

THE PERMEABILITY OF POROUS SOLIDS TO GASES AND LIQUIDS.*

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INTRODUCTION.

CALCULATIONS reveal that the rates at which fluids flow through sand formations are extremely small. Thus an oil-well flowing, say, at 2000 tons/day from a sand 30 feet thick may be considered to be a fairly prolific producer. Yet, if the specific gravity of the oil is 0.8, the mean linear velocity at a distance of only 3 feet from the centre of the well is of the order of 0.05 cm./sec. The speed of flow is inversely proportional to distance from the well and, hence, it can be seen that in wells of more normal size the mean linear speed of the fluid in the body of the sand quickly assumes exceedingly small values. In laboratory work, however, there are advantages in maintaining fairly high rates of flow as the measurements become relatively simpler to take and the accuracy easier to maintain. With these considerations in mind, it was deemed necessary to investigate the validity of certain principles connected with the flow of fluids through porous media, when the rates of flow become very low. To attain easily measured pressure drop across the samples at low rates of flow of air through them, highly impervious samples were chosen. Liquids were excluded from the studies on rock samples for two reasons: (1) liquids introduce complex extraneous factors, such as the swelling of certain minerals, which factors may mask fundamental deviations in the hydrodynamics of the system; (2) certain measurements have already been taken by earlier workers. To obtain some relationship between the flow of air and the flow of liquids a Jena glass filter was used. In this case the difficulty mentioned above was eliminated.

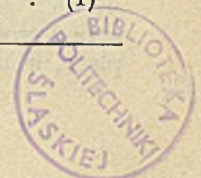
Permeability is the property of porous materials, which permits the flow of liquids through these materials. A porous material is permeable by virtue of its porosity, but any attempt to express permeability as a function of porosity has failed so far. Clays, for example, having a porosity of 50-60 per cent. are practically impermeable, while sandstones with a porosity of 30 per cent. are quite permeable. However, it can be safely stated that permeability is a function of the dimensions and intercommunication of the pores, factors which in most cases cannot be determined.

Theory.

The fundamental principle governing the flow of fluids through porous media, when the flow is in the viscous region, is "Darcy's law."¹ This law in its simplest form states:

$$\frac{dp}{dx} = Cv \dots \dots \dots (1)$$

* Received October 30th, 1941.



where $\frac{dp}{dx}$ = pressure gradient along sample ;

v = macroscopic velocity = $\frac{\text{quantity passing/unit time}}{\text{cross-sectional area}}$;

C = a constant.

The constant C contains a physical characteristic of the fluid, *i.e.*, its viscosity μ . It is usually assumed that separation of μ from the constant C frees the latter from any dependence on the nature of the fluid. In a more elaborate form Darcy's law becomes

$$K = \frac{Q\mu}{A} \cdot \frac{1}{\Delta P} \dots \dots \dots (2)$$

where K = permeability—*i.e.*, a characteristic of the porous medium ;

Q = volumetric of flow with respect to time ;

μ = viscosity of the fluid ;

A = cross-sectional area of the sample ;

ΔP = pressure drop per unit length.

In the case of flow of gases the quantity Q is not constant, but increases with the pressure drop, according to Boyle's law, in the majority of cases. It is therefore necessary to correct this quantity, as measured at the outlet, to the mean pressure. Assuming isothermal expansion :

$$\bar{Q} = \frac{2QP_2}{P_1 + P_2} \dots \dots \dots (3)$$

where \bar{Q} = mean quantity flowing per unit time ;

$P_1 + P_2$ = absolute pressures at inlet and outlet respectively.

For gases, therefore, Darcy's law becomes :

$$K = \frac{\bar{Q}\mu}{A} \cdot \frac{1}{\Delta P} \dots \dots \dots (4)$$

It must, however, be pointed out that Darcy's law is, in fact, another expression of Poisseuille's law of flow through a number of capillaries :

$$Q = \frac{nR^4\pi\Delta P}{8\mu} \dots \dots \dots (5)$$

or
$$\frac{nR^2}{8} = \frac{Q\mu}{\pi R^2\Delta P} \dots \dots \dots (6)$$

where

n = number of capillaries ;

R = average radius of capillaries.

Therefore

$$K = C' \times \frac{nR^2}{8}$$

where C' is a constant introduced by the fact that in Darcy's law, not the actual cross-sectional area of the capillaries through which flow is taking place, is used, but the macroscopic cross-sectional area (*i.e.*, the cross-

sectional area of the sample) and further, the cross-section of the capillaries is neither uniform nor circular.

This relationship between Darcy's and Poisseuille's laws will later be used to find the correct values of certain criteria which were found to be controlling factors of the conditions of flow.

In the c.g.s. system K is measured in darcies, when Q (or \bar{Q}) is measured in c.c./sec., A in cm.², μ in centipoises, and ΔP in atmosphere per centimetre length. The practical unit is the millidarcy = 10^{-3} darcy.

The absolute validity of Darcy's law was challenged by early workers, who found that the quantity v did not vary linearly with $\frac{dp}{dx}$, but varied according to an exponential law. One form ² proposed was :

$$\frac{dp}{dx} = av^n \dots \dots \dots (7)$$

where a and n are constants.

Another form ³ given to this equation was :

$$\frac{dp}{dx} = av + bv^2 + cv^3 \dots \dots \dots (8)$$

where a , b , and c are constants.

Based on an analogy with the flow of fluids through pipes, the following form is far the most popular ^{1, 2}

$$\frac{dp}{dx} = av + bv^2 \dots \dots \dots (9)$$

where a and b are constants.

Based on the above analogy and on mathematical analysis, it is believed that for low velocities the fluid is in a state of "viscous flow," governed almost entirely by the first term of equation 9. As the velocity increases the fluid changes to a state of "turbulence" governed by the second term of equation 9. M. Muskat limits the importance of the linear term to systems with Reynolds' criterion lower than 1. The parameter for length in the criterion has hitherto been difficult to determine, so that this figure may not represent any strict limitation of the conditions under which viscous flow changes to turbulence.

OBJECT OF INVESTIGATION AND CHOICE OF MATERIAL.

As has already been mentioned, it was the object of the following investigation to test the validity of Darcy's law for rock samples, which, due to their small pore diameter, will, under test conditions, give non-turbulent flow.

Oolitic limestone was chosen, which is known to have approximately 73 per cent. of its total porosity in the form of micropores, with an equivalent diameter smaller than 0.005 mm. The results were to be correlated by tests on limestone, magnesium limestone, fine (siltstone-like) sandstone, and coarse (well-cemented) sandstone. The impervious samples were used to yield extremely low rates of flow, whilst the relatively permeable sandstones were used to correlate low and high rates in one system.

A Jena glass filter (commercial specification 11G3) was used to correlate the flow of air and of aqueous solutions and to study the permeability to liquids of different surface tensions.

EXPERIMENTAL WORK ON GAS FLOW.

The cores were cut by means of a special cutter, and whenever necessary subjected to Soxhlet extraction, according to a standard procedure.⁴ The dimensions of each sample were taken by means of a micrometer graduated in millimetres. Length and diameter were measured in five different planes, and the mean of five readings taken. The results are given in Table I.

TABLE I.

Sample.	Lithological species.	Length, cm.	Diameter, cm.	Cross-sectional area, cm. ² .
1	Oolite	3.1936	2.9533	6.8500
2	Oolite	3.1991	2.9656	6.9074
3	Oolite	3.1916	2.9528	6.8478
4	Oolite	3.1996	2.9728	6.9411
5	Limestone	3.2536	2.8589	6.4192
6	Very fine sandstone	1.9684	3.1003	7.5491
7	Mg. limestone	3.0304	2.8390	6.3258
8	Coarse sandstone	2.3879	2.9663	6.8799
9	Coarse sandstone	2.3499	2.9668	6.9130

The samples were thoroughly dried for 6 hours at about 70° C., and always kept in a desiccator over calcium chloride. The sample was placed in the special sample holder, and air under pressure passed through. Keeping the pressure constant, measurements were taken simultaneously for : barometric pressure, temperature, inlet and outlet pressures and rate of flow.

Special precautions were taken to keep the sample in a state of dryness throughout the experiment, firstly by passing the air through a calcium chloride container, and secondly by interposition of calcium chloride tubes whenever there was communication to measuring instruments containing water.

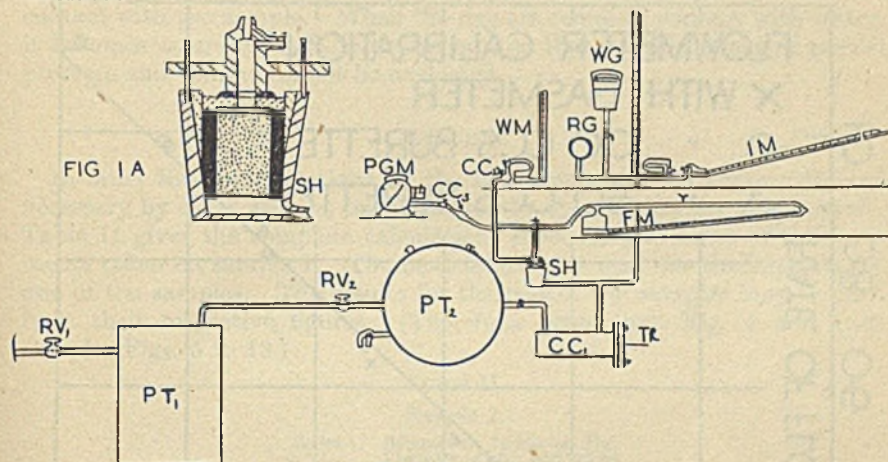
APPARATUS.

The apparatus (Fig. 1) may be sub-divided into three sections :

- (1) Source of pressure and sample holder ;
- (2) Pressure-measuring section ;
- (3) Flow-measuring section.

(1) Air under pressure from a compressor passes through two reducer valves (RV_1 and RV_2) and two pressure tanks (PT_1 and PT_2) into a calcium chloride container (CC_1). The latter also holds the thermometer (Th), which measures the temperature of the stream of air. Passing through a filter of cotton-wool, the air goes through a T-piece to the sample holder and to the pressure-measuring section.

The sample holder (*SH* and Fig. 1A) consists of a steel container and different brass tubes and rings. Rubber packings are provided to prevent any possible leakage. This holder has the advantage that a constant check on the possibility of leakage can be maintained simply by covering the top part with water, or putting the whole in a water-bath, the temperature of which can be accurately measured. If the holder is of brass, troubles of oxidation and rusting which result in the case of iron holders can be avoided.



FIGS. 1 AND 1A.

(2) For the measurement of inlet pressure, the following set of gauges and manometers was provided :

- (a) Rough gauge (*RG*) for the rough estimation of pressure.
- (b) Calibrated Alex. Wright metal gauge (*WG*), for pressures from 130 to 300 cm. Hg.
- (c) A straight mercury manometer (*MM*), for pressures from 25 to 130 cm. Hg.
- (d) A manometer (*IM*) with an inclination of 1 in 4, for pressures from 0 to 25 cm. Hg.

Outlet pressure was measured by means of a water manometer (*WM*), separated by a calcium chloride tube (*CC*₂) from the sample holder.

(3) Up to rates of flow of 1 c.c./sec. a calibrated flowmeter (*FM*) was used, consisting of a resistance to flow (*r*), represented by a capillary of 0.1 cm. diam. and an inclined (1 in 10) toluene manometer.

Higher rates of flow were measured by means of a Parkinson gasmeter (*PGM*) and a stopwatch. The gasmeter gave one revolution for 0.5 l. gas. It was separated from the sample holder by a calcium chloride tube (*CC*₃).

To make the measurements on the glass filter the whole sample holder was replaced by the glass filter which was connected to the apparatus in an appropriate way.

CALIBRATIONS.

(1) The Alex. Wright metal gauge was calibrated against a mercury manometer and the calibration checked for hysteresis.

All the readings were converted into true values by means of a chart.

(2) The Parkinson gasmeter was found to read correctly for 2 l. of air, which were collected under water, and for 4 l. which were displaced from a standard flask by water.

(3) Calibration of the flowmeter was carried out for the two purposes :

(a) To ascertain that the flow of air through the flowmeter within the required range was viscous, as already calculated by ascertaining

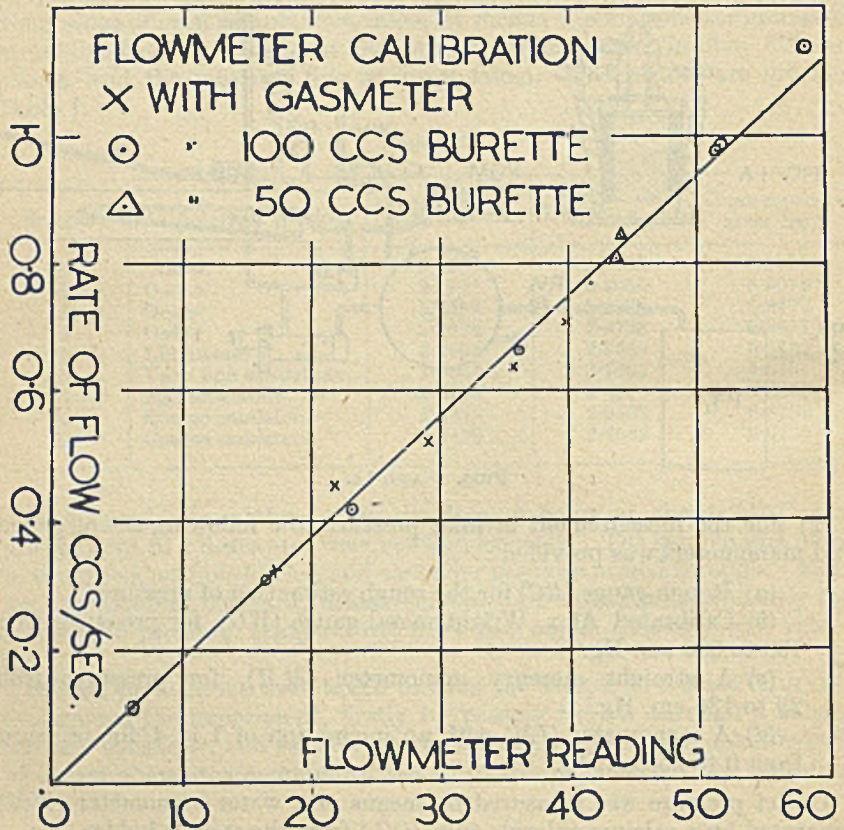


FIG. 2.

the Reynolds' number for the maximum rate of flow to be measured by the flowmeter.

(b) To obtain the equivalence of the flowmeter readings in c.c./sec. Calibration was first carried out by means of the gasmeter, and then by means of a 200-c.c. burette, which was filling with water from a constant pressure head, acting across a fine jet, while the air so displaced was passed through the flowmeter.

At the end of the investigation the calibration was verified by means of a 50-c.c. burette, collecting the air, issuing from the flowmeter, under water. In all cases the time was taken by means of a stopwatch. The calibration is shown graphically on Fig. 2.

CORRECTIONS.

Rate of flow as measured by the apparatus was in all cases converted to \bar{Q} , for considerations already given.

Whenever measurements of air were taken in contact with water the appropriate correction for water-vapour pressure at test temperature was applied—i.e., the volume was reduced by the partial volume of water-vapour. This was considered necessary, because only dry air came in contact with the sample. When the dry air comes in contact with water, it becomes saturated with water-vapour, so that considerations of partial pressure and volume cannot be neglected.

RESULTS.

In order that recalculations, or the introduction of corrections deemed necessary by other workers but neglected by the authors, may be possible, Table II gives the complete calculations sheet for one series of measurements taken on sample 1. The next tables give only the final results for one of the samples. The results for the rest of the samples may be seen from their respective figures. (The Jena glass gave Fig. 4 and rock samples Figs. 5 to 13.)

TABLE II.

Sample I.

Series 1. Barometer : 74.955 cm. Hg.
Viscosity of air : 0.01773 cp.
Temp. : 12.9° C. \pm 0.1° C.

Inlet press., cm. Hg.	Flow-meter reading.	P_1 , atm.	P_2 , atm.	Q , c.c./sec.	\bar{Q} , c.c./sec.	$P_1 - P_2$, atm.	$\frac{\bar{Q}}{A} \times 10^4$.	$h\Delta P$, atm. cm.
196.5	0.05	3.5718	0.9864	0.1128	0.04870	2.5854	12.60	0.8100
193.0	5.93	3.5258	0.9864	0.1106	0.04830	2.5394	12.52	0.7960
188.4	5.74	3.4658	0.9863	0.1070	0.04730	2.4795	12.25	0.7860
184.5	5.57	3.4138	0.9863	0.1038	0.04650	2.4275	12.04	0.7610
181.5	5.44	3.3738	0.9863	0.1012	0.04580	2.3855	11.87	0.7490
165.4	4.77	3.1658	0.9862	0.0881	0.04190	2.1796	10.61	0.6820
160.0	4.55	3.0918	0.9862	0.0850	0.04100	2.1056	10.61	0.6800
153.8	4.34	3.0080	0.9862	0.0810	0.03990	2.0226	10.33	0.6340
149.5	4.15	2.9558	0.9862	0.0774	0.03870	1.9696	10.03	0.6170
144.4	3.98	2.8868	0.9862	0.0741	0.03780	1.9006	9.78	0.5960
140.4	3.84	2.8358	0.9861	0.0670	0.03700	1.8497	9.68	0.5800
133.4	3.58	2.7438	0.9861	0.0643	0.03540	1.7577	9.16	0.5510
130.5	3.46	2.7048	0.9861	0.0643	0.03440	1.7187	8.90	0.5380
116.3	2.98	2.5178	0.9861	0.0550	0.03100	1.5317	8.03	0.4800
108.8	2.74	2.4178	0.9860	0.0510	0.02960	1.4318	7.66	0.4490
103.2	2.54	2.3448	0.9860	0.0472	0.02790	1.3588	7.22	0.4250
97.9	2.42	2.2748	0.9860	0.0450	0.02720	1.2888	7.05	0.4040
92.7	2.24	2.2058	0.9860	0.0418	0.02590	1.2198	6.71	0.3820
86.0	2.09	2.1208	0.9860	0.0391	0.02480	1.1348	6.42	0.3560
82.4	1.95	2.0688	0.9860	0.0362	0.02340	1.0828	6.06	0.3400
75.7	1.77	1.9818	0.9859	0.0331	0.02200	0.9950	5.70	0.3120
70.0	1.64	1.9068	0.9859	0.0307	0.02090	0.9209	5.41	0.2880
64.8	1.47	1.8388	0.9859	0.0275	0.01920	0.8529	4.97	0.2670
64.5	1.46	1.8348	0.9859	0.0273	0.01910	0.8489	4.95	0.2660
58.1	1.32	1.7508	0.9859	0.0249	0.01790	0.7649	4.64	0.2400
52.8	1.19	1.6808	0.9859	0.0222	0.01640	0.6949	4.25	0.2180
47.6	1.05	1.6123	0.9859	0.0197	0.01500	0.6264	3.88	0.1965
42.4	0.94	1.5443	0.9859	0.0178	0.01380	0.5584	3.58	0.1750
37.2	0.84	1.4733	0.9858	0.0158	0.01270	0.4895	3.29	0.1535
33.4	0.74	1.4253	0.9858	0.0141	0.01160	0.4395	3.01	0.1380
28.8	0.64	1.3648	0.9858	0.0120	0.01000	0.3790	2.59	0.1190
25.2	0.59	1.3173	0.9858	0.0111	0.00950	0.3315	2.46	0.1040
20.9	0.44	1.2608	0.9858	0.0083	0.00730	0.2750	1.89	0.0862
14.9	0.29	1.1819	0.9858	0.0058	0.00528	0.1961	1.37	0.0615
12.7	0.26	1.1530	0.9858	0.0050	0.00461	0.1672	1.19	0.0524
10.7	0.23	1.1267	0.9858	0.0044	0.00411	0.1409	1.06	0.0441

THE FLOW OF AQUEOUS SOLUTIONS.

The Jena glass filter was used for two purposes :

- (1) To study the flow of aqueous solutions and to establish if possible the relationship between the flow of gases and that of liquids.
- (2) To measure the average pore diameter and the number of pores, so as to assign the correct value for the parameter of length in the criteria governing flow.

The apparatus used is shown on Fig. 3. It represents an ordinary flow-measuring apparatus, and is characterized by a constant-temperature control.

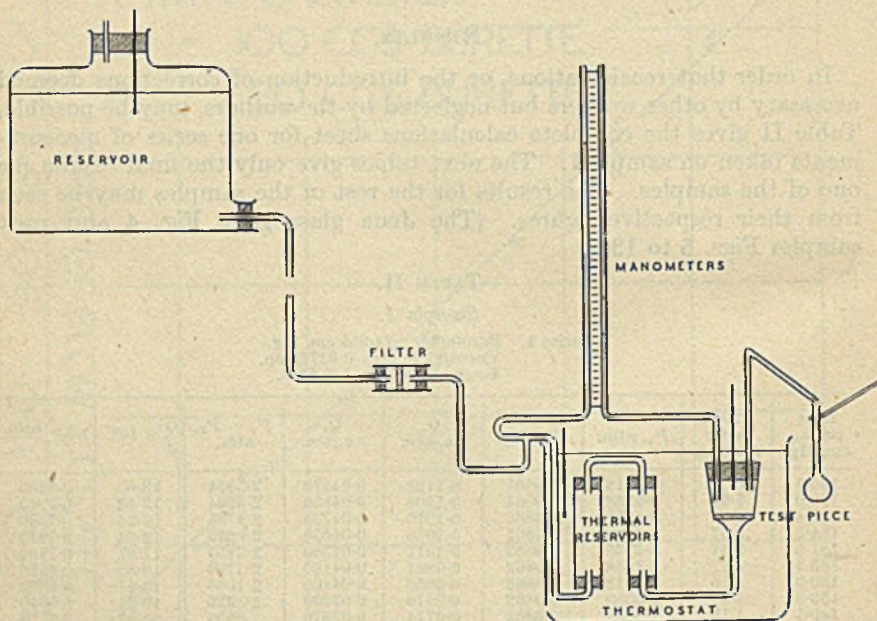


Fig. 3.

Four solutions were tested : (1) distilled water, (2) 2 per cent. *n*-amyl alcohol solution, (3) two sodium chloride solutions (0.960 and 0.614 N). The choice of these solutions was made so as to observe the influence of surface forces on the flow of liquids through porous media. Fig. 14 shows that the flow under test was non-turbulent. A certain deviation of individual results from the straight-line law can be observed.

Measurement of Pore Diameter and Calculation of the Number of Pores of the Jena Glass Filter.

