment. Consequently it is possible to increase the accuracy with which the average dipole moment is estimated by the following procedure.

The dielectric constant which is found is used to check whether the relationship between density and dielectric constant holds. This being the case, the average dipole moment is calculated with that value of the dielectric constant which is obtained from the more exact density with the aid of Fig. 6.*



It is possible to explain this linear reaction between dielectric constant and density in the following way. The general scheme of reaction is given by :

a molecules oil + b molecules oxygen $\longrightarrow c$ molecules polar oil + d molecules water.

We can easily show that the increase of density $\Delta \rho$ is given by

$$\Delta \rho = x \frac{b}{a} m_{0_{B}},$$

where x is the number of oil molecules oxidized and m_{0_2} the mass of an oxygen molecule.

The increase of the polarization per unit volume is given by :

$$\frac{\Delta\varepsilon}{\varepsilon_0+2} = \frac{4n}{3} \times \left(\frac{c}{a}A_p + \frac{d}{a}A_w - A_0\right)$$

where $\Delta \varepsilon =$ the increase of the dielectric constant, $\varepsilon_0 =$ the dielectric constant of the unaltered oil, and A_0 , A_p , and $A_w =$ the polarization per molecule of the oil, polar oil, and water respectively.

^{*} Further research is necessary to investigate if the same relation may be accepted for oils which contain aromatic rings (ordinary lubricating and transformer oils) respectively if the tangent of the straight line drawn in Fig. 6 is a function of molecular weight. This being known, the procedure becomes very simple, as the measurement of the dipole moment may then be substituted by a determination of density.

From these two relations we see that $\frac{\Delta \varepsilon}{\Delta \rho}$ is in first approximation a constant. If we substitute the values for ε_0 and m_{0_2} , we find :

$$\frac{\Delta\varepsilon}{\Delta\rho} = 0.46 \ . \ 10^{24} \Big(\frac{d}{a} A_w + \frac{c}{a} A_p - A_0 \Big). \label{eq:eq:alpha_p}$$

J. W. Williams ⁹ measured the value for A_w , and from our measurements we can calculate A_0 .

If we estimate $A_p \sim 2A_0$ (which is probably in connection with figures available in literature for the organic compounds in question), and if we introduce from Fig. 6, for $\frac{\Delta \varepsilon}{\Delta \rho} \sim 20.77$ we find :

2a+2b=4c+1d.

Now, in our case we study the oxidation of a molecule composed of naphthenic rings and paraffinic side-chains. That the first attack will take place at the paraffinic side-chain is very probable.

According to the literature, peroxides, aldehydes, ketones, acids, and water are also formed. If we give equal probabilities on the occurrence of the reactions :

oil	+	$oxygen \longrightarrow$	peroxides	+	water
oil	+	$oxygen \longrightarrow$	aldehydes	-+-	water
oil	+	$oxygen \longrightarrow$	ketones	-+-	water
oil	+	oxygen \longrightarrow	acids	+	water

we get an average :

7 oil + 12 oxygen \rightarrow 9 polar compounds + 5 water

This is not so far from the scheme required by our function ε from ρ . If we had taken $A_p \sim l_2^1 A_0$ we would find a similar result.*

As already stated, the increase on the average dipole moment $\overline{\mu}$ per unit of time at a given temperature is a quantity proportional to the mean reaction velocity. This quantity is in our experiments a constant value up to an average dipole moment of 0.7-0.8. 10⁻¹⁸ e.s.u. is reached. This appears from Fig. 7.

In this figure we plotted the increase of the average dipole moment per unit of time as a function of the reciprocal value of the absolute temperature at which the experiments were carried out. A straight-line relation is found which confirms the results obtained by Ornstein and co-workers,¹⁰ who studied the oxidation of transformer oils, using a method corresponding to that of Titoff.¹¹ From the slope of the straight line we compute an energy of activation of 21,300 calories per gram molecule.

If we continue the same experiments when the oil is oxidized further, we find the dotted line. Within a close range of the average dipole

For the polar compounds in which we are interested $\epsilon \sim 3$, thus $\frac{\epsilon - 1}{\epsilon + 2} \sim 0.4$. Therefore we choose $A_p \sim 1.5/2 A^0$.

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^{*} For the original oil we find $\epsilon = 2.19$; $\frac{\epsilon - 1}{\epsilon + 2} \frac{1.19}{4.19} = 0.285$.

moment $\overline{\mu}$ we obtain again a straight line (dotted line in Fig. 7). From the slope of this line we calculate an energy of activation of 27,600 calories per gram molecule.

We doubt the comparison of these two energies of activation, for if we connect in Fig. 7 the values found for subsequent dipole magnitudes, then it appears that each following value is somewhat higher than could be expected if the straight-line relation with foregoing measurements strictly hold.

It is quite possible that this phenomenon may be attributed to an increasing influence of the rupture of the molecule, resulting in the introduction of two polar compounds into the system instead of one. The



same alternative would explain why the acid value indicates relatively high figures for oxidation stages lying above the corresponding dipole moment of about 0.7 D. If we accept this hypothesis as true, it is evident that for the calculation of the energy of activation only these reaction velocities may come into account which are obtained at early oxidation stages of the oil.

The same phenomenon may be observed if, at a same temperature, the test is prolonged too long. Then, too, one may obtain figures which show a tendency to lie above the line found at the beginning of the test. Therefore it is of importance, if measurements of reaction velocity are realized by our method, to agree to which maximum stage of oxidation one wants to go. In our case we accepted as a limit 0.7-0.8 D. Only figures which are obtained beneath this limit were included in the straight-lined average relationship.

PART II.-THE INFLUENCE OF COPPER AND TIN.

We now go on to the influence of metals on the rate of reaction and on the length of the period of induction. This investigation is of importance as often, in literature, the catalytic action of certain metals (e.g. copper) is mentioned.

Our results, of course, are valid only for the oil which we investigated. However, data mentioned in the literature suggest that similar phenomena exert their influence during the oxidation of ordinary oils. The research will be extended to these oils.

In a first series of experiments copper filings (electrolytic copper) were used. These filings were passed through a sieve with 400 openings per sq. cm. The conditions of the test were : temperature 100° C.; stirring velocity 1500 revs. per min.; oxygen pressure 5 cm. Hg. Tests were



carried out without the addition of any metal, and subsequently with oils containing an increasing quantity of metal.

The progress of $\overline{\mu}$ was measured every five hours, and thus it was possible to deduce at the end of the experiment both the length of the induction period and the reaction velocity. The magnitude of the reacting surface of the filings is proportional to the number of grams which are added. After establishing the velocity of the reaction in the presence of metal (dotted lines in Fig. 8) the experiment was discontinued. The oil was then divided among four centrifuge tubes and centrifuged at a rate of 1500 revs. per min. The experiment was then continued with the supernatant oil, in which no solid metal was present. From this the lines drawn in Fig. 8 were obtained. The lines marked D_{6a} and D_{6b} refer to experiments with metal-free oil in different quantities (respectively 250 and 125 cm.³). The lines marked D_2 , D_3 , D_4 , and D_5 refer to experiments in which respectively 10, 5, $2\frac{1}{2}$, and $1\frac{1}{4}$ gm. of copper filings are added to 250 cm.³ of oil.
Line S refers to an experiment with tin which is mentioned below. The magnitude of the tin surface in this experiment is comparable with that of the copper surface in experiment D_4 . The figures which were obtained are given in Table IV.

Test.	Cm. ³ of oil.	Copper, gm.	Time = dipole moment (D) .	Reaction velocity.	Induction period, hrs.
Dea	250	0	$67 = 0.17^5, 72 = 0.31^1, 77 = 0.41^5,$	1.21	60
D_{ab}	125	0	$82 = 0.53^{\circ}$ $67 = 0.21^{\circ}, 72^{\circ}_{2} = 0.35^{\circ}, 78 = 0.47^{\circ},$	1.23	$58\frac{1}{2}$
D.	250	1.25	$\begin{array}{l} 83 = 0.60^{4} \\ 20 = 0.14^{0}, 25 = 0.27^{1}, 30 = 0.39^{3}, \end{array}$	1.23	14
D 5	250	2.50	$35 = 0.50^5, 40 = 0.64$ $12 = 0.06^5, 19 = 0.25^4, 26 = 0.41^6,$	1.25	9
D4	250	5	$31 = 0.54^{\circ}, 36 = 0.67^{7}$ $10 = 0.10^{\circ}, 15 = 0.23^{\circ}, 21 = 0.38^{\circ},$	1.27	6
D_3	200	10	$26 = 0.49^{9}, 31 = 0.63^{4}$ $10 = 0.10^{5}, 15 = 0.34^{7}, 20 = 0.47^{9}$	1.33	91
D_2	250	10	$10 = 0.13^{\circ}, 10 = 0.34^{\circ}, 20 = 0.47^{\circ}, 25 = 0.59^{\circ}, 30 = 0.73^{\circ}$	2.00	22

TABLE IV.

From the experiments D_{6a} and D_{6b} it follows that, during the period of induction, the law of mass-working is obeyed. From the experiments D_2 , D_3 , D_4 , and D_5 one has to conclude that the main effect of copper is, in our case, a shortening of the period of induction. A very small increase in reaction velocity was noted, however, up to and including the experiments with 5 gm. of copper filings. This increase is so small that it is within the accuracy of the test.

In these experiments the increase in density, viscosity, acid value, peroxide number, and saponification number were also estimated. All these figures were absolutely insensible for the presence of either copper or tin, provided one takes into account the length of the period of induction.

For an oxidation stage, corresponding with an average dipole moment of 0.5 D some constants are collected in Table V.

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M	etal			μ.	Acid value.	Saponifi- cation number.	Kinematic viscosity, 20° C.	$\underset{\overset{20}{4}}{\overset{20}{4}}$
Tin . Copper No metal Original oil	• • •	•••••	• • • •	0.5 D 0.5 D 0.5 D	$0.6 \\ 0.5 \\ 0.5 \\$	2.0 2.1 2.0 -	245 c.st. 241 c.st. 243 c.st. 2161 c.st.	0.8866 0.8866 0.8866 0.8833

Neither copper nor tin, therefore, has any practical influence on the reaction velocity of the system. Only in the most extreme case may we expect even a small increase with copper—an increase, however, which can be neglected with respect to the primary effect resulting in a shortening

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of the period of induction. In Fig. 9 the length of the period of induction is plotted as a function of the number of grams of copper filings which are added.

It appears that there is no straight-line relationship between the length of the induction period and the surface of copper which is added. The first quantities of the copper surface are the most active. This suggests the possibility of adsorption phenomena. To verify this suggestion the same quantity of copper filings $(2\frac{1}{2} \text{ gm.})$ was brought into contact with the oil for a different length of time. This contact was realized within the usual test-stirring conditions at 100° C. After the chosen length of time the experiment was discontinued. The copper filings were removed





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ime of d), hrs.

In Fig. 10 the length of the induction period is graphically plotted as a function of the time of contact.

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Thus it appears that the length of the period of induction is practically the same, either for a time of contact of, say, 1 hour, or for a time of contact corresponding with the complete length of the period of induction. Fig. 10 is a common curve of adsorption. To be absolutely sure, an experiment was carried out in which the contact of metal and oil was realized in a nitrogen atmosphere for 2 hrs. In this case, too, the induction period decreased from 60 hrs. for the original oil to 17 hrs. * for the metal-treated oil. This proves that we are justified in referring to the case as adsorption.



It seems very probable that certain compounds existing in the oil, which are able to delay or to prevent the oxidation for a certain length of time, are partly adsorbed by the copper surface.

If we accept the theory of C. Moureu and C. Dufraisse¹² † as correct, it

* In these 17 hrs. the time of contact is, of course, not included, as the oil was treated in a nitrogen atmosphere.

† The scheme of reaction, introduced by Moureu and Dufraisse is :

 $\begin{array}{c} A + O_2 \longrightarrow A[O_2] \\ A[O_2] + B \longrightarrow A[O] + B[O] \end{array} \xrightarrow{\text{acceleration}} \begin{array}{c} B[O] + A \longrightarrow B + A[O] \\ A[O] \longrightarrow A \cdot O \text{ (stable)} \\ \text{retardation} \\ \text{or} \\ \text{prevontion} \end{array} \begin{array}{c} B[O] + A[O] \longrightarrow A + B + O_2 \end{array}$

In this scheme B is the anti-oxidant and A the oxidizable compound. If O is placed between parentheses this means "not stable."

between parentheses this means not studie. The objection against this theory is that $A(O_2)$ ought to meet quickly a *B* molecule as $A(O_2)$ may only be considered to be possible for a very short time.

as $A(O_2)$ may only be considered to be possible for a very latter where $A(O_2)$ may only be considered to be possible for a very latter where $A(O_2)$. However, anti-oxidants exert their influence even in extremely low concentrations. Then considerations about reaction velocities led to the conclusion that a $A(O_2)$ molecule will be surrounded by 40,000 molecules in a non-activated state. That is to say, that B is separated from the non-stable $A(O_2)$ molecule by a layer of, say, is evident that—a metal surface being present—the length of the period of induction is a function of the time necessary to destroy that part of the anti-oxidant which is not absorbed.

The largest quantity of anti-oxidant is adsorbed by the first sq. cms. of metal surface (largest concentration of anti-oxidants). This explains why the first quantities of metal which are added exert such a great effect. The subsequent quantities of metal meet with lower concentrations of the anti-oxidant, thus the adsorption, and consequently its effect on the length of the period of induction, decreases.

After passing the induction period the metal is apparently completely inert; it is therefore entirely unjustified to speak about a catalytic effect in our case.

It is quite possible that previous workers, when concluding that a catalytic effect was exerted by copper, were deceived by its influence on the length of the period of induction.* Especially in experiments carried out at relative low temperatures at which the length of the period of induction is of great importance, neglecting this phenomenon may lead to serious mistakes.

A corresponding experiment was carried out with Chempur tin.⁺ This was of interest, as tin, contrary to copper, is regarded by some investigators as a retarder. The results are given in Table VII.

TABLE	VII.	
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Test.	Length of period of induction, hrs.	Reaction velocity.
Oil without any metal . $2\frac{1}{2}$ gm. of tin filings added to 250 cm. ³ of oil . Corresponding surface of copper filings added	$\frac{58\frac{1}{2}-60}{36}$	$1 \cdot 2^2 \\ 1 \cdot 2^0$
to 250 cm. ³ of oil	8	1.25

Thus with tin, too, a similar result was obtained-a shortening of the period of induction and practically no influence on the reaction velocity.

Tin is evidently less active than copper with regard to the shortening of the induction period. As most of the anti-oxidants contain polarizable nitrogen containing groups,¹³ these experiments affirm the well-known fact of a higher relative adsorption affinity for these compounds in the case of copper compared with that of tin.

Certain investigators supposed that the action of metals on oil would

20 molecules thick. In this case the collision change is rather small, and yet, to explain the phenomenon, it ought to be large. The aid hypothesis that the reaction will take place at the interface liquid-gas, which means a larger concentration, and, consequently, a larger collision change, is not acceptable according to our measurements.

It is possible that the assumption of reaction chains, which may be broken by

* Compare Fig. 4 in Part I of this paper. \uparrow Composition according to Quin's "Metal Handbook and Statistics," 1939: Sn = 99.989 per cent.; Sb = 0.005 per cent.; As = nil; Pb = 0.002 per cent.; Bi = 0.0007 per cent.; Cu = 0.0004 per cent.; Fe = 0.002 per cent.; Ag = nil; S = 0.001 per cent.

take place in the dissolved state, and to study this they added copper stearate in their experiments.

In connection with this we remark that a solution of copper during our experiments is quite possible, as a certain corrosion of the metal was observed. Yet we experienced no influence on the reaction velocity. It may be possible that an influence exists if one adds such compounds as copper stearate. However, it is good to realize that in this case a strange substance (stearate) is introduced into the system so that the phenomenon of induced oxidation is not excluded.

As long as no certainty exists with regard to the absence of induced oxidation, we consider the addition of soluble organic metal compounds for the study of specific metal action to be incorrect.

Rotterdam, Laboratory for Fuel and Oil Research. Utrecht, Physical Laboratory of the University.

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THE BLENDING OCTANE NUMBERS OF FURAN AND FURFURYL ALCOHOL.*

By HUGH B. NISBET, D.Sc., Ph.D., F.I.C., F.R.S.E.

SUMMARY.

Furan. Furan was added in various concentrations to motor spirit blends of different octane numbers, and it was found that in blends of low octane number the addition of small proportions of furan caused a big rise in octane number. This relative rise decreased with increasing proportions of furan, until when 30 per cent. was reached the rise became negligible.

The addition of furan to blends of high octane number caused only a slight increase in octane number, and when added to commercial iso-octane, a decrease in octane number was observed.

Furfuryl Alcohol. Owing to the insolubility of furfuryl alcohol in motor spirit of an aliphatic nature, the investigation was limited to the comparison of the blending values of furfuryl and ethyl alcohols in 10 per cent. blends in spirit containing benzole. The blending octane numbers of furfuryl alcohol in these blends are not as high as those of ethyl alcohol.

INTRODUCTION.

FROM the information which has been made available recently regarding the blending octane numbers of hydrocarbons and other compounds it has become apparent that this property is improved when (1) the molecule of an aliphatic hydrocarbon is highly centralized, (2) in addition to centralization in the open-chain hydrocarbon molecule there are also present one or more unsaturated linkages, (3) cyclic hydrocarbons contain unsaturated linkages and when the nature of the cyclic hydrocarbon becomes fully aromatic. It is also known that certain alcohols, particularly the lower aliphatic compounds, and also some ethers—e.g., isopropyl ether—possess high-blending octane numbers (Table I).

It has also been stressed, however, that the blending octane number of a compound is useless if no mention is made of the basis-fuel and the quantity in which the compound in question is blended,⁷ for the antiknock effect of added compounds is not linear with concentration. Moreover, the blending octane number is not the same in basis-fuels of low and high initial octane numbers. Indeed, this value may increase, decrease, or be fairly constant with increasing proportions of the blending agent (Curves A, B, and D respectively, Fig. 1). It may be low in blends with fuels of low octane number and high in blends with fuels of high octane number (Curves A and C, Fig. 1), or, vice versa, high in blends with fuels of low octane number and low in blends with fuels of high octane number (Curves E and F, Fig. 2).

In the present investigation the effect of combining a ring structure containing conjugated double bonds with an ether linkage as found in the molecule of furan (I), and the combination of this structure with an

^{*} Paper received 3rd February, 1941.

TABLE I.

Blending Octane Numbers of Certain Hydrocarbons, Alcohols, and Ethers.

-				
No.	Compound.	Blending octane number.	Conditions.	tef.
1	n-Octane, CH ₃ CH ₃ CH ₃ CH ₂ CH ₃ CH ₃ CH ₂ CH ₂ CH ₃	-19	Approx. 20 per cent. in fuel of octane number approx. 50; 212 jacket temp.	1
2	2:2:4-Trimethylpentane, CH,	100	27 27 27 27 27 I	L
	CH ₃ -C-CH ₃ -CH·CH ₃ 		and the second particular	
3	1-Octene, CH ₃ =CHCH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	25	» » » » 2	
4	4-Octene, CH ₃ CH ₂ CH ₃ CH CHCH ₂ CH ₂ CH ₃ CH ₃	91	»» » » » » 2	
5	2:2:4-Trimethyl-3-pentene, CHa	144	** ** ** ** 2	
	CH ₃ -C-CH=C-CH ₃			
6	n-Hexane, CH ₃ CH ₃ CH ₃ CH ₃ CH ₃ CH ₃ CH ₃	29	²³ 23 23 23 1	
7	2:3-Dimethylbutane, H H	124	11 11 11 11 11 1	
	CH ₃ -C-CH ₃ CH ₃ CH ₃		restance when a private of	
8	1-Hexene, CH ₂ =CHCH ₂ CH ₂ CH ₂ CH ₂ CH ₃	85		
9	2-Hexene, CH ₃ CH=CHCH ₂ CH ₂ CH ₃	100		
10	3-Methyl-2-pentene, CH _a	109	·· ·· ·· ·· 2	
11	CH ₃ CH=C−CH ₃ CH ₃			
	CH ₂ CH ₂ CH ₂ CH ₂	85.2	3	
12	cycloHexene, CH ₂ CH ₁ -CH ₁ -CH ₁ CH ₂ -CH ₂ CH ₂	101.5	3	
13	Benzene, CH_CH_CH_CH	101ª	(a) 20 per cent. blend in .42, octane number 48.4; 212° jacket temp.; cthyl gasoline S.30	
	And the first state of the second	87.56	(b) 20 per cent. blend in spirit of octane number 70, C.F.R. Motor Method.	
14	Ethyl alcohol, CH ₃ CH ₄ OH	154	15 per cent. blend in fuel of octane number 63; C.F.R. Motor	
15	isoPropyl ether, [(CH ₃) ₂ C] ₂ O	105	20 per cent. blend in fuel of octane number 70; C.F.R. Motor Method.	

alcoholic group, as in furfuryl alcohol (II), on the octane blending number has been studied from various angles.



PREPARATION OF FURAN AND FURFURYL ALCOHOL.

Furoic acid and furfuryl alcohol were prepared from furfuraldehyde by Cannizaro's reaction.¹² The alcohol obtained was distilled under reduced pressure and had b. p. 75–77°/15 mm.



EFFECT OF VARYING PERCENTAGE IN BLENDS ON BLENDING OCTANE NUMBER FOR VARIOUS BLENDING AGENTS.

The furoic acid was decarboxylated following the method of Gilman and Louisinian,¹³ substituting diethanolamine for the heavy coal-tar bases used in the original method when equally good results were obtained. The furan obtained had b. p. 31–35°, and was freshly distilled to remove any gum before being used in the engine tests. Table II gives the physical constants of furan and furfuryl alcohol taken from the literature.

NISBET : THE BLENDING OCTANE NUMBERS OF TABLE II.

Physical Constants of Furan and Furfuryl Alcohol.					
	Furan.	Furfuryl alcohol.			
B. p. ° C./mm. S.G. 20/4° Heat of combustion Cp.	31/745 0·9366 5001 cals.	170/760; 75–77/15 1·1285 6128 cals.			

The volatility and high specific gravity made it impossible, owing to carburation difficulties, to determine accurately the octane numbers of furan itself * or of blends containing more than 50 per cent. of the hetero-



EFFECT OF INCREASING PERCENTAGE OF FURAN AND ETHYL ALCOHOL ON THEIR BLENDING OCTANE NUMBERS, IN VARIOUS BASIS FUELS.

cyclic compound. A blend of 20 per cent. of furan in Fuel A (vide infra) had a vapour pressure of 8.5 lb./sq. in. (Reid).

DETERMINATION OF OCTANE NUMBERS AND BLENDING OCTANE NUMBERS.

Octane numbers were determined by the C.F.R. Motor Method, using the following as reference fuels :---

Fuel	A			Octane]	No. 52.5	
	B	•	•	,,	99.3	(Commercial iso-octane)
,,	E.		•		80	(A blend of 60 per cent. A and 40 per cent. B)
**	1		•	7 9	68.7	(Pool spirit containing benzole)
4.1	12	•	•	7 3	69.8	(A blend of 40 pts. benzole and 50 pts. A)

* Furan was found to have an octane number of the order of 90.

Blending octane numbers were calculated using the formula of Garner, Evans, Sprake, and Broom.¹⁴

RESULTS.

Furan.

Table III gives the results for furan added to a fuel of low octane number.

TABLE III.

Furan Blended with Fuel A.

Furan added,	Fuel A added, %.	Octane number of blend.	Blending octane number of furan.
10 20	90 80	64·7 74-0	174·5 160
30 40 50	60 50	79.5 81.5 82-0	$142 \cdot 5$ 125 111 \cdot 5

The effect of adding TEL to a blend of 10 per cent. furan and 90 per cent. Fuel A (octane number 64.7) is shown in Table IV.

г	AD	TE	T	17 -
	<u>a</u>		-	

TEL added to Blend of 10 per cent. Furan and 90 per cent. Fuel A.

TEL added, mls./imp. gall.	Octane number of blend.
0	64·7
1	71·8
2	76·0
3	79·5

In Table V are given the results for blends of furan with fuels of high octane number.