The measurement of the pore radii was made according to the "bubble-pressure method" as developed by Cantor, Bechold, and others. This method is based on the following principle :

If a liquid, *A*, filling a capillary is subjected to the pressure of air, of a gas or a liquid *B*, immiscible with *A*, then the pressure required to displace

liquid *A* from the capillary must be equal or slightly higher than the pressure caused by the interfacial tension of the two phases across the curved meniscus. There is a definite relationship between the pressure required, *p*, the radius of the capillary, *R*, and the interfacial tension, σ . This relationship may be expressed by :

$$R = \frac{2\sigma}{p} \dots \dots \dots (10)$$

The Jena filter was saturated with a liquid of known surface tension, and pressure by air was then applied. The break-through pressure was

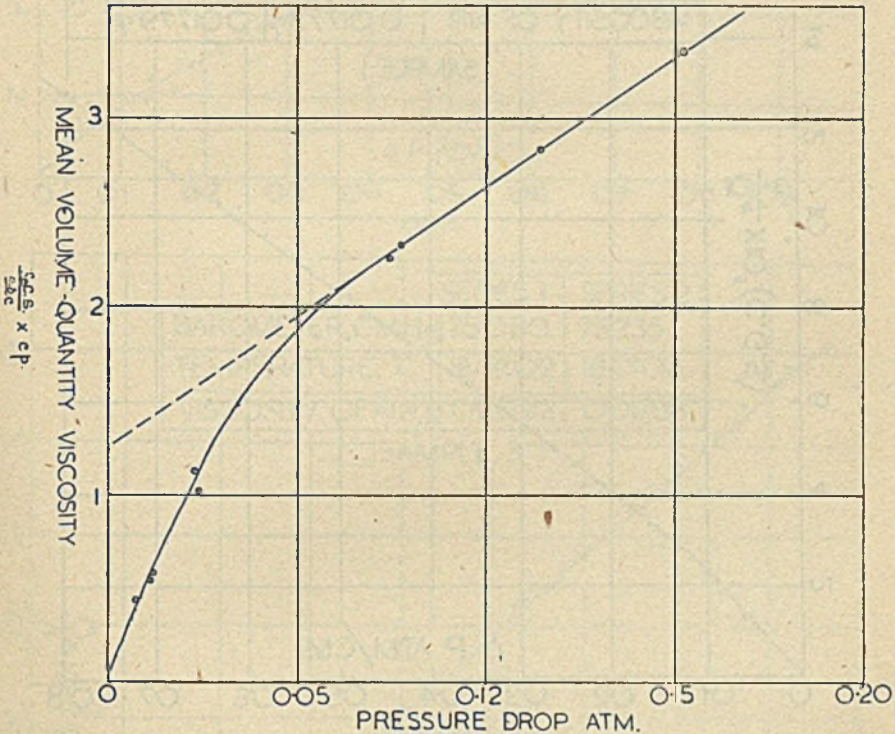


FIG. 4.
FLOW OF AIR THROUGH JENA GLASS FILTER.

observed, together with the number of capillaries through which flow of air took place—*i.e.*, capillaries having approximately equal pore radii. The experiments revealed that the variation in pore diameter was very small. All except thirty-two pores had radii between 1.0 to 1.2×10^{-3} cm.

Substituting a value of 10^{-3} for the pore radius in Poiseuille's formula (equation 5), *n*, the number of capillaries, could be ascertained, and it was found to be 1.4×10^5 as an average of several experiments using different liquids. (This gives the equivalent circular pores. The assumption of circularity constitutes a severe weakness in the calculations but is made

for expediency, as (1) no other method is known, and (2) the calculations are of secondary rather than primary importance in the present work.)

The quantity flowing through a single capillary, and hence the actual (not the macroscopic) mean linear velocity in the different experimental results for the flow of air through the Jena glass filter, could be calculated.

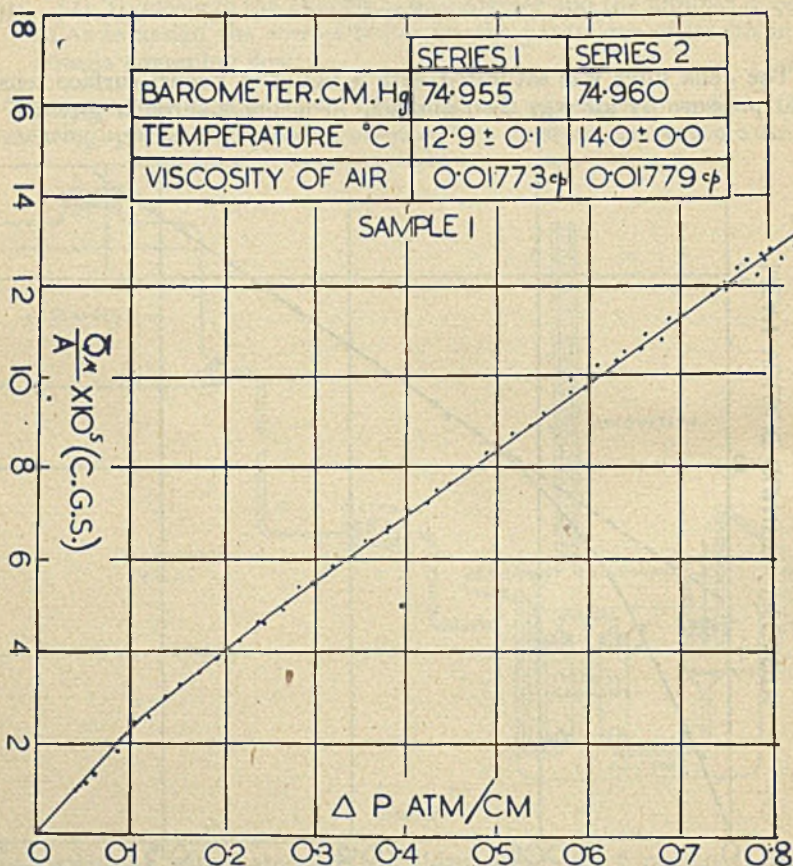


FIG. 5.

DISCUSSION ON THE FLOW OF AIR.

In all cases the plot of rate of flow *vs.* pressure drop yielded curves passing through the origin, but not in a single case could the test results be represented by a single straight line passing through the origin. As the regime was certainly sub-turbulent, these anomalies (on the basis of Darcy's law) assume significance which has to be elucidated.

Before considering the anomalies, it is well to study possible sources of systematic or accidental errors which may have given rise to the apparent anomalies. The barometer was recently checked, and found accurate, and the thermometer was calibrated against N.P.L. thermometers, and found

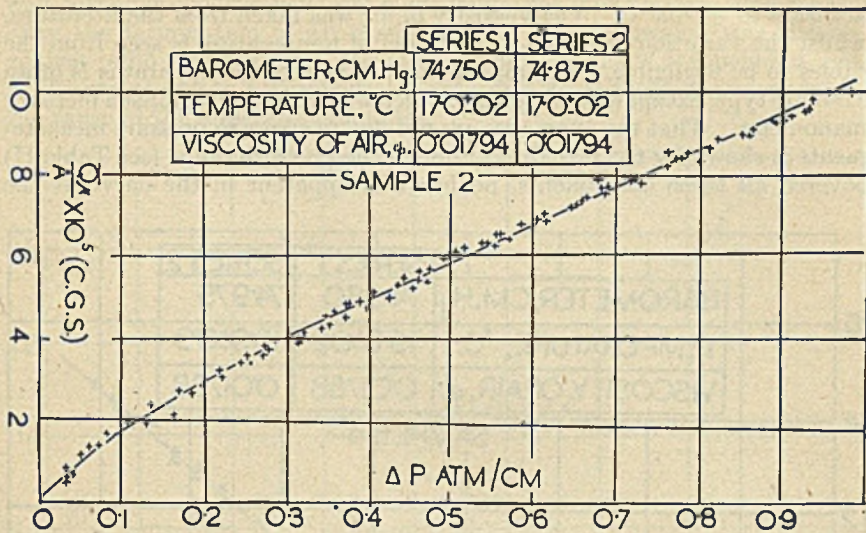


FIG. 6.

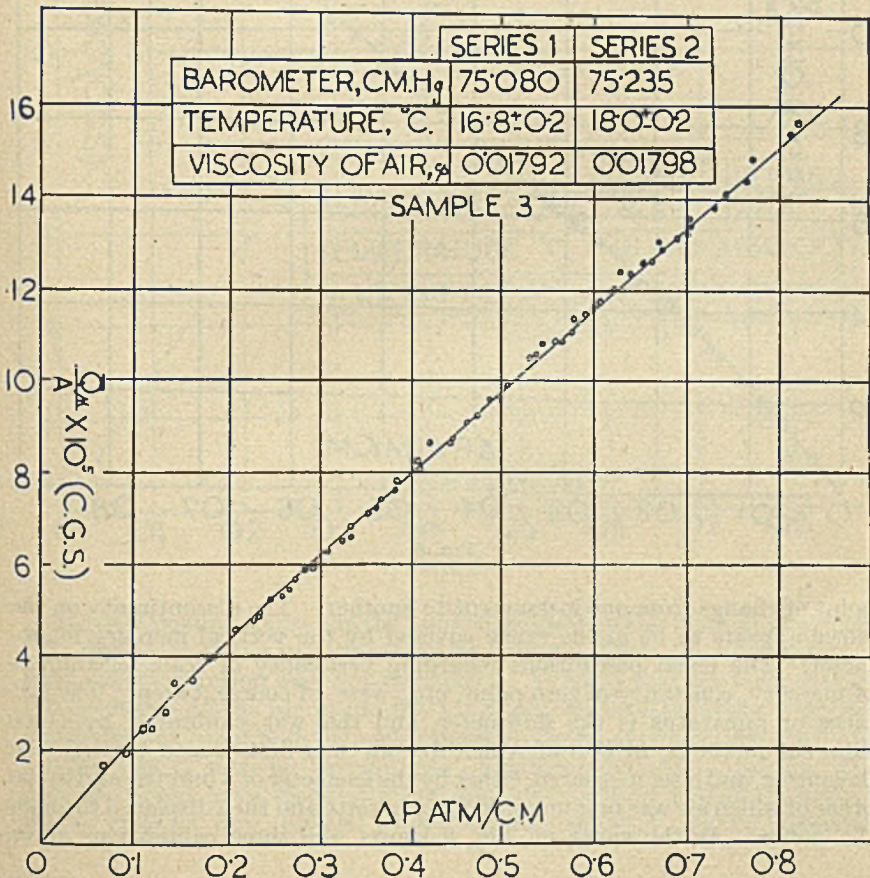


FIG. 7.

accurate to $\pm 0.05^\circ \text{C}$. The viscosity of air was taken from the literature, whilst the variation in it due to variation of temperature is seen from the tables to be negligible. The manometric section of the apparatus is of an absolute type, except the steel gauge, which was calibrated against a mercury manometer. That the anomalies are not due to errors in pressure measurements is shown by the fact that although the pressure range (see Table II) covered all three instruments, no break is apparent in the curve at the

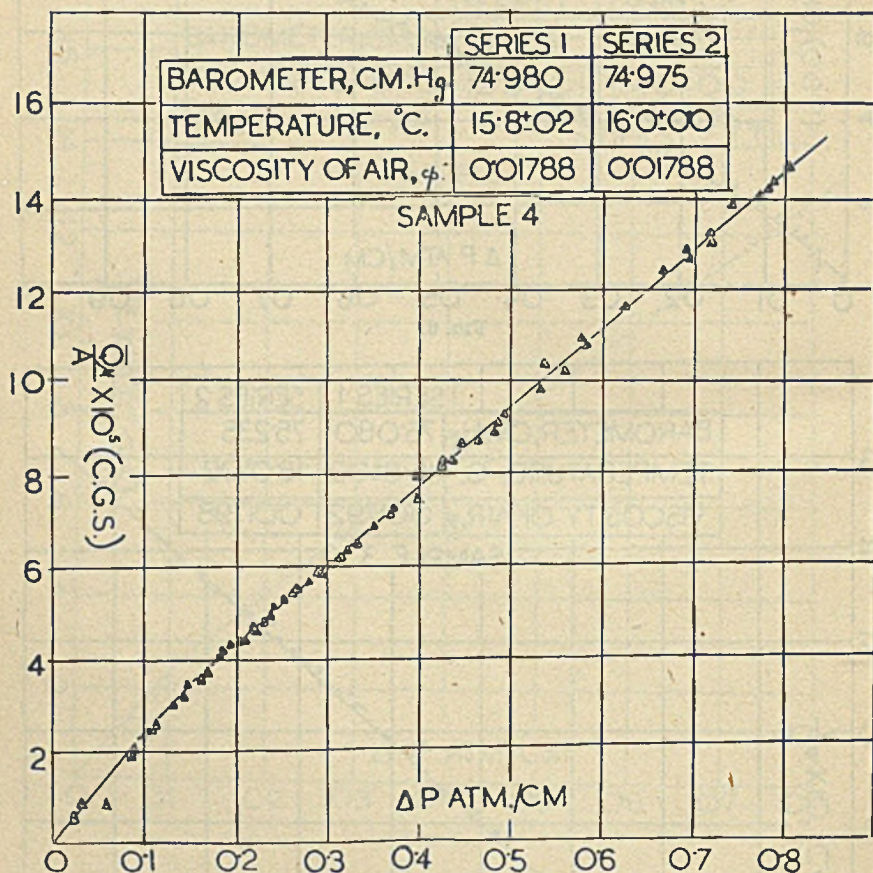


FIG. 8.

point of change from one instrument to another. The discontinuity on the curve appears to be in the range covered by the vertical mercury manometer. The usual precautions regarding verticality of scale, cleanliness of mercury, constancy of zero point, etc., were, of course, taken. The last piece of apparatus is the flowmeter, and this was calibrated by three different methods, in two of which dry air was first passed through the flowmeter, and later measured, either by the gasmeter or a burette, and in the other of which air was first measured in a burette and then displaced through the meter. As the curve on Fig. 2 shows, the three calibrations agree

well, although the first two were made before the investigation, and the last after the termination of all these studies. The stopwatch was checked against radio signals over a period of 3 hours. Thus it is concluded that, whilst errors due to instrumental inexactitudes are there, these cannot be the cause of the apparent anomalies.

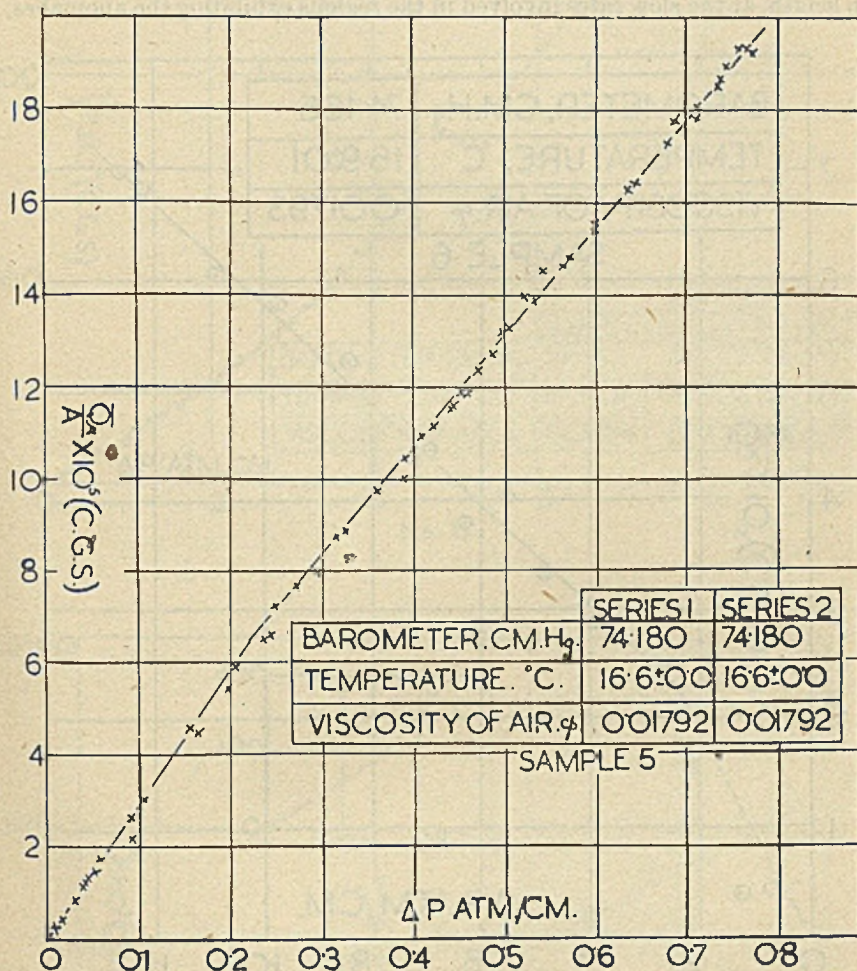
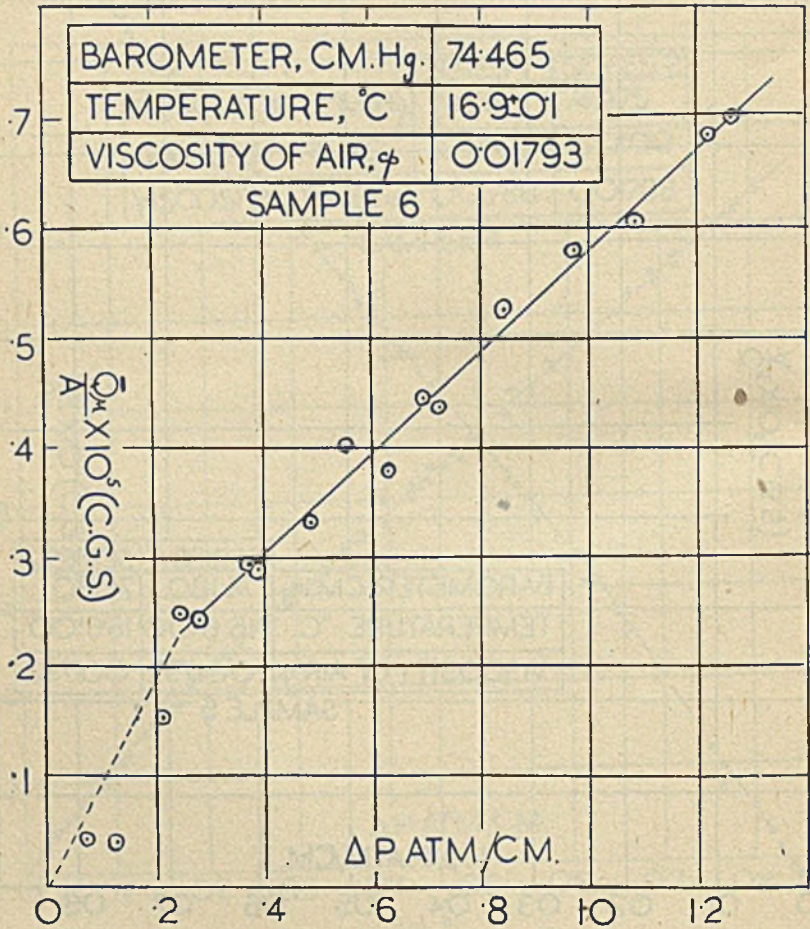


FIG. 9.

Another possible cause for the anomalies may be the method of calculation and corrections introduced or neglected. Thus, the assumption of isothermal expansion may not be correct. It is felt that the facts that the temperatures of the air inside the tank and in the laboratory were substantially the same and the small pressure drops at which the anomalies appear, justify such an assumption. Further, adiabatic expansion, if it existed, would have resulted in an apparent *increase* in permeability at higher rates of flow, instead of the *decrease* shown.⁵ Again, deviations

from Boyle's law at the pressures used are negligible for air. Again, the broad policies involved in the method may be questioned. Foremost in this section is the possible condensation of water-vapour on expansion. Whilst the air used was not tested for complete dryness, it was felt that passing it through the calcium chloride dryer, 6 cm. in diameter and 16 cm. in length, at the slow rates involved in the regions exhibiting the anomalies,



would completely eliminate this source of error. No access of water-vapour to the sample through back vapour pressure was allowed. Again, the possibility of plugging by solid particles was investigated by the several repetitions of the measurements going over the high- as well as the low-pressure differential range (see Table III). Constant check against the possibility of leakage was maintained as a matter of routine. Thus it was concluded that the anomalies exhibited in these tests were not fortuitous, but represented fundamental characteristics of the systems studied. To

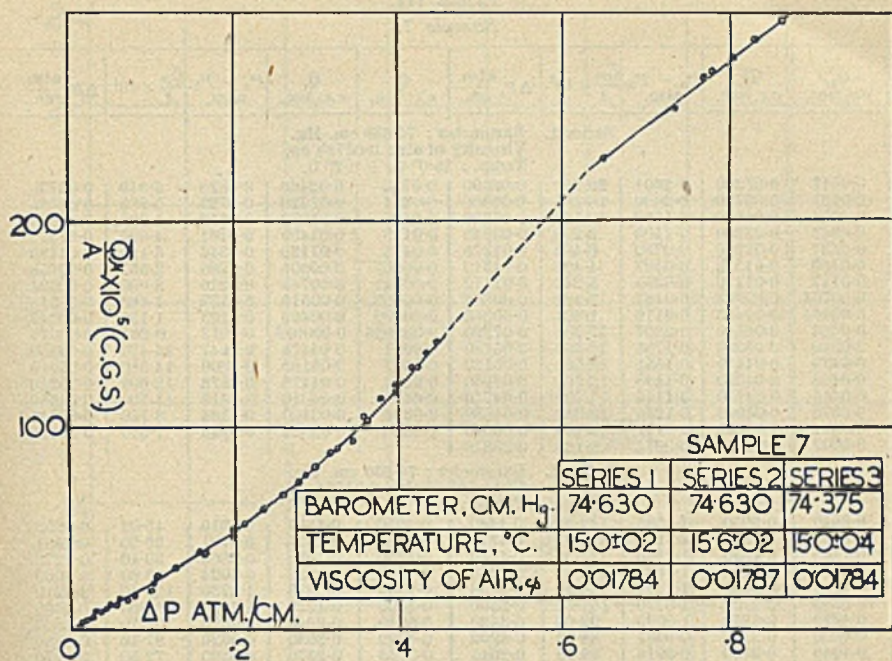


FIG. 11.

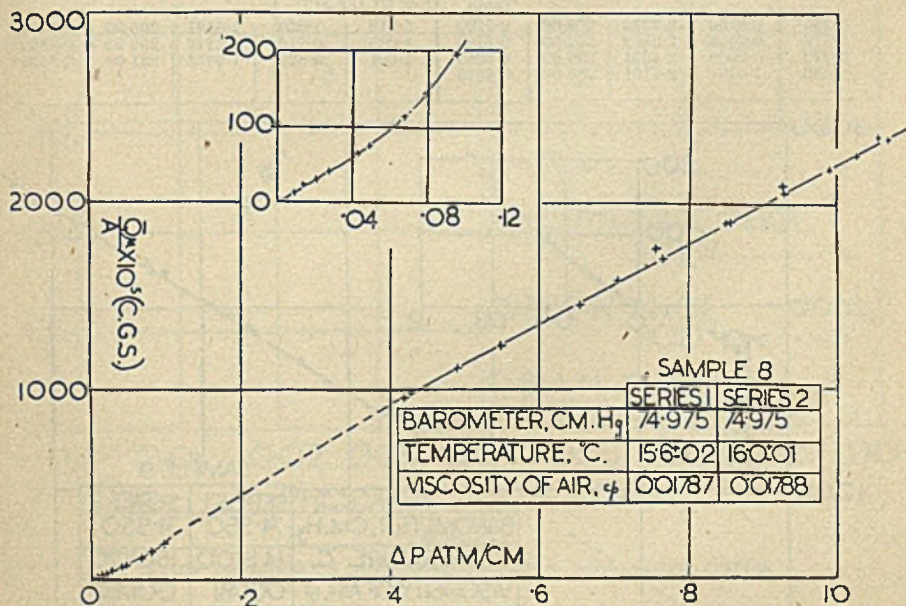


FIG. 12.

TABLE III.

Sample 7.