TAB	LE N	7.

Furan Blended with Fuels of High Octane Number.

Basis	Octane number	Furan in	Octane number	Blending octane	
fuel.	of basis fuel.	blend, %.	of blend.	number of furan.	
Fuel C Fuel B .	80 80 99·3	10 20 20	86-0 88-5 96-5	$140 \\ 122 \cdot 5 \\ 85 \cdot 3$	

The values given in the Tables indicate that furan has a very high blending octane number when added in small percentages to a fuel of very low octane number (Curve E, Fig. 2), but that the relative rise in octane number of blends decreases with increasing proportions of furan, until when 30 per cent. of furan has been added the rise becomes negligible. The experimental values for blends of 40 per cent. and 50 per cent. furan with Fuel A are probably low due to carburation difficulties. It is possible that the extrapolated figures indicated in Curve E' more truly represent the blending octane numbers of furan in these blends.

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NISBET : THE BLENDING OCTANE NUMBERS OF

The blending octane number of furan falls rapidly as the octane number of the blending fuel is raised (Curve H, Fig. 3). The blending octane numbers of furan in 20 per cent. blends with Fuels A and C are higher than most of those recorded for the compounds in Table I, and in Fig. 2 it is clearly shown that with fuels of low octane number furan is a better blending agent than ethyl alcohol in corresponding percentages, when considered from this aspect. In the blends with fuels of octane number 52.5 and 80 (Fuels A and C, respectively) which have been examined the



effect on blending octane numbers, of blending furan and benzene in $20^\circ_{,o}$ with basis fuels of different octane numbers.

blending octane number of furan is higher than that of *iso*propyl ether when used in blends with spirit of octane number 70 (Curves D, E, and F, Figs. 1 and 2). A 10 per cent. blend of furan with Fuel A shows quite a good response to TEL—comparable, indeed, with the responses of other blends of somewhat similar composition. This is brought out in Fig. 4, in which it is to be noted the results plotted are for mls./imp. gallon for the furan blend and mls./Amer. gallon for the other blends, and so are slightly adverse to furan.

Furfuryl Alcohol.

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At the outset it was found that furfuryl alcohol was not completely miscible with motor spirit. It did not mix at all with Fuel A, and only

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approximately 16 per cent. could be dissolved in Fuel D, which contained benzole.

The investigation was limited, therefore, to a comparison of the blending values of furfuryl alcohol and ethyl alcohol in 10 per cent. blends in Fuels D and E. The results are indicated in Table VI, and show that furfuryl alcohol is slightly inferior to ethyl alcohol in these blends.

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EFFECT OF ADDITION OF TEL TO 10% blends of several blending agents in various basis fuels.

In addition, it is interesting to note the relationship between the blending octane numbers of furan and furfuryl alcohol in 10 per cent. blends with various basis fuels as shown in Table VII. Although both furan and furfuryl alcohol show high blending octane numbers in these blends, in view of the difference in the nature and octane numbers of the basis fuels it is not possible to reach any conclusion as to the effect on the blending value of introducing the alcoholic group $-CH_2OH$ into furan.

TABLE VI.

Furfuryl Alcohol and Ethyl Alcohol in 10 per cent. Blends with Fuels containing Benzole.

Blending	Basis	Octane number	Octane number	Blending octane
alcohol.	fuel.	of basis fuel.	of blend.	number of alcohol.
Furfuryl Ethyl . Furfuryl Ethyl .	Fuel D Fuel E "	68·7 68·7 69·8 69·8	72·2 74·5 77 0 78·0	104 127 142 152

TABLE VII.

Furan and Furfuryl Alcohol in 10 per cent. Blends with Fuels of Different Octane Numbers.

Blending agent.	Basis fuel.	Octane number of basis fuel.	Octane number of blend.	Blending octane number of blending agent.	
Furan . Furfuryl alcohol . ""	Fuel A ,, C ,, D ,, E	52·5 80 68·7 69·8	$ \begin{array}{r} 64.7\\ 86\\ 72.2\\ 77.0 \end{array} $	$ \begin{array}{r} 174 \cdot 5 \\ 140 \\ 104 \\ 142 \end{array} $	

The author desires to thank Messrs. Scottish Oils, Ltd., and Dr. G. H. Smith for arranging for, and Mr. J. S. Tripney for making the engine tests recorded here. He is also indebted to Dr. R. G. M. Dakers and Mr. J. Harkess for help with the preparation of furan and furfuryl alcohol.

Heriot Watt College, Edinburgh, 31st January, 1941.

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THE VISCOSITY OF RUSSIAN AND RUMANIAN LUBRICATING OILS AT HIGH PRESSURE.*

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By R. B. Dow, J. S. MCCARTNEY, and C. E. FINK.

INTRODUCTION.

WHILE it has been realized for some time that viscosity of oils increases rapidly with increase of pressure, it is only within the past few years that any laboratory has made an intensive study to correlate this pressure effect with the chemical and physical properties of mineral oils. Previous reports by the senior author and his colleagues 1, 2, 3, 4, 5 have discussed pressure characteristics and these properties of mineral oils refined from American crudes, as well as the methods of measurement that have been used. In particular, it was found that for two oils of the same initial viscosity at the same temperature at atmospheric pressure, the one having the greater content of paraffinic compounds had the smaller pressure coefficient of viscosity at some higher pressure. But while it was apparent that high paraffinicity was accompanied by a lower pressure effect, it was not clear as to the relative contributions of naphthenic and aromatic compounds for greater pressure effects. Since the ratio of percentage composition of these latter compounds does not vary widely in oils refined from American sources, the need was felt for more extensive tests with oils from other fields. Through the kindness of several individuals. whose co-operation is acknowledged at the end of this paper, it has been possible to obtain samples of European and Asiatic oils for this study.

The viscosities of four Russian and three Rumanian oils have been determined at temperatures of 100° , 130° , and 210° F. at various pressures up to 46,000 lb./in.². In addition to the viscosity measurements, it has been possible to obtain other important physical and chemical data for these oils. These include the important items of molecular weight and structural analysis, as well as the more usual inspection data that have been made possible through the co-operation of Dr. M. R. Fenske of the Petroleum Refining Laboratory of this College.

It is necessary, for obvious reasons, that information as to the exact geographic location of refineries and facts regarding trade names must be omitted. For the purpose of this paper it is sufficient to identify the oils by number, and to state that they are typical, conventionally refined oils from crudes of the well-known fields of Russia and Rumania. Some data on the refining processes as given by the respective contributors of the samples will be included with the chemical and physical properties that have been studied by the authors.

DATA AT ATMOSPHERIC PRESSURE.

No details of the refining process for the Russian oils have been furnished to the authors, but the contributor characterized them as typical

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of the more important oils of that country. The Rumanian oils are typical lubricating oils obtained from non-paraffinic crudes by vacuum distillation. The distillate was neutralized with caustic soda and then vacuum redistilled into cuts. Sample 1 is a first-cut spindle oil; sample 2 is a more viscous cut, and sample 3 is a cylinder oil which remained as bottoms after the fractionating process was completed. Samples 1 and 2 were conventionally treated with sulphuric acid and then neutralized with caustic soda.

Table I is a summary of the tests and subsequent computations made for the oils at atmospheric pressure. These include the conventional

TABLE 1.	
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Gravity A.P.I	27·1 0·9234 0·9085 0·8980 0·8711	24.0 0.9101 0.8952 0.8846	$25 \cdot 4 \\ 0 \cdot 9020 \\ 0 \cdot 8869$	24-6 0·9064	20·9 0·9283	17·3 0·9509	15.6
Sp. gr. 60/60° F Density, 100° F , 130° F	0.9234 0.9085 0.8980 0.8711	0.8952	0.9020	0.9004	0.9283	0.9509	
Density, 100° F , 130° F	0.9085 0.8980 0.8711	0.8952	0.8869	0 0014	0.0100	0 0000	0.9021
, 130° F.	0.8980	0.8816	0.0805	0.8914	0.9133	0.9360	0.9474
910° F	0.8711	0 0010	0.8765	0.8808	0.9029	0.9257	0.9370
210 F	O OITI	0.8573	0.8489	0.8534	0.8761	0.8993	0.9108
Viscosity (c.s.) 100° F 20	00.70	99.30	37.53	258.40	23.09	486.40	1731.0
130° F.	74.50	41.30	18.50	188.00	11.90	142.00	403.6
210° F 1	12.92	5.85	5.19	28.82	3.69	17.22	35.39
Viscosity index	38	49	66	84	35	-36	-25
A S.T.M. nour point. ° F. +	- 5	-15	-25	+20	-25	+30	+40
ASTM. colour	71	3	21	73	41	51	black
Aniline noint ° C	92.2	94.3	88-0	120.1	60.8	77.8	80.4
Refractive index 20° C	1.5084	1.4993	1.4959	1.4983	1.5167	1.5263	1.5365
Molecular weight 4	35	393	364	666	285	409	511
Rings per molecule	3.13	2.75	2.48	3.40	2.18	3.45	4.05
n in CaH(an a)	31.7	28.5	26.4	48.1	20.9	30.0	37.7
min C H(m m)	1.8	6.0	6.0	7.9	7.5	11.3	16-2
Daraffing per cent	58	50	60	70	54	51	53
Naphthenes per cent	30	33	30	21	21	20	21
Aromatics per cent	19	8	10	6	22	20	26

Data on Russ	ian and	Rumanian	Oils	at A	tmospheric	Pressure.
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density and viscosity measurements (kinematic) made with 5-c.c. pycnometers and modified Ostwald pipettes, respectively, at the given temperatures. Viscosity index was computed from :

$$V.I. = \frac{(100^{\circ} \text{ F. vis. of } 0 \text{ V.I. oil}) - (100^{\circ} \text{ F. vis. of unknown oil})}{(100^{\circ} \text{ F. vis. of } 0 \text{ V.I. oil}) - (100^{\circ} \text{ F. vis. of } 100 \text{ V.I. oil})} \times 100$$

by means of conventional tables for the viscosities of the 100 and 0 V.1. oils, $e.g.,^{6}$. The A.S.T.M. calculations require no explanation. The computations for structural characteristics were made after the manner of Waterman and his associates.⁷

HIGH-PRESSURE MEASUREMENTS.

The viscosities of the four oils were measured at pressures ranging from atmospheric to $46,000 \text{ lb./in.}^2$ in a modified form of the rolling-ball viscometer of Hersey.⁸ The theory of the viscometer is quite simple, viscosity being determined from the time of roll of a ball down a tube inclined at a small angle to the horizontal. The roll time can be observed with a high degree of accuracy by any of the well-known methods of

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measuring time intervals that vary from a few seconds to 10 or 15 minutes. But for short roll times the viscosity is not simply related to them; also, since the roll time depends on other variables, such as ratio of diameter of bore to diameter of ball, it is evident that the viscometer must be calibrated for every change of geometry and of tube. Hersey ⁹ resorted to dimensional analysis to find the proper combinations of variables. But if the same tube be used, and a calibration curve determined for each change of ball diameter and angle of roll—the conditions under which the instrument is used by the authors—it is possible to find a simple relation from first principles between roll-time and viscosity.

Considering the motion of the ball to be one of rotation only about the instantaneous axis, the gravitational torque is :

 $\rho_0 V gr \sin \theta \quad . \quad . \quad . \quad . \quad (1)$

where ρ_0 = density of ball, V = volume of ball, r = radius of ball, g = accel. due to gravity, θ = angle of inclination to horizontal.

The opposing torque due to buoyancy is

where $\rho = \text{density of liquid.}$

The opposing torque required to change the angular momentum of the liquid will be denoted by L; it is impossible to evaluate it uniquely.

For uniform motion down the tube, the resultant of these torques must be balanced by the viscous torque

where $\mu = \text{coefficient}$ of viscosity, L' = length of roll-path, T = roll-time. The functional relation $f\left(\frac{A}{d}\right)$, between effective area and thickness of film of liquid is also unknown.

Equating torques in the two directions of rotation, and substituting the constant K for the combination of V, g, L', and $f\left(\frac{A}{d}\right)$:

K can be considered to be constant over a wide range of experimental conditions. For example, a temperature change of 212° F. causes an error of only 0.2 per cent. in K, and a pressure change of 5000 atmospheres causes like error of 0.2 per cent.

For large values of T, L becomes negligible and a linear relation exists between $T(\rho_0 - \rho)$ and μ . For short values of T, L becomes appreciable and it becomes necessary to determine μ graphically from a calibration curve. Fig. 1 is a calibration curve for a 0.635-cm.-diameter ball in a tube of 1.072 cm. diameter at an approximate angle of 6.3°. It is the practice of the authors to calibrate the viscometer for each ball diameter and angle of inclination, and then to compute μ from the slope of the linear portion of the curve, or to read it directly from the curve when the inertia effect is large enough to cause the curve to deviate from linearity.

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CALIBRATION CURVE FOR ROLLING-BALL VISCOMETER.

DATA AT HIGH PRESSURE.

The viscosity-pressure-temperature data for the seven samples are collected in Table II. The viscosities were computed from equation (4), as explained previously, by putting L = 0 for long roll times; or were read directly from the calibration curve when μ fell on a non-linear portion of the curve. Densities of the liquids at the various pressures and temperatures were computed from the equation of Dow and Fink.¹⁰ Pressures were measured by means of a manganin gauge coil that was inserted in the pressure line connecting to the viscometer. The change of resistance is known to bear a linear relation to change of pressure,¹¹ and the method of calibration against a dead-weight gauge is done according to standard procedure. Corrections for initial acceleration of the ball and change of path length were made as previously described (1). The other corrections are negligible for the pressure and temperature ranges that have been used.

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RUSSIAN AND RUMANIAN LUBRICATING OILS AT HIGH PRESSURE. 305

TABLE II.

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Viscosity-Pressure Data. Viscosity in centipoises.

Pressure in lb./in.².	Russian '' 00.''	Russian ''1.''	Russian ''2.''	Russian '' Bright Stock.''	Ru- manian ''1.''	Ru- manian ^{(''} 2.''	Ru- manian '' 3.''
			10	0° F.			
$\begin{array}{c} 14.3\\ 1000\\ 2000\\ 3000\\ 4000\\ 5000\\ 6000\\ 7000\\ 8000\\ 9000\\ 10\times 10^3\\ 12\\ 14\\ 16\\ 18\\ 20\\ 22\\ \end{array}$	$180 \\ 230 \\ 285 \\ 355 \\ 435 \\ 529 \\ 642 \\ 788 \\ 940 \\ 1160 \\ 1410 \\ 2090 \\ 3090 \\ 4900 \\$	$\begin{array}{c} 91\\ 112\\ 133\\ 161\\ 195\\ 255\\ 283\\ 340\\ 410\\ 490\\ 590\\ 845\\ 1210\\ 1740\\ 2460\\ 3490\\ \end{array}$	$\begin{array}{c} 32\\ 37\\ 45\\ 54\\ 65\\ 76\\ 91\\ 107\\ 125\\ 148\\ 174\\ 240\\ 333\\ 452\\ 610\\ 840\\ 1160\\ \end{array}$	$512 \\ 590 \\ 705 \\ 855 \\ 1030 \\ 1245 \\ 1505 \\ 1820 \\ 2190 \\ 2610 \\ 3130 \\ 4750 \\ 1000$	$\begin{array}{c} 21 \\ 24 \\ 28 \\ 33 \\ 39 \\ 46 \\ 54 \\ 63 \\ 74 \\ 87 \\ 103 \\ 142 \\ 197 \\ 270 \\ 370 \\ 509 \\ 703 \end{array}$	453 595 780 1010 1330 1725 2230 2905 3810 5010 6520	No data
			13	30° F.			
$\begin{array}{c} 14\cdot 3\\ 1000\\ 2000\\ 3000\\ 4000\\ 5000\\ 6000\\ 7000\\ 8000\\ 9000\\ 10\times 10^3\\ 12\\ 14\\ 16\\ 18\\ 20\\ 22\\ 24\\ 26\\ 28\\ 30\\ 32\\ 34\\ 36 \end{array}$	$\begin{array}{c} 67\\ 80\\ 97\\ 118\\ 140\\ 168\\ 201\\ 240\\ 289\\ 340\\ 400\\ 548\\ 760\\ 1070\\ 1500\\ 2070\\ 2880\\ 4060\\ 5470\\ \end{array}$	$\begin{array}{c} 35\\ 42\\ 50\\ 60\\ 70\\ 83\\ 97\\ 114\\ 135\\ 159\\ 187\\ 255\\ 350\\ 478\\ 650\\ 885\\ 1200\\ 1600\\ 2300\\ 3150\\ \end{array}$	$\begin{array}{c} 16\\ 18\\ 21\\ 24\\ 27\\ 31\\ 36\\ 41\\ 48\\ 55\\ 64\\ 86\\ 112\\ 149\\ 195\\ 253\\ 329\\ 429\\ 555\\ 715\\ 930\\ 1195\\ 1535\\ 2000\\ \end{array}$	$174 \\ 200 \\ 240 \\ 280 \\ 332 \\ 396 \\ 468 \\ 550 \\ 650 \\ 765 \\ 900 \\ 1230 \\ 1670 \\ 2250 \\ 3010 \\ 4000 \\ 5340 \\ $	$\begin{array}{c} 11\\ 12\\ 14\\ 16\\ 18\\ 21\\ 24\\ 32\\ 37\\ 42\\ 55\\ 72\\ 95\\ 125\\ 164\\ 215\\ 283\\ 371\\ 492\\ 652\\ 861 \end{array}$	$135 \\ 160 \\ 200 \\ 250 \\ 310 \\ 390 \\ 495 \\ 630 \\ 790 \\ 990 \\ 1225 \\ 1900 \\ 2980 \\ 4700 \\ 7340 \\ \end{cases}$	383 490 630 795 1000 1265 1590 2005 2510 3170 3990 6310 9940
			21	0° F.			
14·3 1000 2000 3000 4000 5000 6000 7000 8000 9000	$ \begin{array}{r} 12 \\ 13 \\ 158 \\ 17 \\ 20 \\ 23 \\ 26 \\ 6429 \\ 33 \\ 37 \\ 37 \\ - \end{array} $	8 9 10 11 13 15 15 17 19 21 23	4 5 6 7 8 9 10 11	$25 \\ 28 \\ 32 \\ 37 \\ 43 \\ 49 \\ 56 \\ 64 \\ 73 \\ 82$	4 4 5 5 5 6 6 7 8	16 18 21 24 28 33 38 44 51 59 $ 59 $	32 38 44 52 63 74 87 102 120 142

TABLE II-continued.

Pressure in lb./in. ² .	Russian ''00.''	Russian '' 1.''	Russian ''2.''	Russian '' Bright Stock.''	Ru- manian '' 1.''	Ru- manian '' 2.''	Ru- manian '' 3.''
10×10^{3}	41	26	12	93	9	69	168
10 × 10	52	33	15	116	10	94	231
14	67	41	19	145	12	128	314
14	85	51	23	190	15	175	423
10	107	64	27	236	19	238	592
10	132	80	32	290	23	320	790
20	170	101	39	360	27	430	1070
22	221	129	46	450	32	575	1470
24	283	160	56	545	38	770	1990
20	357	194	68	670	46	1050	2680
20	445	237	82	830	56	1420	3630
20	555	289	100	1020	68	1930	4899
94	690	354	120	1240	82	2610	6550
26	863	444	143	1520	100	3530	
38	1085	562	170	1850	120	4800	
49	1690	840	244	2720	172		
46	2620	1170	352	3950	243		
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Viscosity in centipoises.

The equation relating viscosity to pressure is not known accurately. It has been proposed by several investigators that

where μ_0 is the coefficient of viscosity at a certain temperature at atmospheric pressure. Differentiation of (5) shows that *a* equals the pressure coefficient of viscosity, considered to be constant. However, *a* is but an approximation, holding exactly in no case; at low pressures *a* departs noticeably from constancy.

The data of this paper, as well as many other, fit the following relation more accurately

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at all three temperatures.

Likewise, the relation between viscosity and temperature is not known exactly, although empirical relations such as the log log chart of the A.S.T.M., for example, are quite accurate over a moderate temperature range at atmospheric pressure. Since only three temperatures were used in this investigation, no attempt has been made to correlate the temperature characteristics of viscosity.

The data of Table II at 100° and 210° F. have been used to compute the constant *a* of equation (6), and the curves at 210° are shown in Fig. 2, in which the ratio of the common logarithms of the viscosity under pressure to the viscosity at atmospheric pressure is plotted against pressure.

The average slopes of the curves at 100° and 210° are given in Table III.

Table IV contains the average temperature coefficient of viscosity computed between 100° and 210° F. for constant pressures of 1000, 10,000, and 20,000 $\#/\text{in.}^2$.



RATIO OF THE COMMON LOGARITHMS OF THE VISCOSITY UNDER PRESSURE TO THE VISCOSITY AT ATMOSPHERIC PRESSURE PLOTTED AGAINST PRESSURE.

TABLE III.

Oil.			Slope $\times 10^5 = 10^5$	$1/p\Big(\frac{\log_{10}\mu}{\log_{10}\mu_0}-1\Big).$
			100° F.	210° F.
Russian "00"			4-10	4.80
** ** 1 **			4-17	5.50
			4.92	7.64
" BS "			2.81	3.79
Rumanian "1"			5-11	6.29
·· · · · 2 · ·			4.38	5.26
			-	4.65

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Average Slope of Viscosity Curves at 100° and 210° F.

TABLE IV.

Mean Temperature Coefficient of Viscosity between 100° and 210° F.

Oil.	$rac{1}{\mu_{100}} \Big(rac{\partial \mu}{\partial au} \Big)_{1000} imes 10^5.$	$rac{1}{\mu_{100}}\left(rac{\partial\mu}{\partial au} ight)_{ m 10,000} imes 10^{5}.$	$rac{1}{\mu_{100}}\left(rac{\partial\mu}{\partial au} ight)_{ m 20.000} imes 10^5.$
Russian "00".	858	883	
	836	869	888
	786	847	875
""BS".	866	882	_
Rumanian "1"	758	830 *	868
··· 2 ·· .	882	900	
""3"*.	1153	1197	_

* Between 130° and 210° F.

DISCUSSION.

The linearity between $\frac{\log_{10} \mu}{\log_{10} \mu_0}$ and pressure in Fig. 2 indicates that

equation (6) represents the data of Table II to a high degree of accuracy. The internal consistency of the data can be judged by the deviation of the single values of the slopes used in computing the average values. In no case did a single value deviate from the mean by more than 9 per cent., and the average of all the maximum deviations from the mean was of the order of 5 or 6 per cent. Of the seventy-eight values of the slopes computed at 100° and 210° F., only one had to be discarded in the averaging process. Consequently, in the opinion of the authors, equation (6) adequately represents the data at the three temperatures over a present range exceeding 40,000 lb./in.².

Inspection of Tables I and III shows little correlation between the data at atmospheric pressure and viscosity at higher pressures. In general, the viscosity at atmospheric pressure is related to the slope of the viscosity line in that they increase or decrease inversely but not uniformly. For example, Rumanian "1" at 100° and 210° F., as well as at 130° F., has the smallest initial viscosities but the greatest slopes. There appears to be little direct relation between viscosity index and the pressure effect. This is not unexpected, since it is realized that this quantity has little commonly in the oil industry for comparison purposes. There is good correlation between viscosity slope and molecular weight, and some correlation with number of "rings per molecule," but due to deviations from smooth curves, as well as lack of sufficient data, it is impossible to find mathematical correlation for these data.

It has previously been mentioned that oils of higher paraffinic composition have lower relative viscosities under pressure, and that the relative contributions of naphthenic and aromatic compounds towards higher viscosity have not been determined. The Waterman data of Table I bear out these conclusions regarding paraffinicity, as it can be seen that the viscosity slopes for the four Russian oils are less than those for the Rumanian oils at 100°, although it is interesting to note that the distinction is not so clear at the higher temperature. It is to be noted in this respect that the viscosity slope at both temperatures for Russian "Bright Stock" is the smallest of those given in Table III. It is disappointing to observe that the effects of naphthenes and aromatics cannot be separated in these cases. The sum of the two is practically the same for the Russian samples, and there is no noticeable difference in the viscosity slopes at 100° except for "Bright Stock," which has a high relative paraffin content. Likewise for the Rumanian samples, any possible separation of these effects is not valid, since the oils have lower paraffinic content. The authors hope to throw additional light on this interesting question in a further communication which will discuss the viscosity characteristics of Burma oils.

Since the properties of Pennsylvania oils have been studied intensively by the authors, it may be of interest to compare the viscosity-pressuretemperature characteristics of them with the present oils. For seven Pennsylvania samples,^{1,3} ranging in viscosity from 14 c.p. to 415 c.p. at 100° F., it has been found that the viscosity slope at that temperature varied between 2 and 4×10^{-5} . The viscosity index was between 100 and 127 for the individual samples, and the paraffin content was from 77 to 80 per cent. At 210° F. the viscosity slope had increased in each case, varying from 3 to 7×10^{-5} . It can then be seen that the viscosity slopes of the Russian and Rumanian oils are considerably larger on the average than those for typical paraffinic oils. Naphthenic oils from American crudes have viscosity slopes of about 5×10^{-5} at 100° F., and, in relation to the Pennsylvania or paraffinic oils and the present oils, it can be said that the Russian and Rumanian values are less on the average than those of typical naphthenic samples, but greater than those of paraffinic ones.

The average temperature coefficients of viscosity of Table IV are similar in magnitude to those for Pennsylvania oils, with the exception of the coefficient for Rumanian "3," which is unusually large. The coefficient increases with pressure in the normal way, but non-linearly for these oils.

ACKNOWLEDGMENTS.

The authors appreciate the co-operation of the Secretary of the Institute, Mr. S. J. Astbury, in procuring the oil samples. To Mr. E. E. Manning of Lubricating and Fuel Oils, Ltd., London, and Mr. C. R. Young of Romano-Americana, Teleajen-Ploesti, Rumania, they are greatly indebted for donation of the oil samples.

December 16, 1940.

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Pennsylvania State College, State College, Pa.

OBITUARY.

ANDREW CAMPBELL.

WITH the death of Andrew Campbell, which occurred at his home at Beckenham on 16th February, 1941, a great pioneer is lost to Petroleum Technology. Andrew Campbell had his roots in the Scottish shale industry. and all that was good in that industry he translated into petroleum practice. Born in Edinburgh in 1868, Andrew Campbell gained his early experience as a chemist with the Linlithgow Oil Company, after serving his apprenticeship with the well-known Edinburgh City Analyst, Mr. I. Falconer King. At the age of twenty-one he joined the Burmah Oil Company as Assistant Chemist to that company, with whom he remained until 1913, and afterwards served as their Advisory Chemist. During his years with the Burmah Oil Company he was actively engaged in refinery management, and was always greatly interested in new developments. I remember with what keenness he watched over efforts to separate aromatic hydrocarbons from Iranian gasoline by means of liquid SO₂. He was, in effect, well ahead of most of his colleagues in the industry, reading widely and travelling extensively. It is of some interest to note that when he took charge of the Burmah Oil Company's original refinery at Dunneedaw the throughput was less than 1,000,000 gallons per month and the original scheme was for refined kerosine, jute batching oil, wax candles and coke. Before he retired from Burma he brought this figure up to over 14,000,000 gallons per month, divided between the Dunneedaw Refinery and the Company's new one at Syriam. He developed the original idea of Dr. Hood's bauxite refining method into a works process, and this is of interest, too, in view of the recent revival towards bauxite as an adsorbent in the United States of America. He took an active interest also in experiments, carried out on a semi-plant scale, of a pioneering cracking process called the Noad, owned by the Burmah Oil Company through a subsidiary company formed to develop it. However, the war of 1914–18 intervened, and by the end of it other, and more fully developed, processes seemed to make further experimenting scarcely worth while.

In 1908, because of the Burmah Oil Company's interest in what was to become the Anglo-Iranian Oil Company, he visited Iran and drew up plans for a refinery at Abadan for a throughput of 2,000,000 gallons monthly—a figure which was vastly increased even before erection began. After the last war he visited Rumania with a deputation of oil technologists for the assessment of war damage.

Still later he became the Managing Director of National Oil Refineries, Ltd., and in this capacity built and equipped the great refinery at Swansea.

Some of Andrew Campbell's aphorisms remain in my mind today, especially the one "distillation is the cheapest method of refining." How prophetic was that saying, and how likely it is to become more and more effective when one considers the isolation of special and particular "chemical bricks " from the crude oil ! Andrew Campbell was a founder member of the Institute and a member of Council from 1916 to 1926. His rather remarkable paper on refining, which was later expanded into a useful monograph, showed his interest in the subject and his lucidity as an expounder and his acumen in foreseeing future developments. In Council he was a very Nestor, sane in judgment, equally balanced in knowledge and wisdom. He was always kindly, courteous and helpful, especially to his younger colleagues. Very open-minded and always ready to give the freest scope to his associates, he was a veritable father to his flock. Personally, as one who came into the industry with merely an academic background, I feel I owe him more than I can express, and these few words are a heartfelt tribute to one of whom it can fairly be said, "He made men."

A. E. DUNSTAN.



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Geology and Development.

682.* Major Tectonic Provinces of Southern Oklahoma and their Relation to Oil and Gas Fields. E. A. Paschel. Bull. Amer. Ass. Petrol. Geol., January 1941, 25, 1-22.-Southern Oklahoma and adjoining areas are divided into five tectonic provinces, which, from east to west, are the Ouachita Mountains province, the Arkansas Valley geosyncline, the Hunton-Tishomingo uplift, the Andarko-Ardmore geosyncline, and the Amarillo-Wichita-Red River uplift. One is considered a part of the Appalachian-Ouachita-Marathon homogeneous mobile belt which extends across the Continent from Eastern Oklahoma; the other four are regarded as having the features of a heterogeneous mobile belt and are treated by the author as two "uplifts" and two "geosynclines," being compared with similar provinces in California. Evidence is offered to show that the Andarko-Ardmore geosyncline has been compressed or squeezed between the Hunton-Tishomingo uplift to the north-east and the Amarillo-Wichita-Red River uplift to the south-west. The local structures within the "geosynclines" are regarded as having been formed primarily by compression, whereas those on the "uplifts" are regarded as having been formed by "vertical uplift." Local structures of the two uplift provinces are considered as having possibilities of more prolific oil production than those within the geosynclines. Boundary and topographic maps are given, and it is considered that with the improved drilling now available the Ordovician beds at 10,000 ft. will prove profitable for development.

R. J. W.

638.* Traverse of Upper des Moines and Lower Missouri Series from Jackson County, Missouri, to Appanoose County, Iowa. L. M. Cline. Bull. Amer. Ass. Petrol. Geol., January 1941, 25, 23-72.- A summarization, carried out for the Iowa Geological Survey Department, of a traverse of the Pennsylvanian upper Des Moines and lower Missouri series made along the strike from near Kansas City, Missouri, to Appanoose County, Iowa, an outcrop distance of 180-200 miles, in order to correlate the hitherto unknown Iowa section of the Des Moines series with that of West Central Missouri, The work has in general substantiated previous work of the Missouri survey, and correlated for the first time some of the higher Des Moines Beds in the areas surveyed. Eleven generalized columnar sections are described, and show regional variations in lithology and thickness. Further work in the same series from the south and west area of Kansas City into South-eastern Kansas is still required to tie up more exactly the status of Blackjack Creek, Houx, Higginsville, Myrick Station, Worland, and Exline Limestones. The Ardmore, which is the most important limestone in the Cherokee group, and, despite its thinness, has remarkable distribution from the vicinity of Tielsa, Oklahoma, to Guthrie County, Iowa, and throughout the area, is a valuable marker where persistent and diagnostic units are generally lacking.

R. J. W.

684.* Position of San Andres Group, West Texas and New Mexico. F. E. Lewis. Bull. Amer. Ass. Petrol. Geol., January 1941, 25, 73-103.—The result of the study of this wide area has led the author to conclude that the San Andres group should be placed in the Guadalupe series instead of the Leonard series. His correlations were supplemented by palzontologic information. Stereograms were made of a wide area of the South Permian basin to gain a regional perspective of the Upper Permian stratigraphy. Certain major structural features were recognized and were controlling factors in Permian deposition, and the stratigraphic phenomena of the Permian basin are related directly to lateral gradation. Surface studies and subsurface work reveal that, as a result of this gradation, many of the facies are time equivalents, unconformities being found the best time-markers because of the changing facies. The stereograms as used were on blue-paper prints in three sheets of 72 \times 42 in., 48 \times 40 in., and 32 \times 20 in., respectively. Vertical scale 1 in. = 1000 ft., the price being §4.25 the set. R. J. W.

685.* Edna Gas Field, Jackson County, Texas. M. M. Kornfield and C. R. Steinberger. Bull. Amer. Ass. Petrol. Geol., January 1941, 25, 104-119).—This gas-field was dis-

covered in 1919 by means of surface geology, and is 7 miles north-west of the town of Edna, Jackson County, Texas, adjacent to the west bank of the River Lavaca, and in the area which includes the lakes locally known as the Horseshoe, Alligator, and Blackberry. In 1909 gas seepages were noted along the river near the present field, and these, together with the topographic features, suggested the existence of oil or gas. Following a report written by S. G. Drushel of Edna in 1919, the first well was drilled in 1921 to a depth of 2670 ft., where it blew out and the hole lost. A second hole was drilled 125 ft. east to a depth of 4019 ft., when a blow-out junked the hole. Further drilling in 1926 established a commercial gas-well in a sand at The well was located 1200 ft. to the west of the other two wells, and 2650 ft. although lasting only a few months (the gas being piped to Houston), it established the existence of gas in commercial quantities. Further drilling was carried out, and between 1919 and 1932 fifteen wells were drilled to gas sands varying from 2600 to 4100 ft. in depth, eight of which produced gas; the others failed because of blowouts, etc. A well was drilled in the neighbourhood to 6425 ft., but ran into heaving shale, and was plugged back and completed at 5367 ft., where it sprayed 5 brl./day of 39° oil. Further wells were drilled to 7146-7155 ft., but heaving shale caused fishing jobs and abandonment as oil-producers; gas was obtained from 4637 to 4650 ft. by perforating casing. The sand locally was known as Rogers sand. A well costs about \$25,000. 80-100 ft. of 16-in. conductor pipe is set, 1000 ft. of 103 in. to shut off artesian water sands and production string, 5-7-in. casing to $2-2\frac{1}{2}$ in. tubing being used with Christmas tree connections tested 6000 lb.; wells produce through a 500-lb. separator. A tank of 65-250 brl. is erected to save the small amount of condensate produced with the gas, producing pressures being 1875 lb. on tubing and 1925 lb. on casing through $\frac{1}{4}$ -in. chokes; open flow 32 million cu. ft. of gas daily. The Houston Gulf Gas Co. contract for the gas at a price of 5 cents per 1000 cu. ft. Condensate is sold for tractor fuel. Sands have been logged at the following depths: 2600, 3570, 3850, 3955, 4105, 4640, 4750, 4960, 5360, and 5780 ft. Sands above 4200 ft. were developed during the early history of the field within a restricted area, but since 1936 the lower sands were produced and the area extended. It is believed that careful and extensive coring, supported by electrical well logging, will add a number of producing gas-sands and possibly oil-sands uncovered in the section now considered gas-bearing only. Life of individual wells should lengthen with improved completion methods and restricted flowing rates of the gas as com-R. J. W. pared with heavy unrestricted withdrawals in the older wells.

686.* Geology of Wind River Mountains, Wyoming. E. B. Branson and C. C. Branson. Bull. Amer. Ass. Petrol. Geol., January 1941, 25, 120-151.-The paper is a summary of research to date, with preliminary conclusions, which for several years have been planned by the authors, on the geology of the Wind River Mountains. The mountains are eroded from a north-west to south-east trending anticline, and lie entirely within the boundaries of Freemont County, Wyoming, the range being 150 miles long and about 40 miles wide. Maximum elevation is 13,800 ft., and on the east it rises above a general level of approximately 5000 ft. and 7000 ft. on the west, the largest town on the east side being Lander, and Pinedale on the west side. Wind River and its tributaries drain the north-east side and Green River the south-west side, whilst Sweetwater River drains the south end and part of the south-west side. The range consists of a core of pre-Cambrian granodirite and metamorphics on which are developed the higher parts of the range and the glaciated peaks. Palæozoic sediments form foothills on the north-east side and some resistant beds support long dip slopes to the plains. Mesozoic sediments underlie hogbacks and valleys paralleling the axis of the range. Dips of the sediments on the north-east flank range from 10° to 15°, covering Cambrian to late Cretaceous in age, only Silurian being absent. Eocene, Oligocene, Pliocene, and Pleistocene overlap older formations in some places. On the east side a series of anticlines parallels the main range about 25 miles from the summit. Anticlines on the east side are affected by minor faults, as is also the main ridge, and the pattern of the lakes indicates much faulting in the pre-Cambrian core. The main uplift and folding of the range came at the close of the Mesozoic, but minor uplifts occurred during the Cenozoic. These uplifts were probably irregular, as indicated by the absence of Ordovician and Devonian strata at the south end and the pinching-out north of the range of the Tensleep, Phosphoria, and Chugwater formations.

The Lander Sandstone, at the base of the Ordovician, on the south end of the Wind River mountains, is absent at the north end and thickens to 80 ft. or more on the east side of Big Han Mountains.

Glaciation and peneplanation are worthy of fuller discussion, and the development of drainage lines east of the range requires fuller treatment than could be given in this paper.

Known oil-bearing formations on the east flank are : Madison, Tensleep, Phosphoria, Dinwoody, Sundance, Dakota, Mowry, and Frontier.

An areal geology map of the Wind River Mountains is given, in addition to a columnar section of the formations exposed, and formation names and various cross-sections. R. J. W.

687.* New Source for Sodium Sulphate in New Mexico. W. B. Lang. Bull. Amer. Ass. Petrol. Geol., January 1941, 25, 152-150.-Sodium sulphate-bearing brines have been discovered west of the Pecos River in south-east New Mexico within a short distance of the potash mines at Carlsbad. The brines are found in the Castile formation, where weathering has altered the anhydrite, and are probably the accumulations of the dense derivatives of percolating ground water through gravity differences retained in traps which temporarily at least preserve these concentrations from flushing by normal ground-water circulation. These brines are therefore considered as residual accumulations by differential gravity, a process relatively unique in the concentration of economic mineral matter in a dissolved form. The materials essential to the formation of such a brine are dolomite and gypsum with contained accessories, chief among which is halite, the place of lodgment of the brines being at or near (above) the surface of alteration of anhydrite in the Castile formation to Gypsum, where the surface is not more than 100-300 ft, below ground surface. If sufficient reserves can be located there is promise for commercial development. A map with a diagrammatic cross-section is given of the area concerned, and the paper also summarizes sodium sulphate production in other south-western States. R. J. W.

688.* Estimating Oil Reserves. F. H. Lahee. Bull. Amer. Ass. Petrol. Geol., January 1941, 25, 164–166.—The author stresses the importance of estimators stating by which method they have reached their figures, prior to publication of same. Estimates, he states, should be made by either the "probable area method." or the "proved area method." The former is the one often applied in calculating reserves on incompletely developed properties; the latter, which is conservative and relatively safe from large errors, is more often applied to proved areas, although with reasonably active wildcatting and development it is likely to show larger increments in reserves through extension of developed territory. Oil reserves may be figured :

(a) By the old method of decline curves;

(b) By multiplying together a number of factors previously studied and carefully measured, such as porosity, permeability, sand thickness, areal content, and recovery factor;

(c) By detailed analysis of production history, including data on gas-oil ratios, bottom-hole pressures, etc., and projection of this history into the future.

Whilst there may be room for considerable difference in the figures and estimates used, once the basis figures are agreed on there is a fair degree of similarity between the results obtained by different workers. R. J. W.

689.* Miocene of Caliente Range and Environs, California. J. E. Eaton, U. S. Grant, H. B. Allen. Bull. Amer. Ass. Petrol. Geol., February 1941, 25, 193-262.—An exhaustive paper with maps, sketches, and many photographs, including plates of the various faunas to be found. Caliente range and environs is considered to furnish what is believed to be the best Triocene record for California. Approximately 180 molluscans and echinoderm faunas, representing forty-seven nearly consecutive horizons, from that of Turritella inezana var. hoffmani upward to well above that of Astrodapsis tumidus, have been obtained from a Miocene succession locally about 13,800 ft. in thickness.

The district lies at the junction of the three largest Miocene provinces of the State, linking their histories. A long, narrow, and deep upper Oligocene and Miocene trough about 300 miles in length and 20 in width, apparently extending from the Santa Cruz region south-east to Caliente Range, is the area the authors have discussed. Evidence obtained in Caliente Range and environs, in combination with state-wide data, suggests the history as follows :---

In the lower Oligocene California appears to have been completely emergent, with continental deposits being locally laid down near the present coast.

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In the upper Oligocene the sea invaded the State as a narrow inlet occupying the newly initiated Caliente trough, continental deposition continuing in most former areas of that nature. The marine Miocene of California is a transgressive series, conformation basinward, but revealing strandward the occurrence of two oscillations which respectively inaugurate and divide its upper third, comprising three nearly equal major natural divisions, the Vaqueros (Lower Miocene), Temblor (Middle Miocene), and Monterey (Upper Miocene). Each of these has a more or less distinctive epeirogenic history, fauna, and average physical aspect. The sea transgressed during both Lower Miocene and Middle Miocene periods, with some regression during the latter period. It advanced once again widely during early Upper Miocene time, and reached its widest extent during this epoch. Progressively cooler waters are recorded during the Miocene series, the earlier tropical fauna being replaced by subtropical fauna with slightly hardier fauna at a later period. Each fauna changed relatively slowly during its stage, with hardier forms with the cooler waters, the Miocene series of California being divided into approximately equal thirds as regards major physical and coincident faunal incidents. Wide regression, resulting in complete emergence of California, separates the Miocene series from the markedly different and more restricted Pliocene series. The authors state that, except for parts of the Bilter Creek area, their field-work over twelve, seven, and three years, respectively, represents only a rapid reconnaissance made a few days at a time, but they regard this as providing preliminary framework for future investigation. R. J. W.

690.* Micropaleontology and Stratigraphy of a Deep Well at Niceville, Okaloosa County, Florida. R. Hendee Smith. Bull. Amer. Ass. Petrol. Geol., February 1941, 25, 263-286.—A water-well was drilled at Niceville to a depth of 524 ft. on April 1939, cuttings were taken approximately every 10 ft. and saved and carefully examined, thus enabling the author to establish some dip and strike control of the formations, and giving the first occurrences of some typical forms in the column where previously in the Upper and Middle Miocene sections considerable doubt had existed as to the thicknesses and depth of the beds and ranges of many of the microfossils. Formerly, owing to the rarity and scattered nature of good outcrops in Western Florida, stratigraphic work had been based almost entirely on palæontology, little attempt being made to ascertain thickness and amounts of dip. A standard section for the Middle Miocene of the Gulf Coast had previously been set up by two geologists, largely from outcrops in the area. The present work serves as a useful point of departure for correlation of wells in other parts of the Gulf Coast, as it aids in establishing the relative position of points in the palæontological time scale previously known only from inferential evidence. Map cross-section and charts are given. R. J. W.

691.* Pre-Cambrian Zeolite Opal Sediments in Wichita Mountains, Oklahoma. C. A. Merritt and W. E. Ham. Bull. Amer. Ass. Petrol. Geol., February 1941, 25, 287-299.—The Wichita Mountains are located in south-western Oklahoma, principally in the counties of Kiowa and Comanche. The mountain system forms a physiographic unit of irregular peaks and low knobs with a maximum relief of about 1000 ft. The width is nowhere more than 28 miles and the extent some 65 miles to north-west and south-east, the peaks being separated by flat valleys or plains. The Wichita Mountain igneous rocks are Pre-Cambrian in age, and are composed chiefly of granophyres and gabbro-anorthosite. Rocks of a unique type have recently been discovered, composed principally of zeolites and opal, with variable amounts of dolomite and calcite, occurring as four scattered outcrops in Kiowa County. They appear to be stratified and to have a maximum thickness of 47 ft., and are given the name of "Tapee Creek." Evidence is given to show that the zeolites and opal have formed by the alteration of a sediment which was essentially an anorthosite-graywacke with some beds containing dolomite and perhaps limestone. The zeolites, chiefly natrolite, and the opal are secondary and partly diagenetic. R. J. W.

692.* La Rosa Field, Refugio County, Texas. B. Fisher. Bull. Amer. Ass. Petrol. Geol., February 1941, 25, 300-317 .- This paper described the La Rosa field, discovered in 1938 as a result of geophysical work preceded by detailed surface mapping. The field is located in the southern part of Refugio County in the lower Gulf Coastal region of Texas. It is found in the so-called Frio trend, which is characterized by a maximum development of the sands on the Frio formation which shale out within short distances both up and down the dip. Most of the fields along this trend are very prolific and produce an excellent grade of crude oil. The use of electrical logs and careful coring have made the interpretation of structural conditions a relatively simple problem, whilst core analysis has provided valuable information concerning characteristics of the oil-sands. The reflection seismograph is given credit for the field's discovery. In all, some seventy-two oil-wells are producing from six separate sands, ranging in depth from 5400 to 6300 ft.; there are also six gas-wells completed in three different gas-sands. The 5900 ft. or discovery sand is clean, coarse-grained sand from 80 to 100 ft. thick and containing a maximum oil column of 30 ft., with a gas-cap, 25 ft. thick, on top. Sand averages 32 porosity and permeability 2000 milli-darcys. Ultimate recovery from this sand is indicated to be 975 brl./ft. Gas-oil ratio averages 500 cu. ft. gas per brl. oil produced which has a 42° A.P.I. R. J. W. gravity.

693.* Future of Field Geology. R. Dana Russell. Bull. Amer. Ass. Petrol. Geol., February 1941, 25, 324-326.-The author refers to a discussion published in the August 1940 number of the Bulletin in which leading geologists expressed the opinion that field geology as a technique for the discovery of oil-fields has not only passed its peak, but has practically exhausted its usefulness, except in foreign work. The author challenges this conclusion, and wonders whether the decline may not be ascribed to other factors, and stresses the value of careful surface mapping, illustrating this by enumerating fourteen areas where oil and (or) gas occurs. In only two can discovery be ascribed to surface geology alone, with surface indications aiding in the discovery of six others, but all could have been found by surface mapping. He also mentions Mississippi, which has been covered several times by geophysical surveys, yet it remained to a surface geologist to discover the first oil-field of this State. In conclusion the author's complaint is against the implication that field methods are no longer useful as a means of finding oil except in unknown foreign areas. Surface mapping, being by far the cheapest of exploration methods, should not be abandoned in favour of more expensive techniques until its possibilities have been exhausted.

R. J. W.

694.* Upper Paleozoic of Western Australia. Correlation and Palæogeography. C. Teichert. Bull. Amer. Ass. Petrol. Geol., March 1941, 25, 371–415.—This paper was originally presented in January 1939 to the Geological Section of the Australian and New Zealand Association for the Advancement of Science. Further field-work carried out during 1939 and 1940 has rendered it necessary for the author to thoroughly revise and alter his previous presentation.

The paper deals with those rocks in Western Australia which were—as elsewhere on the Continent—until recently classified as Permo-Carboniferous. There has been a growing tendency in recent years to include these rocks unrestrictedly in the Permian, and in a later section of the paper the author discusses whether this is justifiable. The strata and their fossils are described in broad outline, and a correlation is suggested for the three important districts of Western Australia : Irwin River, North-west Division, and West Kimberley Division, which are compared with those of Eastern Australia, particularly of New South Wales, and it is indicated that the general succession of the Hunter River area in New South Wales can be recognized in West Australia—namely, Lower Marine-Lower Coal Measures-Upper

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Marine. A physiographic map of Western Australia and a sketch-map of same showing the distribution of outcrops of Upper Palæozoic rocks, etc., together with an extensive bibliography, are included. R. J. W.