Q_1 , c.c./sec.	\bar{Q} , c.c./sec.	$P_1 - P_2$, atm.	$\frac{\bar{Q}\mu}{A} \times 10^4$	ΔP , atm. cm.	Q_1 , c.c./sec.	\bar{Q} , c.c./sec.	$P_1 - P_2$, atm.	$\frac{\bar{Q}\mu}{A} \times 10^4$	ΔP , atm. cm.
Series 1. Barometer : 74.630 cm. Hg. Viscosity of air : 0.01784 cp. Temp. : 15.0° C. \pm 0.2° C.									
0.0817	0.07220	0.2601	20.380	0.08590	0.0256	0.02460	0.0828	6.040	0.02735
0.0631	0.05710	0.2090	16.100	0.06900	0.0231	0.02220	0.0723	5.980	0.02385
0.0504	0.04600	0.1630	13.130	0.05390	0.0194	0.01880	0.0617	5.300	0.02035
0.0343	0.03260	0.1103	9.200	0.03650	0.0149	0.01450	0.0461	4.090	0.01522
0.0237	0.02280	0.0750	6.430	0.02475	0.0115	0.01130	0.0342	3.190	0.01130
0.0160	0.01580	0.0487	4.400	0.01610	0.00907	0.00906	0.0290	2.560	0.00958
0.0117	0.01150	0.0355	3.245	0.01172	0.00741	0.00740	0.0210	2.000	0.00694
0.00704	0.00703	0.0184	1.982	0.00806	0.00520	0.00519	0.0157	1.460	0.00518
0.00464	0.00463	0.0119	1.304	0.00393	0.00409	0.00409	0.0105	1.150	0.00347
0.00683	0.006140	0.2207	17.300	0.07290	0.000925	0.000925	0.0013	0.2610	0.00043
0.0640	0.05890	0.1735	16.600	0.05730	0.0601	0.05470	0.1947	15.430	0.06430
0.0479	0.04430	0.1551	12.500	0.05120	0.0557	0.05100	0.1800	14.380	0.05940
0.0408	0.04350	0.1498	12.260	0.04950	0.0484	0.04470	0.1578	12.600	0.05210
0.0445	0.04150	0.1446	11.700	0.04770	0.0430	0.04010	0.1418	11.300	0.04680
0.0378	0.03560	0.1236	10.030	0.04080	0.0328	0.03100	0.1134	8.750	0.03740
0.0344	0.03260	0.1117	9.190	0.03680	0.0293	0.02800	0.0946	7.900	0.03120
0.0302	0.02880	0.0973	8.120	0.03210					
Series 2. Barometer : 74.630 cm. Hg. Viscosity of air : 0.01784 cp. Temp. : 15.0° C. \pm 0.2° C.									
0.8510	0.5050	1.3585	142.40	0.4480	0.2050	0.1595	0.5619	45.00	0.1958
0.8030	0.4820	1.3127	136.00	0.4340	0.1620	0.1310	0.4701	36.90	0.1551
0.7460	0.4550	1.2590	128.30	0.4160	0.1290	0.1080	0.3863	30.40	0.1273
0.6750	0.4210	1.1944	118.80	0.3950	0.0962	0.0835	0.3024	23.60	0.1000
0.6190	0.4000	1.1367	114.40	0.3750	0.7560	0.0835	1.2730	129.40	0.4210
0.5590	0.3700	1.0770	104.30	0.3560	0.6800	0.4220	1.1994	119.00	0.3960
0.4910	0.3260	1.0033	92.00	0.3420	0.5640	0.3640	1.0820	102.70	0.3580
0.4650	0.3120	0.9684	88.00	0.3200	0.4600	0.3090	0.9626	87.10	0.3180
0.4040	0.2780	0.8918	79.40	0.2945	0.3660	0.2570	0.8300	72.50	0.2770
0.3820	0.2600	0.8579	75.00	0.2830	0.2830	0.2080	0.7054	58.60	0.2330
0.3260	0.2340	0.7732	66.00	0.2550	0.2280	0.1740	0.6037	49.10	0.1993
0.2810	0.2070	0.7025	58.40	0.2320	0.1600	0.1340	0.4771	37.80	0.1574
0.2450	0.1850	0.6346	52.10	0.2090	0.1100	0.0952	0.3094	26.90	0.1020
Series 3. Barometer : 74.375 cm. Hg. Viscosity of air : 0.01784 cp. Temp. : 15.0° C. \pm 0.4° C.									
2.135	0.9550	2.3392	260.00	0.7700	2.512	1.050	2.6101	296.00	0.8630
2.172	0.9650	2.3592	272.00	0.7780	1.986	0.916	2.2243	255.50	0.7350
2.270	0.9900	2.4391	270.00	0.8050	1.681	0.820	1.9673	231.00	0.6495
2.380	1.020	2.5191	288.00	0.8310					

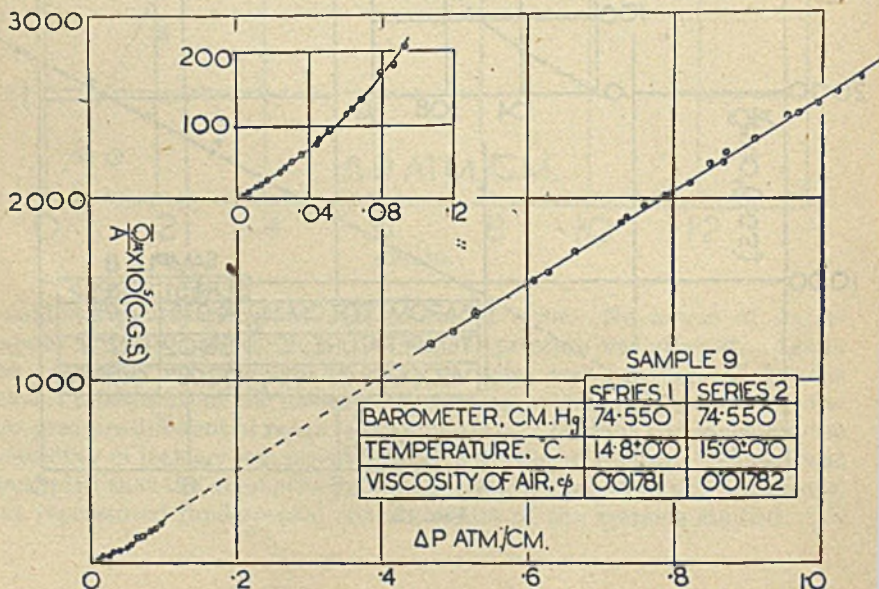


Fig. 13.

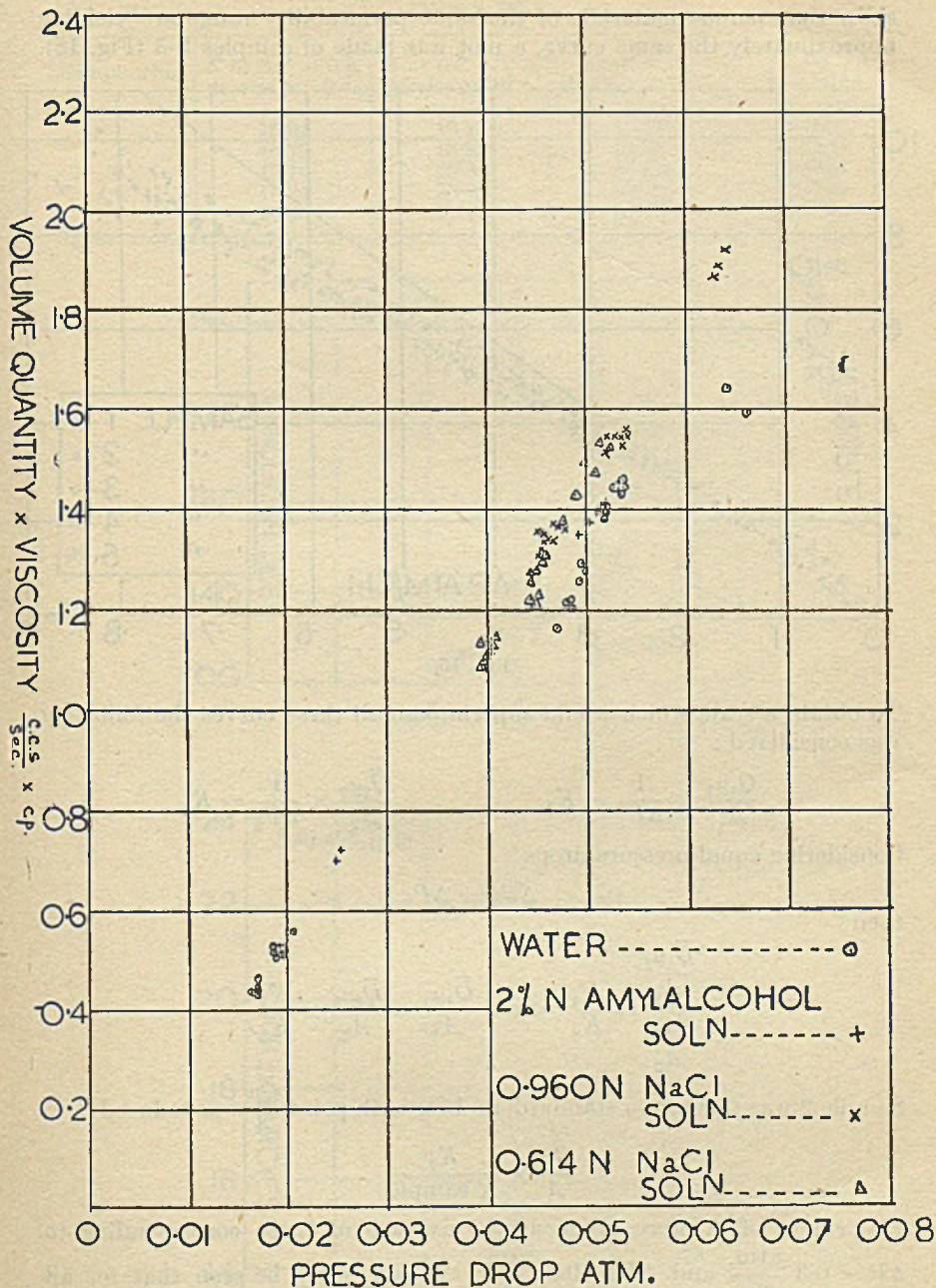


FIG. 14.

FLOW OF AQUEOUS SOLUTIONS THROUGH JENA GLASS FILTER.

show that porous materials of the same permeability range are yielding approximately the same curve, a plot was made of samples 1-5 (Fig. 15).

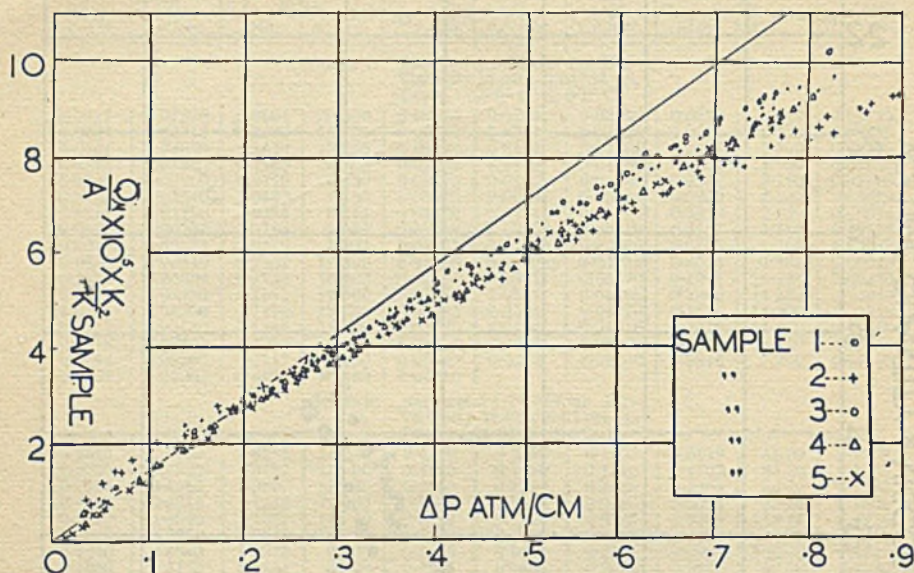


FIG. 15.

To obtain a scale which would superimpose all these curves the following was considered :

$$\frac{\bar{Q}_1 \mu_1}{A_1} \times \frac{1}{\Delta P_1} = K_1 \qquad \frac{\bar{Q}_2 \mu_2}{A_2} \times \frac{1}{\Delta P_2} = K_2$$

Considering equal pressure drops

$$\Delta P_1 = \Delta P_2$$

then

$$\frac{\bar{Q}_1 \mu_1}{A_1} = \frac{K_1}{K_2} \quad \text{or} \quad \frac{\bar{Q}_1 \mu_1}{A_1} = \frac{\bar{Q}_2 \mu_2}{A_2} \times \frac{K_1}{K_2}$$

Sample 2 was taken as a standard, and for each point $\frac{\bar{Q} \mu}{A}$ was reduced to

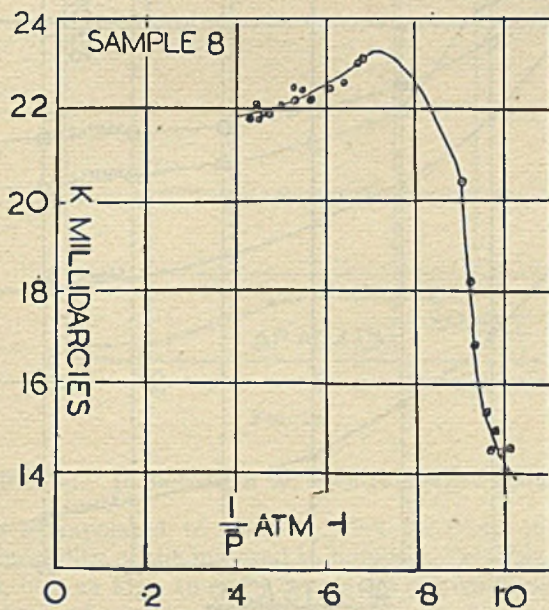
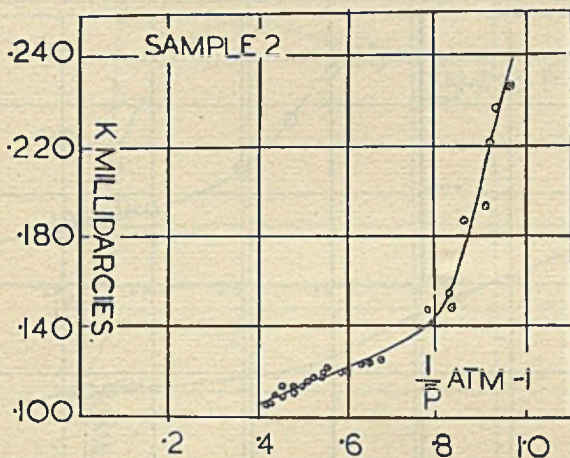
$$\frac{\bar{Q} \mu}{A} \times \frac{K_2}{K_{\text{sample}}}$$

The values of K were taken as the average of those corresponding to $\Delta P = 0.3 \frac{\text{atm.}}{\text{cm.}}$ and $\Delta P = 0.8 \frac{\text{atm.}}{\text{cm.}}$. It can easily be seen that for all these samples a change in permeability occurs at approximately $\Delta P = 0.2 \frac{\text{atm.}}{\text{cm.}}$

Table IV gives the necessary data for this plot.

TABLE IV.

Sample No.	K at $\Delta P = 0.8$, darcies $\times 10^{-5}$.	K at $\Delta P = 0.3$, darcies $\times 10^{-5}$.	Average K , darcies $\times 10^{-5}$.	$\frac{K_2}{K \text{ sample}}$
1	15.92	18.35	17.13	0.7500
2	10.79	13.35	12.07	1.0000
3	19.10	20.85	19.88	0.6500
4	18.26	20.26	19.26	0.6300
5	25.30	27.40	26.35	0.4580



FIGS. 16 AND 17.

Corresponding data for samples 6-9 are given in Table V.

TABLE V.

Sample No.	K at $\Delta P = 0.8$, darcies $\times 10^{-5}$.	K at $\Delta P = 0.3$, darcies $\times 10^{-5}$.	Average K , darcies $\times 10^{-5}$.	$\frac{K_2}{K \text{ sample}}$
6	0.625	0.867	0.796	15.1630
7	354.0	263.5	308.75	0.0391
8	2224.0	2272.0	2248.0	0.00537
9	2530.0	2600.0	2565.0	0.00471

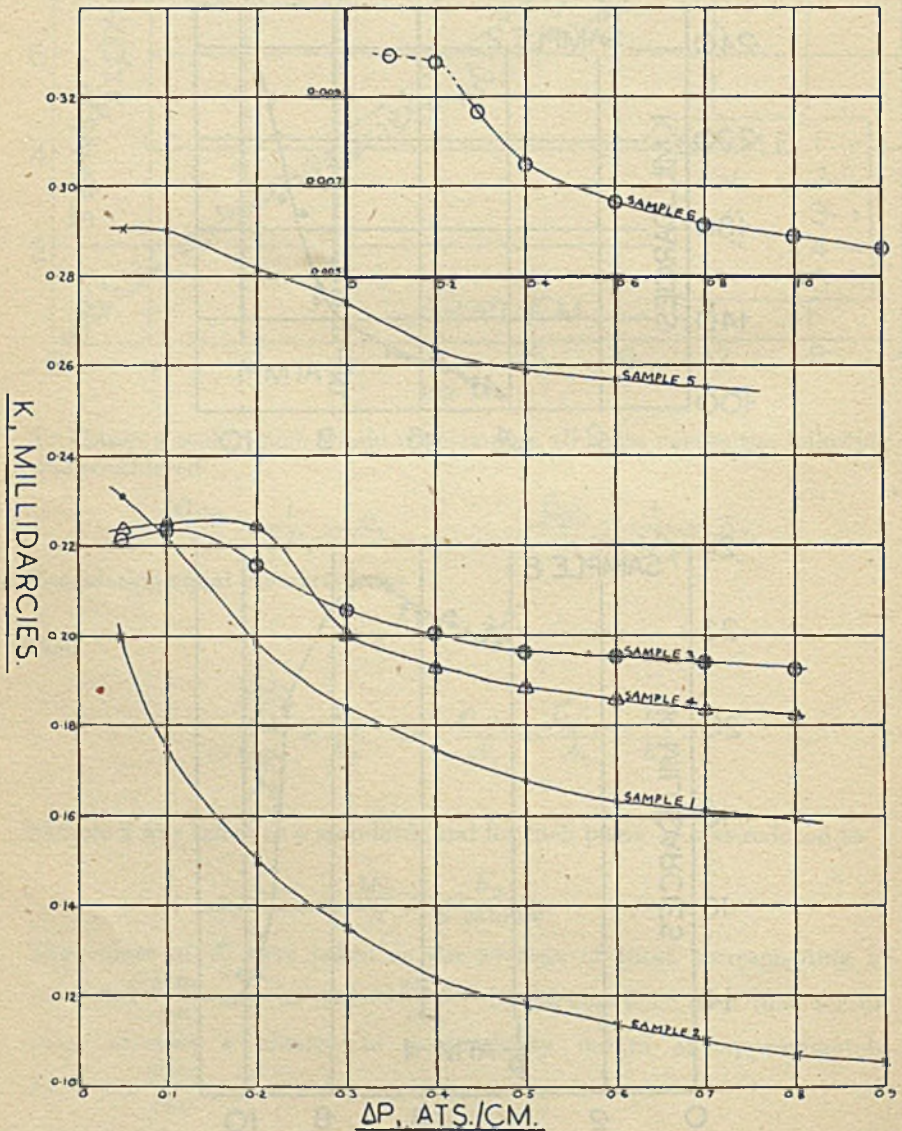


FIG. 18.

An attempt was made to investigate the experimental results from the point of view of the mean free-path theory put forward by Klinkenberg.⁶ This theory proposes that the permeability of porous media to gases is a linear function of the reciprocal of the mean pressure, but not a function

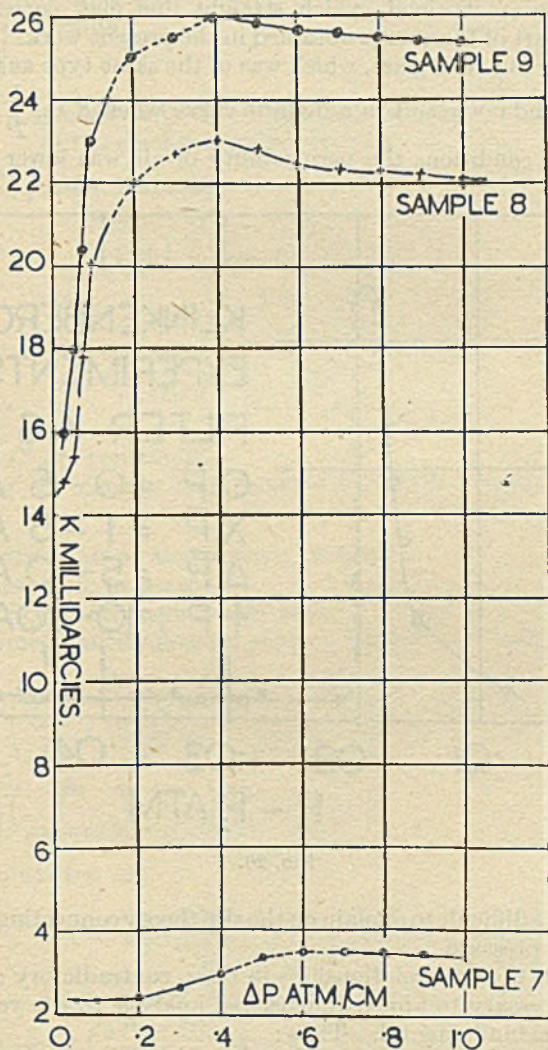


FIG. 19.

of the pressure drop. In plotting K vs. $\frac{1}{P}$ a straight line should be obtained, which, when extrapolated to zero—*i.e.*, infinite mean pressure—should give the permeability of the material to liquids. This method of plotting was adopted, but, as Figs. 16 and 17 show, no straight line was obtained. The curves obtained are actually the mirror images of the curves K vs. ΔP , as shown on Figs. 18 and 19. By plotting some of Klinkenberg's results

as K vs. $P_1 - P_2$ (i.e., the equivalent of ΔP (Fig. 20)), it was observed that there was some relationship between the variation of permeability and the pressure drop. For very small values of pressure drop an increase of permeability with pressure drop becomes evident, while at greater values a straight line is obtained, which straight line may correspond to the asymptotic part of the curves obtained in the present work.

The tests on the Jena glass, which was of the same type as those used by Klinkenberg, did not result in a definite curve when K vs. $\frac{1}{\bar{P}}$ were plotted. Under certain conditions the permeability of air was lower than that to

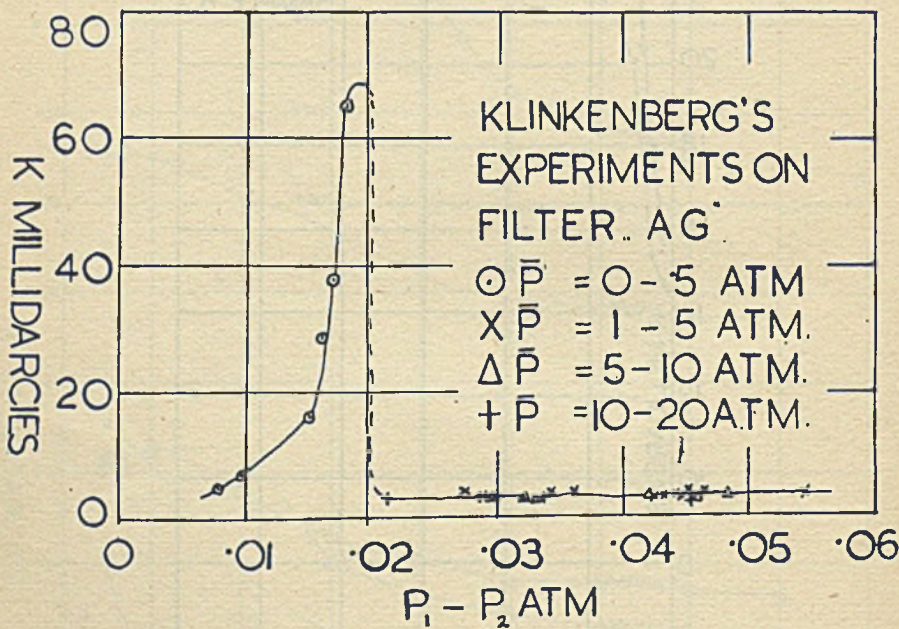


FIG. 20.

liquids, which is difficult to explain on the slip theory connecting permeability and the mean pressure.