695.* Some Problems of Appalachian Structure. R. E. Sherrill. Bull. Amer. Ass. Petrol. Geol., March 1941, 25, 416-423.-The Applachian foreland is a broad, gentle, spoon-shaped synclinorium, the lowest part of which is in northern West Virginia and lies north and west of a closely folded and faulted mountain zone. Search for oil and gas production from deeper formations has emphasized the importance of a better understanding of the structure of this area. In his paper the author stresses the structural complexity of the Appalachian foreland, mentions some of the problems involved, and considers the origin of the folds, including direction of stress and mechanics of the folding, effects of rotational stresses, date of folding. These problems are, he states, not limited to the foreland, but are part of their entire concept of mountain deformation. Foreland problems having received scant attention in the numerous theories of orgeny, he considers that further geophysical, well record, and general stratigraphic data are needed in working towards a solution of these problems. Also important are the accumulation, correlation, and interpretation of data on the joints, local faults, and areas of exceptionally steep surface dips, it being necessary that each structure and problem be regarded as part of a large regional picture into which it must fit. R. J. W.

696.* Silurian Production, Shipley Field, Ward County, Texas. C. P. Cordry and M. E. Upson. Bull. Amer. Ass. Petrol. Geol., March 1941, 25, 425–427.—The development of production from the 7000-ft. level in a white limestone of Silurian age in the above area represents the first commercial production found in the State from beds of this age. The well was completed on 13th December, 1940, in a pay-zone between 7010 and 7060 ft., after having been drilled to a total depth of 9187 ft. and plugged back to 7075 ft. 7-inch casing was comented at 6968 ft., and after being acidized and thoroughly washed, the well flowed 1595 brl. of oil during a period of 12 hr. Gravity of the oil was 32° Be. The area in which this deep test is located has for ten years been producing oil from sandstone beds of the Whitehorse group, the base of which was found in this well at 2900 ft. Below this depth to 6030 ft. a succession of dolomite and limestone beds of Permian age was penetrated. From 6330 to 6930 ft. siliceous limestone in three different units were found, which correlate with a well on the McElroy field in Western Upton County, 32 miles farther east, at a depth of 10,167–11,153 ft. A white and slightly pinkish, coarsely crystalline limestone was encountered up to 7110 ft., whilst strata of Upper, Middle, and Lower Ordovician were penetrated up to 9187 ft., when, owing to an accident, the well was plugged back to test an upper oil zone. R. J. W.

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697.* Correlation of Crude Oils with Special Reference to Crude Oil of Gulf Coast. D. C. Barton. Bull. Amer. Ass. Petrol. Geol., April 1941, 25, 561-592.—This paper represents a compilation with minor revision of the notes used by the author in his presidential address to the Association at Oklahoma on 22nd March, 1939, and the manuscript of a preliminary draft of a comprehensive paper planned for later publication before death intervened. The late author's assistant, Virgil Moore, and W. P. Haynes rearranged and edited the manuscript and drew the accompanying charts, preserving as far as possible the diction and arrangement of the author.

In an introduction it is stated that discussion of the source and migration of crude oils is invariably beclouded by the lack of any reliable criterion which will serve to distinguish one crude from another, or will permit the identification of a given crude oil throughout all stages of its life-history. Many believe that crude oils migrate upwards across bedding planes from great depths, but this belief rests on indirect evidence. It is seldom possible to identify a given shallow occurrence certainly with the deep-lying counterpart or parent accumulation from which it is believed to be derived. So far we cannot identify a given crude oil with its parent or distinguish crude oils of diverse parenthood, but if it is possible to establish the existence of, and learn to recognize some type of invariant property in crude oils that remains constant and unchanging throughout the course of their normal evolution, a solution would be expedited.

The author suggests a "gravity-interval pattern" to serve as such an invariant characteristic for the identification of crude oils. This gravity-interval pattern is based on analyses made by the United States Bureau of Mines by the Hempel method, where a distillation cut is taken at 50° C. and at every 25° C. thereafter up to 275° C. under atmospheric pressure, and at 200° C. and every 25° there-after up to 300° C. at a pressure of 40 mm. of mercury. The A.P.I. gravity of each of these cuts is determined, and this record serves for the portrayal of the gravityinterval pattern of each crude oil. All analyses were classified according to type of base-that is, paraffin or naphthene. For this purpose the A.P.I. gravity of key fraction No. 1-the last fraction obtained when distilling at atmospheric pressure by the Hempel method-is taken as an index. All crude oils in which key fraction No. 1 has an A.P.I. gravity of 40° or lighter are called paraffinic; those between 33° and 40° are classed as intermediate, and those of 33° gravity or heavier are called naphthenic. All analyses of crude oils with the same gravity for key fraction No. 1. measured in degrees A.P.I., are then taken, and the interval in degrees A.P.I. between each cut is noted. These intervals are averaged and plotted in graph form using the gravities of key fractions No. 1 as ordinates and the gravity intervals as abscissæ. The irregular graph for each interval is then represented by a smooth curve, and the mean values of the intervals in A.P.I. degrees listed in tabular form for ready reference for various other crude oils. From the graphs the author can establish from various samples-not identical-a family resemblance. Numerous graphs of oils from different fields well serve to illustrate results of the author's studies employed by him as a standard for identification of crude oils. R. J. W.

698.* North Cowden Field, Ector County, Texas. S. C. Gresey and F. F. Fulk. Bull. Amer. Ass. Petrl. Geol., April 1941, 25, 593–629.—This field is on the eastern margin of the Central basin platform in North-central Ector County, Texas, 18 miles north and west of Odessa and 30 miles north-west of Midland. In 1924 and 1925 the field first attracted attention, but leasing was carried on slowly and without boom semblance. Ten-year leases were taken, and the nearest producing wells were 125 miles south-east, in the Reagan County at Big Lake field. The discovery well was completed on 11th September, 1930, drilled with a standard rig, with a natural daily flow of 272 brl. On 16th January, 1934, it was shot with 160 quarts of nitroglycerine, and the well received a new proration potential of 777 brl. daily. Numerous and erratic water-bearing strata caused operators to turn to the rotary system of drilling, and during the latter part of 1935 drilling spread in all directions, and a large number of wells brought in. Most operators circulate with live oil to protect porous beds when drilling in with the rotary.

All production of gas and oil in the field is from the Grayburg formation of the Whitehorse group. There are four pay-sands in the first 400 ft. of the Grayburg. The first pay is 50–70 ft. thick; the second about 55 ft.; the third from 10 to 40 ft., as also the fourth. Wells showing considerable anhydride in the pay section make excellent producers. Depth is about 3615-3875 ft. but thickness of Grayburg formation has as yet to be determined. Original reservoir pressure is thought to have been 1750 lb. per sq. in. Up to July 1938 212 wells had been drilled, mostly by rotary, and a deviation of no more than 5° max. is allowed. Drilling time rotary 42 days. Wells are spaced one well per 40 acre unit and 440 ft. from lease lines. 66% of the wells are connected to a natural-gasoline plant of the absorption type with a capacity of 50 million cu. ft. per day against a 30–40 lb. back pressure. R. J. W.

699.* Page Field, Schleicher County, Texas. R. Simpson. Bull. Amer. Ass. Petrol. Geol., April 1941, 25, 630-636.—This field is in Schleicher County, Texas, 9 miles southeast of Eldorado and 45 miles due south of San Angelo. It is on the western edge of the eastern platform and near the eastern edge of the Black shale basin in the physiographic province known as the Edwards plateau. It is about 70 miles west of the nearest outcrop of igneous rock of the Llano uplift. The discovery well was commenced in 1929, but at 5055 ft. was shut down. In May 1934 the well was deepened, and at 5402 ft. a sweet gas, with a distillate content of 0.7 gal. per 1000

cu. ft., was struck in the following month. The well was carried to 6257 ft. and then plugged back to 5550 ft. and shot with 200 quarts of nitroglycerine at 5400-5445 ft. and, following acidization with 3000 and 8000 gal. of hydrochloric acid, was completed in 1936 as a gas-distillate well with an open flow of 16 million cu. ft. Of the seven wells drilled, four are gas, one oil, and two dry. The four gas-wells have a potential gas production of 170 million cu. ft. One oil-well has a potential of 259-2 brl. of 37° gravity crude. It is now producing 37 brl. daily, with 15 brl. of salt water. A 45-mile 8-in. gas line (welded) from field to San Angelo has been completed for an electric generating and water-pumping plant there. Gas occurs in porous limestone in the Straun series. It is the author's belief that the Page field is not primarily a fold, but rather a reef or depositional "high," possibly over an old positive area with some later folding. R. J. W.

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700.* Summary of Faunal Studies of Navarro Group of Texas. L. W. Stephenson. Bull. Amer. Ass. Petrol. Geol., April 1941, 25, 637-643.-The Navarro group in Eastcentral Texas is the uppermost major geologic unit of the Upper Cretaceous series of Texas. Its area of outcrop forms a relatively narrow, sinuous band extending from Red River in Bowie County in the north-east to the Rio Grande in Maverich County in the south-west. The group has been divided into four formational units in ascending order, Neylandville marl, Nacatoch sand, Corsicana marl, and Hemp clay, all of which are of marine origin. The sediments composing them are medium- to finegrained, and were deposited in waters covering a continental shelf, the limiting depths of which have not been precisely determined, but the character of the fossil faunas suggests that the waters were not deeper than those of the Continental Shelf off the present Atlantic Coast. Recent palæontologic studies have resulted in 411 named species and varieties of the larger invertebrate fossils being recognized. A further 100 poorly and incompletely preserved forms are assigned to genera, but too imperfect for specific identification. Fully 90% of the Navarro fauna as at present known is restricted to the Navarro group and its equivalents. Only one specimen is known to range upward into sediments of Tertiary age. The group is correlated with the Maestrichtian of Europe. R. J. W.

701.* Analysis of Midway Fauna of Western Gulf Province. J. Gardner. Bull. Amer. Ass. Petrol. Geol., April 1941, 25, 644–649.—In the Midway fauna of the Western Gulf province about forty-seven superspecific groups of pelecypods and about sixtyfive of gastropods, two of scaphopods, one of cephalopods, and one of Vermes have been recognized. No single species in the Gulf province is certainly known to bridge the rift between the Cretaceous and the Tertiary. The value of the superspecific groups in determining the relationship of the Palæocene fauna to those which precedo and follow varies widely. They may be segregated into seven more or less clearly defined assemblages, as follows :—

(1) Genera recorded in the Midway that have persisted from Cretaceous to Recent times;

(2) Those restricted to Cretaceous and Palæocene;

(3) Those restricted to Cretaceous and early Tertiary;

(4) Those restricted, at least in the Gulf Province, to Palæocene and early Eocene;

(5) Those restricted to the Palæocene and Eocene;

(6) Those restricted to the Palzocene, Eocene, and Oligocene;

(7) Those initiated in the Palæocene and continuing to the Recent.

R. J. W.

702.* Simpson Group of Arbuckle and Wichita Mountains of Oklahoma. Charles E. Decker. Bull. Amer. Ass. Petrol. Geol., April 1941, 25, 650-667.—The deep interest in the Simpson group manifested for many years has been steadily increasing. This is due to the various oil and gas formations contained over wide areas, to its asphalt deposits, its excellent glass sand, and to its numerous fossils, making possible correlations both local and widespread.

Because of recent road-cuts it is possible to present several detailed sections;

whilst restudying old sections new information is presented indicating changes in formation contacts, relative thicknesses of formations and extension eastward of the Tulip Creek formation. Additional evidence for earlier omission of Falls as a formation name for the Simpson group is found to be more fully justified, the group consisting of a remarkable series of alternating limestones, sandstones, and shales. The paper includes a graphic section showing Simpson group formations, and several revised detailed sections of the same are given. R. J. W.

703.* Devonian Subsurface Strata in Western Kentucky. L. B. Freeman. Bull. Amer. Ass. Petrol. Geol., April 1941, 25, 668–712.—The purpose of this investigation is to correlate the subsurface Devonian strata in the Western Kentucky basin with the equivalent beds in the generally distant outcrops. Samples from about forty wells were studied, zoned on the basis of general lithology and insoluble residues, and a tentative correlation of these zones with the outcrop material was suggested. Formations recognized at the surface in Southern Illinois can be traced into the subsurface in Western Kentucky. A map showing area included in this study and its relation to areas of Devonian outcrop is given and a Palæostratigraphic map of the Devonian of Western Kentucky shows probable Pre-Chattanooga distribution of Devonian and subjacent Silurian formations, with sections across same, together with a composite correlation diagram to illustrate the relationship. The paper includes detailed sections of wells examined, also a bibliography. R. J. W.

704.* Study of Sedimentation and Stratigraphy of Lower Mississipian in Western Michigan. L. Hale. Bull. Amer. Ass. Petrol. Geol., April 1941, 25, 713-723... Formations representing the lower Mississippian in Michigan have always been considered as unimportant shale sections and have received very little study. Recent drilling developments in Allegan, Kent, and Ottawa Counties have provided good samples, proving that this western area differs markedly in its sedimentary history and presents several interesting stratigraphic problems.

The formations discussed comprise the Coldwater, Ellsworth shales and the upper part of the Antrim formations

The basal member of the Coldwater is red fossiliferous limestone with some red shale; the "Coldwater lime" in many places is light grey dolomite rather than limestone, and has embedded crystals of secondary dolomite and "pepperings" of glauconite. The Ellsworth is present only in the western part of the State, and is grey and greyish-green shale with grey dolomite zones.

The green shales of the Ellsworth grade into, and alternate with, the black shales of the Antrim, making it difficult to determine the top. The oldest formation discussed is the Antrim shale, which caps the producing Traverse limestone, and is considered to be the source bed of the Transvaal. A further detailed account of the Antrim-Ellsworth-Coldwater shale formation by Eleanor Tarbell is discussed on pages 724-733. R. J. W.

705.* Olla Field, La Salle Parish, Louisiana. S. A. Packard and H. R. Kamb. Bull. Amer. Ass. Petrol. Geol., April 1941, 25, 747-750.—The Olla field is 4 miles east of the Urania field, and 3 miles south-east of the town of Olla, being on the north-east edge of what is called the Central Louisiana district. This new field is the first large producer of oil from sands below the top of the Eocene Wilcox group. Previous important Wilcox fields such as Urania and Eola found production only in the top sand member. The Olla zone is about 470 ft. below the top of the Wilcox, and averages 300 ft. in thickness. Five producing oil and gas sands are known at present within the zone, which is characterized by the presence of glauconitic and calcareous sands and marks suggesting it is part, at least, of shallow marine origin. The field lies on a narrow, elongate north-south anticlinal ridge of small closure along the east side of the so-called Urania uplift.

To 25th November, 1940, seventy-four oil-wells and one gas-well have been completed, forty-four produce from the "upper or lower Central sands," eleven from the nest sand, known as "Mathews sand," nineteen from the next lower sand, known as "Cruse sand," and one from the lowest, known as "Good Pine sand." The average depth is 2250 ft. and wells take about two weeks to complete. A selected

section 40-150 ft. of the Ulla zone is cored, and then an electric survey made before setting the pipe. The wells come in flowing 50-300 brl. daily through a $\frac{1}{4}$ -in. choke. Gas-oil ratio is 250 to 1. One well to 40 acres is the spacing, and some $5\frac{1}{4}$ miles long north to south and $\frac{3}{4}$ -2 miles wide east to west are the present limits of the field. Crude averages 31.5° gravity for all sands except the "Good Pine," which is 27° (average). R. J. W.

706.* Formation Samples from Gun Perforators. J. T. Richards. Bull. Amer. Ass. Petrol. Geol., April 1941. 25. 752-759.—During the past few years gun perforators have been used in petroleum development work for two general purposes: first, to explore possible producing formations cased off during drilling of old wells, and second, for perforating casing opposite recently drilled producing formations to produce more efficiently oil or gas from the formations, or to eliminate mechanical difficulties.

The author has summarized the result of an examination made by him of the material from 293 spent shells. The material represented 175 ft. of strata from three wells, and included limestone, shale, sandstone, cement, and mud. He established the fact that rock material in quantities sufficient for microscopic examination does collect in the combustion chamber of spent shells, and that this material represented the formation opposite the shell at the time of firing. In all cases material derived from the mud was much less than in ordinary rotary samples of good quality. The following hypothesis formulated by him as a probable explanation of the accumulation of uncontaminated rock samples in the shells:

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(1) On penetrating the formation, the bullet displaces by compression, consolidation, and brecciation, the material occupying the space in its path; the loosened material exists in the form of rock dust and rock fragments.

(2) Due to the velocity of the bullet and the vacuum immediately behind a travelling projectile, some of the loosened rock material is drawn into the space opened by the bullet. Possibly gravity pulls some fragments into the space.

(3) The loosened rock material is suspended briefly in the gases propelling the bullet.

(4) The propelling gases contract immediately after full expansion generating a suction from the formation to the shell.

(5) Since this suction is strong enough to carry bullets from the formation back into the shell, it is also strong enough to carry loosened, shattered rock fragments into the shell.

The author explains his methods of treating the samples which were obtained from one area in the Mid-Continent field, and considers that if similar data from other area were obtained by the same means, the result might add materially to knowledge of underground strata and conditions. R. J. W.

707.* Geology of Western Nebraska Demands Careful Prospecting. W. V. Howard. Oil Gas J., 1.5.41, 39 (51), 11.—The granite ridge running from the Barton Arch of Kansas to the Black Hills of South Dakota is readily delineated, but the location of producing horizons connected with it is more difficult. Tests so far show that practically all the producing horizons of the Cretaceous, Jurassic, Pennsylvanian, and older beds, which might be expected in this area, wedge out on the flanks of the high or are truncated by erosion. Only the basal sand—the Reagan or La Motte sand—can be expected over the arch. Hence the search is not so much a matter of finding highs on the arch, as of locating minor flank structures and stratigraphic traps. The cloak of unconformable Tertiary beds renders surface geological work practically useless here, and the erosion of limestones and their coming into contact in places make the interpretation of geophysical work very difficult. Hence stratigraphical tests and detailed subsurface geology are of the main importance. Accurate correlation is essential.

In Nebraska unconformities occur at the base of the Tertiary and the base of the Jurassic, with the Triassic, Jurassic, and Tertiary pinching out irregularly. The Quaternary consists of sands and clays, whilst the uppermost Tertiary is mainly composed of sands. In parts the Niobrara, Carlile, Greenhorn, and much of the
Graneros of the Cretaceous are missing. Indeed, some wells fail to find Cretaceous, The Sundance and Morrison occur, the latter being shaly but becoming sandier to the east, in which direction it overlaps the red beds of the Triassic. In the Permian and Pennsylvanian the Minnekahta limestone, and the Opeche and Hartville forma. tions, have been observed. These may rest directly on the basal sand overlying the granite. The possibilities of Pennsylvanian production seem good in the south-west part of the arch near the Kansas State line, but on the east flank it may be necessary to go 50 ml. east of the crest. Some wells fail to get Mississippian or older Palæozoic beds, but others have found Arbuckle and possible Simpson. The basal sand-a sand, conglomerate, or granite wash-occurs in most wells, and is productive in the Ray Pool. G. D. H.

A map and cross-section are included.

708.* U.S.S.R.-Greater Use of Natural Gas Reserves Planned. Anon. Oil Gas J., 1.5.41, 39 (51), 21.-The production of gas in the Azerbaidzhan fields has increased sharply, and all the fields are said to have exceeded their quotas under the third Five-Year plan during the second half of 1940. However, much remains to be done. especially with regard to reducing waste. Closed pipe-line systems are to be introduced in the Baku, Grozny, Maikop, Ishimbai, and Buguruslan areas, and the recovery of gasoline from natural gasoline is planned.

In the western Ukraine gas is produced for local industrial needs, but the supply G. D. H. far exceeds the demand.

709.* Creole Report Reviews Operations in Venezuela. Anon. Oil Wkly, 28.4.41, 101 (8), 51.—In 1940 Quiriquire produced 21,676,451 brl. of oil, and Oficina and San Joaquin production began to move through the 16-in pipe-line to Guanta. Two wildcats were drilled at Socororo, 22 ml. west of Oficina, one being dry and the other only a minor producer. Early this year a third well was completed as a dry hole. In Central Venezuela a wildcat, Gorrin 1, 160 ml. west of Socororo, was dry. In the Leona area a 1000-brl, well was brought in.

Thirty-six producers were completed at Jusepin and eight in the San Joaquin district (Roble and Santa Ana). Nine wells were completed by Standard at Oficina, one at Cumarebo, and a dry hole at Temblador. G. D. H.

Drilling.

710.* Unnecessary Drilling. Anon. Oil Wkly, 19.5.41, 101 (11), 11.-Among the more serious evils which directly or indirectly arise from the drilling of unnecessary wells are the following: (1) A large and wholly unnecessary increase in the cost of developing the oil and gas reserves of each pool; (2) an unavoidable steady decrease in the allowable well, not only in a given pool, but also in the state as a whole, resulting in a long-delayed pay-out of wells; (3) an unnecessary and undesirable postponement of full development of pools, resulting in congested drilling in some parts of a pool and insufficient development in other parts of the same pool, causing an inefficient and consequently wasteful use of reservoir energy; (4) a curtailment in discovery and development of new reserves occasioned by the dissipation, in drilling of unnecessary wells, of the funds which would otherwise be available for that purpose.

The drilling of unnecessary wells is occasioned largely through (1) the failure of operators to adopt proper well-spacing programmes, and (2) the allocation of allowable production on the basis of individual well potentials or some combination of factors which give excessive weight to the well without giving proper weight to attributable acreage and reserves.

The writers of this report, the Independent Petroleum Association of America's Committee on Unnecessary Drilling, recommend the following programme : (1) That the orderly development of pools by the adoption of proper spacing programme be encouraged, so that reservoir energy will be efficiently used; waste minimized and maximum ultimate recovery assured to operators and royalty owners alike. (2) That all oil reservoirs be developed with the fewest possible wells, in order that the largest

quantity of proven reserves be made available at the lowest cost. (3) That on the discovery of each new pool, and before a second well is commenced therein, each and every operator who owns acreage within the probable limits of the pool take the initiative in working out a well-spacing programme coupled with a plan for allocating allowable production in the pool which will eliminate, or at least discourage, the drilling of unnecessary wells. (4) That all operators actively undertake a programme of education for the purpose of fully informing all landowners, royalty owners, and the public generally of the substantial benefits to all concerned which will result from orderly development and production methods as against the wasteful practice of drilling unnecessary and unprofitable wells. A. H. N.

711.* Drilling Costs Cut by Feed-Water Heating System. G. M. Wilson. Oil Wkly, 19.5.41, 101 (11), 13.-The system, due to the raising of the feed-water temperatures before it reaches the boilers, permits the use of one less boiler at each setting; a normal installation of four boilers, for example, is now cut down to three on a certain deep-drilling test in San Joaquin Valley. Naturally, a saving is made in both fuel and installation costs; but an important additional operating advantage is gained by the fact that much less fluctuation of the water in the gauge-glass results when hot instead of cold water is pumped into the boiler.

Exhaust steam from the mud pumps and mud-mixing pumps is collected in a gathering system of light-weight 8-in. welded conductor pipe running along the surface of the ground to a unitized heat exchanger, in which much of the heat is imparted to the circulating boiler feed-water. The heat exchanger is described.

Exhaust steam from the two feed-water pumps is also utilized by allowing it to pass through a coil of pipe laid in the bottom of the skid-mounted water-supply tank spotted near the boiler setting. Water from the water well coming out at approximately 60° F. is raised in this preliminary heating stage to approximately 80-90° F. This warmed supply water is then taken up by the feed-water pump and forced through the large exchanger; while passing through this latter system the water temperature rises to 200-218° F. The final temperatures in all cases vary 10-20° either way, depending on the rate of drilling and the consequent volume of exhaust steam that is made available to the heat exchanger. A back pressure of approximately 15 lb. is built up in the steam-gathering system, due to the restriction formed by the exchanger. A. H. N.

712.* River-bed Drilling. J. A. Kornfeld. Oil Wkly, 19.5.41, 101 (11), 15. A description of the rig and practices followed in a river-bed drilling programme in a part of Kansas is given. Derrick, rotary table, draw-works, motors, and slush-pump are unitized on one large skid. This is easily skidded into position on the pile structure, making for a minimum of rigging-up time. The front end rests out over the river on the pile structure, whilst the rear end rests on the river-bank. The chief advantages of the rig are the brief time required for rigging up and tearing down, and elimination of expense for derrick erection. The rig can be moved from one completion on to the next location in approximately 48 hrs.