To bring out the true relationships in these contradictory results, it was considered necessary to apply dimensional analysis to the various factors, which might be fundamental. Thus :

$$f(K, \bar{P}, \Delta P, v, D, \rho, \mu) = 0 \dots \dots (11)$$

where D = average diameter of the capillaries ;
 ρ = density of the gas ;

while the notation of the other factors remains as previously given. The different dimensionless functions were determined and tested for validity.

Buckingham's π Theorem ⁷ had to be employed, as the number of factors exceeded five. The functions obtained were :

$\pi_1 = \left(\frac{K}{D^2}\right)$, which is in accordance with the definition of the coefficient of permeability;

$\pi_2 = \frac{\bar{P}}{\rho v^2}$
 $\pi_3 = \frac{\Delta P}{\rho v^2}$ } functions which will have to be tested on the experimental results;

$\pi_4 = \frac{\mu}{vD\rho}$, Reynolds' criterion, which has always been considered as one of the chief controlling factors.

Hence the equation becomes :

$$f \left[\left(\frac{K}{D^2}\right), \left(\frac{\bar{P}}{\rho v^2}\right), \left(\frac{\Delta P}{\rho v^2}\right), \left(\frac{\mu}{vD\rho}\right) \right] = 0 \quad \dots \quad (12)$$

or

$$K = CD^2 f \left[\left(\frac{\bar{P}}{\rho v^2}\right), \left(\frac{\Delta P}{\rho v^2}\right), \left(\frac{\mu}{vD\rho}\right) \right]$$

$$= C' f \left[\left(\frac{P}{\rho v^2}\right), \left(\frac{\Delta P}{\rho v^2}\right), \left(\frac{\mu}{vD\rho}\right) \right] \quad \dots \quad (13)$$

where C and C' are constants.

Considering the density and pressure at which volume measurements were taken :

- ρa = density of air at atmospheric pressure ;
- Pa = atmospheric pressure ;
- va = velocity at atmospheric pressure ;
- Qa = volume quantity flowing per unit time at atmospheric pressure,

$$K = C' f \left[\left(\frac{\bar{P}}{\frac{\rho a \bar{P}}{Pa} \times \frac{va^2 Pa^2}{\bar{P}^2}}\right), \left(\frac{\Delta P}{\frac{\rho a P}{Pa} \times \frac{va^2 Pa^2}{\bar{P}^2}}\right), \left(\frac{\mu}{vD\rho}\right) \right]$$

$$= C' f \left[\left(\frac{\bar{P}^2}{\rho a P a v a^2}\right), \left(\frac{\Delta P \times \bar{P}}{\rho a P a v a^2}\right), \left(\frac{\mu}{vD\rho}\right) \right]$$

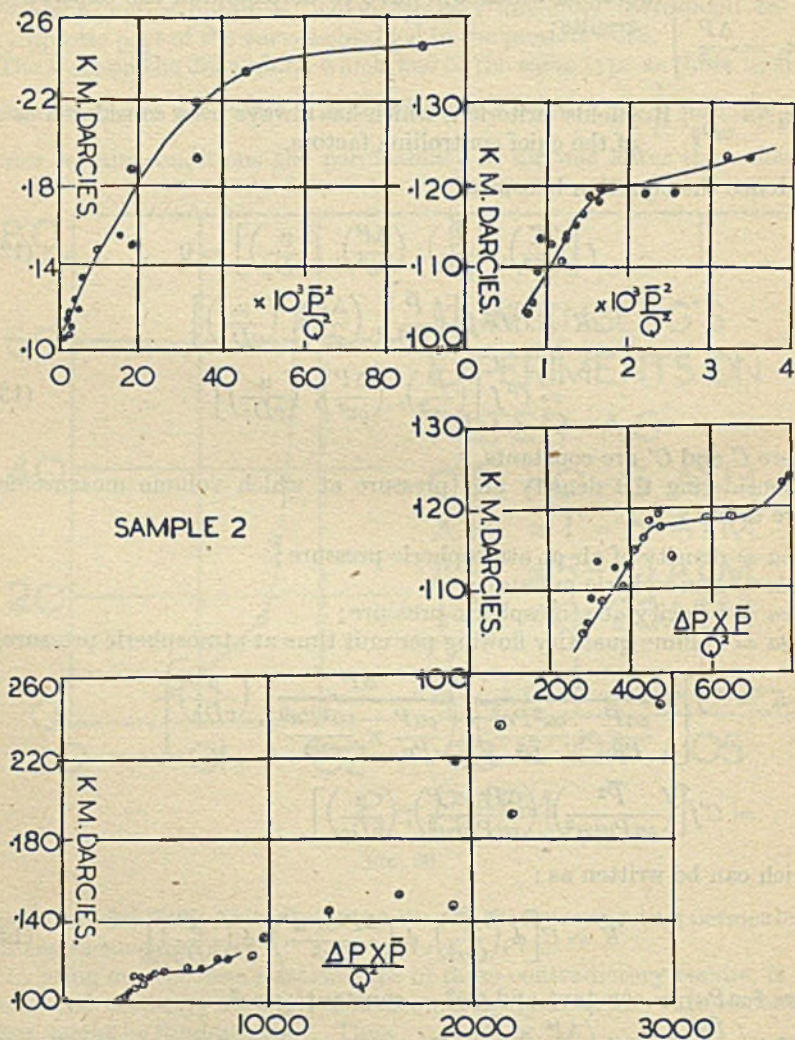
which can be written as :

$$K = C \left[\phi_1 \left(\frac{\bar{P}^2}{Qa^2}\right), \phi_2 \left(\frac{\Delta P \times \bar{P}}{Qa^2}\right), \phi_3 \left(\frac{\mu}{vD\rho}\right) \right] \quad \dots \quad (14)$$

since $(\rho a Pa) = \text{constant}$ and $Qa^2 = \text{constant} \times va^2$.

If $\phi_1 \left(\frac{\bar{P}^2}{Qa^2}\right)$ and $\phi_2 \left(\frac{\Delta P \times \bar{P}}{Qa^2}\right)$ affect the value of K fundamentally, they will give definite curves on plotting K vs. function, while if this is not the case, a spread of the points will be observed. In other words, the true relationship between K and \bar{P} and between K and ΔP will be shown plotting K vs. the two dimensionless functions obtained, and not vs. \bar{P} or ΔP alone. Figs. 21, 22, and 23 show the application of these considerations to the experimental results of samples 2, 7, and 8. The functions are not shown for the other samples, as the three samples shown typify the others.

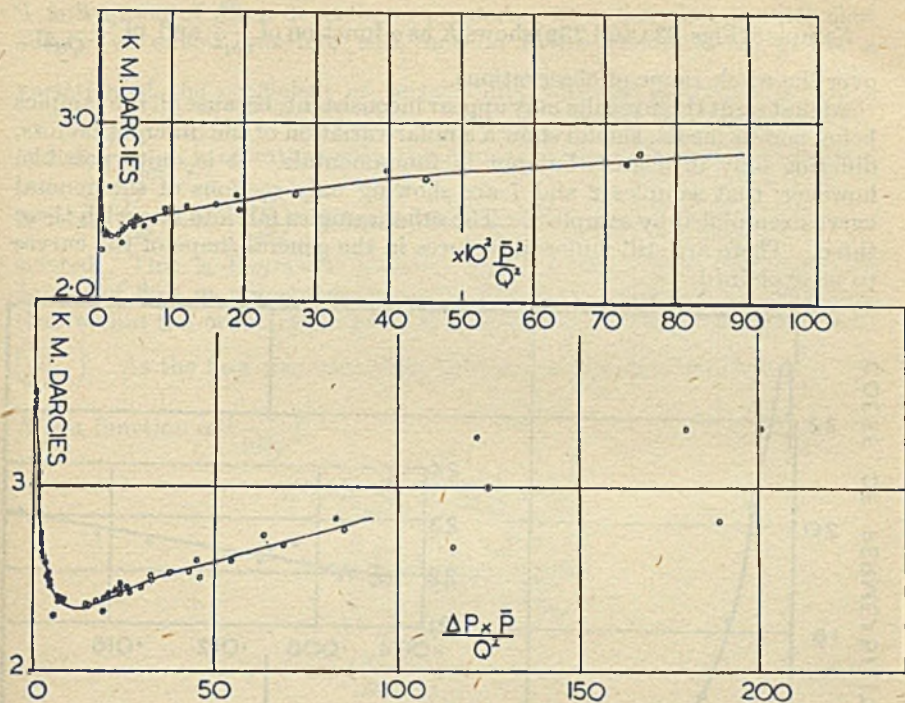
Sample 2 (Fig. 21) shows that the permeability coefficient K is a function of $\frac{P^2}{Qa^2}$ over the whole range of the curve, while K is a function of $\left(\frac{\Delta P \times \bar{P}}{Qa^2}\right)$ over a limited range only. The two functions where any curve is obtainable



FIGS. 21A AND 21B.

are similar. Where there is spread in the points, the accuracy of measurements was lowest.

Sample 7 (Fig. 29) shows K as a function of $\frac{\bar{P}^2}{Qa^2}$ and of $\frac{\Delta \bar{P} \times P}{Qa^2}$, over part of the range of observations. Again there is a portion of the plot where no curve can be drawn, and this portion is of lowest experimental accuracy.



FIGS. 22A AND 22B.

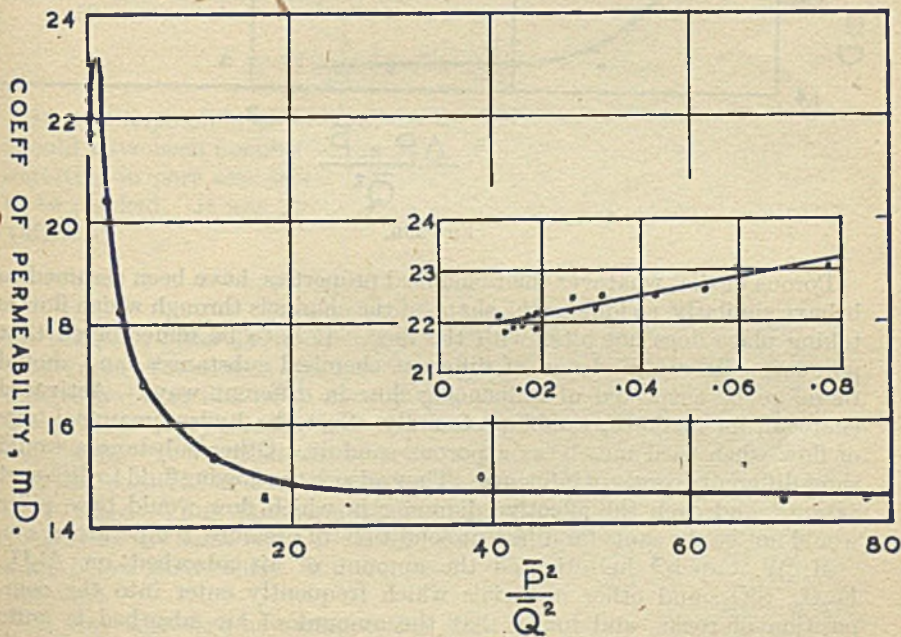


FIG. 23A.

Sample 8 (Figs. 23A and 23B) shows K as a function of $\frac{\bar{P}^2}{Qa^2}$ and of $\frac{\Delta P \times \bar{P}}{Qa^2}$ over the whole range of observations.

At first sight these results may appear inconsistent, because all the samples being porous media, should show a similar variation of the different factors, differing only in degree, but not in fundamentals. It is quite possible, however, that samples 2 and 7 are showing only sections of the general curve exemplified by sample 8. The other samples fall into line with these three. There are still minor differences in the general shape of the curves to be explained.

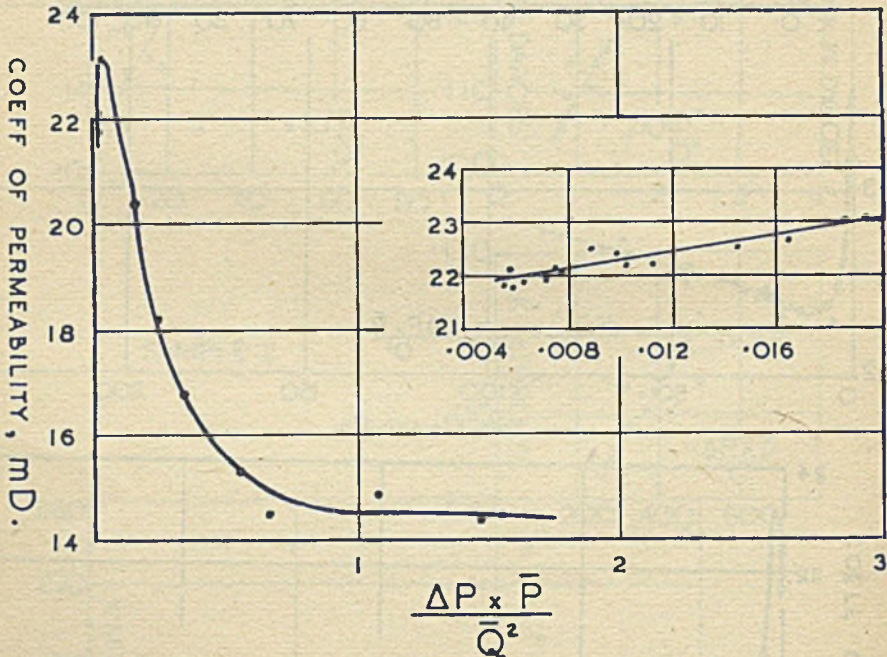


FIG. 23B.

Porous media, whatever their chemical properties, have been assumed to behave similarly, so long as the shape of the channels through which flow is taking place does not alter with the flow. It is to be remembered that porous media are made up of different chemical substances, and should therefore be suspected of influencing flow in different ways. Activated charcoal, for instance, would profoundly affect the hydrodynamical laws of flow when used merely as a porous conduit. Other substances would show different degrees of influence. They adsorb the flowing fluid to different extents, and even the effective diameter in which flow would take place would not be the same for different conditions of pressure, temperature, etc.

M. W. Capek⁸ investigated the amount of air adsorbed on Al_2O_3 , Fe_2O_3 , SiO_2 , and other materials which frequently enter into the composition of rocks, and found that the amount of air adsorbed is quite considerable.

Adsorption of gases depends on pressure. It is therefore possible that adsorptive effects interfere with normal hydrodynamic flow, giving a variation of the coefficient of permeability with the functions $\phi_1 \left(\frac{P^2}{Qa^2} \right)$ and $\phi_2 \left(\frac{P \times \bar{P}}{Qa^2} \right)$, or rather with the dimensionless and more fundamental criteria $\left(\frac{P}{\rho v^2} \right)$ and $\left(\frac{\Delta P}{\rho v^2} \right)$. Finally, the third function $\phi_3, \left(\frac{\mu}{vD\rho} \right)$ was considered. This is Reynolds' criterion, which is believed to determine the nature of flow in porous media under different conditions. It is known that within the ordinary range of the viscous region K is invariant with $\left(\frac{\mu}{vD\rho} \right)$. As the flow was very slow, however, it is pertinent to assume that K is a function of $\left(\frac{\mu}{vD\rho} \right)$.

$$\begin{aligned}
 K &= f\left(\frac{\mu}{vD\rho}\right) = f\left(\frac{\mu}{D} \times \frac{1}{v\rho}\right) \\
 &= f\left(\frac{\mu}{D} \times \frac{1}{\frac{vaPa}{\bar{P}} \times \frac{\rho a \bar{P}}{Pa}}\right) \\
 &= f\frac{\mu}{D} \times \frac{1}{va\rho a} \dots \dots \dots (15)
 \end{aligned}$$

Since $\frac{\mu}{\rho a}$ is constant, it may be written :

$$K = Cf\left(\frac{1}{Dva}\right) = C'f\left(\frac{D}{Qa}\right) = C''f\left(\frac{Qa}{D}\right) \dots \dots (16)$$

It was impossible to evaluate D for the rock samples. Even if this should have been possible by the method used for the Jena glass filter, the variation in pore size would have been too great to allow any conclusion to be reached. It was therefore thought advisable to evaluate the correct values of

$$\frac{vD\rho}{\mu}$$

for the Jena glass filter plotting it *vs.* K . This gave a curve showing a maximum. It was then assumed that an average value of D existed for every sample and that this value was constant for every sample. Thus, plotting Qa *vs.* K for every sample, curves were obtained showing a minimum and a maximum. It was then assumed that the maximum obtained with the rock samples occurred at the same value of Reynolds' number as that for the glass filter. Thus the permeability function of the rock samples were plotted on the same chart as that of the rock samples, so that the maxima were below each other. Fig. 24 shows the similarity of the curves thus obtained.

It may therefore be assumed that a general curve exists on which the coefficient of permeability drops to a minimum at a value of Reynolds'

criterion of about 0.2, rising to a maximum at a value of Reynolds' criterion between 1 and 2 (taking the parameter for length the mean diameter of the pores). For higher values of Reynolds' criterion the value of K becomes more and more independent of the criterion, assuming a constant value, which would correspond to true viscous flow. It may therefore be concluded that there is the probability of the existence of a regime of *subviscous flow* for gases, where the relationship between the pressure drop and the velocity of flow is not governed by the simple linear equation of

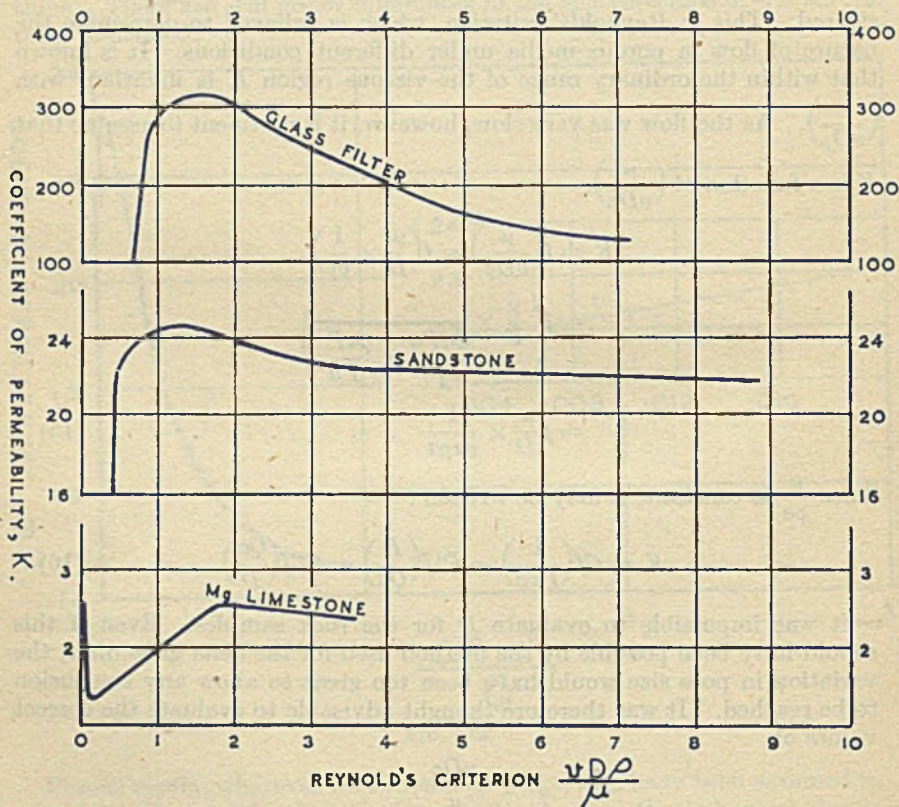


FIG. 24.

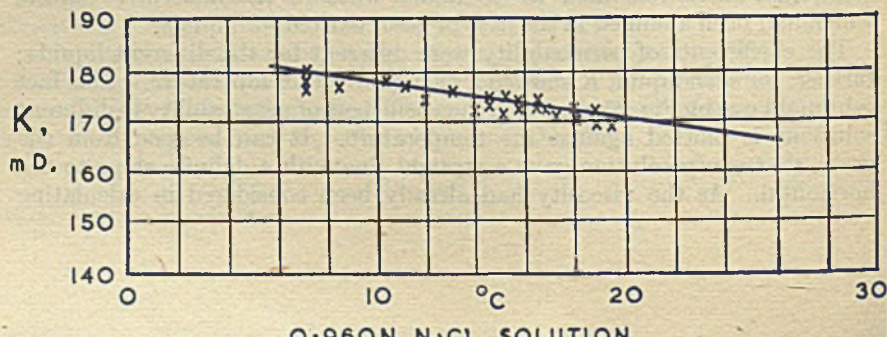
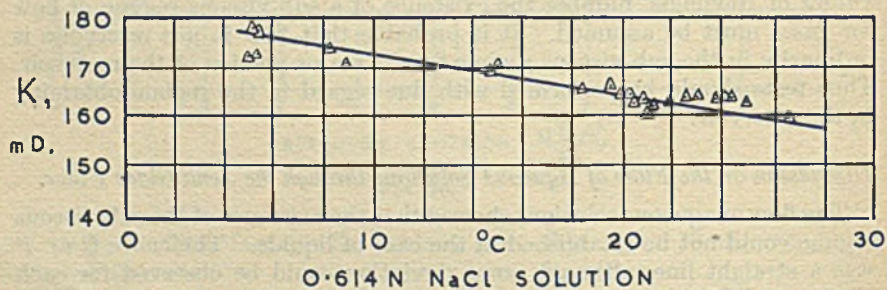
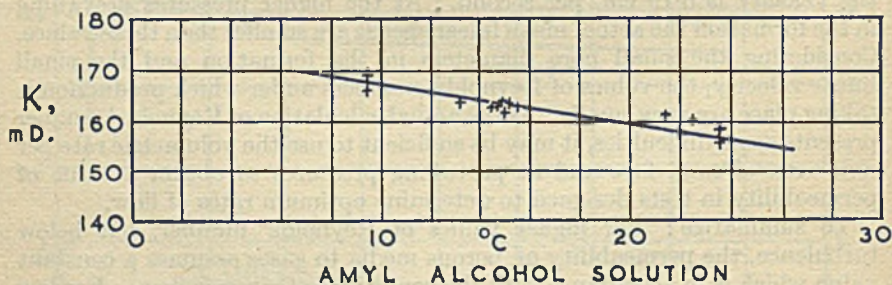
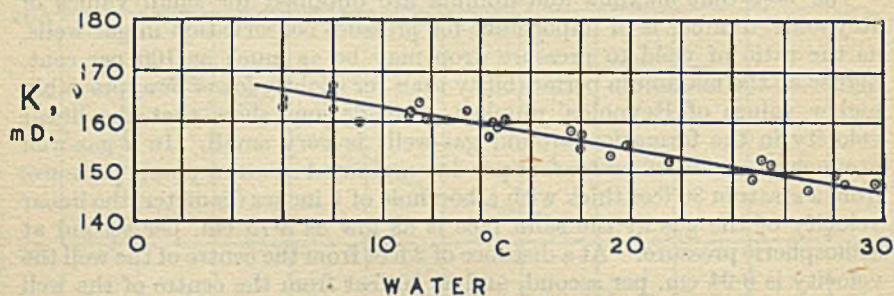
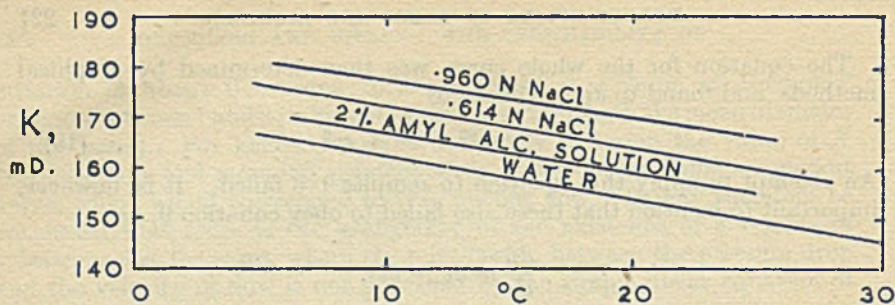
viscous flow. This fact is also evident from Figs. 4 to 13 directly, as discussed above.