Drive-pipe practice in one well called for $43\frac{1}{2}$ ft. of 13-in. casing cemented with seventy-five sacks. However, all subsequent wells were drilled with from 40 to 70 ft. of 10-in. 40-lb. seamless casing. This pipe is driven by the piling-driving contractor at the same time as the piling is driven. A steel-drive shoe is used on the bottom joint, and a steel-drive head in the top collar. The collars on each joint are welded, and alignment is checked closely during the driving, so as to keep the pipe vertical. The drive-pipe facilitates drilling through the loose river-bed sand; it also prevents washing sand from below the immediate surface of the river-bed. Since the pipe is driven until a solid foundation is reached, there is a variation in length.

and a Drilling and cementing operations are briefly discussed. A. H. N.

tion at 10 713.* Cement Spray Bailer Used to Combat Caving Shale. A. C. MacIntyre. Oil Gas J., 1.5.41, 39 (51), 36.—The device does not completely eliminate the problem, and there are times when there is no other remedy than to cement and drill through the troublesome sections; but it has proved effective in many cases.

The cement spray-bailer, as its name implies, sprays a thin coating of cement on

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the face of the shales and forms a crust which aids in preventing caves. The cost of such spraying is much less than that of a full-hole cementing job and drilling through. The shales can be sprayed much faster than the time required for a full-hole job. Use of the device thus reduces drilling time lost in cementing in, and also provides a better hole, often obviating costly fishing jobs.

There are several types of bailers on the market. One consists of two attachments which screw on the top and bottom of several joints of 3-in. tubing. One contractor generally uses three joints, each about 20 ft. long, thus giving him a bailer about 60 ft. long. One type trips, opening the jets, when it strikes the bottom of the hole. Another is operated by a weight dropped down the line. In one type the cement is ejected from two holes, one directly opposite the other. In another type there is a ring of holes around the bottom of the bailer.

The cement is sprayed on the face of the shales as the bailer whirls in the hole, rotated by the spinning of the sand-line, which turns when a weight is suspended from the wire. The rate of the spin lessens as the bailer becomes lighter, due to the cement emptying from the bailer.

Details of cement consistency and operation of bailer are given. A. H. N.

714.* Directional Drilling of Holes through Hard Formations. H. F. Simons. Oil Gas J., 8.5.41, 39 (52), 50.—Probably the most outstanding job in hard-rock country in recent years has been the drilling of wells under Lake Centralia in the Salem, Illinois, field. All wells were directionally drilled from sites along the lake-shore to predetermined points beneath the lake. These wells were completed by cable tools, and were later deepened to lower pay horizons by the same method. The total controlled footage drilled amounted to 35,000 ft., the total horizontal displacement being 5458 ft. The greatest lateral distance to which a well was directed was 432 ft. The average deflection well was $248\cdot12$ ft.

The principal reason for the increasing use of directional drilling in hard-rock areas is the improved technique, which has reduced the cost and time required to complete the job. A desired objective may be gained by using as few as four whip-stocks, where formerly a large number might have been employed. This saving is accomplished by studying the formation and taking advantage of the normal dip if it is possible to do so. The study of normal bit action and the tendency of a hole to drift have also been helpful, and a better knowledge of the effect of weight on the bit has been acquired.

Directional holes have been drilled with a deviation from the vertical of as much as 45° , and some engineers believe that it is easier to maintain a high angle than a lesser one. Other engineers prefer to start higher and maintain a lesser angle over a greater distance. The claim for this method is that it requires fewer whipstocks and less time, and the wear on the drill pipe and equipment is reduced. Experience has shown, however, that drift angles at about $8-10^{\circ}$ maintain direction very satisfactorily in most conditions.

Certain details of the mechanics and operations of directional drilling are discussed. Side-tracking, straightening, and controlled directional drilling are discussed under three separate sections, giving the usual procedures followed. A. H. N.

715.* Effect of Crooked Wells on Exploitation. H. C. H. Thomas. J. Inst. Petrol., May 1941, 27 (211), 157-164.—Attention is directed to the adverse effects of unintentionally deviated wells on the orderly exploitation of an oil-field. These effects comprise: incorrect spacing at the production level, resulting in inefficient drainage; incorrect interpretation of structure; errors in forecasting; failure to complete the well; failure to produce the completed well to exhaustion. It is shown that a directional survey of every well drilled is not only of considerable value to the exploitation geologist, but is the only way in which progress towards the dilling of straighter holes can be assessed. B. M. H. T.

716.* Slim-hole Drilling on the Gulf Coast. I. W. Alcorn. Petrol. Tech., March 1941, A.I.M.M.E. Tech. Pub. No. 1305, 1-14.—On the Gulf Coast probably the optimum size of slim-hole would have $8\frac{4}{3}$ -in. surface casing with a $7\frac{3}{4}$ -in. hole, and the minimum hole size would be $6\frac{1}{4}$ in. Not until 1937 was serious consideration given

to the use of slim-holes for drilling to 7000-9000 ft. Points in favour of their adoption were as follows: On the Gulf Coast new discoveries represent odds of about 7 to 1 against the discovery of commercial production, and 10,500 ft. represents the lower limit of economical production, with the odds increased against even finding oil production below that depth. Thus a rig with a drilling limit of 10,500 ft. or less will suffice, and a smaller and compact diesel or gas-engine rig is satisfactory, and reduces the cost of foundations, fuel, and moving in. Reduction of the hole-size reduces the cost of bits, drilling, reaming, casing, and mud. Coring is also reduced large hole.

Comparison of data for a series of wells of similar depths and other characteristics, but of different sizes, shows that reduction in size reduces casing and fuel costs, time, bit changes, reaming, footage and mud costs, and increases the footage/hr.

Electrical logging, mud-stream sampling, and side-wall sampling and coring have reduced the amount of ordinary coring necessary. Gun-perforating has changed completion programmes and reduced rig times and overall cost. Improved cementing technique has reduced gas and water encroachment hazards. A 136-ft. derrick with a 26-ft. base and 85-h.p. engine is common, and there has been a trend towards the use of hydraulic couplings. 81 in. seems to be the minimum size for digging below the surface with rock-bits.

Numerous tables and curves set out the data relevant to the drilling of holes of different sizes. G. D. H.

717.* Flow of Muds, Sludges, and Suspensions in Circular Pipes. D. H. Caldwell and H. E. Babbitt. Industr. Engng Chem., 1941, 33, 2, 249.-A theoretical analysis of the flow of sludges in circular pipes is presented. Two types of flow-plastic and turbulent-are shown to occur, the change from one type to the other taking place at the critical velocity. The application of the plastic flow equation to a problem involves a knowledge of the coefficient of rigidity and the tangential unit shearing stress of the sludge. The value of these constants may be determined experimentally in a modified Stormer viscometer. Details of experiments on the flow of sludges of different types in pipes of various diameters at several rates of flow are given, and these data are shown to be in excellent agreement with the theoretical analysis of plastic flow. Theoretical equations supported by experimental evidence are given for the determination of the critical velocity. Under turbulent flow conditions the viscosity of the sludge dispersal medium governs the flow, and the ordinary Reynolds Number-Fanning friction faction relationship may be used. Experimental evidence in support of this is also given. J. W. H.

718. Measuring Particle-Size Distribution and Colloid Content of Oil-Well Drilling Fluids. G. L. Gates. U.S. Bureau of Mines, Report of Investigations, No. 3549, February 1941.—This report emphasizes the importance of the colloid content as a constituent of mud-fluid for well-drilling. Without colloids the solids in the fluid would rapidly settle, and consequent deterioration in sealing and wall-building properties would ensue.

During the course of investigations by engineers of the Bureau of Mines concerning characteristic properties of mud fluid, the need arose for a rapid, reliable method of measuring particle-size distribution and determining colloid content. Studies were accordingly made of published methods, and a standard procedure based on the hydrometer method of analysis was evolved. The procedure differs from previous methods mainly in the manner in which the sample is prepared for analysis, in the absence of a deflocculating agent, the application of a correction factor for dissolved materials which occur in most mud fluids, and in measuring the viscosity of the suspension.

Although results obtained by the hydrometer method are not absolute, they agree closely with those obtained by the pipette method, which is a direct method of particlesize analysis. Moreover, size-distribution curves plotted from results of nearly all the samples tested by the Bureau indicate that the cumulative weight percentages determined by the hydrometer method of analysis form a continuous relationship with the cumulative weight percentage determined by sieve analysis.

Advantages of the hydrometer method equally include simplicity of equipment and test procedure; easy and quick calculation of results of analysis by means of a slide rule and tables; and provision of a means of prediction of possible behaviour of the fluids after accumulation of sufficient data. H. B. M.

719. Patents on Drilling. R. Neuhaus. U.S.P. 2,239,826, 29.4.41. Appl. 15.7.40. Tool-joint with a coupling member with larger diameter than pin members adapted to receive wear incident to operation.

F. Stone and A. L. Stone. U.S.P. 2,239,942, 29.4.41. Appl. 17.5.39. Well pipejoint.

J. F. Chappell. U.S.P. 2,239,996, 29.4.41. Appl. 25.5.36. Drilling apparatus comprising a bit on a drill-pipe with another pilot bit being located on another pipe which is inserted inside the first pipe.

L.H. Giles. U.S.P. 2,240,095, 29.4.41. Appl. 25.8.38. Rock drill-bitcone-catcher which is to be used as a fishing-tool.

R. Ring. U.S.P. 2,240,417, 29.4.41. Appl. 7.10.38. Apparatus for surveying wells by means of a pendulum having a point contact with a record and a low voltage current inducing electrolytic changes on the record chart, thus marking it.

A. R. Reed. U.S.P. 2,240, 519, 6.5.41. Appl. 31.8.38. Drill string-shock absorber adapted for flow of slushing fluid through it.

F. J. Young. U.S.P. 2,240,737, 6.5.41. Appl. 14.4.37, Draw-works having an enclosure surrounding the transmission element.

J. A. Dunn. U.S.P. 2,240,738, 6.5.41. Appl. 14.7.37. Rotary drilling rig with the drill-string extending into the kelly, which is aligned by a taper with the swivel.

J. D. Spalding. U.S.P. 2,240,741, 6.5.41. Appl. 5.2.40. Draw-works with two shafts, one of which is adapted to convey a fluid.

J. C. Mason. U.S.P. 2,240,794, 6.5.41. Appl. 11.3.40. Drilling lift consisting of a pair of hydraulic cylinders attached to the derrick legs and containing pistons connected to lift-cables.

C. J. Moon. U.S.P. 2,240,852, 6.5.41. Appl. 20.1.40. Derrick structure which is capable of being raised from horizontal to vertical position.

J. Neufeld. U.S.P. 2,241,154, 6.5.41. Appl. 1.10.38. Well-surveying method and apparatus to determine the nature of formations penetrated by the drill-hole by measuring the fluorescence of substances present in the formation and the depth simultaneously.

A. D. Garrison. U.S.P. 2,241,255, 6.5.41. Appl. 17.8.39. Oil-base drilling fluid.

W. W. Robinson and R. R. Crippen. U.S.P. 2,241,273, 6.5.41. Appl. 1.7.39. Method and apparatus for treatment of drilling mud.

G. A. Severson. U.S.P. 2,241,274, 6.5.41. Appl. 27.9.38. Safety device adapted to disconnect the engine from the draw-work and to apply the brakes in cases of emergency.

E. Shinn and E. Shinn, Jr. U.S.P. 2,241,275, 6.5.41. Portable hoisting apparatus. A. H. N.

Production.

720.* Oil Recovery by Air and Gas Drive in Pennsylvania. R. B. Bossler and P. A. Dickey. Oil Gas J., 1.5.41, 39 (51), 32. Paper Presented Before American Petroleum Institute.—There appears to be a definite relation between ultimate oil recovery and well spacing. If the well spacing is decreased to small values and the distances between wells becomes absurdly short, the oil recovery will increase more and more

slowly, tending to approach as a limit the total amount of recoverable oil in the sand. On the other extreme, where the spacing becomes so great that the input wells do not affect the producing wells, the recovery will approach zero.

A curve of this shape may be expressed by the general formula : $y = ae^{-bxP}$.

A reasonable value for a must be assigned by deducting the unrecoverable oil from the total oil in the sand. In the Venango district the constant a becomes 140. Values may be assigned as follows: y = R = cumulative ultimate recovery, brl./acre-ft. x = F = square root of product, acres/oil wells times acres/air well. a = 140. e = 2.7183 (base of Naperian logarithms). b and P = constants depending on local conditions.

It is necessary to relate the spacing to the fraction of total recoverable oil that will be recovered, instead of to the actual oil recovered. The equation becomes: $R = e^{-0.29F^{1.49}}$, where R equals fraction of total recoverable oil recovered at geometric mean spacing F.

A formula is developed for optimum well spacing for any set of conditions. This formula leaves out consideration of the beneficial effect of close spacing, as the leases studied did not allow derivation of a quantitative relation between spacing and time of recovery. The authors' data showed clearly that close spacing increases the rate of recovery and accelerates the rate of production decline, so that not only does close spacing result in greater ultimate recoveries, but the oil is recovered faster.

If a certain development will produce a certain quantity of oil in 10 years from a given area, with oil production declining in a logarithmic manner, the present worth of the future income will be about 85% of to-day's value of the total quantity of oil. If 20 years is required to recover the same amount of oil from the same property, the present worth of the future income will be about 65% of to-day's value of the oil. If other conditions are the same, it is about 25% more profitable to extract the oil from a property in 10 years rather than 20 years.

Closer spacing and more rapid recovery will result in decreased lifting costs and more efficient extraction of the oil in the sand. Use of high pressures at the start will result in the removal of some of the oil from the less permeable sections of the sand.

The paper also includes a discussion of the various gas- and air-drives in Pennsylvania outside the Venango district. A. H. N.

721.* Automatic Controls Close Wells when Tank Battery is Filled. D. H. Stormont. *Oil Gas J.*, 1.5.41, 39 (51), 35.—A two-well tank battery has been equipped with valves and controls for automatically shutting in the wells when the tank battery is filled. This experimental equipment has been satisfactorily operating for 10 months. The equipment also provides means whereby individual wells may be stopcocked from the central tank-battery manifold. Judging from operations of the experimental battery, installation of this equipment at each tank battery on the Cowden lease will, it is estimated, result in switchers' labour being reduced by about 40%, and, by reducing the number of trips to open and close the wells, car mileage of the pumpers should be reduced by almost half. Tests indicate also that, through use of stopcocking, the gas-oil ratios of the wells can be reduced by almost 100 cu. ft./brl.

The equipment consists of (1) an 8-in. liquid-level controller with pilot on the tank battery; (2) a single-seated diaphragm-operated pressure regulator and oil-valve installed between the manifold and separator; (3) a 1500-lb. working-pressure regulator installed behind a positive choke, which follows an adjustable choke, at each of the wells; (4) standard separator float control; (5) a spring-loaded relief valve on a by-pass around the pressure-regulator at the tank-battery manifold. The working of the equipment is described and illustrated.

The equipment is of particular value where wide well-spacing is practised or where a lease is remotely located. A. H. N.

722.* Cathodic Protection to Prevent Corrosion of Gas-Well Casing. W. E. Huddleston. Oil Gas J., 8.5.41, 39 (52), 59. Paper Presented Before American Gas Association.—The theory of corrosion and of cathodic protection is explained. After discussing the practicability of protecting gas-well casing cathodically, the following conclusions are reached :—

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With certain limitations, cathodic protection may provide an economical means of combating corrosion on gas-well casing.

Many problems, however, arise out of the design of a cathodic protective system for this application, the most serious of which is a source of power for supplying the protective energy. Other problems arise in the manner of determining the necessary load requirements for a given string of casing, the fabrication of a suitable lowresistance anode in locations having adverse soil conditions, and the question of being able to apply cathodic protection to a corroding well in sufficient time to save the casing from penetration.

In view of the results obtained by insulating, it is quite apparent that casing corrosion can be mitigated sufficiently by this method alone to prolong the useful life of the casing for several years, provided the well is insulated before the casing wall has reached penetration or near penetration. Obviously the most satisfactory practice would be to insulate new wells as they are completed. Experience gained from insulating gas-wells during the past 4 years indicates that, in general, the useful life of well-casing can be at least doubled (even when it is subject to severe attack), provided the well is insulated at the time it is connected to the gathering system, or within a few weeks after.

Multiple wells connected to the same gathering system demand special consideration, as the corrosion rate on the uninsulated wells will usually be accelerated by insulating all or part of the other wells.

The economic benefits gained by insulating a number of wells can only be determined by actual tests in the field, for some wells corrode at a much higher rate than others. A. H. N.

723.* Intermittent Injection of Air Aided by Electric Clocks. A. C. MacIntyre. Oil Gas J., 8.5.41, **39** (52), 70.—In order to determine the optimum intermitting schedule in a particular field, the operator used a number of synchronous clocks which operate on a 110-v. 60-cycle current, throwing a switch either at 30-min. or 1-hr. intervals. The clocks were arranged to open a solenoid valve, and could be so adjusted that the valve closed at the will of the operator.

After various "on" periods were tried, a schedule of 8 min. "on" and 22 min. "off" was adopted. The intake pressure used allowed 45,000 cu. ft. of air to be admitted to the sand each 24 hr. In 62 weeks of operation the production from wells surrounding this arrangement amounted to 6730 brl. of crude. This compared with 1560 brl. of crude for 62 weeks under continuous repressuring, or a gain in production by the intermittent repressuring of about 432%.

It is noted that with regular injection a pressure of only 20 lb. was required, whilst a pressure of 125 lb. was used with the intermittent injection.

It was not necessary to attach the electric clock to all the wells to obtain results. All were affected by the rise and fall in pressure as the valve was opened and closed by the electric clock.

The theory behind the experiment is that the Venango third sand has a very extreme range of permeability. Probably the oil strata being worked at 20 lb. was not more than 4 or 5 ft. thick, out of a total of 32 ft. of exposed section. The injection of air in intermittent slugs caused a Jamin action in the more permeable strata of the sand, and thus permitted injected air to be introduced into the less permeable area. These less-permeable strata have a higher oil content, and thus the production was increased. A. H. N.

724.* Electric Power Pumping-Plant Designed for Present and Future. G. B. Nicholson, Gil Wkly, 5.5.41, 101 (9), 14-16.—A wide diversity of well characteristics is a peculiarity of many wells producing in the East Texas field. All producing from the Woodbine sand and apparently completed similarly, many wells bear only the slightest resemblance to their neighbours. Productivity varies sharply; in the pumping wells, fluid-levels and water-content are widely divergent. With sixty wells on the leases an inefficient pumping assembly would result in considerable waste expenditure in equipment and man-power.

An electric-generating power-plant with individual electrically controlled units at the wells was solected as the power. This typo installation offers considerable flexibility in operation. Constructed with the idea that future power requirements may be greater than those at present, the assembly will permit expansion at low cost when occasion arises. A detailed description is given of the major items of the plant. A. H. N.

725.* Dehydration Units for Individual Gas Wells. R. B. Anderson. Oil Wkly, 5.5.41, 101 (9), 17-19. Paper Presented Before American Petroleum Institute.—A dehydration plant located at isolated wells must be designed to meet the following conditions: (1) It must be completely automatic and require no more than casual inspection by the regular field force. (2) It must be simple in operation, so that unskilled common labour can understand its operation and make adjustments when necessary. (3) It must obtain what power is required from gas pressure; no other is available. (4) Water for cooling or steam is not available. (5) The solution must not be corrosive, and must be such that if over-concentration does occur, no harm will result. (6) The method must appreciably depress the dewpoint, so that small quantities of untreated gas can be mixed without raising the dewpoint of the mixed gas above the minimum ground temperature. (7) It must be inexpensive.

The paper describes a well-head dehydrator that was finally adopted to meet the above conditions. There is really nothing new in the method employed. It is the conventional diethylene-glycol dehydration plant. It is unique only in various features of its design to meet the limiting factors of a well-head dehydration unit.

Gas saturated with water vapour enters the contactor through the inlet pipe above the base of the contactor, and passes up through three bubble-trays, where it contacts the diethylene glycol solution that is flowing down through the contactor. This contact is sufficient to absorb all the water the diethylene glycol is capable of absorbing from the gas.

There has been developed another type of unit that is adaptable to dehydrating gas at the well that meets all the limiting factors for such plants.

The unique feature of this design is that no pump is required and the still is operated at line pressure, the water removed and condensed under pressure and discharged through a trap from the unit.

Gas enters the contactor near the base, where it contacts the diethylene glycol solution. The solution passes up through the trays of the tower to the top tray, where it drains through an overflow line to an "adjustable flow control." The adjustable flow-control is a chamber in which is located an adjustable weir which controls the volume to be discharged to the still. The solution passes to heating coils in a hot-oil bath and then to the still under full pressure. A. H. N.

726.* Gas-Well Spacing. W. P. Smith. Oil Wkly, 5.5.41, 101 (9), 20-21. Paper Presented Before American Petroleum Institute.—The problem is studied from an economic viewpoint focussed upon experience gained from Elk-Poca field. Although there have been some few notable exceptions, in general up to the present the development of the Elk-Poca field, near Charleston, West Virginia, has been on a rational basis, and is on the whole economically sound. However, caution will have to be used henceforth in order to avoid some of the costly uneconomic results of poorly planned well spacing.

There is probably no general formula which can be made to fit all cases in determining the optimum in well spacing. Each company or operator should, for his own, as well as for the common welfare, seek to follow a programme of well spacing which will, so far as is predictable, serve his needs, and at the same time conflict as little as possible with the development programme of his neighbour. In other words, unnecessary overcrowding of offset wells should be avoided. It is not recommended that any operator or group set up a fixed and inflexible well-spacing programme, because each one has problems as to acreage, location of acreage, market demand, and reserves which are peculiar to his own operation. It is recommended that careful study be given all available field and production data, to the end that each operator may estimate for bimself the economic factors relating to his own part in the development of new sources of production.

One of the most obvious needs of the operators in the development of new deep producing structures is for unitization of small contiguous acreage groups, wherever possible, into sufficiently large blocks to avoid unnecessary and uneconomic overdrilling due to requirements for offset wells.

The belief is expressed that the industry will find it ultimately of great general benefit to undertake a programme of education for the royalty owners and of self-education for the industry, to conserve and prolong the useful life of producing fields through adequate and economically sound spacing of wells, bearing in mind that what may be sound economics for one company or one operator may not necessarily be so for another. A. H. N.

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727.* Minor Sands Water-flooded with Success. F. R. Cozzens. Oil Wkly, 5.5.41, 101 (9), 28.—In redrilling many of the minor fields which had been abandoned for 20-40 years, operators were surprised to find in the sand of a newly drilled well a head of fresh, lively oil, somewhat resembling the original flush production. Gas, too, was commonly in evidence, and often in amounts sufficient to operate the equipment. The same operators were far more surprised when, after a few months' to a year's pumping, the oil and gas suddenly gave way to floods of fresh water, and the well was ruined. The cause was easily determined. Many of the original wells, being carelessly plugged, had filled with water, and its weight and volume had been sufficient, over the course of years, to penetrate the sand for a considerable distance, pushing the oil and gas before it. This gradually resulted in an extremely rich pay in the sand-body between the old holes, and a newly drilled well invariably tapped it.

Old wells had been drilled on an average of 200 ft. apart, and the crooks and width of the pay formation had been fairly well determined. New wells could be drilled at costs ranging from \$300 to \$1000, and, while short-lived, each could be expected to yield 1000 or more barrels of oil before the water came through. The recovery plan which was then mapped out, and is now being followed, is to drill or stagger new wells as nearly as possible in the centre of the sand-streak, and midway between two of the old locations. The drill invariably brings oil, and the narrowness of the streak is an advantage, since the incoming water volume is confined to restricted areas. The new wells are given a light charge of nitroglycerine and pumped vigorously for the duration of their life, which may vary anywhere from a few months to five years. The speed at which the water travels through a formation depends on the depth and texture of the sand, and the number of old wells which are taking water. Some wells, of course, have been plugged sufficiently to prohibit the drainage of water into the sand. A. H. N.