An attempt was made to obtain some kind of mathematical formulation connecting the pressure drop with the velocity of flow.

An increase of permeability could only be expressed by the presence of a fractional power of v in the permeability equation. Examining the lower portions of the curves of samples 7-9, on which the increase of permeability is quite conspicuous, they were found to approximate to

$$P = av^{0.85} \dots \dots \dots (17)$$

where a was a constant.



the coefficient of permeability, it was postulated that the viscosity was not the only property influencing flow.

The conclusion reached was that the effective cross-section under viscous flow was different for different liquids, due to differences in surface energy and consequent differences in thickness of adsorbed layers. As the pressure drop varied with a high power of the radius, small differences in the thickness of these layers could account for the variation in K observed.

A physical interpretation of this fact may be obtained by dimensional analysis. It may be assumed that instead of the viscosity being the sole criterion as a property of liquids governing flow, viscosity μ , density ρ , and the product of surface tension and the average pore diameter d , are all important. Then a dimensionless function obtained is :

$$\left(\frac{\mu^2}{\rho(\sigma d)}\right)$$

As d is a constant for each rock sample, and is unknown for different samples, it is omitted from the criterion. Thus :

$$K = f\left(\frac{\mu^2}{\rho\sigma}\right) \dots \dots \dots (19)$$

It is to be remembered that this function is only dimensionless when the product (σd) is used to derive it. No dimensionless function can be obtained from μ , ρ and σ alone.

It is found experimentally that :

$$\log K = \log K_1 + 0.1 \log \left(\frac{\mu^2}{\rho\sigma}\right) \dots \dots \dots (20)$$

Thus the dimensions of K_1 are those of K . To render the equation dimensionless in both variables, K and $f\left(\frac{\mu^2}{\rho\sigma}\right)$,

$$\log \left(\frac{K}{K_1}\right) = 0.1 \log \left(\frac{\mu^2}{\rho\sigma}\right) \dots \dots \dots (21)$$

Fig. 26 gives the plot for this equation, and it is seen that all four liquids yield points falling on a single curve. The function is in reality $\left(\frac{\mu}{\rho} \cdot \mu \cdot \frac{1}{\sigma d}\right)$, and thus may be taken as the ratio of resistance due to kinematic and absolute viscosity to that due to surface-energy effects. K is then a measure of permeability as governed mostly by viscosity phenomena, and K_1 of permeability as governed by surface energy. In other words, where μ and $\frac{\mu}{\rho}$ are small and σ is large, flow is affected to a greater extent by surface-energy effects than in cases where μ and $\frac{\mu}{\rho}$ are large and σ is small. This is in accord with ordinary experience.

It was concluded that the coefficient of permeability assumes different values with different liquids, and is also dependent on the temperature for each liquid. The slope of the graphs of K vs. temperature in degrees

Centigrade is the same for all the liquids tested and is equal to $0.80 \text{ md}/^\circ \text{C}$. Thus :

$$\begin{aligned} k &= a - b (t^\circ \text{C}) \\ &= a - 0.80 (t) \end{aligned} \quad \dots \quad (22)$$

where a is a characteristic constant of the liquid used. It is to be noted that if this equation is the same for all liquids and media used, then from a determination of permeability of a medium to a particular liquid at a single

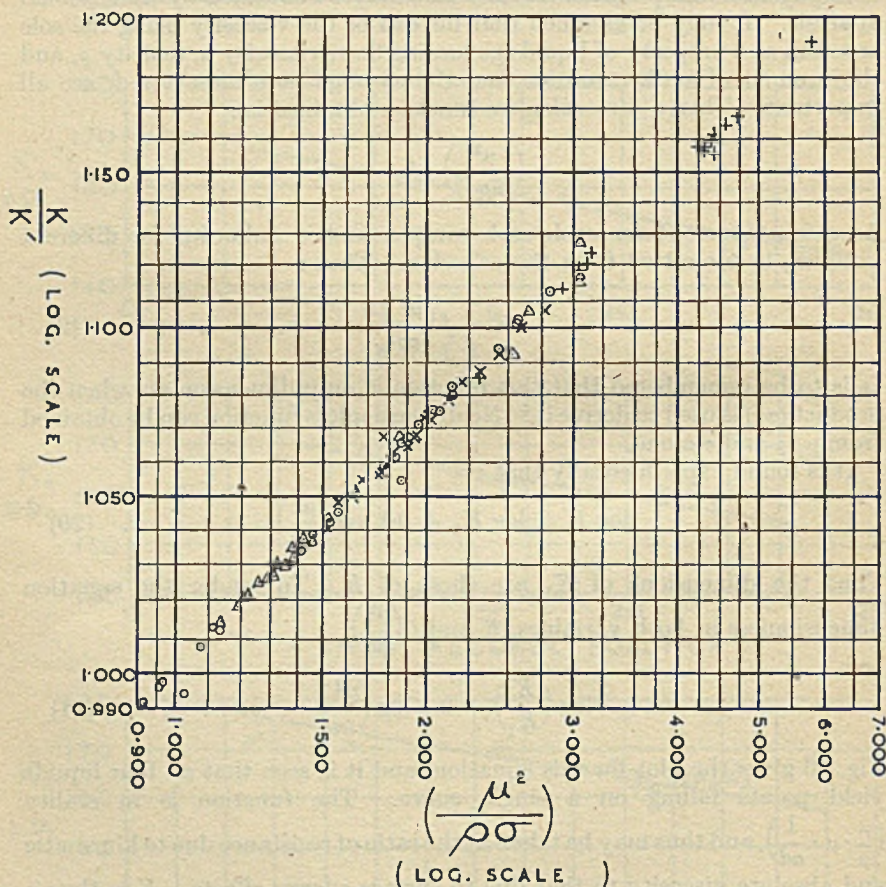


FIG. 26.

temperature the permeability at other temperatures can be calculated. Further work is necessary, however, before this condition can be assumed to be operating.

CONCLUSIONS AND RECOMMENDATIONS.

(1) The permeability of porous media to gases and liquids presents two different problems and in the present work no correlation between these two is apparent.

(2) Permeability to gases is dependent mainly on Reynolds' number, which at small values gives rise to maxima and minima. For higher values of Reynolds' number, but preceding the turbulent regime, permeability assumes a constant value corresponding to viscous conditions. Thus for low rates of gaseous flow in rocks, tests should be carried out at Reynolds' numbers corresponding to those obtaining underground. The "Reynolds' number" may be taken simply as the volumetric rate of flow per unit area of sand, the area being perpendicular to the main line of flow. In other words, the mean linear speed of the gas is taken as the "Reynolds' number." It is further recommended that tests be carried out under a mean pressure equal to that existing underground.

(3) Permeability to liquids is dependent not only on the viscosity, but also on other properties of the liquid which cause a variation in the effective cross-section of the pores under viscous flow. The coefficient of permeability assumes different values for different liquids having different surface-tension values. A single curve was obtained for the different liquid used by plotting against the criterion $\left(\frac{\mu^2}{\rho\sigma}\right)$. The permeability also varies with the temperature for the same liquid, but a correction for this can be obtained for each liquid:

$$K = a - b t^{\circ} \text{C.} \\ = a_1 - b_1 t^{\circ} \text{F.}$$

Further work is necessary before these equations can be taken as universal. The effects of the temperature are fully accounted for in the criterion $\left(\frac{\mu^2}{\rho\sigma}\right)$. Thus for correlation between different liquids at different temperatures this criterion should be used. For correlation with the same liquid at different temperatures the more specific temperature equation may be used.

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THE PHASE TRANSFORMATIONS OF NORMAL PARAFFINS.

By C. G. GRAY, B.Sc., A.H.-W.C., A.I.C.

INTRODUCTION.

IN recent years a considerable amount of information has been published on the crystalline habits of normal paraffins and other long-chain compounds. These studies have shown that polymorphism is common in such compounds, and that crystalline transitions frequently occur in the solid phase. The solid phase transitions have been studied in some detail by various experimenters, each working with a more or less restricted range of compounds, but no attempt appears to have been made to correlate the results observed in these restricted zones and to form a complete picture of the solid phase relationships for a given class of compound. This task is attempted for the normal paraffins in the present paper.

The study of the solid phase relationships in the normal paraffins throws some interesting light on a number of difficulties and apparent inconsistencies in the literature on the crystallography of petroleum waxes. The crystallography of the pure *n*-paraffins is in itself a subject of some complexity; it is therefore not surprising that the interpretation of results on commercial waxes is full of pitfalls.

THE CRYSTALLINE MODIFICATIONS OF NORMAL PARAFFINS.

Pure normal paraffins are known to crystallize in at least four distinct modifications:—

(1) *Hexagonal System*, the hydrocarbon molecules being packed side by side "like hexagonal pencils" (Müller), the long axes being perpendicular to the planes containing the ends of the molecules. This is shown diagrammatically in Fig. 1a. The molecules rotate freely about their long axes.

(2) *Orthorhombic System* (Fig. 1b). In this modification the molecules are packed side by side perpendicular to the planes containing their ends, *i.e.* the (001) planes, but the packing is no longer hexagonally symmetrical. Two unequal side spacings are shown. The molecules do not possess freedom of rotation, but show libration about their mean positions.

(3) *System uncertain* (monoclinic or triclinic). Two unequal side packing spaces are shown, and the molecules are tilted at an angle of 73° to the planes containing their ends (Fig. 1c).

(4) *System uncertain* (monoclinic or triclinic). Two unequal side spacings are shown, and the molecules are tilted at an angle of $61^\circ 30'$ to the planes on which their ends are situated (Fig. 1d).

In the literature, a great deal of confusion exists over the nomenclature of these four modifications. In the subsequent discussion, the following

nomenclature will be used throughout, and it is suggested that it would provide a convenient standard notation:—

- α form: Vertical rotating chains (hexagonal).
- β form: Vertical non-rotating chains (orthorhombic).
- γ form: chains tilted 73° to (001) planes.
- δ form: chains tilted $61^\circ 30'$ to (001) planes.

The various crystalline modifications described above are not observed in all normal paraffins, the crystalline habit being governed by the number

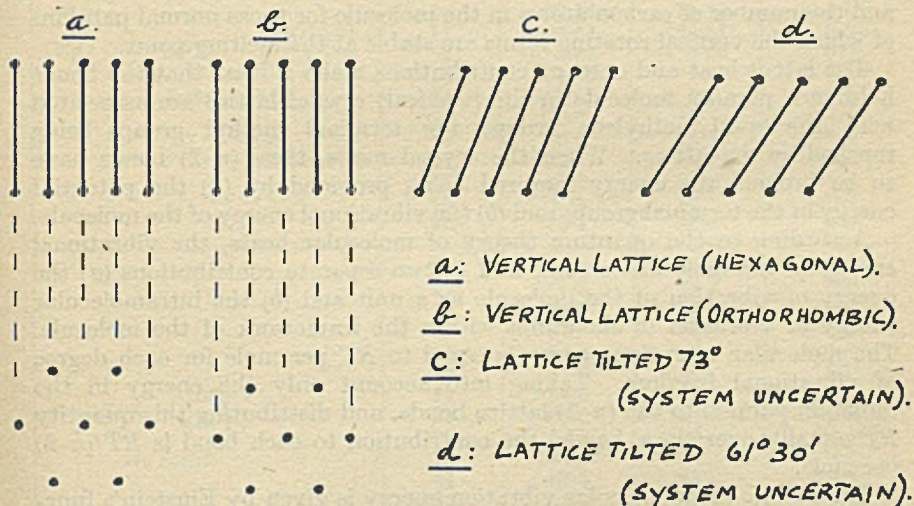


FIG. 1.

CRYSTAL SYSTEMS OF NORMAL PARAFFINS.

of carbon atoms in the molecule. The ranges of n in which each modification has so far been observed are as follows:—

- α : Odd paraffins from C_{11} upwards; even from C_{18} upwards.
- β : Odd from C_{11} upwards; even from C_{18} upwards.
- γ : Odd from C_5 to C_9 inclusive; even from C_6 to C_{22} inclusive.
- δ : Even only, C_{24} to C_{36} inclusive. This modification has been obtained only by crystallization from solvents. It has not been obtained by crystallization of melts or by transition from one of the other modifications.

THE MELTING POINTS OF n -PARAFFINS.

The melting points of the normal paraffins below C_{20} show odd-even alternation, the values lying on two smooth curves, that of the even members lying above that of the odd. The two curves converge at $n = 20$. Above $n = 20$ the values for both odd and even members lie on one smooth curve. This curve has been assumed to continue up to the highest known paraffins, although erratic values have been found in the region C_{30} to C_{40} .

THEORY OF MELTING.

W. E. Garner and his co-workers have shown that the heats of crystallization of the vertical rotating (α) forms of normal paraffins increase linearly with the number of methylene groups in the molecule.¹ The two terminal methyl groups, on the other hand, contribute a negative quantity to the molecular heat of crystallization. The contributions to the entropy of crystallization are in a similar sense, and it is concluded that "there is a marked tendency for these ends to enter the liquid state."

These facts throw light on the relationship between the melting point and the number of carbon atoms in the molecule for those normal paraffins of which the vertical rotating forms are stable at the melting point.

The latent heat and entropy contributions make it clear that the bonds holding a paraffin molecule in the (vertical) crystal lattice are associated with the $(n-2)$ methylene groups, the terminal methyl groups being repelled by the lattice. When the crystal melts, these $(n-2)$ bonds have to be broken, the energy required being provided by (a) the potential energy of the terminal groups and (b) the vibrational energy of the molecule.

According to the quantum theory of molecular heats, the vibrational energy of the molecule is composed of two separate contributions (a) the energy of vibration of the molecule as a unit and (b) the intramolecular energy of vibration of the atoms within the framework of the molecule. The molecular vibration energy is equal to RT per mole for each degree of vibrational freedom. Taking into account only the energy in the direction parallel to the $(n-2)$ lattice bonds, and distributing this quantity RT equally over these bonds, the contribution to each bond is $RT/(n-2)$ per mole.

The atomic intramolecular vibration energy is given by Einstein's function $h\nu/e \frac{h\nu}{\kappa T} - 1$, and it is known that except in the region of absolute zero this energy approximates closely to $R(T-C)$ per mole for each degree of freedom, where C is a constant for a given molecular structure. The total vibrational energy in the direction of the lattice bonds is therefore $R(T-C) + RT/(n-2)$ per bond per mole.

The fact that the heats of crystallization of the methylene groups and of the terminal groups respectively are constant above C_8 , irrespective of the temperature of crystallization, shows that the bond energy and the potential energy of the terminal groups are constant for similar crystalline forms, irrespective of the temperature of crystallization.

Let the bond energy be E_1 per mole and the potential energy of the methyl groups distributed over the $(n-2)$ bonds, be $2E_2/(n-2)$ per bond per mole. It is reasonable to assume that at melting, the bond energy is neutralized by the combined potential and vibrational energies, so that

$$E_1 = \frac{2E_2}{(n-2)} + R(T-C) + \frac{RT}{(n-2)}$$

This equation reduces to the form

$$T = A - B/(n-1) \text{ where } A, B, \text{ are constants.}$$

Over the range C_{20} to C_{36} , the vertical rotating forms of the n -paraffins

TABLE I.
 Melting Points of Normal Paraffin Hydrocarbons.

	<i>n</i> .	M. pt., t° C. (calc.).	M. pt., t° C. (obs.) (2).	Δt° C. (calc. minus obs.).	
Even: $t = 126.81 - \frac{2143.41}{n + 3.7069}$ (δ form)	6	-94.0	-94.0	0.0	
	7	-93.66	-90.05	-3.61	
	8	-56.3	-56.8	+0.5	
	9	-53.32	-53.69	+0.37	
	10	-29.56	-29.72	+0.16	
	11	-25.61	-25.61	0.00	
	Odd: $t = 123.7 - \frac{1908.86}{n + 1.779}$ (α form ?)	12	-9.65	-9.65	0.00
		13	-5.39	-6	+0.6
		14	+5.8	+5.5	+0.3
		15	10.0	10	0.0
16		18.0	18.1	-0.1	
17		22.1	22	+0.1	
18		28.1	28.0	+0.1	
19		31.9	32	-0.1	
20		36.4	36.4	0.0	
$t = 123.4 - \frac{1659}{n - 1}$ (α form)		21	40.45	40.4	+0.05
	22	44.4	44.4	0.0	
	23	48.0	47.4	+0.6	
	24	51.3	51.1	+0.2	
	25	54.3	53.3	+1.0	
	26	57.0	57	0.0	
	27	59.6	60	-0.4	
	28	62.0	61.6	+0.4	
	29	64.1	64	+0.1	
	30	66.2	66	+0.2	
	31	68.1	68.4	-0.3	
	32	69.9	70.3	-0.4	
	33	71.6	71.6	0.0	
	34	73.1	73	+0.1	
	35	74.6	74.6	0.0	
	36	76.0	76	0.0	
	$t = 137.4 - \frac{2266.7}{n}$ (β form ?)	37	76.1	76.3	-0.2
38		77.8	77.1, 79.3 *	+0.7	
39		79.3	78.9	+0.4	
40		80.75	80.75	0.00	
41		82.1	80.7, 82.5 *	-0.4	
42		83.4	82.9	+0.5	
43		84.7	83.3, 83.8 *	+0.9	
44		85.9	86.4	-0.5	
50		92.1	92.1, 93.0 *	0.0	
52		93.8	94	-0.2	
54		95.4	95	+0.4	
60		99.6	98.9	+0.7	
62		100.8	100.5	+0.3	
64		102.0	102	0.0	
66	103.1	103.6 †	-0.5		
67	103.6	104.1 †	-0.5		
70	105.02	105.25	-0.23		

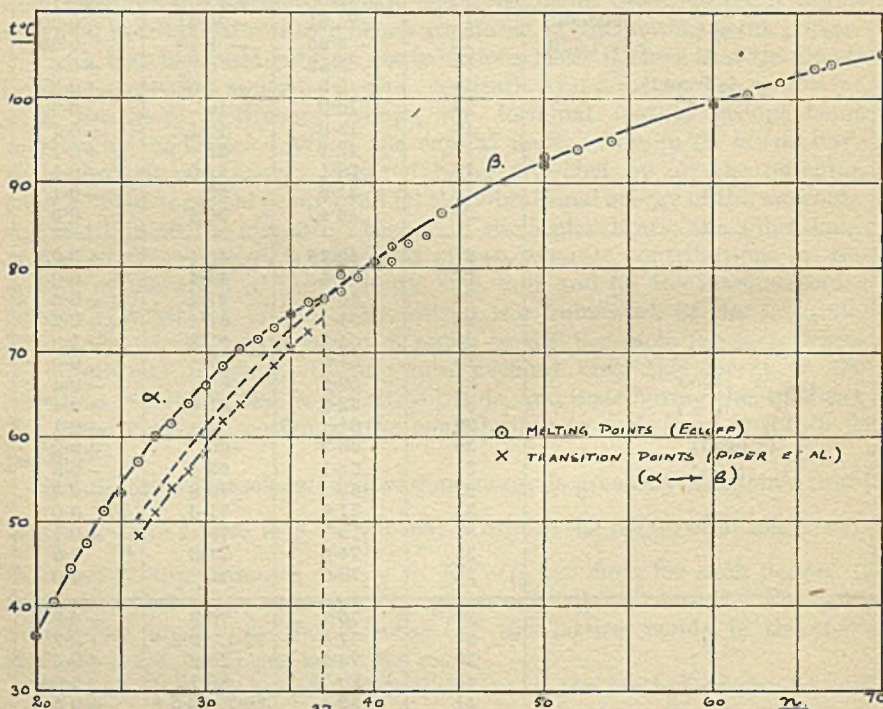
* Egloff quotes two values without discrimination.

† According to Egloff, "impure."

are stable at the melting point, and the melting points for this range, calculated from the equation $T(^{\circ}K) = 396.4 - \frac{1659}{n-1}$, are shown in Table I,

together with the observed melting points published by Egloff.² The constants A and B were evaluated by substituting the observed values of T for C_{22} and C_{36} .

Above C_{36} , and below C_{20} , the values of T calculated from this equation show marked deviations from observed values. It is known that the even paraffins below C_{20} crystallize with tilted chains, the melting point curves of the vertical and tilted forms intersecting at about C_{20} .³ The odd paraffins above C_9 do not crystallize with tilted chains; nevertheless, the melting point curve of the odd paraffins also shows a discontinuity at



GRAPH 1.

INTERSECTION OF α - AND β -MELTING POINT CURVES AT C_{37} .

about C_{20} . The equations of the "odd" and "even" curves in this zone have been calculated from the observed values, and it has been found that these curves are give by the equations:—

$$T(^{\circ}K) = 396.77 - \frac{1908.86}{n + 1.779} \quad \dots \quad \text{odd series, } C_{7-19}.$$

$$T(^{\circ}K) = 399.81 - \frac{2143.41}{n + 3.7069} \quad \dots \quad \text{even series } C_{6-20}.$$

The melting points calculated from these equations are compared with observed values in Table I.

The data available on the paraffins with more than thirty-six carbon

atoms in the chain are neither so complete nor so reliable as those for the lower members. Nevertheless it is here suggested that the discontinuity at C_{36} is due to a definite change in the form of crystal which is stable at the melting point above C_{36} . The evidence for this suggestion will appear in the next section. The melting points in the zone above C_{36} lie on the curve: $t^\circ \text{C.} = 137.4 - \frac{2266.7}{n}$ as is shown in Table I and in Graph 1.

THE SOLID PHASE TRANSITIONS.

The curve for melting point above C_{36} depressed through 2.4°C. , continues as a transition in the solid phase for paraffins below C_{37} . The "first transition points on cooling" reported by Piper and his associates⁴ for C_{26} - C_{32} , C_{34} - C_{36} are plotted in Graph 1, and are compared in Table II with values calculated from the equation

$$t^\circ \text{C.} = 135 - \frac{2266.7}{n}.$$

Piper and his co-workers confirmed that for paraffins above C_{26} this transition was from the vertical rotating form to the vertical non-rotating form. The tilted forms (angle of tilt $61^\circ 30'$) obtained by crystallizing the even paraffins in this range from solvents pass monotropically to the vertical rotating forms, the temperatures at which this takes place laying 0.5 - 1.5°C. above the "First transition on cooling" line, except for C_{26} and C_{28} , which show a difference of about 3.4°C. between the two transitions.

TABLE II.
 $\alpha \rightarrow \beta$ Transition Temperatures.

<i>n.</i>	Piper's "transition point, cooling."	Calculated transition point ($\alpha \rightarrow \beta$) $t^\circ \text{C.} = 135.0 - \frac{2266.7}{n}$	Δt observed minus calculated.
26	48.3	47.8	+0.5
27	51.0	51.0	0.0
28	54.0	54.1	-0.1
29	55.8	56.8	-1.0
30	58.0	59.4	-1.4
31	61.8	61.9	-0.1
32	63.9	64.2	-0.3
34	68.5	68.3	+0.2
35	70.5	70.2	+0.3
36	72.5	72.0	+0.5

Piper's "first transition point on cooling," with the nomenclature adopted in the section on Crystalline Modifications, is the $\alpha \leftarrow \rightarrow \beta$ transition for both odd and even series. The continuity of this $\alpha \leftarrow \rightarrow \beta$ transition line with the melting-point line for paraffins above C_{37} is a strong indication that the β form crystallizes from the melt above C_{37} , and not the α form,

as in the C_{20-37} range. Piper's "transition on heating" at which the δ form passes to α lies a little above the β setting-point line in the solid phase, but King and Garner¹ have pointed out that for the longer chains the vertical forms are probably stable at the melting point.

The identification of Piper's "cooling" and "heating" transitions with the $\alpha \longleftrightarrow \beta$ (odd-even) and $\delta \longrightarrow \alpha$ (even) changes, respectively, immediately raises the question of the nature of the transition line which runs roughly parallel to and some 5° C. below the α melting point curve in the range $C_{18}-C_{28}$, as this line has been assumed to be the line of transition from α to β in this range.⁵ This transition has apparently been noted in even paraffins only, no data on odd paraffins in the range having been traced.

Kolvoort⁵ and Müller⁶ examined the phase transitions of $n-C_{24}H_{50}$, and found that the two transitions, which take place approximately 5° and 10° C. respectively below the melting point, are reversible. On the other hand, the upper transition point in C_{26} and C_{28} is monotropic, as shown by Piper. Above C_{23} this transition does not appear at all. Piper and his associates regarded their sample of triacontane as anomalous in this respect, and continued the curve of the upper transition for C_{26} and C_{28} to join up with those of C_{32} and C_{34} . The evidence available, however, indicates that the upper transition below C_{30} does not correspond with the upper transition in C_{30} and higher hydrocarbons. This is shown in Fig. 2, which shows the observed transition points over the range $C_{20}-C_{36}$, and the suggested scheme of correspondence between them.

It is perhaps significant that the melting-point curve for C_{36} and over cuts the line of upper transition temperatures for C_{28} and under at the point corresponding to C_{29} , at which point the upper transition (heating) is suddenly depressed (Piper), and is thereafter identified as the ($\delta \longrightarrow \alpha$) transition.

The γ melting-point curve for even paraffins intersects the α melting-point curve at C_{19} approximately,³ and it is suggested here that the upper transition in the range $C_{20}-C_{28}$ is the continuation of this line as a transition $\alpha \longleftrightarrow \gamma$ for even members. Data on odd members do not appear to be available. The odd members above C_9 , however, are not known to exist in a tilted form.

This interpretation is at variance with the conclusions of Kolvoort,⁵ who classified the upper transition for $n-C_{24}$ as the point of (enantiotropic) conversion from hexagonal α to orthorhombic β . Kolvoort did not, however, claim to have established the crystalline systems in which his preparations separated. His observations were confined to the angles between the lines of intersection of the (001) and ($hk0$) planes, and were thus incapable of differentiating between vertical and tilted forms. It was assumed that Müller's X-ray data on C_{29} would also be applicable to C_{24} . This assumption, however, is no longer justified.

Müller showed that the lower transition in C_{24} corresponded with the sudden displacement of the (200) reflection in the X-ray spectrum (40-41° C.). Thereafter, with rising temperature, the (200) spacing increased continuously until it became identical with the (110) spacing (46° C.), this being interpreted as a continuous transition of an orthorhombic structure into a radially symmetrical (hexagonal) form in which the chains

are free to rotate. It is, however, possible that the lower transition is from one tilted modification to another (*e.g.* triclinic \rightarrow monoclinic), and that the chains do not assume a position vertical to (001) until the upper transition point is reached, at which point the rotation sets in and the molecules take up a vertical position. This point can only be settled

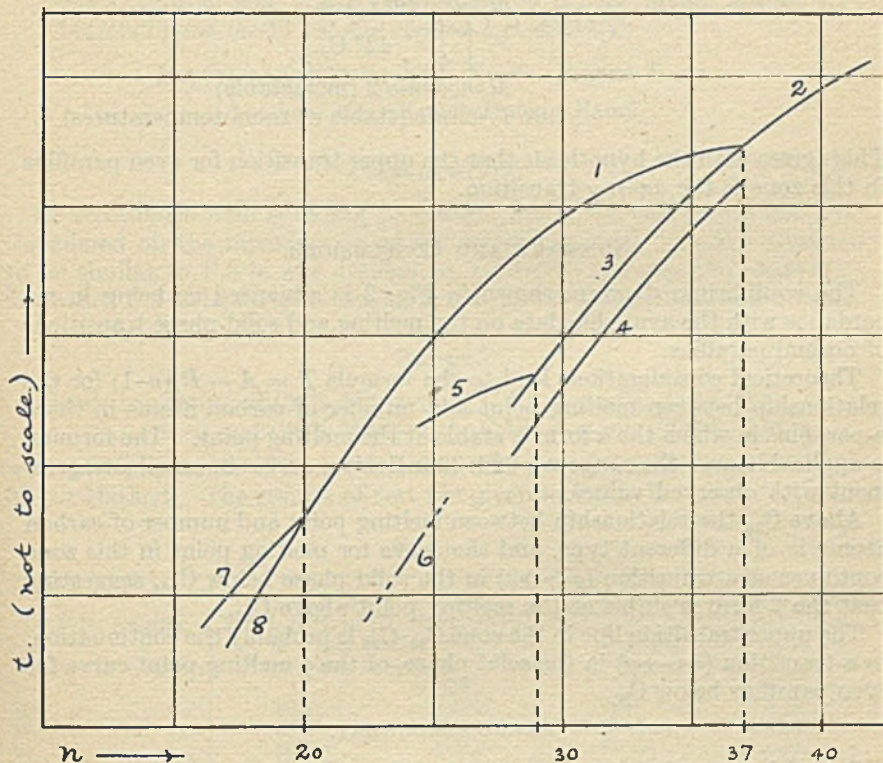


FIG. 2.

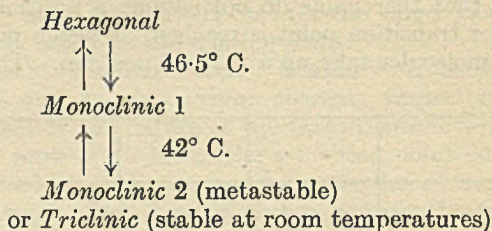
PHASE TRANSFORMATIONS OF NORMAL PARAFFINS.

- 1: α m.pt. ($\alpha \leftrightarrow$ liquid).
- 2: β m.pt. ($\beta \leftrightarrow$ liquid).
- 3: β m.pt. (odd) ($\beta \rightarrow \alpha$).
- δ m.pt. (even) (monotropic) ($\delta \rightarrow \alpha$).
- 4: β set pt. (odd-even) ($\alpha \rightarrow \beta$).
- 5: γ m.pt. (enantiotropic below C_{26}) (even) ($\alpha \leftrightarrow \gamma$).
- 6: δ m.pt. (enantiotropic below C_{26}) (even) ($\gamma \leftrightarrow \delta$).
- 7: γ m.pt. (even).
- 8: α m.pt. (odd).

by measurement of the long spacings over the temperature range involved, evidence from short spacings being insufficient to settle the question definitely.

Yannaquis⁷ and Bijvoet⁸ concluded from X-ray data (the latter on pure n - C_{21}) that the upper transition point in this range corresponds with a change from a hexagonal α form to a tilted form. According to Yan-

naquis the tilted form is triclinic; according to Bijvoet it is monoclinic for C_{24} . Bijvoet gives the following scheme for C_{24} .



This agrees with the hypothesis that the upper transition for even paraffins in this zone is the $\alpha \leftrightarrow \gamma$ transition.

SUMMARY AND CONCLUSIONS.

The equilibrium diagram shown in Fig. 2 is advanced as being in accordance with the available data on the melting and solid-phase transitions of normal paraffins.

Theoretical considerations lead to the formula $T = A - B/(n-1)$ for the relationship between melting point and number of carbon atoms in those n -paraffins in which the α form is stable at the melting point. The formula is applicable over the range $n = 20-36$ inclusive, and is in excellent agreement with observed values.

Above C_{36} the relationship between melting point and number of carbon atoms is of a different type, and the curve for melting point in this zone continues as a transition ($\alpha \leftrightarrow \beta$) in the solid phase below C_{36} , suggesting that the β form is stable at the melting point above C_{36} .

The upper transition line in the zone $C_{20}-C_{28}$ is probably the continuation, as a transition ($\alpha \leftrightarrow \gamma$) in the solid phase, of the γ melting-point curve for even paraffins below C_{20} .

ACKNOWLEDGMENT.

Grateful acknowledgment is made by the author to the directors of the Asiatic Petroleum Co., Ltd., and of the Bataafsche Petroleum Maatschapij, for permission to publish this survey.

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CALIBRATION OF C.F.R. REFERENCE FUELS.

Calibration of Secondary Reference Fuel F.4 + 4 mls. T.E.L./Imp. Gln. and C.12 + 4 mls. T.E.L./Imp. Gln. by C.F.R. Motor Method I.P. 144/42(T) and the 17° Motor Method I.P. 43/42(T).

Report of Sub-Committee No. 5—Engine Tests.

Aviation Fuel Knock-Rating Panel.

INTRODUCTION.

IN accordance with standing procedure, the above calibration has been considered on the introduction of F.4 Reference Fuel. As F.4 appeared to be similar to F.3 it was decided to determine whether the calibration for leaded F.3-C.12 would be accurate enough for use with the latest batch.

TESTS.

Blends consisting of (50% F.4 + 50% C.12) + 4 mls. T.E.L./I.G.
and (90% F.4 + 10% C.12) + 4 mls. T.E.L./I.G.

were rated in terms of leaded F.3 and C.12 in ten C.F.R. engines by 17° Motor Method. The results of test are given in Table I.

TABLE I.

C.F.R. Engine.	(50% F.4 in C.12) + 4 mls. T.E.L./I.G. in (% F.3 in C.12) + 4 mls. T.E.L./I.G.		(90% F.4 in C.12) + 4 mls. T.E.L./I.G. in (% F.3 in C.12) + 4 mls. T.E.L./I.G.	
		Diff.		Diff.
A	49.8	-0.2	89.6	-0.6
B	50.3	+0.3	91.0	+0.8
C	52.2 *	+2.2	93.0 *	+2.8
D	50.0	0	90.0	-0.2
E	50.4	+0.4	90.0	-0.2
F	50.3	+0.3	90.3	+0.1
G	49.7	-0.3	90.0	-0.2
H	49.8	-0.2	90.2	0
I	50.0	0	90.0	-0.2
J	50.0	0	91.0	+0.8
Average	50.0	—	90.2	—

* Ratings on Engine "C" have not been included in the average, as they were obviously in error.

CONCLUSION.

As the average difference is negligible (less than 0.1 O.N.), it is recommended that the calibration tables issued by the Institute of Petroleum for F.3 + 4 mls. T.E.L./I.G. in C.12 + 4 mls. T.E.L./I.G.* shall be employed for leaded F.4 and C.12.

* *J. Inst. Petrol.*, 1941, 27 (211), 192.

The amended Table is reproduced herewith as Table II.

TABLE II.

Octane-Number Calibration Tables C.F.R. Motor Method (I.P. 44/42(T)) up to 100 O.N., thence by "17° Motor Method" (I.P. 43/42(T)).

F.4 + 4 mls. T.E.L./I.G. in C.12 + 4 mls. T.E.L./I.G.

% F.4 + T.E.L.	O.N.	% F.4 + T.E.L.	O.N.
0	93.3	50	103.0
2	93.7	52	103.4
4	94.0	54	103.9
6	94.4	56	104.4
8	94.8	58	104.8
10	95.2	60	105.2
12	95.6	62	105.7
14	96.0	64	106.2
16	96.4	66	106.6
18	96.8	68	107.0
20	97.2	70	107.5
22	97.5	72	108.0
24	97.9	74	108.5
26	98.3	76	109.0
28	98.7	78	109.5
30	99.1	80	110.0
32	99.4	82	110.5
34	99.8	84	111.0
36	100.2	86	111.5
38	100.6	88	112.1
40	101.0	90	112.7
42	101.4	92	113.3
44	101.8	94	114.0
46	102.2	96	114.6
48	102.6	98	115.3
		100	116.0

ABSTRACTS.

	PAGE		PAGE
Geology and Development	291 A	Chemistry and Physics of Hydro-	
Geophysics	300 A	carbons	311 A
Drilling	301 A	Analysis and Testing	314 A
Production	304 A	Special Products	314 A
Synthetic Products	308 A	Book Review	315 A
Refining and Refinery Plant	308 A	Books Received	316 A

AUTHOR INDEX.

The numbers refer to the Abstract Number.

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

Attaway, D., 744	Griswold, J., 760, 764	Ludwig, E. E., 760	Simons, H. F., 727
Bandy, A. M., 748	Hare, D. G. C., 739	Maler, A. R., 739	Smith, R. H., 740, 745
Bonnell, W. S., 761	Henderson, B., 748	Mannion, P. P. Jr., 740,	Spangler, F. L., 735
Boynton, A., 739, 748	Henderson, H., 733	745	Stevenson, H. M., 748
Brattain, R. R., 768	Higgins, C. F., 766	McKean, E. K., 748	Swetland, R. M., 753
Briggs, F., 746	Hoffoss, J. E., 739	McKean, J. H., 748	Taylor, I., 761
Bullum, S., 748	Holloway, C., 762	McTee, A. R., 713	Thompson, R. R., 748
Buttram, F., 709	Howard, W. V., 730	Mounce, W. D., 739, 748	Tipton, R., 748
Canon, A. B., 739	Huggins, M. L., 749	Nelson, E. E., 761	Trager, L., 748
Cooke, E. F., 739	Huntington, R. L., 741	Noble, W. B., 739	Trusty, A. W., 767
Dent, G. M., 750	Jones, D. J., 716	O'Donnell, J. P., 729	Uren, L. C., 723, 737
Downing, L. R., 739	Jones, R. N., 769	Ottenweller, J. H., 762	Volpin, A. S., 739
Eckhardt, E. A., 732	Kallam, F. L., 755	Pendleton, W. W., 770	Weinaug, C. F., 763
Egloff, G., 771	Katz, D. L., 763	Peterson, L. F., 740, 745	Weinrich, W., 762
Elkins, L. E., 740, 745	Kennedy, H. T., 748	Piety, R. G., 739	White, R. E., 739
Evans, P. M., 748	King, S. P., 736	Pirson, S. J., 708	Williams, N., 742, 743
Faust, P. H., 765	Kornfeld, J. A., 718	Roach, E. J., 739	Wilson, G. M., 746
Fearon, R. E., 739	Levine, S., 757	Sawdon, W. A., 722, 734	Wilson, J. H., 739
Germany, A., 748	Lvorsen, A. I., 711	Scherbatskoy, S. A., 739	Wood, L. A., 766
	Liljestrand, W. E., 739	Schmer, J., 747	Wyszynski, Z. S., 706
	Logan, L. J., 710, 714		Zobell, C. E., 717
	Lucous, J. C., 748		

Geology and Development.

706. Deposits of Natural Gas in Poland. Z. S. Wyszynski. *Min. and Pet. Tech. Mag.* (University of Birmingham), 1943, 41.—The geology of the Polish Carpathian and preCarpathian Oil and Gas zones is outlined. The reserves of natural gas in Poland are then discussed in a little detail. The uses to which natural gas was put are enumerated. (1) As fuel (boilers, house heating, etc.). (2) As Fuel for internal-combustion gas engines (heavy rail and road vehicles, stationary motors). (3) For lighting purposes. (4) For extracting of natural-gasoline ("wet" gas only). (5) For enrichment of coal-gas (gas works at Luck, Rowne, Torun, Bydgoszcz, Gdynia, Czestochowa, and other towns, sometimes hundreds of miles away, were supplied with liquid natural gas in special steel bottles under pressure). (6) In metallurgical processes (carburation of steel). (7) As raw material for chemical industries (fabrication of NH_3 from CH_4).

A. H. N.

707.* Oil Reserves in the United States. Anon. *World Petrol.*, April 1943, 14 (4), 64.—The annual report of the A.P.I. committee on petroleum reserves estimates the U.S. reserves at the end of 1942 to be 20,082,793,000 bbl., 493,497,000 bbl. more than at the end of 1941. The 1942 production was 1,385,479,000 bbl. Therefore the increase in visible reserves in 1942 was 1,878,976,000 bbl., 260,051,000 bbl. of which was attributed

to oil found in entirely new pools, and the rest to upward revision of the amount of oil known to be contained in old fields.

The estimates of proved reserves do not reflect the availability or the rate at which the reserves can be produced, with or without physical waste.

Tables give by States the proved reserves at the beginning and end of 1942, the proved new reserves and production in 1942, and a summary of the A.P.I. committee's annual reports covering the period 1937-1942.

G. D. H.

708.* Oil Supply Problem Demands Early Solution. S. J. Pirson. *Oil Wkly*, 5.4.43, 109 (5), 51.—The maintenance of known unproduced oil supplies adequate for all long- and short-term eventualities and properly situated geographically is a problem aggravated, but not created by the U.S. participation in the war.

In recent years about 10% of all wells drilled in U.S. have been wildcats, and about one in ten of the latter has been successful. Until 1941 the discovery rate of oil remained above the rate of consumption; in 1942 the deficiency of discoveries compared with production may be 585 to 1068 million barrels, although exploratory drilling in 1942 was at a record high. The fields discovered in 1942 were small, and indicate the efficiency of modern discovery methods.

There have been cycles of efficiency in the discovery of oil. The successive peaks can be associated with the use of the non-technical wildcatter, surface geology, sub-surface geology, and geophysics. Now hopes are centred on the geological theories of stratigraphic accumulation, and on new prospecting techniques (deep electrical resistivity and geochemistry). In stratigraphic prospecting new tools as well as refined older techniques are brought into use.

Reserve estimates are based on the use of the best production practices, and withdrawals at rates above the optimum may reduce the visible reserves by 15-20%. Hence the reserve problem also involves the question of an adequate rate of productivity.

Synthetic oil might be made to improve the oil situation, but it is expensive, requires expensive plant and a large number of workmen, and the situation is similar with regard to oil from shales. Secondary oil-recovery methods require favourable sand conditions, and shallow sands (for water-flooding to be economical), and even then are unlikely to give a suitably high rate of production. Increased wildcatting may solve the problem if undiscovered reserves remain and they are largely in stratigraphic traps. Stratigraphic traps seem likely to hold the bulk of the undiscovered oil. They may be lenses formed in a variety of ways, truncations, pinch-outs, etc.

The geological search for stratigraphic traps would entail the location of surface and subsurface uplifts, the construction of detailed palaeogeographical maps, and the construction of isopachous maps, supplemented by core-drilling for geological data, the borings being surveyed by appropriate methods.

At present three-quarters of the oil discoveries are made by small independent operators and companies. Wildcatting will only be encouraged by hopes of substantial financial returns. Increases in the price of crude oil, and in the depletion allowance, and the allowance of large production for discovery wells with exemption from taxes on the profit they give, are possible stimulants for wildcatting.

Wildcatting must be controlled to avoid wastage, and at the same time the controlling authorities could provide and co-ordinate vital information.

G. D. H.

709.* Increased Costs and Low Prices Destroying Discovery Machinery. F. Buttram. *Oil Wkly*, 5.4.43, 109 (5), 73.—Many have tried to convince war-emergency authorities in charge of price control that the oil producer is limited in his effort by the margin between operating costs and the cash realized from the sale of his crude oil. Crude-oil prices were "frozen" about eighteen months ago, and since then Congress committees have studied the matter, and the Army and Navy authorities have expressed concern over the supply position. Increased wildcatting has been called for.

The deficiency of discovery, abandonment of stripper wells, and idle secondary-recovery reserves are all consequences of low oil prices.

Two-thirds of the 1942 discoveries were made by independent operators, and for several years independent operators have found over 70% of the new fields.

Wildcaters are going out of business, and so the various parts of the machinery of discovery effort are becoming scattered. Hence it is not surprising that a quarter of

1943 has gone without any sign of the revival and increase in wildcatting which have been called for.

Scarcity of materials, inability to compete in the labour market under present conditions, and threats of an attack on the depletion allowance and on the intangible-expense option are further problems of the oil industry.
G. D. H.

710. Oil Men Vote Increased Crude Prices as Most Important of Possible Stimulants to Wildcat Drilling. L. J. Logan. *Oil Wkly*, 5.4.43, 109 (5), 42.—A ballot paper on the possible stimulants for increasing wildcatting was sent to companies and operators that drilled fifteen or more wells in 1942, and to outstanding wildcaters, drilling contractors, and others. The ranking of possible stimulants was sought, but in determining the aggregate result of the ballot unplaced possible stimulants were ignored. The proposition to stimulate wildcatting by increased crude prices was placed well ahead of all other propositions. Second in rank was the "Proclamation of a sympathetic and reasonably long-range government policy with regard to wildcatting and the development of new fields, which will dispel misgiving over controls and discretionary powers of administrative agencies." The making of materials and equipment more readily available nearly tied for second place. The fourth place was held by the proposition of more liberal daily allowables for new producing areas, towards the end of hastening pay-out of investments, and a close fifth was the alleviation of existing or prospective manpower shortage. In the sixth place was the giving of "greater assurance of pipe-lines or other market outlets for any production established."

Many balloters called for the retention of depletion allowance and deduction of intangible drilling costs in determining income tax, and for the decentralization and simplification of P.A.W., these points occupying ninth and tenth places respectively without having been printed on the original ballot paper. Motor transport was considered as only a minor obstacle to wildcatting.

"Government subsidies to aid in drilling of promising prospects" and "The setting up of a government owned and controlled operating company, to participate in active search for new fields" were two propositions scratched out or ignored by many voters as unworthy of consideration as possible stimulants.
G. D. H.

711.* Discovery Thinking. A. I. Levorsen. *Oil Wkly*, 12.4.43, 109 (6), 11; 19.4.43, 109 (7), 14; 26.4.43, 109 (8), 12. See abstract No. 620.—The article in the *Oil Weekly* gives greater detail on some points, and has more diagrams than that in the *Oil and Gas Journal* (8.4.43, 41 (48), 38).
G. D. H.

712.* March Drilling Results in Completions Gain. Anon. *Oil Wkly*, 12.4.43, 109 (6), 42.—1476 wells were completed in U.S.A. in March 1943, compared with 1280 in February. The main gains were in Illinois, Oklahoma, and Texas, which had rises of 40, 31, and 42 respectively. Supply difficulties and transport questions are undoubtedly holding back drilling.

A table gives details by States and districts of the completions in March 1943, with comparative totals for February 1943, and March 1942, as well as the cumulative 1943 completions.
G. D. H.

713.* Declining Output of Illinois and Oklahoma Becomes Serious. A. R. McTee, *Oil Wkly*, 19.4.43, 109 (7), 9.—The present daily output of Oklahoma and Illinois is 100,000 bbl. below the level of a year ago, and is still declining. This fall is complicating the problem of moving available production and products to the East Coast, and throwing a heavy burden on other oil States. Unsatisfactory exploratory results in 1942 in these two States indicates a probable continuation of the downward production trend.

Compared with the first quarter of 1942 the Illinois production has fallen by 114,000 bbl./day, and that of Oklahoma by 57,000 bbl./day. Kansas, the third largest producing State of P.A.W. District 2, has been able to assist in offsetting the decline by increasing its output by 60,000 bbl./day, but it is now probably producing practically at its maximum rate. Additional supplies will therefore have to come from Texas, which is not well located geographically for meeting the deficit. At the same time Texas will have to supply 300,000 bbl./day to the 24-inch pipe line, and 200,000 bbl./day to the 20-inch product line.

At the end of 1942 the Illinois crude reserves were estimated at 306,778,000 brl., a fall of 26,939,000 brl. during the year. The Oklahoma reserve at the end of 1942 were 968,927,000 brl., 66,893,000 brl. less than a year earlier. The Kansas reserve changed but little in 1942, and amounted to 686,975,000 brl. at the end of the year.

A committee has suggested to P.A.W. that the ceiling price of crude oil should be advanced 25 cents, and that secondary recovery methods should be applied as a means of increasing production.

Tables show the trend of District 2 crude production and stocks in 1941, 1942, and 1943, and the trend of reserves and discovery rates in 1938, 1939, 1940, 1941, and 1942. G. D. H.