728.* Unsteady Flow of Heat through Porous Media. H. B. Harbut, D. C. Cain, and R. L. Huntington. Industr. Engng Chem., 1941, 33, 2, 257.—The investigation was undertaken with the object of obtaining data applicable to the recovery of oil from spent oil-sands. The data given are, however, applicable to any large-scale porous media heating problems. The relative rates of heat-flow through porous media of different pore-size and of different interstitial fluid fillings are presented. The results indicate that in the case of the smaller grains conduction is the factor governing heat transfer, whereas in the case of large spheres convection in the liquid filling the interstices governs the heat-transfer rate. J. W. H.

729* Development and Application of Subsurface-pressure Data in Kettleman Hills. E. W. McAllister. Petrol. Tech., March 1941, A.I.M.M.E. Tech. Pub. No. 1303, 1-16.—The first subsurface pressure measurements at Kettleman Hills were made in 1932, and in 1933 they became part of the routine. The productivity index is the number of barrels of oil and/or water which will enter the well per day per lb./in.² pressure drop at the well-face. This index was found generally to decrease with time and to vary with the rate of flow. Static pressure measurements were also made with the wells shut in, and the flow-pressure gradient was determined in the flowstring. From these data the potential of a well can be computed, for it is equal, theoretically, to the product of the productivity index and the maximum mean pressure draw-down that can be made opposite the producing interval of the well. An example is given of such a computation. The potential decline and "absolute" potential decline can also be plotted, the latter being the potential if all pressure could be removed from the surface of the producing sand.

In the development of Kottleman Hills it has been the policy of the Kettleman North Dome Association to complete only enough wells to maintain a 60 lb./in.² (surface producing pressure) field potential, and to determine the number of drilling strings necessary, a potential-decline curve for the field is plotted, based on individual well potentials derived from production and subsurface data. Superimposed on this curve are the expected increases in potential from future completions for different numbers of drilling strings. Thus the drilling programme can be drawn up.

Subsurface pressure data are valuable in the solution of gas-lift problems such as tubing depths, surface pressures, etc. In wells of small production rates, intermittent gas-lift is more efficient than straight gas-lift, and generally increases production.

The distribution of production and acreage amongst the various leaseholders is discussed in detail. Concentration of production in competitive areas has given an unbalanced condition of reservoir pressure, and excessive gas production has reduced the ultimate oil recovery. G. D. H.

730.* Some Factors in the Economics of Recycling. E. Kaye, *Petrol. Tech.*, March 1941, A.I.M.M.E. Tech. Pub. No. 1304, 1–10.—To determine the amount of distillate in place involves a knowledge of acreage, sand thickness, reservoir pressure and temperature, porosity and connate water content of the sand, and an estimate of the distillate content of the gas. This last is the most difficult measurement. An ultimate distillate recovery depends also on the maintenance of pressure above the dew-point, otherwise there is loss by condensation in the sand.

Recovery plant size is determined by the extent of the reserves, gas market, cost of production and condensate market. Plant cost is discussed and ranges \$-\$13 per 1000 cu. ft. of gas capacity/day. Operating costs per unit of capacity vary with reservoir pressure, condensate content of gas, extraction efficiency, character of condensate, and gas capacity of the wells. Costs range \$0-0201-\$0-0246/gal, with condensate worth \$0-025/gal, depreciation and raw material being allowed for.

Typical condensates are composed essentially of hydrocarbons boiling within the motor-fuel ranges (75%), with various percentages of natural gasoline (10%) and kerosine distillate (15%). Condensates are neither particularly volatile nor high in anti-knock. They more nearly approximate to the products of simple distillation of crude oil. Condensate is not sought by refiners, even though it appears to be more valuable than crude oil, and consequently plants have been designed to distil the condensate into its components, producing reasonably satisfactory fuels, including leaded grades, entirely without reforming.

Soon there will be a production of 50,000 brl./day of condensate from thirty plants, and this, considered as crude oil, should not present a producing or marketing problem, although if converted into end-products a problem does arise.

The appendix deals with gas-sampling methods and condensate recovery costs, and lists the recycling projects in operation, under construction, and planned.

G. D. H.

731.* Proration—Part 1. O. W. Willcox. World Petrol., May 1941, 12 (5), 36-41.— The author suggests that proration in the oil industry suffers shortcomings which could be eliminated if a system similar to that of the sugar industry could be adopted. Judged by standards set in the world sugar industry, the system of proration now found in the American petroleum industry has the following principal shortcomings: (1) It is not nation-wide; the prorating laws passed by individual States have no effect beyond their own boundaries, and the oil producers of non-prorating States remain free to throw upon the market whatever amount of oil they please. Moreover, the prorating States are not always of one mind as to the proper basis of proration, especially as regards the allowables that are prescribed from time to time. (2) The amount of oil coming on for sale is out of control not only as regards the unlimited production of the non-prorating States, but also as regards new production anywhere. Whenever a new oil-pool is discovered or a new well is opened in an old field, this new production may and does claim a place in the existing scheme of proration; to give the new oil its place, previous allowables must be reduced. This

continual whittling away of allowables continually reduces current earnings and prolongs the time required for the operator to pay-out his investment, and not infrequently removes the possibility of a reasonable pay-out. (3) Due to the pressure of non-prorated oil and to new flush production, the visible stock of petroleum products is subject to comparatively large variation, with a strong tendency to overhang the market. Prices vary with each change in the statistical position, alternately squeezing the oil producers and the consumers. This uncertainty and instability of oil prices has a disturbing effect on the economics of investment, production processing, and consumption.

An outline is given of the concepts of proration to be adopted, as these concepts found world-wide success in the sugar industry. Of these concepts, two—the sixth and seventh—are new and controversial to oil-men. They are : (1) (concept No. 6) the business of the industry belongs to the whole industry as it stood at the time it was constituted as a unit. Once the industry has been recognized as a contractual entity, the membership list is closed, and is not reopened except when additional facilities for production are required to meet an increased demand, or for some exceptional reason. (2) (concept No. 7) The prices which the industry shall charge the public for its products will be named in the contract or agreement with the public authorities, and will not be subject to change except at stated periods and after prior consultation between representatives of the industry and the public; and these prices will be uniform throughout the country.

These are discussed in detail.

A. H. N.

732. Patents on Production. W. H. Hunter. U.S.P. 2,240,780, 6.5.41. Appl. 5.1.39. Flat-groove valve-body and packing means therefor, forming a pump plunger.

W. Ferris. U.S.P. 2,240,901, 6.5.41. Appl. 20.2.36. Hydraulic transmission adapted to be lowered into an oil-well consisting of hydraulic motor, pump, and valve mechanisms.

M. De Groote and B. Keiser. U.S.P. 2,241,011, 6.5.41. Appl. 23.10.39. Process for resolving petroleum emulsions of the water-in-oil type.

J. R. Henry and R. P. Downing. U.S.P. 2,241,090, 6.5.41. Appl. 3.1.39. Pumping unit consisting of supports carrying a shaft with an eccentric which has a roller on it connected to a crosshead, which is in turn connected to the polished rod.

T. W. Murray. U.S.P. 2,241,153, 6.5.41. Appl. 9.4.40. Well-pump operating equipment for operating the sucker-rods consisting of a shaft and at least three wheels, two to oscillate the shaft and the third to be connected to the rods.

A. D. Garrison. U.S.P. 2,241,253, 6.5.41. Appl. 10.6.38. Method of treating wells to convert a water wet producing sand into one which is preferentially wettable by oil.

A. D. Garrison. U.S.P. 2,241,254, 6.5.41. Appl. 6.7.38. Method of treating oil wells.

J. R. Yancey. U.S.P. 2,241,288, 6.5.41. Appl. 26.1.40. Apparatus for completing wells.

R. Smith. U.S.P. 2,241,333, 6.5.41. Appl. 24,7.34. Well-head. A. H. N.

Crude Petroleum.

733. Analyses of Crude Oil from Phillips Co., Kansas. Anon. Petrol. Engr., Jan. 1941, 12 (4), 64.—Phillips County crude oil from the Logan Pool, Kansas, is an intermediate base crude with S.G. 0.867, sulphur 0.57%, carbon residue 5.3% and viscosity S.U. at 77° F. and 100° F. of 100 sec. and 72 sec., respectively. A Bureau of Mines analysis gives the following yields : Light gasoline 7.3%, total gasoline and naphtha 24.0%, kerosine distillate 8.8%, gas oil 14.7%, non-viscous lub. dist. 10.2%, medium lub. dist. 7.5%, and residuum 33.8%.

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734. Hydroforming is New Dehydrogenation Process. D. J. Smith and L. W. Moore. Petrol. Engr, April 1941, 12 (7), 23.-The first commercial hydroforming plant has been put into operation at a Texas City Refinery, and is capable of reforming 7500 brl./day of heavy mixed cracked and straight-run naphtha of 40-45 O.N. giving an 80% yield of gasoline of about 80 O.N. The process consists of treatment at a high temperature with the hydroforming catalyst resulting in ring closure and dehydrogenation, the hydrogen produced being partly recirculated with the fresh feed in order to control the rate and extent of dehydrogenation. The gasoline produced contains a high percentage of aromatic hydrocarbons and only a small quantity of aliphatic unsaturates, and is sufficiently stable for direct blending into gasoline. Fresh feed and hydrogen-rich recycle gas are heated by heat exchange and passed to a two-coil furnace, mixed and passed to the high-pressure catalytic reactors, conditions being designed to avoid thermal cracking before contact with the catalyst. The hot reaction products are cooled and passed to a gas separator, the liquid from which is stabilized and re-run to remove heavy polymers. Coke deposition on the catalyst reduces its activity, but this is restored by burning off the reactors with flue gas and air under carefully controlled conditions. Typical analyses of (a) charge and (b) hydroformed product are as follows: Gravity A.P.I. (a) 51.4, (b) 51.3; O.N. (a) 47.2, (b) 77.0; Reid V.P. (a) 0.4 lb., (b) 8.2 lb.; I.B.Pt. (a) 222° F., (b) 79° F.; 50% dist. to (a) 292° F., (b) 270° F.; and F.B.Pt. (a) 436° F., (b) 368° F. The hydroformed product contains 40-50% aromatics, of which 15-20% are toluene, the rest being predominantly xylenes and higher. The flexibility of the process allows either straight-run or cracked naphthas to be reformed to produce motor spirit or aviation gasoline which require no refining. By modifying conditions a product with 80% of aromatics can be produced, thus providing an important source of toluene. The products from the plant in question alone contains a quantity of toluene equal to 25° of the U.S. production for 1939 (20 million gallons). C. L. G.

735. Patents on Cracking. C. Arnold. E.P. 535,662, 17.4.41. Appl., 12.10.39.— Process of cracking high-boiling hydrocarbon oil to produce gasoline-like products. The oil is subjected to treatment with liquefied normally gaseous saturated hydrocarbon solvent, preferably propane. Thereafter the paraffinic constituents are separated from the solvent and subjected to an elevated temperature in the presence of a cracking catalyst to convert them into relatively high anti-knock gasoline-like products. The non-paraffinic constituents also obtained are subjected to a relatively high cracking temperature in the absence of a catalyst to convert them by pyrolytic cracking into lower-boiling hydrocarbons comprising gasoline-like constituents. These gasoline products are recovered and finally blended with the other gasoline-like products obtained.

Standard Oil Development Co. E.P. 535,895, 25.4.41. Appl. 19.9.39. Production of high knock rating gasoline from heavy hydrocarbon oil by heating the oil to a cracking temperature between 850° and 1000° F. and thermally converting a substantial proportion thereof into gasoline. The heavy residue is then separated from the cracked vapours, and the latter cooled to a temperature within the range 700-800° F. and contacted with a mass of desulphurizing catalyst. Finally the treated vapours are conducted to a fractionating zone, where separation of gasoline from unconverted heavy oil is effected. The latter is then recycled to the cracking zone.

W. Kaplan. U.S.P. 2,240,160, 29.4.41. Appl. 26.8.35. Method of cracking residue oils in the vapour phase by injecting them into a high-temperature stream of hydrocarbon vapour passing through a long tube of restricted cross-section mounted in a heating zone. The residue is intimately sprayed into the stream and in such a ratio to the stream that it is instantly vaporized. The heating of the stream is controlled and maintained above the dew-point of the mixture, and the process continued for a sufficient period of time to convert a substantial proportion of the oil residue into constituents boiling within the gasoline range. H. B. M.

Hydrogenation.

736. Hydrogenation of High-temperature Tar from By-product Coke Ovens. H. H. Storch, I. L. Hirst, C. H. Fischer, H. K. Work, and F. W. Wagner. Industr. Engng Chem., 1941. 33, 2, 264.—Industrial aromatic solvents can be produced by the hydrogenation of high-temperature coke-oven tar. Catalytic hydrogenation is effected in two stages : liquid-phase hydrogenation at 450° C. with 2 hr. contact time, followed by a vapour-phase hydrogenation at 510° C. with 0.5 min. contact time. Details of the various experiments carried out to investigate the variables—catalyst, contact time, conversion, and character of products—are given. The aromatic solvents produced by this process possess high solvent power and will be of value in the resin and lacquer industries. J. W. H.

Synthetic Products.

738. Synthetic Hydrocarbons. A. E. Williams. Engineering, 1941, 151, 394.—A description of the Fischer-Tropsch process for the synthesis of hydrocarbons and carbon monoxide and hydrogen derived from coal or natural gas is given. The effect of pressure on the yield and character of the products is discussed, and details of loss in catalyst activity and a gas desulphurisation process are given. J. W. H.

739. Physical Characteristics of Synthetic Rubbers. J. N. Street and J. H. Dillon. J. appl. Physics, 1941, 12, 45.—The nature and application of the more important types of synthetic rubbers are discussed. Summarized physical properties are given, together with the results of comparative tests in the following specific fields of application : motor-car types, petrol, oil and ozone resisting rubber-wear.

J. W. H.

740.* Properties of Synthetic Lubricating Oils. Synthesis and Properties of 11-normaldecylocosane. S. Klos, E. Neyman-Pilat, and S. Pilat, J. appl. Chem. U.S.S.R., 1940, 13 (a), 1369–1374. Translated by A. A. Boehtlingk, For. Petrol. Tech., Nov.-Dec. 1940, 8 (11–12), 438.—The difficulty encountered in the separation of individual chemical compounds from lubricating oils induced the authors to propare synthetically a number of hydrocarbons similar to those of petroleum oils. Numerous determinations of the molecular weights carried out by one of the authors had indicated that saturated hydrocarbons containing more than 30 carbon atoms in the molecule may have properties similar to those of lubricating oils. On the basis of this fact, the authors chose as the first object of their experiments one of the *iso*-hydrocarbons of the fatty series with 32 carbon atoms in the molecule—viz., 11-n-decyldocosane.

This report gives a detailed account of the synthesis and properties of this hydrocarbon. B. M. H. T.

Refining and Refinery Plant.

741.* Functions of Refrigeration in Petroleum Refining. W. R. McGinnis. Refiner, May 1941, 20 (5), 143-146.—With some exceptions, refrigeration is used in the refinery to provide control of chemical reactions or to remove certain components, a large part of the original material then going to further processing at higher temperature, or to a storage at atmospheric temperature. In such cases the cooled material is available to precool incoming material by heat interchange, reducing the amount of direct refrigeration required.

A number of refrigerants are available, and may be selected according to their suitability for the conditions under which they are to operate.

The most commonly used is anhydrous ammonia, which may be used either with compression or absorption cycles. Ammonia is suitable for temperatures ranging down to -80° or -90° F. The pressures are moderate, leakage is easily detected, and fire hazard is but little. It is not a diluent for lubricating oil, therefore lubrication of compressors is not a difficult problem. Forrous materials are inert to ammonia, but copper bearing alloys are subject to corrosion by ammonia.

Propane, which shows a flatter pressure-temperature curve than ammonia, fre-

quently is used, particularly in propane dewaxing systems as a diluent, and, by evaporation from the solution, as a direct refrigerant. Propane is also used in the conventional compression cycle.

Carbon dioxide is used for some special processes, but is not in general use. It requires equipment construction for high pressure and more power than that required for commonly used refrigerants.

Liquid sulphur dioxide is used in the Edeleanu process for solvent separation and also as a direct refrigerant by evaporation from the mixture. It is not ordinarily used below -20° F. In some cases, where lower temperatures are required, an indirect refrigerating system using a suitable refrigerant is employed. Sulphur dioxide with water is corrosive to ferrous materials, and must therefore be perfectly dry in the refrigerating system. Leakage absorbs water from the atmosphere, causing some external corrosion.

Freon 12 and Freon 11 are generally used for air-conditioning applications, being non-toxic, non-corrosive, and non-inflammable; but they may be used for other purposes where these qualities are desirable. Freon 12 is a moderate pressure refrigerant suitable for piston compressors, and standard equipment is available in a large range of sizes. Freon 11 is a low-pressure refrigerant, particularly suitable for centrifugal compressors, because of its large vapour volumes. In addition to the above refrigerants, ethane and ethylene are being used for low-temperature applications.

The power required to produce refrigeration at any definite condition of evaporator and condenser temperatures is not affected to any considerable extent by the selection of refrigerant; the power being nearly the same for the commonly used refrigerants at ordinary temperatures, except CO_2 , which is not frequently used.

Details of design and principles of absorption refrigeration systems are given.

A. H. N.

742.* First Hydroformer Unit Put on Stream. J. V. Hightower. Refiner, May 1941, 20 (5), 153–156.—The process of hydroforming differs from thermal reforming in three respects. In the first place it is catalytic rather than thermal. In the second place it involves circulation of hydrogen in admixture with the heated fresh charge as the mixture passes over the granular catalyst. Finally, the gasoline produced is less olefinic, chemically speaking, than gasoline of the same octane number produced by thermal reforming, and has an appreciably higher content of aromatics—45–50 vol.- $\frac{0}{6}$.

The unit brings about an interesting conversion of the low-grade naphtha used as a feed-stock. There is an apparent paradox in the use of hydrogen produced in the operation, for it might seem that this gas would cause the process to be essentially one of hydrogenation. Such is not the case, however. The net result of the operation is to remove a portion of the hydrogen from the naphtha feed. As the feed passes over the catalyst after leaving a preheating furnace, the catalyst causes a chemical change, resulting in the splitting off of hydrogen atoms. By introducing a given quantity of recycled hydrogen into the chamber under definite conditions of temperature and pressure, the rate and nature of the chemical change produced by the catalyst are controlled, so that the production of unsaturated hydrocarbon materials is held to a minimum. This is a point of considerable difference between hydroforming and thermal reforming, since the gasoline made by thermal reforming contains a higher percentage of unsaturated materials. Because of the low rate of production of unsaturates in the hydroforming process, the rapid formation of heavy, tarry material on the surface of the catalyst is avoided and the activity of the catalyst prolonged.

The paper describes the operation of the first unit put up in Texas City.

The hydroforming process is capable of producing gasoline of aviation grades, although as operated at present the unit at Texas City is making motor fuel only. Octane rating of the gasoline may be raised by altering operation conditions.

The fact that there is a large amount of toluene in the gasoline is of importance. On the basis of charging 7500 brl. daily of naphtha feed, it is estimated that the potential toluene production of the hydroformer amounts to about 5,000,000 gal./year, approximately a fourth of the total toluene produced in the United States during 1939. It is readily apparent that the installation of a few large units provided with equipment necessary for the recovery of nitration-pure toluene could meet any conceivable need for toluene for military purposes. A. H. N.

743.* Fractionation and Condensation Recover Distillate from Doctor Solution. Anon. Refiner, May 1941, 20 (5), 157–158.—Recovery of distillates from spent doctor solution is being accomplished through a series of heaters, flash and fractionating chambers, and a water-cooled vapour condenser. Since the solution is used at a once-through contact, pumped from the supply tank to the distillate contactors, settling drums and spent storage, the partly emulsified solution entrains a substantial quantity of the treated gasoline that is not broken out in the settling tanks. The recovery system is connected into the transfer line which leads the spent doctor heater, a combination flash, heating and stripping column, and a water-cooled condenser for recovered vapours mounted above an accumulator drum. The spent doctor is then led to the same tank as before, from which it is subsequently recirculated through a regeneration unit for reconditioning.

The plant is described in detail. The steam used to heat the doctor solution in the first heater and in the base of the flash-stripper column is taken from the plant main, but is not super-heated. The temperature maintained on the stream of doctor through both heaters is approximately 215° F., above the boiling point of water but below the boiling point of the doctor solution itself. Pressures maintained through the system are as near atmospheric as possible, so that the distillate in the doctor solution will distil without the hindrance of back pressure. A. H. N.

744.* Compressor Losses Caused by Orifice Meters. J. G. Burnham and V. E. Middlebrook. *Refiner*, May 1941, 20 (5), 167–169. *Paper Presented before Natural Gasoline Association of America.*—The effect of an orifice inserted in a line carrying gas will be to produce a final downstream pressure which is lower than the upstream pressure.

In the case of an orifice meter, which is usually installed relatively close to the compressor suction header, the final downstream pressure will be essentially the intake pressure of the machines. If there were no orifice in the line, the upstream or higher pressure, not the final downstream pressure, would then take to the machines.

If the orifice plant is eliminated, one of the following conditions will prevail: (1) The machine will handle more gas, due to an increase in volumetric efficiency, or (2) less horsepower, either total or per million, will be required to boost the same volume to a specified discharge pressure.

For the case given in this paper, of a 12-in. line carrying 3000 M.C.F. of gas available at 8-in. vacuum, the percentage of volumetric capacity lost will range from 1% at 5 in. differential to 15% at 50 in. The percentage increase in H.P./M.M.C.F. required to boost to 40 lb. varies from about 1% at 5 in. to 11% at 50 in.

If the orifice is removed from the master meter, the total incoming gas volume can be determined by two meters; one installed on the absorber residue, the other on the stabilizer tops. A factor calculated from a fractional analysis of the finished product may be used to convert the gallons of stabilized gasoline into equivalent cu. ft. of gas. The total of the two metered volumes plus the factored volume will equal the volume of gas entering the plant. A. H. N.

745.* Performance of Bubble-plate Columns. W. D. Harbert, E. S. Homan, D. D. Rosebery, and R. L. Huntington. *Refiner*, May 1941, 20 (5), 170–174.—There are two principal factors which determine the capacity of a bubble-plate column, such as a fractionator or an absorber: (1) The maximum quantity of liquid which can be passed downward through the downspout; (2) the maximum quantity of vapour or gas that can be passed upward through the bubble-plate.

Both of these maxima are fixed by the limit above which the column will no longer function in a normal manner. These two fluids—i.e., the downward-flowing liquid and the upward-flowing vapour—are mutually interdependent on each other, in so far as their performance in the tower is concerned.

The counter-current flow of air and kerosine has been observed in several plate-toplate sections of a 12-in.-inside-diameter bubble-tray tower under a wide range of liquid and gas-flow rates. It has been found that the ability of a downspout to disengage vapour from the frothy mixture flowing from the tray above determines in a large measure the gas and liquid capacity of a tower. Froth heights in the downspouts may vary considerably without the occurrence of priming or flooding; however, on the trays themselves it was seen that once froth began to build up, there was no stopping until the entire plate-to-plate section was filled with a frothy fluid mixture, whereupon the tower ceased to function counter-currently.

Reference is made to similar work carried out by Souders and others, and it is concluded that the behaviour of the flow of the liquid and froth in the downspout conformed closely to the mechanism described by these previous workers.

A. H. N.

746.* Y.P.F. Enlarges Capacities of Three Refineries. J. P. O'Dennell. Oil Gas J., 20.3.41, 39 (45), 28.—The three refineries of the Y.P.F. at La Plata (near Buenos Aires), Salta (North Argentine), and Mendoza (in West Argentine) are being considerably enlarged. At La Plata a vis-breaker handling 5000 brl. per day of $13\cdot5^{\circ}$ A.P.I. cracked fuel oil or a 7:3 mixture of heavy fuel and asphalt is being installed. A distinctive feature of the plant is the generation of steam from water, preheated by waste heat from the circulating fuel oil, in the convection section of the heater, 10,000 lb. of 190-lb. gauge steam at 386° F. being produced daily.

At Salta a 2000-brl.-per-day combination topping and cracking unit operating on Rio Pezcado and Vespucio crude has been installed. (The San Pedro crude from Vespucio is of 45.5° A.P.I. with a paraffin base, and has an unusually high gasoline content.)

At Mendoza a 3200-brl.-per-day combination topping, vis-breaking, and cracking unit operating on Tupungato and Cachueta crude has been installed. (The Tupungato crude has a paraffin base, and gravity 30.2° A.P.I., and the Cachueta crude is mixed base of slightly higher gravity.) At the present rate of increase of refining capacity the country should be entirely self-sufficient in a few years. C. L. G.

747. Petroleum Refineries, including Cracking Plants, in the United States. 1st January, 1941. G. R. Hopkins and E. W. Cochrane. U.S. Bureau of Mines, Information Circular No. 7161. April 1941.—Statistics compiled by the Bureau of Mines, and included in this report in the form of summary tables, indicate that during 1940 the number of refineries in the United States increased from 557 to 562. This slight gain was maintained in spite of the fact that a number of plants were dismantled in Texas and other States.

Approximately 50 refineries closed down during the year, largely owing to low gasoline prices, competition for crude-oil supplies, and the termination of a favourable distributing arrangement for independent plants in the Los Angeles area. This was reflected in the number of operating plants, which declined from 461 to 420, and in the number of idle plants, which increased from 86 to 136.

Equally, operating capacity declined from 4,196,694 brl. daily on 1st January, 1940, to 4,180,588 brl. daily on 1st January, 1941, and idle capacity increased from 431,952 brl. to 538,381 brl. during the year. Even so completed capacity was 2% more on 1st January, 1941, than in the previous year.

Of the ten refining districts, four showed declines in total capacity. The largest gains were reported in the East Coast and the Texas Gulf Coast.

Completed cracking capacity again increased by 5%, and idle capacity decreased to the low level of 82,042 brl., of which 85% was reported to be in "good shape."

H. B. M.

748. Patents on Refining and Refinery Plant. Universal Oil Products Co. E.P. 535,656, 17.4.41. Appl. 14.9.39.—Process for separating a stream of conversion products essentially consisting of relatively heavy normally gaseous hydrocarbons, lighter gases, and hydrocarbons boiling within the gasoline range into more than three fractions of different composition.

Standard Oil Development Co. E.P. 535,664, 17.4.41. Appl. 16.10.39. Process of contacting hydrocarbons with mineral acids under conditions which cause degradation of the acid, and in which a requisite acid strength is maintained by replacing part of it with fresh acid. The invention relates specifically to the reaction between isoparaffins and olefins when it is customary to employ a high ratio of acid to olefin and to recover the product by withdrawing a portion of the reaction mixture containing acid, reaction product and unreacted material, allowing the mixture to settle to an acid layer and a hydrocarbon layer and returning the acid to the system.

Houdry Process Corp. E.P. 535,803, 22.4.41. Appl. 11.9.39. Treatment of heavy hydrocarbons, including tarry and asphaltic bottoms and similar hydrocarbon residues, to separate the same into solid and fluid parts. The invention is characterized by controlling the operating conditions, so that the temperature of the coking zone does not fall below 800° F. nor rise above 950° F.

E. H. Records and J. E. Louttit. U.S.P. 2,239,859, 29.4.41. Appl. 16.8.38. Refining hydrocarbon oils containing sulphur compounds by treating with a catalyst, including a metal salt selected from the group consisting of ferric chloride, aluminium chloride, and a dispersing agent, consisting of sulphonated castor oil, at an elevated temperature. The sulphur compounds are thus converted into soluble form.

R. Rosen and C. A. Cohen. U.S.P. 2,240,577, 6.5.41. Appl. 4.6.38. Method of separating and recovering constituents of petroleum products by intimately contacting the product in liquid form with an alkyl ester of citric acid, in circumstances permitting development of a two-phase liquid, and separating the two phases by gravity. H. B. M.

Chemistry and Physics of Petroleum.

749.* Recent Progress in Chlorination. E. T. McBee and H. B. Hass. Industr. Engng Chem., 1941, 33 (2), 137.—Recent progress (1937–1940) in the chlorination of hydrocarbons is reviewed, and some of the recent discoveries are discussed. Among these discoveries may be mentioned the substitutive chlorination of olefines, peroxidecatalyzed chlorinations with sulphuryl chloride, chlorinations in intimate contact with a liquid mass of metallic chlorides, preparation of polychloropropanes, chlorination of natural gas, chlorination of aromatic compounds, chlorinolysis of paraffin hydrocarbons, high-pressure chlorination of paraffin hydrocarbons, hexachloroethane as a chlorination agent, the use of a capillary for introducing chlorine into material to be chlorinated, chlorination of esters, and chlorination of rubber. H. E. T.

750.* Synthesis of Phenol by Partial-Pressure Evaporation. D. F. Othmer and C. E. Leyes. *Industr. Engng Chem.*, 1941, 33 (2), 158.—Phenol has been synthesized by partial-pressure evaporation methods in both the sulphonation and fusion steps.

Benzene is sulphonated in the presence of a high-boiling naphtha fraction; then the sodium benzene sulphonate is neutralized and fused with caustic soda under kerosine. In each case the water of reaction or of solution is removed by partialpressure evaporation. A comparison with other sulphonation methods is included, and the technical and economic advantages of this process (Kokatnur) are indicated. For the Kokatnur process good yields and low process costs are the principal merits. It is shown that the primary sulphonation step in the manufacture of phenol can be carried out with the theoretical molecular ratios of benzene and sulphuric acid, whereas in the fusion operation, aqueous caustic solutions and aqueous solutions of sodium benzene sulphonate can be employed directly, also in practically theoretical proportions.

High-speed (1000 r.p.m.) emulsifying stirrers with naphtha cuts boiling in the range $170-200^{\circ}$ C. gave optimum results in sulphonation with either 94°_{00} or 98°_{00} sulphuric acid. Sulphones were not formed unless a large excess of benzene was employed. The small amount of charring which occurred was completely removed during neutralization.

The best results in the secondary, or fusion stage, were obtained with 50% aqueous

caustic soda (1.5%) excess) and of sodium benzene sulphonate. In this case also high-speed emulsifying agitators were employed, allowing a reduction in the volume of kerosine and giving a sintered, readily soluble product. Exclusion of air during the fusion stage prevented oxidation of the sodium phenolate, an added attraction for the process. H. E. T.

751.* Aromatic Mercuration. K. A. Kobe and T. F. Doumani. Industr. Engng Chem., 1941, 33 (2), 170.—Mercuration is of sufficient general application and importance in the aromatic series to be regarded as a typical substitution reaction, like nitration, sulphonation, or halogenation.

In general mercuration proceeds easily, with formation of mono-, di-, and polymercurated compounds. The ease of formation of di- and poly-mercurated compounds in many cases makes the formation of mono-mercurated compounds extremely difficult, so that the formation of mono-mercurated compounds in satisfactory yield by direct mercuration is impossible. The various methods for direct mercuration have been tabulated for hydrocarbons, amines, phenols, acids, nitro-compounds, and heterocyclic compounds. In addition, the various indirect methods of mercuration are mentioned.

752.* Utilization of Polychloropropanes and Hexachloroethane. E. T. McBee, H. B. Hass, T. H. Chao, Z. D. Welsh, and L. E. Thomas. *Industr. Engng Chem.*, 1941, 33 (2), 176.—A new term, "chlorinolysis," has been proposed to describe the process of chlorinating an organic compound under conditions which rupture the carboncarbon bonds and yield chlorocarbons with a smaller number of carbon atoms than were contained in the starting material. The term "chlorinolysis" is analogous to the familiar terms hydrogenolysis, hydrolysis, alcoholysis, and ammonolysis.

Chlorinolysis of polychloropropanes has been carried out in a nickel apparatus in the temperature range $300-360^{\circ}$ C. at a pressure of 1250 lb. per sq. in. Nickel has little effect on the dechlorination of partly chlorinated hydrocarbons and subsequent polymerization of the chlorolefines to carbonaceous material. The reaction temperature may be varied considerably, but below 300° C. substitution occurs very slowly, whilst above 400° C. undesirable side reactions take place. There also appears to be no limiting pressure, except that imposed by the material of which the apparatus is constructed.

The chief product obtained from the chloronolysis of propane and chlorides of propane was octachloropropane in good yield.

A careful investigation of the pyrolysis of octachloropropane was then undertaken, and the main products produced were carbon tetrachloride and tetrachloroethylene.

In addition, hexachloroethane and 1: 2-dichloropropane were pyrolized to obtain useful products in good yield. H. E. T.

753.* Chloronolysis of Chloropentanes. E. T. McBee, H. B. Hass, and E. Pierson. Industr. Engng Chem., 1941, 33 (2), 181.—High-temperature, high-pressure chlorination of chloropentanes has resulted in the formation of hexachloroethane, carbon tetrachloride, and hexachlorobutadiene. Explosions during the chlorinolysis of the chloropentane are prevented by use of excess chlorine. At 400° C. and under a pressure of 1000 lb. per sq. in. the conversions into carbon tetrachloride and hexachloroethane are approximately 90%, and the potential yield of these products approaches the theoretical value. H. E. T.

754.* High-Pressure Chlorination of Paraffins. E. T. McBee, H. B. Hass, and J. A. Pianfetti. Industr. Engng Chem., 1941, 33 (2), 185.—Liquid phase chlorination of paraffin hydrocarbons yields a higher percentage of primary substitution products than are obtainable in vapour phase at the same temperature. Thus, in the thermal chlorination of paraffin hydrocarbons, high pressures may be desirable in order to obtain a liquid phase. In vapour-phase chlorination of saturated hydrocarbons increased pressure causes increased relative rates of primary substitution. Since there appears to be a direct correlation between the change in the relative chlorination rate and in the molar volume of the hydrocarbon with increasing pressure, it

appears that pressure alters the relative chlorination rate by effecting a greater absolute concentration of the hydrocarbon in the vapour phase.

The effect of temperature and pressure on the relative chlorination rates of hydrogen atoms in propane, *n*-pentane, and *n*-heptane carbon has been fully investigated; the temperature range being $150-200^{\circ}$ C. and the pressure range 250-4000 lb. H. E. T.

755.* Relation between Free Energy and Structure of Organic Molecules. P. F. Bruins and J. D. Czarnecki. Industr. Engng Chem., 1941, 33 (2), 201.—Equations are derived from existing molecular free-energy equations to express the amount by which the free energy changes on the formation of the following bonds: C-H, C-C, C=C, C-CH₃, C-OH, C-CHO, and C-CO₂H. The value of the atomic linkage equations, compared with the general free energy equations, which are expressed as a function of the number of carbon atoms in the molecule, is that the bond equations are not restricted to a single homologous series, but have a more extended application in thermodynamic calculations. J. W. H.

756.* Generalized Equation for Activity Coefficients of Gases. S. H. Marron and D. Turnbull. Industr. Engng Chem., 1941, 33 (2), 246.—In a recent article in Industr. Engng Chem., 1941, 33, 69, the authors showed that the activity coefficients of gases can be calculated from an approximate form of the Beattie-Bridgeman Equation of State, if the constants are known. Newton (*ibid.*, 1935, 27, 302) has shown that all gases under similar conditions of reduced temperature and pressure have the same activity coefficient. The present paper serves to correlate the two ideas by deriving an activity coefficient equation from the Beattie-Bridgeman equation in which the only variables are reduced temperature and pressure. J. W. H.

757. Infra-Red Spectra of Rubber and High Polymers. W. C. Sears. J. appl. Physics, 1941, 12, 35.—The transmission spectra of thin films of crude rubber, soft and hard vulcanized rubber, thermoprene, polyvinyl chloride, neoprene, and pliofilm have been measured in the 2-15 wave-length band. The spectrum of rubber resembles the long-chain paraffins more closely than any of the other polymers. The polymers containing chlorine have distinctive spectra. J. W. H.

758. Heat of Wetting of Wood Charcoal by some Common Liquids. R. L. Razouk. J. phys. Chem., 1941, 45 (2), 179.—Measurements were made of the heat of wetting of four samples of charcoal by water, methyl, ethyl, n-propyl, n-butyl, and isobutyl alcohols, benzene, pyridine, and carbon tetrachloride. The apparatus was so arranged that the charcoal could be completely outgassed before the determination. The measurements were made at 25° C. and 30° C. Observations were also made on the time required for the development of the full heat of wetting for the thoroughly outgassed charcoal. This was found to vary from a few minutes for water and methyl alcohol, up to 30 min. for benzene.

An account is given of previous work and of the various theories of wetting.

P. D.

759.* Studies on the Separation of Paraffin Waxes. Part IV. The Sweating of War-Oil Mixtures. M. F. Sawyer, T. G. Hunter, and A. W. Nash. J. Inst. Petrol., 1941, 27 (210), 143–154.—A previous paper indicated that an investigation of the factors affecting the efficiency of the sweating process in which the same oil and wax-stock and also the same sweater are used throughout, resolves itself into a consideration of the effects of the following variables :—

(1) Amount of oil in the oil-wax mixture.

(2) Rate of sweating.

(3) Rate of extent of cooling of the oil-wax mixture before commencing to sweat, and

(4) Viscosity of the oil.

These factors are here considered. It is shown that-

(1) The sweating of an oil-wax mixture is considerably easier to control than the fractional melting of an oil-free wax, a fact of particular industrial importance.

(2) The yields of the various melting-point waxes, calculated as a percentage of the wax content of the oil-wax stock, are considerably lower than for the corresponding waxes, and obtained by the fractional melting of the oil-free wax stock at the same rate;

(3) Under the same conditions of sweating, the efficiency of the process is dependent on the oil content of the stock.

(4) Rate and extent of cooling of the sample prior to sweating have little effect on the yield and oil content of the various waxes produced.

(5) For corresponding melting points, the yields of waxes obtained by sweating at 5% and 10% per hour are similar, but those from the faster process are of slightly higher oil content.

(6) In the limited experimental work performed on viscosity, results indicate that oil of higher viscosity is more difficult to remove from the wax, and the resulting wax is therefore of higher oil content. B. M. H. T.

Analysis and Testing.

760.* Improve Pharmacopoeia Tests for Petroleum Products. Anon. Nat. Petrol. News, 1941, 33 (6), R-47-48.—Changes in tests for the 12th revision of the U.S.P. are now under consideration. Proposed versions for a number of these concerning petroleum products are given. For paraffins, the m.-p. range is widened to $47-65^{\circ}$ C., and the A.S.T.M. method recommended for their determination. In the test for carbonizable substances the strength of the acid and the manipulative details of the method are more rigidly defined. Allowance is made for the possible formation of paraffin/sulphuric acid emulsions in the matching of the colour produced against the standard.

A broader range for petrolatum is also recommended, the sp. gr. range widening to 0.815–0.865 at 60° C., and m.-p. range to 38–60° C. The A.S.T.M. method is proposed for m.-p. determinations.

In the case of liquid petrolatum, proposals include the substitution of the A.S.T.M. viscosity conversion table for that in use at present, the replacement of the term "opalescent" in the test for solid paraffin by the definition "Newsprint viewed through the diameter of the test-tube containing liquid petrolatum should be readable," and more rigid definitions of the details of the test for carbonizable substances. T. T. D.

761.* Mobile Unit for Studying Condensate Recovery. H. M. Nelly, Jr., and M. Benedict. *Refiner*, May 1941, 20 (5), 159-163 (cf. also *Oil Gas J.*, 8.5.41, 39 (52), 73).—When the type of equipment described in this article is run on the feed for the commercial unit, utilizing the same type of process at the same temperature and pressure, the results will be directly comparable with those which would be obtained in the commercial unit, thus eliminating all uncertainties in equilibrium constants. Furthermore, the products obtained will have the same characteristics as those which will be produced by the commercial installation.

The unit is a complete recovery plant mounted on a truck, which can be driven to a point where the high-pressure condensate stream to be studied is available. It has been so designed that it can be operated in any one of the following three conventional types of recovery processes :---

Atmospheric temperature absorption. Low-temperature absorption. Low-temperature separation.

The unit can be operated over the following range of variables : Well-head pressure : up to 6000 lb./sq. in. Primary tower pressure : up to 5000 lb./sq. in. Primary tower temperature = 10 to $\pm 120^{\circ}$ F. Feed rate : 500-1200 Standard cu. ft./hr. Lean Oil rate : 0 to 5 gall./hr.

The units proper—*i.e.*, the towers, piping, valves, and meters—are located in the rear compartment of the truck body. Forward of these is the control compartment,

in which are mounted instruments for the measurement and automatic control of pressures, temperatures, liquid levels, and rates of flow. In the front compartment is located the equipment for providing utilities. This equipment consists of an air-cooled gasoline engine, which is the prime mover for the unit, generator, lean-oil pump, air compressor, and refrigerating apparatus. It should be noted that the unit is entirely self-contained and requires no external utilities.

The control of the operation of the unit has been made as nearly automatic as possible. This results in even operation and reduces the operating personnel to a minimum.

To illustrate the type of information which can be obtained from the operation of the unit, the results of two typical test-runs are presented. Both tests were absorption runs made on the same feed under identical operating conditions, with the exception of the temperature of the absorber. The operating conditions and principal results of these runs are given in outline.

The accuracy of the results obtained from the unit depend not only on its operation, but also on the ability to collect a representative sample, to transport it without leakage or contamination to the laboratory, and to analyse it correctly. There are certain checks which can and should be made before the data are accepted.

A. H. N.

Motor Fuels.

762. Patents on Motor Fuel. C. E. Every. E.P. 535,768, 22.4.41. Appl. 19.9.39. Preparation of a fuel for use in internal-combustion engines consisting of an emulsion of water as the disperse phase and hydrocarbon oil as the continuous phase. An amino-compound soap is mixed with the hydrocarbon oil, water added to the mixture, and the whole agitated to form an emulsion.

Standard Oil Development Co. E.P. 535,975, 29.4.41. Appl. 24.10.39. Production of a gasoline of full boiling range—*i.e.*, about 80–410° F.—and of high octane number by separating the C_s and lower hydrocarbons and reacting the heavier hydrocarbons to produce alkylated aromatics having a boiling range which complements that of the C_s-C_s fraction previously recovered to yield a gasoline having a satisfactory distillation curve and high octane number.

L. C. Kemp. U.S.P. 2,238,860, 15.4.41. Appl. 15.8.39. Process for the conversion of natural gasoline hydrocarbons into high-octane motor fuel. Initially the gasoline is fractionated to separate therefrom fractions respectively rich in normal butane and *iso*butane and to produce a fraction of hydrocarbons mainly of higher molecular weight than butane. The normal butane fraction is then submitted to isomerization to produce *iso*butane. The fraction consisting of hydrocarbons, and the products of conversion fractionated to produce therefrom a fraction comprising C_3 and C_4 hydrocarbons, including olefins, also a high-boiling fraction comprising motor-fuel hydrocarbons of relatively high octane rating. Finally the C_3 and C_4 fraction is subjected to alkylation with the *iso*butane, and the products of alkylation fraction a fraction comprising hydrocarbons suitable as aviation motor fuel of high octane value.

G. Egloff. U.S.P. 2,240,134, 29.4.41. Appl. 21.3.40. Treatment of petroleum fractions to produce therefrom substantial yields of essentially paraffinic motor fuel having relatively high anti-knock value. An intermediate-boiling-range petroleum fraction is treated at an elevated temperature, and in the presence of a catalyst consisting essentially of a mixture of ferric chloride and aluminium chloride with a minor amount of hydrogen chloride, to produce a substantial yield of *iso*butane and normal butane. The *iso*butane and normal butane are then separated and the latter cracked at an elevated temperature to produce a substantial yield of of elefinic hydrocarbons. The *iso*butane is alkylated with the olefinic hydrocarbons, and the products of alkylation fractionated to recover high anti-knock value gasoline.

F. R. Moser. U.S.P. 2,240,145, 29.4.41. Appl. 22.8.39. Production of a liquid fuel for compression ignition engines. Incorporated in the fuel is a small amount of

Gas, Diesel and Fuel Oils.

763. Patents on Gas, Diesel and Fuel Oil. M. L. Chappell. U.S.P. 2,238,553, 15.4.41. Appl. 14.3.38. Method of increasing the cetane number of a petroleum diesel-oil fraction. The oil is treated with a diazonium salt at a temperature below 40° F. Thereafter the mixture is neutralized, and the water, containing dissolved salts of the reaction, separated from the diesel oil fraction.

C. Ellis. U.S.P. 2,240,558, 6.5.41. Appl. 7.2.36. Improving the ignition quality of a diesel fuel by mixing with dilute nitric acid in proportions ranging from about equal volumes of the diesel oil and acid to 5 vol. of oil to 1 of acid. H. B. M.

Lubricants and Lubrication.

764.* Trends of Lubricating Oil Manufacture and Utilization. M. H. Tuttle. Refiner, May 1941, 20 (5), 164–166. Paper Presented before Western Petroleum Refiners Association.—The trend to-day in the field of engine design continues to be towards higher temperatures and higher pressures, and this must continue, because this is in the direction of greater fuel economy. The limit is only that imposed by the materials for construction, the combustion characteristics of the fuels, and the lubricating characteristics of the oils. Since engines are now designed on the basis of the higherquality oils, it becomes necessary for the manufacturers of the lower-grade oils to suit their product to the engine.

By the solvent treatment of properly selected stocks, oils of high viscosity index and of excellent stability can be produced. Additives should be employed to supplement deficiencies of the raw stock, and not to replace the best refining methods.

The value of the lowest viscosity oils now in use is questioned, but if their use is to be continued, it is proposed that extensive engine tests be conducted to determine the film-stabilizing effect of including in such oils solvent-refined residual fractions.

Before the advent of solvent extraction, lubricating-oil quality was almost entirely a matter of crude source. To-day oils of equal paraffinicity are produced without regard to crude source, although yield of paraffinic oil and resistance to oxidation are greatly affected by crude source. Little is known about this quality of some oils of high viscosity index to be more resistant to oxidation than others, but frequently high stability has been found together with high sulphur, which would indicate the presence in some crudes of sulphur-type oxidation inhibitors.

Since the high-yield stocks do not necessarily produce the most stable oils, it is important that the crude sources be investigated with regard to each of these characteristics. A. H. N.

765.* Extreme-Pressure Addition Agents. E. A. Evans and J. S. Elliott. J. Inst. Petrol., May 1941, 27 (211), 165–180.—Patented additions to extreme-pressure lubricants may be classified generally into groups comprising sulphur, chlorine, phosphorus, and nitrogen compounds. The sulphur compounds may be sub-divided into derivatives of mineral oils, fatty oils, organic acids, esters, polymers, and a variety of specific aliphatic and aromatic compounds. Representative addition compounds from each of these groups were tested for film rupture strength in the Almen Machine, and the efficiency of the compound in promoting the load-carrying capacity of the oils in which they were incorporated assessed and discussed in relation to structure.

B. M. H. T.

766. Patents on Lubricants and Lubrication. Standard Oil Development Co. E.P. 535,777, 22.4.41. Appl. 21.9.39. Preparation of an improved lubricating composition for use in internal-combustion engines, and comprising a mineral lubricating oil and small amounts of salts or soaps of at least two polyvalent metals selected from

the three groups consisting of (1) aluminium, (2) nickel, and (3) a group comprising the alkaline earth metals and magnesium.

A. H. Gleason. U.S.P. 2,238,638, 15.4.41. Appl. 23.12.37. Preparation of an improved lubricant consisting of a viscous waxy hydrocarbon oil containing a small proportion of a polymerized oxygen-containing aliphatic compound having an oxygen atom connected only to carbon and having a chain of more than ten carbon atoms. The polymer product contains a substantial proportion of fractions with a molecular weight above about 600, and soluble in the oil.

C. Clar, N. Geiser, and P. Kühnel. U.S.P. 2,238,846, 15.4.41. Appl. 9.8.37. Production of lubricating oils by catalytically hydrogenating carbon monoxide, cracking the non-gaseous hydrocarbons obtained, and converting the cracking products by means of a polymerizing agent, containing a substantial proportion of aluminium chloride, into lubricating oil. During the process it is found that the oils are improved by heating in the presence of the polymerizing agent to a temperature between 140° and 240° C., while excluding additions of halogenated hydrocarbons.