714.* Wildcat Activity Declining Instead of Increasing. L. J. Logan. *Oil Wkly*, 19.4.43, 109 (7), 11.—Instead of the sharp increase in wildcatting in U.S. which the Government has called for, there has been a decline from the rates which have held in the past few years. The March rate was only 2800 wildcats/year instead of 4500/year as required. If the necessary number is to be reached, an average of 420 wildcats/month must be drilled during the remaining nine months of 1943. Up to the end of the first quarter of 1943, 674 wildcats were completed exclusive of semi-wildcats, compared with 716 in the corresponding period of 1942. Only 15.1% of the 1943 wildcats were productive, whereas the corresponding figure for 1942 was 18.7%. Many fewer new pays have been found than in 1942, although new oil and distillate fields were at about the same level. In order to replace current production by new reserves, 125,000,000 brl. of oil must be discovered each month, and this figure may have been attained in March, but some would probably place the figure at 50,000,000 brl. About half the March discoveries were in District 2, where they are most needed, and much of the remainder was in District 3. California has had two unimportant extensions of established fields.

Probably the most important March discovery is the Hall's Bayou field of the Texas Upper Gulf Coast, which may produce 20,000,000 brl. The new field at Shuteston, South Louisiana, is regarded as fairly important, and several other Texas Gulf Coast and South-west Texas discoveries may give up to 10,000,000 brl. each. The Hobson field of the Lower Texas Gulf Coast has established good pays in a deeper sand section (Claiborne and Wilcox), opening a new exploration trend.

Tables summarize by States the results of wildcat completions in March and in the first quarter of 1943; they list the March discoveries with details; and show the trend of wildcat completions. G. D. H.

715.* Hungary Furnishing Most Important Developments in Continental Europe. Anon. *Oil Wkly*, 19.4.43, 109 (7), 57.—Plans are being carried out for constructing natural gas pipe-lines from northern Transylvania to Cluj and other Hungarian industrial towns. A lubricating-oil refinery is to be built in Hungary to process domestic crude.

During 1942 Hungary is estimated to have produced 3,800,000 brl. of crude, compared with 2,600,000 brl. in 1941. The 1942 production of petroleum substitutes is estimated at 200,000 brl.—about twice the 1941 figure. The Hungarian oil output has substantially exceeded domestic needs in the last two years, making about 2,000,000 brl. available to Germany in 1942 alone. The Axis petroleum and substitute output was probably 112,000,000 brl. in 1942.

The main Hungarian production is in the Budafapuszta region, around what was formerly known as the Liske field.

In the Lovaszi area oil was found in 1941 at depths of 4950–5400 ft., the early wells giving about 800 brl./day of 39-gravity oil. Liske is reported to have 40 wells on production, and in 1940 was giving about 5000 brl./day from 3950–4950 ft. Across the border the Selenico and Peklenico fields of Yugo-Slavia yield about 10 brl./day each. G. D. H.

716.* Wildcatter's Spirit Must Not Be Crushed. D. J. Jones. *Oil Wkly*, 26.4.43, 109 (8), 14.—It is generally believed that practically all the large structural features of U.S. are known, and so the smaller features and stratigraphic traps must be the source of future oil supplies, with the latter providing most of the new reserves. In order to discover stratigraphic traps an increased number of exploratory wells will have

to be drilled under the supervision of the industry's best-trained technical experts. However, a fair number of these wells should be drilled by the ordinary independent wildcatter, who will play a very important part in discovering adequate reserves, and even when he fails he will add to the industry's stratigraphic knowledge.

The encouragement of wildcatting by bonuses and subsidies seems to require complicated administrative machinery, and may be unfair and impracticable in many cases. The present task of discovering adequate reserves is too big even for the major companies with all their resources of money and men.

Unless some drastic stimulant in the form of an advance in crude oil prices is forthcoming the wildcatter and the individual operator are likely to disappear. Increased cost of labour and materials and man-power shortage are making it very difficult for the smaller operators to carry on. In many cases they are unable, and perhaps unwilling, to embark on secondary recovery projects under present crude price conditions. A rise in price of 50 cents/bbl. is necessary. This will stimulate many to greater efforts, and lead to some tests which will open pools in areas where the best minds of the industry would not recommend drilling.

G. D. H.

717.* **Influence of Bacterial Activity on Source Sediments.** C. E. Zobell. *Oil Wkly*, 26.4.43, 109 (8), 15.—Significant numbers of living bacteria are found in recent marine sediments even at depths of over 3 ml. and at the base of 17-ft. cores. Stratigraphic changes in the organic and sulphate content of cores show that the bacteria are active *in situ*, and their activity may continue although the temperature, pressure, and salinity may vary widely. Many of the bacterial species found in sediments are physiologically versatile, and most are facultative aerobes. The pH of sediments is influenced by bacterially produced acids or bases, and thus chemical reactions and the precipitation or solution of calcium carbonate may be altered. Bacteria tend to create reducing conditions in marine sediments, and such conditions favour the formation of petroleum hydrocarbons. Methane-producing bacteria are widely distributed in the sea. Carbon dioxide, carbon monoxide, hydrogen, and hydrogen sulphide are formed by bacteria, sulphates are reduced, sulphur precipitated, and the aggregation of particles and the lithification of sediments are influenced by them. Bacteria may not produce petroleum directly, but they certainly convert organic matter into substances which are more petroleum-like. They can convert methane into bacterial protoplasm, and may be able to polymerize it to form higher hydrocarbons. Many bacteria liberate fatty acids from fats and oils, and the removal of two oxygen atoms from the fatty acids would result in the formation of fairly long-chain hydrocarbons. Some bacteria destroy petroleum hydrocarbons, a process which may be responsible for the failure of workers to find petroleum hydrocarbons in recent sediments or in experimental material with mixed cultures. This destruction might occur during transport and storage of samples prior to analysis, or might occur *in situ* in all except certain environments (hydrogen sulphide, certain heavy metals and other substances inhibit the oxidation) which are unfavourable to the activity of the hydrocarbon-oxidizing bacteria.

Changes produced by hydrocarbon-oxidizing bacteria in surface soils over subterranean oil deposits from which volatile hydrocarbons are escaping may serve as useful indicators in searching for oil.

G. D. H.

718.* **Frequency of Dry Holes Rises Sharply in Kansas Completions.** J. A. Kornfeld, *Oil Wkly*, 26.4.43, 109 (8), 33.—In 1942 in Kansas dry holes were 41.7% of the total completions, a rise of 15.1% above the 1941 figure. In 1942 90% of the wildcats were failures, and in 1941 85.4%. Few, if any, of the 1942 discovery wells were more than 10 ml. from the nearest developed producing area. The increase in the proportion of dry holes in the state in 1942 is partly due to wildcats being 23.6% of the total completions instead of 12.6% as in 1941. 26.7% of the non-wildcat wells were dry in 1942, compared with 18.1% in 1941.

Tables give the numbers of oil, gas, and dry wells completed each year from 1937, and compare the results of wildcat and pool drilling in Kansas in 1941 and 1942.

G. D. H.

719. **Colombian Activity May be Helped by Proposed Law.** Anon. *Oil Gas J.*, 29.4.43, 41 (51), 38.—The proposed new Colombian oil law minimizes title litigation,

does not require drilling before relinquishing an explored concession, and increases taxes only on new contracts. Production taxes will range 3 to 13%, depending on distance from the petroleum-gathering system, and surface taxes will be 20 centavos in the first two years in the less accessible areas and 30 centavos in others, and 3 pesos in the eleventh year in the former and in the tenth year in the latter. The usual concession area will be reduced from a maximum of 50,000 hectares to 25,000 hectares, and from a minimum of 5000 to 3000 hectares.

The war has virtually stopped oil operations in Colombia by depressing markets and preventing the importation of equipment. The 1942 production was 10,600,000 bbl., compared with 24,650,000 bbl. in 1941. Lack of equipment has prevented complete definition of the new Casabe area, where the discovery well was completed at 8280 ft. in October 1941. Nine wells have been drilled which average 3700 ft. The field produces from exceptionally thick sands, and lies on the west bank of the Magdalena, north-west of Infantas and La Cira.

On the Barco concession producing wells have been completed on or near highs at opposite ends of a 15-mi.-long structure. Two wells have been completed on the Socuavo dome in the north, and three on the Tres Bocas dome in the south, one well in each case proving commercial. Socuavo No. 2 flowed 200 bbl./day of 35° A.P.I. oil from 5575 ft., and Tres Bocas 2-A 1000 bbl./day.

Cimitarra 2 has encountered oil-shows.

G. D. H.

720. Canadian Government Takes Over Operation of Athabaska Oil Sand. Anon. *Oil Gas J.*, 29.4.43, 41 (51), 43.—The pilot plant of Abasands Oils, Ltd., which was destroyed by fire in 1941 and rebuilt in 1942, has been taken over by the Government, \$500,000 having been appropriated for the improvement of plant and processes.

The Athabaska tar-sands are estimated to contain 250,000,000,000 bbl. of oil, and outcrop or lie under 8–200 ft. of overburden. Excavation is by light blasting and power shovelling, the oil then being separated by flotation with recoveries estimated at 28–30 bbl./40 ton of sand. The oil was used chiefly as a diesel fuel on northern river-craft.

The operating problems include winter difficulties, economic mining methods, separation of bitumen from the sands, and treatment of the bitumen to give diesel fuel, gasoline, lubricants, etc., removal of 7–8% of sulphur, location of uniform, rich sands with little overburden, and the disposal of the sands, overburden without polluting streams. The raw sands have been successfully used for surfacing roads when mixed with dry sand and crushed stone. Certain peculiar qualities of the separated crude indicate a possibility of working out a synthetic rubber process in conjunction with a refining plant.

G. D. H.

721. Oil Zones of the United States: Lower Mississippian. Anon. *Oil Gas J.*, 29.4.43, 41 (51), 72C.—In the area between the Appalachians and the Cincinnati Arch sandstones and shales form the bulk of the Lower Mississippian deposits. In the eastern part, the Berea is the only widespread sand, and it occurs in West Virginia, Kentucky, Ohio, and Michigan. The Weir, Squaw, Big Injun, Beckett, and Keener are oil-sands of local importance. Shales form the base of the Mississippian in the Illinois basin, and later there were thick limestones, some of which were separated by unconformities. Some oil has been found in the top of the St. Louis limestone, but the McClosky is the main pay, being an oolitic member of the basal Ste. Genevieve. Some oil is obtained from two upper members of the Ste. Genevieve. West of the Ozarks the main pay is the top of the "Boone" (Mississippi lime or chat), and this is of importance in eastern Kansas. Recently Mississippi lime production has been found on the west flank of the Bond Arch. The Madison limestone (Mississippian) is the oldest known pay of the Rocky Mountain area, providing the main oil at Kevin-Sunburst, and shows on the Baker-Glendive anticline.

There are possibilities of Lower Mississippian production in the Williston basin, in the eastern part of the West Texas basin, on the flanks of the Nemaha Granite Ridge, and in the Illinois-Indiana basin.

There are unconformities within and above each of the four extensive limestone formations between the pre-Cambrian and Upper Mississippian, and each has developed porosity and frequently given oil accumulation. The sediments of the basins between the various broad uplifts which developed in this period cannot be correlated over wide

areas, but they have very similar characteristics. More intense movements occurred after the Lower Mississippian, and conditions changed rapidly, causing the subsequent geological history to be different in the different producing sections of the country.

A map shows the Lower Mississippian outcrops, the structural features, the Lower Mississippian producing areas, and those which are favourable and unfavourable for producing from this system. G. D. H.

722.* Locating Cased-Off Production by Radioactivity Logging. W. A. Sawdon. *Petrol. Eng.*, May 1943, **14** (8), 43.—Gamma-rays originate in the formations, and, passing through the casing and cement, if present, indicate the character of the formation. The neutron curve measures the effect of bombarding the formation by neutrons from a strong source. In general, shales give the highest gamma radiation, and sands and shales less. The hydrogen in a formation is the chief cause of variation in the intensity of the neutron curve. The connate and combined water of a shale, due to the hydrogen, leads to a low intensity of the neutron curve. An increase in porosity of a formation with oil or water in the pores gives low neutron curve intensities, but the curves do not distinguish between oil and water, since both contain hydrogen.

The gamma-ray and neutron curves together may permit the location of porous horizons in a limestone between shales, and are of assistance in selecting points at which to perforate for cased-off production. Both types of curves may be used for geological correlation in a field. G. D. H.

723.* Inspection and Analysis of Formation Samples. L. C. Uren. *Petrol. Engr.*, May 1943, **14** (8), 62.—Before determining the porosity and permeability of a part of the formation sample, any liquids therein must be removed. This is best done in a Soxhlet apparatus, preferably by first extracting with benzene to remove petroleum and petroleum residues, then extracting with acetone to remove water, and finally extracting with pentane to displace acetone. The extracted specimen is then dried below 210° F. Specimens for permeability measurements are cut to a form and size which depend on the core-holder in the permeameter used and on the direction (perpendicular or parallel to the bedding) in which the measurement is to be made. Air is generally the most convenient fluid with which to make the measurement, but at times oil is preferred. The apparatus must provide means for controlling the pressure upstream and measuring the value of the pressures at the up- and down-stream faces of the core, for filtering the liquid used, for measuring the specimen's dimensions, controlling the temperature, and measuring the rate of fluid flow. It is usual to measure the permeability at several pressure gradients, and in the case of gases the preferred value is obtained by plotting the values against the reciprocal of the mean pressure and extrapolating to zero reciprocal mean pressure.

The gross fluid content of the sample is purely the loss in weight on extraction. The water content is determined by submergence in a solvent, such as xylene, and heating to drive off the water and condensing it in a suitable receiver. The oil content is determined by difference. Alternatively both oil and water may be distilled off and collected, certain corrections being made, and the result being checked by weighing the specimen before and after distillation.

The amount of oil in a core is but a poor basis for finding the oil gravity, and it is best to measure gravity on oil produced directly from the formation. Fairly satisfactory results may be obtained by pycnometer measurements on oil distilled from the core, provided that corrections are made to allow for changes in the oil during retorting.

An extensive bibliography is appended. G. D. H.

724. Devonian Production Gaining in Importance in Western Illinois Basin. Anon. *Oil Gas J.*, 6.5.43, **41** (52), 150.—The first Devonian lime oil of the Illinois basin was found at Siosi in south-west Indiana in 1926, and the first important Devonian production in Illinois was found at Centralia in 1940. Since then the Devonian has been found to be productive in more than a dozen fields in Illinois. In Illinois the term "Devonian" is applied to a body of limestone several hundred feet thick immediately below the Kinderhook-New Albany shale, and of Devonian and Silurian age. Both systems are present over much of the basin.

Commercial Devonian production was obtained in the Colmar-Plymouth field in

1914 at a depth of 420 ft. The oil is in the Hoing sand on an anticlinal-type structure, and the ultimate recovery may be 1702 brl./acre. The Martinsville field was opened in 1937 with production from several Devonian sands and from the Trenton. Two Devonian wells were brought in at Decatur. Sorrento has three Devonian wells at depths of 1830 ft. The Sandoval Devonian, opened in 1938, has proved more prolific than many other Devonian fields. The upper horizons were practically drilled up when Devonian production was established at Centralia, where the ultimate Devonian recovery is estimated at 3125 brl./acre for the whole field. The Devonian pay at Salem is an extremely porous limestone at about 2860 ft., and it may yield 6000 brl./acre. The Loudon Devonian pay is about 15 ft. thick and 3000 ft. deep, with an estimated ultimate recovery of 4500 brl./acre. Bartelso, Irvington, and Tonti are other fields with Devonian production.

In most of the Devonian producing fields of Illinois the pay has been found to be in close contact with a water-table of water-drive proportions. Recently Devonian production has been found at Boulder, South Bartelso, and Patoka, but only a few wells have been drilled in these cases. A new area in the northern part of the Illinois basin has been opened to Devonian exploration by a strike in northern Christian county, 50 ml. north of the prolific Devonian area surrounding Loudon and Salem.

A map shows the sites of the Devonian pools in the western part of the Illinois basin.

G. D. H.

725.* Drilling Increases in April ; Wells Completed at Rate of 18,000 Yearly. Anon. *Oil Wkly*, 10.5.43, 109 (10), 63.—The weekly well completion rate in U.S.A. in April was 345, 18% higher than the March rate, but 16% below the April 1942 rate. The weekly rates in January and February 1943 were respectively 346 and 320. During April there were notable increases in field work in Pennsylvania, West Virginia, Kansas, North Louisiana, Michigan, New Mexico, Eastern Texas, and West Central Texas, where there were more completions in four weeks than in the preceding five weeks. There were also increases in the weekly average in Arkansas, Illinois, Ohio, Oklahoma, North Texas, and West Texas.

Details of the April completions are tabulated by States and districts, with total completions for March 1943 and for April 1942, together with cumulative completions for the first four months of 1943, and details of the rigs on 1st May, 1943.

G. D. H.

726.* Canadian Company Drilling Gaspé Peninsula Deep Test. Anon. *Oil Wkly*, 10.5.43, 109 (10), 64.—An 8000-ft. test has been begun on the Galt Brook dome on the Gaspé Peninsula, south of the St. Lawrence. In excavations for the derrick foundations live petroleum was encountered. The hard surface limestone has been penetrated for 26 ft.

G. D. H.

727. New Oil Supplies and Greater Production Efficiency Considered by A.I.M.E. H. F. Simons. *Oil Gas J.*, 13.5.43, 42 (1), 30.—One of the best places in which to seek new oil supplies is in deeper horizons underlying present producing fields, for structural traps often have oil in a number of superimposed traps. Denison considers that no structural trap is condemned until the basement rock is reached. Consequently, in northern Oklahoma and most of Kansas less than 1000 ft. of additional sediments remained to be tested ; in the Seminole area only four tests have gone below the Wilcox and there are about 4000 ft. of sediments below the Wilcox ; in the East Texas basin 4000–10,000 ft. of sediments require prospecting below the Woodbine, and already production has been found in the Paluxy, Glen Rose, and Travis Peak ; on the Gulf Coast 7000–10,000 ft. remain to be tested before reaching the limit of present drilling depths. Near the north edge of the Panhandle oil- and gas-fields, some 6000 ft. of sediments lie above the granite ; a considerably greater depth remains to be tested on some of the large structures of the West Texas basin. Deeper drilling of this type would require little expansion or change of producing organizations, and there would be little need for further geological or geophysical work for this prospecting.

Knowlton considers that all the U.S. oil areas except the Texas, Gulf Coast, and West Texas are producing at or above the maximum efficient rate. The most economical source of additional oil for the war programme, apart from exploratory drilling,

is secondary recovery. It is probable that 70,000,000,000 bbl. of oil remain in present known fields at the end of primary production. 3,000,000,000 bbl. or more of secondary recovery oil could be produced by existing techniques at the present or a slightly increased price.
G. D. H.

728. Oil Zones of the United States: Upper Mississippian. Anon. *Oil Gas J.*, 20.5.43, 42 (2), 68-C.—Upper Mississippian production is restricted to three areas and is important in only one, the Illinois basin. The Maxton sand yields a little oil in the Allegheny Plateau region. In the Illinois basin the Chester consists of clastics and some limestones, especially in the deeper parts, where sands of the upper members form wedge edges. Producing stratigraphic traps in the lower members are nearer to the edges of the basin. The Degonia, Clore, and Palestine sandstones produce in the Wabash River area; Waltersburg and Tar Springs sandstones in the southern part of the basin; the Hardinsburg and Golconda are minor pays; the Cypress is generally productive in the northern part of the basin; the Paint Creek produces in several fields; the Bethel (Benoist) produces widely as does the Aux Vases. Conditions similar to those of Illinois do not seem to have existed elsewhere in the United States in Chester times.

In Upper Mississippian times local uplifts became more intense, and sheet sands and shales over wide areas were replaced by sands pinching out up-dip and grading into shale down-dip, thus giving depositional stratigraphic traps. These offer best chances where intersected by lines of folding.

As a basin fills the stratigraphic traps approach the middle, but greater submergence may interrupt this trend.

A map shows the Upper Mississippian producing areas.

G. D. H.

729. Shell Opens Potential Oil Field in Colombia. J. P. O'Donnell. *Oil Gas J.*, 27.5.43, 42 (3), 32.—1 El Difícil in the Magdalena Department of Colombia has flowed 130 bbl./day of 46° A.P.I. crude with 1,300,000 cu. ft. of gas through a $\frac{3}{8}$ -in. choke. The well has a total depth of 5930 ft. and encountered a gas cap above the 600 ft. of porous limestone from which it is producing. The tubing pressure is 2375 lb./in.² The well is said to be on major structure and may herald a new field. It is 60 ml. from tidewater, and 100 ml. due south of the port of Santa Marta. The construction of a pipe-line through the generally flat country should be easier and less expensive than the other Colombian pipe-lines. 1 El Difícil is about 30 ml. north-west of 1 El Doce, a dry hole completed at 10,046 ft., 20 ml. to the south-east of El Difícil 1 Brillante is being drilled.

Shell discovered the Casabe field which has nine wells but no outlet. This is a little north-east of the De Mares concession. Two promising new producing areas have been found on the Barco concession, but the prospects need confirmation.

Lack of shipping has virtually eliminated Colombia's oil exports and equipment imports. The first quarter's production of 1943 was 1,034,500 bbl. compared with 5,845,000 bbl. for the same period of 1942. The production in the last quarter of 1942 was 570,000 bbl.
G. D. H.

730. More Sedimentary Petrography Needed for Exploration and Development Programmes. W. V. Howard, *Oil Gas J.*, 27.5.43, 42 (3), 38.—Most of the sedimentary petrography now being used falls into three categories: (a) Rapid examination with a binocular microscope or hand lens to detect the appearance of a key horizon or of a lithological change. (b) Breaking up the rock to study grain size and shape. (c) Throwing away much of the rock and studying the remainder in great detail.

Core analysis and the indirect methods of study such as electrical logging, gamma-ray logging, etc., do not add much to the knowledge of the rocks involved.

The geologist uses key horizons for correlation, to tell his structural position, where to case and to core, and when he is near his pay. Cores and mechanical logging information tell the engineer much about the sand productivity, and later will give him data of value in secondary recovery projects.

Most companies separate the exploration and production departments, often losing thereby much information which both could use. There are geological reasons for pressure, interference, water movement, and other irregularities. The reason is not always faulting; it may be changes in lithology. Especially near shore, changes are

likely, and washouts may cut off beds. Detailed studies of the reservoir lithology are frequently very valuable, and in this way the geologist can often solve problems with benefit to the production department. The geologist's attack should be direct, and should not result in a lengthy report with much irrelevant detail, which may be of great scientific interest, but of little practical value.

G. D. H.

731. April Completions Continue Increase Started in March. Anon. *Oil Gas J.*, 27.5.43, 42 (3), 115.—1351 wells were completed in U.S.A. in April, 58 more than in March. 767 were oil-wells, an increase of 61 on the March figure. Illinois completions rose by 21 to 156, Appalachian completions by 52 to 262. The decline in Oklahoma completions continued. The number of wells in the 5000–10,000 ft. class has increased to 206, compared with 179 in March and 144 in February. The rise in this class of wells is seen in the Upper and Lower Gulf Coast fields as well as in South Texas.

1449 wells were completed in April 1942.

A table gives a summary of the April operations by States, with the types of completions, footage, numbers of wells in various depth ranges, and the numbers of wells drilling.

G. D. H.

Geophysics.

732.* Geophysical Operations at Peak Levels During 1942. E. A. Eckhardt. *Oil Wkly*, 5.4.43, 109 (5), 49.—In the early part of 1943 geophysical activity was above the average for the preceding year. The 4500 wildcats asked for in 1943 are almost 50% above the number drilled in any year previously, and need a corresponding expansion of geophysical activity. This expansion may not be possible, for those engaged in geophysical work are especially suited for the armed forces. Only 15–20% of geophysical personnel are eligible for occupational deferment, and already about 40% of the personnel have been lost to the forces or to civilian technical services.