A. W. Lewis. U.S.P. 2,239,752, 29.4.41. Appl. 2.4.37. Lubrication of bearing surfaces having substantially the corrosion susceptibility characterizing cadmiumsilver, cadmium-nickel, and copper-lead alloys. The lubricant employed consists of a mineral hydrocarbon oil to which has been added corrosion inhibiting proportions of benzo-nitrile.

E. W. Cook. U.S.P. 2,239,841, 29.4.41. Appl. 12.12.38. Method of lubricating bearing surfaces, at least one of which comprises an alloy having substantially the corrosion susceptibility of cadmium-silver, cadmium-nickel, and copper-lead alloys. The lubricant has incorporated therein an oil-soluble organic morpholine in corrosion inhibiting proportions.

M. Fairlie. U.S.P. 2,239,953, 29.4.41. Appl. 1.5.39. Preparation of a lubricating composition consisting of a petroleum lubricating oil and chlorocalcium phenyl stearate in which the chlorine is attached to the calcium.

D. E. Badertscher. U.S.P. 2,240,009, 29.4.41. Appl. 26.5.39. Preparation of a mineral-oil composition consisting of a viscous mineral-oil fraction and a minor proportion of the reaction product obtained by dissolving substantially equivalent proportions of an alkali alkyl xanthate and a β -chloroethyl amine in a suitable solvent modium. The mixture is refluxed for sufficient time to precipitate alkali chloride and form the reaction product. Finally the alkali chloride and the solvent are removed from the reaction product.

R. W. Richardson. U.S.P. 2,240,054, 29.4.41. Appl. 4.5.38. Method of improving and refining a lubricating oil by subjecting it to the action of more than 800 cu. ft. of air por barrel of oil at a temperature between 300° and 500° F. in the presence of 0.1% of manganese naphthenate. The air is passed through the oil at the rate of about $4\frac{1}{2}$ cu. ft. of air per barrel of oil, per minute. The oxidized oil is thereafter treated with a solvent mixture to remove undesirable constituents.

R. E. Conary, H. V. Ashburn, and P. S. Stutsman. U.S.P. 2,241,243, 6.5.41. Appl. 25.3.39. Preparation of a lubricating oil comprising a mineral lubricating oil containing 0.01-2.0% by weight of a phosphite ester of an alkyl ether of an alkylene glycol. H. B. M.

Special Products.

767.* Useful Products From Natural Gas. F. H. Dotterweich. Refiner, May 1941, 20 (5), 147-152. Paper Presented before Natural Gasoline Association of America. The non-hydrocarbon constituents, with the exception of carbon dioxide, are found in natural gas in relatively small amounts. Hydrogen sulphide, which is objectionable, due in part to its corrosive nature, may be removed and marketed for agricultural uses. The extremely fine state in which the sulphur is recovered has special value both in liquid sprays and as a solid dusting material. Helium, although present in natural gas in small amounts, is nevertheless of great value, as an oxygen diluent for medical purposes, inflation of lighter-than-air balloons and ships, as a preservative, and in the electric industry. Some wells produce carbon dioxide in relatively large amounts and make possible its recovery and use as a refrigerant, fire extinguisher, food preservative, and beverage carbonator.

The hydrocarbon groups of dry natural gas and bottle gas which are by-products of the natural gasoline industry must be converted into other products before they may be used to manufacture useful products. There are four methods of conversion : decomposition, oxidation, halogenation, and nitration. The four methods are discussed in some detail, with a study of possible products to be obtained commercially.

Synthetic rubber manufacture and utilization under various trade names is discussed.

Ethylene is an important raw material for many types of synthetic resins. This material used in the production of many plastics is obtained from cracked natural gas and refinery gas.

England, faced with a shortage of material for cable sheathing, in that polyvinyl chloride formerly imported from Germany was used for this purpose, has developed one of the latest type of plastics, polythene. This product is made by the direct polymerization of ethylene and possesses rubber-like qualities and excellent insulating characteristics.

Ethylene is the source of an important group of plastics based on vinyl chloride. Vinyl chloride may be manufactured from ethylene by the direct addition of hydrogen chloride to acetylene. In addition, and closely related to ethylene chloride is vinyl acetate. This compound is now chiefly manufactured from acetylene and acetic acid, the acetylene being produced from carbide; however, the future should see large quantities of acetylene, used in this process, produced from natural gas. These compounds, together with polyvinyl butyral, are being marketed and sold in varying proportions under the name of vinylite resins.

One of the most interesting and important applications of these resins is their use as Plexiglas. This product is one of the hardest acrylic resins, a colourless, transparent, thermoplastic solid. In addition, it may be obtained in a number of colours, both transparent and translucent, varying from delicate tints to the deep shades. The thermoplastic property of Plexiglas makes possible its fabrication at ordinary temperatures attained in ordinary ovens. By the use of wood tools, it may be readily machined. The optical and electrical properties of this substance are discussed.

The paper deals with an extensive number of products besides those mentioned above. A. H. N.

768.* Sulphuric Acid from Refinery Sludge. Anon. Chem. Met. Eng., May 1941, 48 (5), 144-147.—The paper consists of a short descriptive part and a detailed flowsheet, illustrated by photographs of an actual plant. When acid sludge is heated to 550° F. it decomposes into sulphur dioxide gas, solid coke, water vapour, and a small quantity of hydrocarbon gases. The sulphur dioxide can be processed in a contact sulphuric-acid plant to give clean sulphuric acid of any desired strength.

In the plant, the granular coke resulting from the decomposition of the acid sludge is fed in regulated quantity into a rotary kiln, where it is ignited and discharged at redheat into a second and smaller kiln by means of a sealed plunger feeder. The heat content of the coke is transferred to the sludge, which is fed into this second kiln in a measured and continuous stream, and the breakdown reaction is quickly completed. The strong gas from the decomposition kiln is cooled to condense out moisture and condensable oil, and then passed through the furnace, where any fixed hydrocarbon gas is burned out. The gas is then cooled, dried, and processed in a contact-acid plant using vanadium catalyst. The coke resulting from decomposition of the sludge is returned to the heating kiln after the excess has been diverted for use elsewhere. A. H. N.

769. Patents on Special Products. H. R. Fife. E.P. 535,588, 15.4.41. Appl. 12.10.39. Preparation of a petroleum composition for protectively coating or binding coal. The composition consists of a petroleum oil having a viscosity between 50 and 150 Saybolt seconds at 60–100° F., charged with added amorphous petroleum wax in such

quantity that the oil at least partly gels at room temperature, but remains capable of being sprayed.

H. R. Fife. E.P. 535,589, 15.4.41. Appl. 12.10.39. Method of protectively coating coke or coal by heating a mixture of petrolatum and water to liquify the petrolatum, and spraying the heated mixture on the fuel under combined extraneous pressure and vapour pressure within the heated liquids.

N.V. de Bataafsche Petroleum Maatschappij. E.P. 536,497, 16.5.41. Appl. 20.11.39. Catalytic treatment of hydrocarbons, consisting of or containing cyclo-paraffinic and/or cyclo-olefinic hydrocarbons, boiling substantially within the gasoline range. The invention particularly concerns the catalytic dehydrogenation of cyclo-paraffins and cyclo-olefins, or mixtures containing these hydrocarbons—e.g., cyclohexane, methyl cyclohexane, and gasolines rich in or at least containing naphthenes, with the object of producing aromatic hydrocarbons.

P. J. Gaylor. U.S.P. 2,238,637, 15.4.41. Appl. 18.8.38. Preparation of an improved oil composition consisting of an insulating hydrocarbon oil and a soluble condensed polynuclear hydroaromatic compound having a molecular weight above about 200, also the property of lowering the viscosity index of the oil and its gas evolution under the influence of an electric discharge. H. B. M.

Detonation and Engines.

770.* Octane Rating Relationships of Aliphatic, Alicyclic, Mononuclear Aromatic Hydrocarbons, Alcohols, Ethers, and Ketones. G. Egloff and P. M. Van Arsdell. J. Inst. Petrol., April 1941, 27 (210), 121-138.—This paper is largely a compilation of the octane ratings, scattered throughout the literature, of hydrocarbons, alcohols, ethers, and ketones.

The data are discussed in relation to the nine rules proposed by Lovell, Campbell, and Boyd concerning the relationship between structure and octane rating. For the pure hydrocarbons it was found necessary to modify somewhat their first and second generalizations, whilst considerations of data on the oxidized compounds showed that these rules were also applicable to the oxidized class of motor fuels. It is shown that the combustion conditions under which the octane ratings are made are the most vital factor in any octane rating given for a chemical compound. The octane ratings given for the various compounds and the generalizations made from them are specific for the test method indicated, and any change in the test method markedly alters the octane rating of the compound. B. M. H. T.

771.* Extension of the Octane Scale above 100 O.N. (Report and Recommendations of the Institute of Petroleum Knock Rating of Aircraft Fuels Panel.) Anon. J. Inst. Petrol., May 1941. 27 (211), 188.—As some experimental types of fuel have anti-knock values better than that of pure *iso*-octane, it has been considered desirable to provide an extension of the octane scale. The scale recommended extends from the O.N. of reference fuel C + 4 mls./T.E.L. Imp. Gal. to that of F + 4 mls. T.E.L./Imp. Gal. (C 12 + 4 mls./Imp. Gal. = 93 O.N. approximately; F 3 + 4 mls./Imp. Gal. = 116 O.N), B, M, H. T.

772.* Tentative Method for Knock Rating of Experimental Aviation Fuels of Over 100 O.N. "17° Motor Method." (I.P.T. Serial Designation G. 396-194° (T). Anon. J. Inst. Petrol., May 1941, 27 (211), 191.—The method is primarily intended for testing experimental types of fuel of over 100 O.N. The apparatus and method are as laid down under I.P.T. Serial Designation G. 39 (T), except that a fixed ignition setting of 17° early shall be used, and the bouncing-pin lower-leaf spring-tension increased to prevent the pin from bouncing as a result of higher combustion pressures. The spring tension may be increased if necessary for stable working up to a maximum of 300 gms. B. M. H. T.

773.* Calibration of C.F.R. Reference Fuels. Anon. J. Inst. Petrol., May 1941. 27 (211), 192–194.—The calibration of F 3 + 4 mls. T.E.L./Imp. Gal. and C 12 + 4 mls. T.E.L./Imp. Gal. has been determined by the C.F.R. Motor Method (I.P.T. G. 39 (T) and I.P.T. G. 39(b) T), and continued up to 116 O.N. B. M. H. T. 774.* Liquid Jets of Annular Cross Section. A. M. Binnie and H. B. Squire. Engineer, 1941, 171 (4448), 236-238.—Experiments made on a water-jet produced by an annular orifice are described. An approximate theory of the form of the annular portion is derived and is compared with experimental observations. J. G. W.

775.* Tests of a Kadenacy High-Duty Moderate Speed Experimental Unit. S. J. Davies. Engineer, 1941, 171 (4448), 238-240.—The results of tests made on a twostroke engine to which the Kadenacy principles of exhausting and charging had been applied are given. The unit had a bore of 4.515 in. and a stroke 6.5 in., and operated at 1000 R.P.M.

The output obtained was exceptionally good and the fuel consumption satisfactory ; with a more efficient supercharger the performance would have been still more striking.

A high standard of reliability was shown on an endurance test, evidenced by the small amount of wear measured, the low consumption of lubricating oil, and the good conditions of the oil at the end of the run. J. G. W.

776.* Temperature and Latent Energy in Flame Gases. W. T. David. Engineer, 1941, 171, 268–270.—Experiments are described confirming the view previously held by the author that the temperature rise resulting from the combustion of an inflammable gaseous mixture increases as the distance of flame travel from the igniting spark increases. This is ascribed to the difference between the mechanism of flame propagation in the early stages of combustion after spark ignition and that in the later stages.

Experiments are also described which show how the temperature attained by the fame gases resulting from the combustion of any given homogeneous inflammable mixture depends greatly on the manner in which combustion takes place. It is shown that under certain conditions, after careful allowance has been made for radiation losses, this temperature may be several hundreds of degrees C. below the calculated value. A theory is advanced to account for this discrepancy.

It is further shown that, owing to latent energy, the ideally calculated pressures are not fully attained in closed vessel explosions even after allowing for the heat loss which takes place during explosion. The measured explosion pressure was found more nearly to approach the ideally calculated value as the size of the explosion vessel was increased, suggesting that little success in determining the specific heats of gases by the explosion method can be expected unless very large vessels are used.

E. F. C.

777. Notes on Recent Developments in Fuel Technology. J. Hiles and J. R. Thompson. *Fuel*, XX, 1941, p. 61.—A brief review is first made of recent developments in the use of protective furnace atmospheres in the heat treatment of ferrous materials. Due to the extensive experience gained in recent years in atmosphere control, it now appears to be possible to produce any desired atmosphere with comparative ease and to conduct heat treatment of the metal without surface damage.

The method of colliery cleaning of anthracite next described consists of feeding the coal in at one end of a large rectangular tank containing a 1-ft. layer of water and underneath this a 2-ft. layer of a parting liquid. This consists of a mixture of pentachlorethane and ethylene dibromide with a sp. gr. of 1-70. As separation takes place, flight conveyors remove clean coal and refuse, which are then washed with water-sprays. Due to special arrangements to conserve the parting liquid in use, the consumption per ton of feed of pentachlorethane is only 8 oz. and of ethylene dibromide only 1 oz.

Experiments carried out with a C.F. R. four-stroke diesel engine in which the oxygen content of the charge could be raised from 21% to 55%, showed that with appropriate fuel injection the B.H.P. increased by 50%. At the same time the maximum cylinder pressure did not vary appreciably, whilst the maximum rate of pressure rise actually decreased up to an oxygen content of 45%. Ignition lag decreased linearly with increasing oxygen content, the lag with 55% oxygen being less than half that with air. Since it appears that oxygen boost may safely be applied for short periods, it is suggested that the method might be applied to assist the take-off of diesel engine directly, so saving considerable engine weight.

E. F. C.

Coal and Shale.

778.* Oil-Shale Deposit of Orepuki, Southland. R. W. Willett and H. W. Wellman. N.Z. J. Sci. and Tech., Sept. 1940, 22 (2B), 84B.—The results expressed in this report are based on information obtained from geological and geophysical surveys carried out in 1939–40. The Orepuki oil-shale lies at the eastern end of Te Wae Wae, Longwood Survey District, Southland. About 14,000 tons of oil-shale were mined and treated during 1899–1903, since which date the plant has been closed.

The rocks of the Orepuki have been divided into three groups. The igneous basal complex, which ranges from noritic to granitic types, is separated by a large unconformity from the shale-bearing Waimeamea Series. Both the above groups were folded and faulted, and suffered considerable erosion before the deposition of the Orepuki Series, which extends indifferently over both the bedrock and the Waimeamea Series, and is penetrated only by the larger streams of the district.

The oil shale occurs near the base of the Waimeamea Series directly overlying the workable coal-seams, and ranges in thickness in the known areas from 4 ft. 6 in. to 8 in. Further information is needed on the thickness of the shale over the entire region, which is only possible by drilling. Suggested drilling sites are indicated. Large-scale distillation tests show that on the average the oil-shale yields 43 gals. crude oil per ton and 26.7 lb. ammonium sulphate per ton. The average sulphur content of the oil shale is 5.9%.

The quantity of oil shale *in situ* lies between a probable maximum of 6,769,000 tons and a probable minimum of 1,770,850 tons. Mining conditions and the possible percentage recovery and probable cost are discussed. B. M. H. T.

Economics and Statistics.

779.* Oil in International Relations. Walter H. Voskuil. Bull. Amer. Ass. Petrol. Geol., March 1941, 25, 353-370.--The importance of petroleum to a nation is not to be gauged only by the demand for gasoline, fuel oils, or lubricants. Importance may also be gauged by critical needs, special functions, irreplaceable services more importantly than by quantity consumed only. Oil is a raw material vital to the welfare, industrial and military strengths of nations even to the very survival of nations. The paper illustrates and describes the various world oil-producing districts and consuming markets, the political impediments to free movement of oil, and some of the international tensions that have risen as a result of the fortuitous and uneven manner in which oil resources are distributed geographically and politically, and is of interest in view of the present international situation in Europe, etc. Maps showing imports into the countries concerned and their usual routes are given. In regard to Russia, the writer states that although she is the biggest producer of oil in Europe and has large reserves, exports of crude and refined products fell from 30°_{\circ} of production in 1932 to 4% in 1938, in spite of increase in crude production. Industrial development, military expansion, and mechanization of agriculture tended to absorb most of the Russian oil output. R. J. W.

780. Petroleum Engineering Education. H. H. Power, *Petrol. Tech.*, March 1941, A.I.M.M.E. Tech. Pub. No. 1312, 1–5.—Engineering colleges render considerable services by the progressive process of selection of career aims. It is essential to eliminate misfits, but enrolments should not be restricted so as to tend to create a group of very independant individuals who lack the incentive to make a record of their own.

The basic principles underlying the work cannot be thoroughly covered in four years, but it is doubtful whether five or six years would give proportional gains to many students. A tentative four-year course distributes time amongst subjects as follows: chemistry (21), engineering drawing (6), economics (3), English (12), geology (18), government (3), mathematics (14), physics (12), civil engineering (12), electrical engineering (3), mechanical engineering (8), petroleum engineering (22). The instruction in chemistry should cover physical chemistry and colloids; in geology it should have a sedimentary bias. Fluid mechanics and thermodynamics are essential. A sound basic training must be given, with an approciation of the importance of cost and practical economics, and the student must acquire the ability to express himself clearly both orally and in writing. G. D. H.

BOOK REVIEW.

Exploration Geophysics. By J. J. Jakosky. Pp. xii + 786. Figs. 411. Printed by Times Mirror Press, Los Angeles, California, U.S.A. 1940. Price \$9.00.

This is the second book on the subject of Geophysical Prospecting or Exploration Geophysics to make its appearance in this country in the past few weeks, and a third on the same subject, already published in U.S.A., may arrive here any day. Whatever the immediate cause for this spate of publication, it indicates at least the great importance which geophysics has attained in its application to problems of economic geology, especially in oil and mining exploration, and also a wide-felt need for a comprehensive and up-to-date book on the subject. Such an inundation might easily have produced some confusion, but from a consideration of the first two books, it is obvious, and indeed fortunate, that they each appeal to a different class of reader, although a certain amount of overlap is inevitable. The treatise by Jakosky is essentially a book for the practising geophysicist and reader actively interested in the application of geophysical methods. Furthermore, the earlier publication by Nettleton is limited to prospecting for oil, whereas this work covers all important economic applications in mining, water supply and civil engineering, in addition to oil prospecting.

The book is divided for the most part according to the geophysical method. Five chapters covering nearly three-quarters of the volume, deal successively and at considerable length with the older methods, grouped in the customary manner as magnetic, gravitational, electrical (two chapters) and seismic methods. Two short chapters are concerned with newer methods, the first with geo-chemical methods, the other with geo-thermal methods. One chapter of fifty pages is devoted to drill or borehole investigations, especially the measurement of electrical resistivities and potentials, which have achieved considerable importance in recent years, and a further chapter of twenty-eight pages discusses physical principles applied to oil production problems. The three remaining chapters apply to geophysical prospecting as a whole. In the introductory chapter the author presents a brief historical review of the development of geophysical methods from remote times up to the present-day, and proceeds to indicate trends in development of future methods. Chapter II, as set out in the caption, deals with the geological and economic background of exploration geophysics, and the last chapter of the book refers briefly to permit and trespass practice and insurance, mainly of concern and interest to geophysical parties operating in U.S.A.

The above brief outline indicates to some extent the comprehensive nature of this book. Not only is the whole field of economic geophysics covered, but each method is described and discussed in unusual detail, and no important aspect of the subject is omitted or neglected. The fundamental principles and theories, the instruments and equipment, the field techniques, reduction of observations and the final analysis and interpretation—all are given full and proper consideration. A particularly noteworthy and valuable feature of the book is the special attention given to the application of the various methods to specific problems of economic geology. The applications are well exemplified by illustrations, records, profiles, plans and maps, many of which are taken from actual field surveys. Suitable charts and diagrams and numerous photographs of instruments, equipment and field operations add greatly to the interest, value and clarity of the book as a whole. Instead of the usual bibliography, a list of patent references is introduced at the end of the appropriate chapter or section. As the author remarks, "Patent specifications . . . tend to be more authoritative than the reports in contemporary literature." Particular attention may also be directed to Chapter II, where the subjects discussed are all of prime importance in the economic and efficient application of geophysical methods to particular geologic problems. Being of a controversial nature, they are all too frequently overlooked or avoided.

Before concluding, mention may be made of one or two features which detract from the general high standard of the book. In various sections the arrangement or sequence is somewhat disjointed, due, it would seem, to a lack of uniformity in the treatment of the various methods. This discontinuity is further emphasized by the fact that there is sometimes no differentiation in type to distinguish main from subsidiary headings. Throughout the text numerous paragraphs appear in inconveniently small closely printed type, for no obvious reason other than the condensation of the subject matter within the 787-page limit of this book.

This elaborate work by Jakosky is unquestionably the most comprehensive and detailed compilation on the subject of Exploration Geophysics which has yet appeared. It is brimful of valuable information, and is altogether a record achievement, for which the author deserves the highest praise.

J. C. TEMPLETON.

PUBLICATIONS RECEIVED.

Australia; Council for Scientific and Industrial Research, 14th Annual Report, 1939-40. Pp. 102. Fep.

The 14th Annual Report covers the entire field of research work carried out under the Council for Scientific and Industrial Research during the year ended 30th June, 1940. Most of the work relates to biological problems, but reference is made to researches on lubrication and wear under the direction of Dr. P. Bowden, of the University of Melbourne, formerly of University of Cambridge. It is believed that the results will be of considerable value in connection with the growth of the Australian aeroplane engine industry. A C.F.R. engine has been installed in the Aeronautical Research Laboratory. A new laboratory is being built for investigations in industrial chemistry.

Empire Mineral Resources and their Relation to the War Effort. Sydney J. Johnston. Institute of Chemistry, 1941. Pp. 85.

This is a reprint of the 23rd Streatfield Memorial Lecture, 1940. The author is Principal, Mineral Resources Department, Imperial Institute, London. The subject is dealt with under three main headings—viz., the Empire's share of mineral wealth; production, uses, and trade in Empire minerals; and Government assistance to the mining industry in the Overseas Empire. The statistical information relates to 1938, and constitutes a useful summary of the well-known annual Mineral Industry published by the Imperial Institute.

Stabilized Roads. R. H. Picher. Canadian Bureau of Mines; Technical Paper No. 800. 1940. Pp. 37.

This Report treats specially of the method of stabilization of graded granular soils with clay binder and moisture film. Brief mention is made of the use of Portland cement and several types of bituminous materials as permanent stabilizers.

B.E.A.I.R.A. 20th Annual Report. Oct. 1939-Sept. 1940. Published by the Association. 1941. Pp. 134.

Under the heading "Insulating Oils" it is stated that a report on the ageing tests of oils from several large power-stations over a period of years is in an advanced stage of preparation. The tests show that the sludge and acidity values of the oils have changed very little during the period.

SCALSKIE!

INSTITUTE NOTES.

JULY, 1941.

STUDENTS' SECTION (BIRMINGHAM BRANCH)

The Annual General Meeting of the Students' Section (Birmingham Branch) was held on May 22nd, 1941, when the following Officers and Committee were elected :

		A. L. CUDE.
		A. W. PEARCE.
er		A. N. NISSAN, Ph.D.
		G. BUXTON.
		L. GRUNBERG.
		M. L. FELLOWES
	er	er

Seven meetings were held during the Session for 1940-41. Papers presented included "Engine Performance and Development," by H. Fossett (Associated Ethyl Company), "The Theory of Surface Catalysis," by S. J. Green, and lectures on their theses and vacation work in Trinidad given by fourth year students. One meeting was devoted to films on various aspects of the petroleum industry.

The average attendance at meetings was twenty-two.

The Section also took an active part in the Mining Society's successful Conversazione held in February last.

ARTHUR W. EASTLAKE, Honorary Secretary.



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