During 1942 an average of 226 seismograph parties were operating in U.S.A., 35 more than in 1941. 42% of all reported seismic activity was in Texas, which probably contributed 40% of the 1942 reserve additions. An average of 58.8 gravimeter parties were operating in 1942, compared with 54 in 1941.

Geophysical supplies are a less serious problem than was generally expected, but man-power is the greatest source of uncertainty in planning next year's geophysical operations.

Diagrams show the number of seismograph parties operating since the beginning of 1938, and the distribution by States or areas of the seismograph and gravimeter parties during 1942.

G. D. H.

733.* Surface Analysis Can Now Tell Hydrocarbon Source. H. Henderson. *Oil Wkly*, 5.5.43, 109 (5), 82.—Stratigraphic traps are generally believed to be the big hope for additional oil supplies in U.S.A., and surface analysis is unique in prospecting, since it will locate stratigraphic traps. During the past eight years progress and improvements have been made in surface analysis, and it is now possible to differentiate between vegetable waxes and the hydrocarbons diffusing from underlying petroleum. Surface concentrations of hydrocarbons such as oil and gas seeps, and paraffin earth have always been considered as indications of oil at depth. This reliability is shown by the fact that in a single geological province they are credited with the discovery of 75 out of the 219 domes found prior to 1936. These may be considered as macroscopic soil-analysis methods. It seems reasonable to suppose that there are low-degree surface concentrations of hydrocarbons indicative of oil at greater depth or under tighter overlying beds.

In 1924 the Tomball field was outlined by the determination of the salinity of near-surface waters, and in 1929 it was found that relatively high concentrations of methane and ethane in the surface soils indicated petroleum at depth. In 1932 the Russians began to measure the concentration of hydrocarbons in surface soils. They fractionated the hydrocarbons and correlated high concentrations of the lighter fractions, such as methane and ethane, with gas at depth, and high concentrations of the heavier hydrocarbons with oil at depth. Work in U.S.A. since 1935 has led to agreement on the leakage of hydrocarbons from subsurface oil deposits, but there is no agreement on the mechanism. The mechanism may be largely diffusion, associated with effusion and permeation. Shallow fields, other things being equal, may be expected to give

greater surface concentrations of hydrocarbons than deep fields, and the escape of the light hydrocarbons may be one of the chief reasons for the low-gravity oil in shallow fields. Recent unconsolidated formations permit much more rapid diffusion than the older more consolidated beds. The pressure gradient, temperature, and formation permeability will affect the rate of leakage, while the retention of the hydrocarbon-gas molecules at the surface will be a function of the absorption characteristics of the surface formation. Thus the concentration of the hydrocarbons over a reservoir is dependent on a number of factors.

The generation of hydrocarbons from decaying vegetation complicates the use of soil analysis. Methane, ethylene, and waxes and fats may be formed from vegetable matter, and in soil analysis these must be distinguished from hydrocarbons from oil reservoirs. Sampling below the surface vegetable hydrocarbon contaminated zone does not give a satisfactory method, and therefore a physico-chemical method has been used to differentiate between vegetable waxes and hydrocarbons which have diffused from petroleum at depth. Relatively recent alluvium and man-made fills will be low in hydrocarbon concentrations.

The form of the hydrocarbon concentration profile is discussed for several simple cases.

Surface analysis is rapid, inexpensive, and does not use large quantities of critical materials, though there remains some doubt regarding its oil-finding power.

G. D. H.

Drilling.

734.* Drilling Well Inside City Limits Made Noiseless and Safe. W. A. Sawdon. *Petrol. Engr.*, March 1943, **14** (6), 47-50.—The paper describes the drilling rig built in the heart of the city of Los Angeles. Because of the location and the restrictions imposed, the surface equipment for this well had to be insulated against noise and fire hazard. The derrick is of standard steel construction, but, after erection, was first enclosed with a wooden framework shown photographically in accompanying illustrations. The inside of the framework was covered with chicken wire to hold a thick covering rock-wool, which was then placed within the frame structure to insulate against sound. Outside of the rock-wool, sheets of transite mineral board were attached to the wooden members to make the structure fire-proof as well as sound-proof. This combined insulation covers the entire derrick structure, including the engine-house. The dog-house with lockers is placed on the ground away from the derrick floor, to provide greater convenience for the men.

The only openings in the derrick structure are a small one at the top above the crown block, and another on the side about derrick-floor level for bringing in pipe, tools, and materials. Electric lights must, of course, be used day and night, but reflectors prevent any upward glow through the small opening above the crown-block. Two fans on the derrick floor circulate the air and keep it moving upward through the opening at the top. The side opening is covered with a vertical sliding door insulated like the rest of the building. As there are objections to opening this door at night, 90-ft. stands of drill-pipe are made up during the day and placed on the rack within the derrick for use when needed. A "mouse-hole," in addition to the rat-hole, has been provided to take one 95-ft. stand of pipe. Details of the constructions are described and illustrated.

A. H. N.

735.* Correct Method of Applying Clips to Wire Rope. F. L. Spangler. *Petrol. Engr.*, March 1943, **14** (6), 58.—By a diagram and a photograph wrong and right methods of applying clips to ropes are given. Particulars for number of clips, etc., are summarized in following table:—

Rope Diameter, in.	Number of Clips.	Spacing of Clips, in.	Length of Wrench, in.
$\frac{1}{4}$ to $\frac{3}{8}$	3	3	12
$\frac{3}{8}$ to $\frac{1}{2}$	4	$4\frac{1}{2}$	18
1 to $1\frac{1}{4}$	4	6	24
$1\frac{1}{4}$ to $1\frac{3}{8}$	4	7	24
$1\frac{1}{2}$ to larger	5 to 7	10	24

736.* Multiple Batch-Squeeze Cementing. S. P. King. *Petrol. Engr*, March 1943, **14** (6), 74.—Multiple batch-squeeze cementing jobs can be more efficiently supervised by utilizing brief forms that convert the entire job into a series of gauge-tank measurements. This technique has been found especially adaptable in foreign fields where native labour and the lack of modern cementing equipment and trained personnel frequently augment the petroleum engineer's responsibility on the job. Many improvised cementing units consisting of pumps, slurry tanks, and mixing hopper mounted on truck or trailer, if properly handled, can function very efficiently. The usual lack of flexibility in pumping, inability to achieve any adequate mechanical control over mixing speed or slurry weight, plus the not infrequent unavailability of a particular type of cement for a specific purpose, tend to complicate a straightforward cement job. In these circumstances it is to the engineer's advantage to organize his work to provide a maximum allowance for any eventualities requiring his personal supervision.

The author illustrates these remarks by giving the details of a typical job, including the calculations which are necessary and the procedure to be adopted. A. H. N.

737.* Recent Developments in Formation Logging. Part 2. L. C. Uren. *Petrol. Engr*, March 1943, **14** (6), 84.—The normal geothermal gradient is about 1° F. for each 60 ft. of depth, in some localities much greater, but this is appreciably altered in the vicinity of formational intervals in wells where gas is expanding or liquids are flowing from the well into the formation, or vice versa, or where chemical change is occurring—as, for example, in the setting and hardening of cement behind casings. Knowledge of these local variations in the normal temperature gradient is of assistance in locating the positions of water, oil and gas sands, or gas-oil contacts in producing reservoirs, in determining variations in permeability of component members of an oil and gas-producing zone, locating casing leaks or the source of water entering a well, or locating the top of a column of cement in the annular space behind a string of casing. Temperature surveys have the advantage over some other methods of gathering subsurface information, in that they can be applied to the inside of casing.

Thermometers used in making temperature surveys in wells are of three types. (1) The maximum mercury thermometer, which, on being lowered into a well and withdrawn, indicates the maximum temperature reached. (2) The self-contained continuously-recording type, which is designed to be lowered through the well on a wire line and indicates the temperature at all depths on a record contained within the instrument, the results being available only after the instrument has been withdrawn to the surface. (3) The continuously-recording type, in which only an instrument responsive to thermal change is lowered into the well, while the temperature is simultaneously indicated or recorded on an instrument at the surface. The three types are described in some detail.

The use of temperature logging for detecting the presence of oil or gas sands, or the level of cement behind casings and for correlation of formations is described.

The paper ends with a discussion of inspection drilling mud as a method of logging with a trailer—mounted set of instruments. In the process of drilling, the bit disintegrates the formation in its path, and fluids present in the pore spaces of the rock become a part of the liquid phase of the drilling fluid. Though the amounts of oil, gas, or salt water thus added to the drilling fluid are small, they are sufficient to be clearly apparent in the delicate tests that are applied to the fluid after it reaches the surface. In order to correlate the fluid detected by such tests with a stratum from which it came, it is necessary to take into account the time intervening between the drilling of the material and its delivery at the surface in the drilling fluid. A log of rate of penetration versus depth is also obtained, and differences in the recorded rate of penetration may be used as an index of the lithologic properties of the strata penetrated. The depth to the top and bottom of each sand stratum is thus disclosed, and sands are clearly differentiated from shales. The test equipment employed in this system of logging may be divided into two groups: that used for detection of oil, gas, and salt water in the drilling-fluid returns, and that necessary in registering the depth of the well, the rate of penetration and rate of drilling fluid circulation. The latter must be known to correlate surface observations with the depths to which they relate. The instruments used are electrically operated, and power for operating them is obtained either from the source that drives the drilling rig, or from a 1½-kw. gasoline-engine-

driven generator carried as a part of the equipment of the trailer laboratory. The measurements taken and the methods used are briefly described. A. H. N.

738.* Special Equipment Controls Shallow Depth Blowouts. Anon. *Oil Wkly.* 26.4.43, 109 (8), 30.—Certain fields in west Texas present a problem of small blowouts due to high-pressure pockets of nitrogen being encountered at shallow depths where the mud head is insufficient to hold the gas down. To minimize the danger and losses due to these blowouts, one company worked out the following system—the mud line was shortened and a section of pipe larger than normal mud outflow line inserted just ahead of the screen. This enlarged section, in addition to providing space for expansion of gas carried in the mud stream, was also opened at the top with a wide cut-away section or slot. A gas-laden charge of mud, reaching this point, would seem to explode, most of the gas and a little mud being blown vertically through the slot, saving the screening equipment just beyond from the force of the blast. A quick-closing valve was installed in the mud flow-line, at a convenient point below the derrick floor, the weighted arm of the unit being normally held up by means of a chain supported in a quick-release fastening set into the derrick floor. Since positive, quick closing was of more importance than positive seal against all flow, the packing on the stem of this valve was left loose enough to insure that binding at this point would not defeat the snap action of the weight in closing it.

While drilling through the danger zone the master bushings in the rotary are locked in place to prevent their being literally blown from their socket by the force of the blow up along the drill-string. Since modern rotary tables provide some means of securing the bushings within the table, this step merely involves provision of proper locking bar and its use through the danger zone. When the blowout is approached, a close watch is kept on the flow-line vent and, if a blowout is indicated, the locking chain is released and the quick-acting valve is closed. This eliminates any possibility of damage to the mud-conditioning machinery and confines the blowout to the cellar area. The drilling fluid is, of course, blown straight up against the locked master bushings—and falls back into the cellar to be recovered. A. H. N.

739. Patents on Drilling. A. Boynton. U.S.P. 2,314,867, 30.3.43. Appl. 22.9.38.—Semi-threadless drill stem.

W. B. Noble and J. E. Hoffoss. U.S.P. 2,314,947, 30.3.43. Appl. 23.11.40.—Core-bit with roller-cutters below the slush passage-ways.

W. D. Mounce. U.S.P. 2,315,127, 30.3.43. Appl. 12.10.39.—Resistance thermometer adapted to be lowered into a hose-hole.

E. J. Roach and E. F. Cooke. U.S.P. 2,315,134, 30.3.43. Appl. 3.11.41.—Well control head for oil.

A. R. Maier. U.S.P. 2,315,157, 30.3.43. Appl. 14.6.41.—Draw-works.

S. A. Scherbatskoy. U.S.P. 2,315,355, 30.3.43. Appl. 30.4.40.—Well surveying method and apparatus using a detector of radioactivity in the drill-stem.

J. H. Wilson. U.S.P. 2,316,304, 13.4.43. Appl. 16.1.40.—Mast pole derrick of the portable type.

D. G. C. Hare, U.S.P. 2,315,329, 13.4.43. Appl. 18.6.40. Subsurface prospecting by investigating the formation surrounding a bore-hole by means of a source of neutrons.

R. G. Piety. U.S.P. 2,316,361, 13.4.43. Appl. 17.3.41.—Method and apparatus for surveying wells by determining the distribution of radioactive material in the earth surrounding the well.

A. B. Canon. U.S.P. 2,316,402, 13.4.43. Appl. 19.8.40.—Cementing wells and using a packer.

L. R. Downing. U.S.P. 2,316,409, 13.4.43. Appl. 5.12.41.—Oil-well straightener to be used above a drill-bit.

R. E. White, W. E. Liljestrand and A. S. Volpin. U.S.P. 2,316,480, 13.4.43. Appl. 3.8.40.—Flat-top slush pump-valve.

R. E. Fearon. U.S.P. 2,316,576, 13.4.43. Appl. 14.8.40.—Well-surveying method and apparatus using an electric circuit with an ionization chamber. A. H. N.

Production.

740.* Mid-Continent Reconditioning Practices Entering New Era. Part 1. L. E. Elkins, R. H. Smith, L. F. Peterson, and P. P. Manion, Jr. *Oil Wkly*, 29.3.43, 109 (4), 22. *Paper Presented before American Institute of Mining and Metallurgical Engineers.*—In order to determine if reconditioning is desirable or possible, certain specific questions must be considered. They may be generalized as follows:—(1) Is the well in good "mechanical" condition, or is some plugging agent or extraneous fluid restricting, in some manner, the otherwise normal flow of oil or gas? (2) Is there sufficient oil or gas remaining in the area of drainage influence of the well in question to justify reconditioning operations? (3) At what interval within the section is the objective oil or gas zone located? (4) Is there sufficient reservoir energy to supply the motivating force to move this oil towards the well-bore? (5) Is the distribution of fluid (oil, gas, and water) in the section of the reservoir around the well, in relation to the permeability profile, such that the desired oil or gas can be selectively withdrawn if necessary? (6) What mechanical operation is required to accomplish the objective? (7) Are the physical characteristics of the pay section, reservoir pressure, and the shape of the penetrating well-bore such that the mechanical operation can be accomplished? (8) Would reconditioning be economic?

Reconditioning operations may be divided into three general classifications, as follows: (1) The problem of eliminating extraneous forces and their restrictive action on the normal flow of oil and gas. (2) The problem of increasing the drainage efficiency of a well by either extending its vertical or lateral sphere. (3) Means of reconditioning wells to establish selective withdrawal, and thus conserve energy or reduce lifting expense through reduction of free gas or excessive water production. Part 1 of the paper deals with class (1), the other two classes being discussed in parts 2 and 3.

The above restrictive forces are primarily plugging agents. They become stuck to, or bridged in, the natural channels of permeability. Many times the restricting action is obvious because of unusual decline in productivity, and its removal is simple, and requires no special innovation. The use of sand-pumps, special bailers, reverse circulation processes, acid-jet guns, wall-scrapers, under-reamers, application of heat, and such, all have their field of application in removal of plugging agents in open hole and sometimes behind the pipe. If the operation is not one of the relatively simple cleanout type as listed above, more basic data and more specialized technique may be required. Complications develop many times when pipe is set through pay formations, or if the plugging agent penetrates into, or is deposited deep in, the channels of permeability. Then the reconditioning either requires removal of the plugging agent by abrasion, or scraping, or by solvent action, or it may be necessary to create new permeable channels by shooting or its equivalent. Plugging back, side-tracking, and re-drilling the pay section may sometimes be justified if the plugging agent is deposited by the oil-stream as it converges on the well-bore. Case histories have been prepared to illustrate how two of these typical problems develop and how they can or might be solved. These case histories are presented with full illustrations. A. H. N.

741. Some Factors Affecting the Economics of Gas Cycling Plant Design. R. L. Huntington. *Refiner*, April 1943, 22 (4), 100-103.—There are a number of engineering studies to be made before final consideration is given towards the design of a condensate and natural-gasoline-recovery plant. (1) The estimation of the condensate, natural gasoline, and dry gas reserves in the field, based on geological and physical test data. (2) An electrolytic model study of the field in order to determine the arrangement of input and producing wells for the best flooding pattern. (3) A study of market outlets for liquefied and gaseous products.

Owing to the heavy demands for the lighter hydrocarbons, the trend in the construction of condensate-recovery plants has been towards the installation of centralized oil-absorption plants. Each field presents its own problems, such as that of the selection of optimum operating pressures and temperatures, depending on the composition of the reservoir fluid to be processed. Other factors, such as the balancing of gas-compression cost against the recovery of condensate and natural gasoline, are

discussed. Mathematical derivations are given for the determination of the optimum inter-stage pressures whenever the ratio of discharge pressure to intake pressure runs too high for economical single-stage operation.

A. H. N.

742. Salt-Water Disposal in Kansas. N. Williams. *Oil Gas J.*, 1.4.43, **41** (47), 29-30.—The fields discussed produce very large amounts of water, and State regulations now prohibit impounding of water or other disposal except in wells. Disposal of water in wells has presented a number of problems, both physical and economic. Not only has it been necessary to provide wells capable of taking the water in sufficient volume, but special precautions have been necessary to insure that injected water would not enter any formation in which fresh-water supplies or oil production would be endangered. Also involved has been the adoption of suitable methods and facilities for handling and treating the water. Chief concern, in view of the comparatively low potential oil recovery remaining in some of these fields, has been the need for holding costs of disposal to an absolute minimum. Principal formations used at this time for water injection are the Arbuckle lime, the granite wash, and the Reagan Sand, which lies below the Arbuckle. The Dakota Sand has been used to some extent in certain areas, but this is a shallow horizon, and is sometimes a source of fresh-water supply. A survey is now under way to determine the extent of potentialities of this sand for water disposal. The Arbuckle lime, usually found around 3250 ft., is the main oil-producing horizon of the area, but it has a very active water drive and is a large producer of water, and with water returned to down-structure locations no complications arise. The Reagan Sand is particularly suitable sand in those fields where it is known not to carry oil or gas. Although various shallow sands have been used, injection to them is rapidly being discontinued in favour of the lower horizons.

The method used is discussed.

A. H. N.

743. Catwalk Facilitates Servicing of Heavy-Duty Pumping Unit. N. Williams. *Oil Gas J.*, 1.4.43, **41** (47), 40.—The maintenance connected with the walking beams of heavy-duty pumps presents a difficult problem of safety. An operator in the Oklahoma city field has solved the problem by providing a catwalk which extends outward in each direction from the Sampson Post position to the ends of the walking beam. It is supported in the structure of the pumping derrick by the side of the walking beam, and at a height convenient for the pumper to lubricate or adjust the working parts. That half of the catwalk which extends inside the derrick to the beam-head assembly over the well is supported on a pivot hinge at the centre point, so that it folds upward against the back of the derrick when not in use. This places it out of the way when the well is in operation, or when rods or tubing are being pulled.

The folding section swings upwards out of the way automatically by means of a counterweight arm extension, which also holds it in its upward position. It is balanced so that only slight effort is required to lower it. The weight of a man holds it downward in working position. The back section extending to the pitman bearings is stationary, and is supported at its outward end by two cables, one on each side, secured into the derrick above, and by two bracing arms on the underside.

A. H. N.

744.* Gas-Oil Ratio Calibrations Used to Measure Gas in Gas-Lift Wells. D. Attaway. *Oil Wkly*, 19.4.43, **109** (7), 18-20.—Measuring gas-flow records into and out of wells on intermittent gas-lift by means of seven-day recording charts gave one company a difficult problem. The cause of this condition was the fact that gas-lift units were equipped with time clocks or automatic injection devices to operate at set intervals, such as 15-minute periods, 10-minute periods, etc. When the valve opened to admit a charge of gas to the well, the gas-flow reached peak velocity immediately and the differential pen swept out to recording position in almost a straight line. Usually the injection period consumed only 2 or 3 minutes and the automatic valve shut off completely, causing the differential pen to fall back almost instantly down the same line it had recorded in ascending. Such a record was certainly unreadable. Dampening plugs and other devices were unsatisfactory, as they actually retarded differential pen movement.

The solution of the problem selected was the use of gas-oil ratio tests. Several special-type clocks were purchased having devices for setting the rotating time at 1-, 3-, or 6-hr. intervals. The process involved a tester or meter man making a visit to the

lease using gas-lift and removing the 7-day clock from the lease meter. A "fast" clock was installed and a chart placed on the meter. The meter was tested for "zero" and then placed in service. The oil-storage tank into which the well was producing was then gauged. Both the injection-gas meter and the production-gas meter could be fitted with the special clock for the test period. If the clock was set for a 1-hr. rotation and the well intermitter operating on a 15-min. schedule, the chart would secure a record of four injections. As the orifice meter clock is running at a very fast speed, the differential hand, in moving out across the chart, covers some distance. If the injection period is as short as 3 or 4 min. almost $\frac{1}{2}$ of the chart surface passes beneath the differential pen during the injection. Such a record is very readable and accurate.

In order to secure an average and representative record of the well's behaviour and operation, a chart might be taken every hour for 3 hrs. In cases of varying recordings, the test might be extended to 6 hrs. Wells having injection periods 30 mins. apart might use a clock rotating in 3 or 6 hrs. Such a clock speed will be ample to record a very readable differential record. At the conclusion of the test, whatever its period, a gauge must be taken of the well's production during the period. Having secured readable charts and knowing the well's exact production, it is possible to calculate the amount of gas required to lift a barrel of oil. Using the production-gas meter, the amount of gas produced with each barrel of oil can be determined.

Typical examples are given.

A. H. N.

745.* Mid-Continent Reconditioning Practices Entering New Era. Part 4. L. E. Elkins, R. J. Smith, L. F. Peterson, and P. P. Manion, jr. *Oil Wkly*, 19.4.43, 109 (7), 21-28. *Paper Presented before American Institute of Mining and Metallurgical Engineers.*—During the natural evolution of petroleum technology, the problem of proper use and conservation of reservoir energy has gradually advanced to a front-line position. Although conservation is usually found enveloped in studies of the reservoir as a whole, the individual well is the means through which conservation must be achieved. The flow of fluid into and from the well results in an expenditure of energy which, in many reservoirs, is at least partly irreplaceable. Therefore the problem of selective withdrawal is one which has rapidly come into focus. In reality, selective withdrawal can be applied in two general ways. It can often be applied to a reservoir as a whole—that is, oil or gas production may be restricted to certain areas in a field in order to limit water or free gas production, an excess of either often representing inefficient use of reservoir energy. This type, to be effective, requires unitization or some type of co-operative operation.

The other type of selective withdrawal is confined to the individual well and, to be realized, frequently requires complex workover operations. This is discussed in great detail under the headings of water shut-off and the exclusion of gas. Ordinary and squeeze cementing are discussed. A number of typical workover cases are quoted and discussed.

It is concluded that the technique of reconditioning oil-wells is rapidly approaching the stage where a minimum of guesswork has to be relied upon to solve the individual problem. This has been brought forth by the initiative and co-ordinated efforts of oil-producing companies and active service companies.

The paper is followed by a discussion on certain of the points raised—mainly on water shut-off jobs.

A. H. N.

746. Loco-Hills Pressure Project Indicates Increased Recovery. G. M. Wilson and F. Briggs. *Oil Wkly*, 19.4.43, 109 (7), 30.—Early realizing that co-operation among themselves would mutually benefit each operator through prolongation of the life of the field, a conservation programme involving a pressure-maintenance project was put into effect in October 1941 in the Loco Hills Field of New Mexico. With the exception of two operators in the field, an association of Loco Hills producers carries on this conservation programme as a non-profit making, incorporated organization, employing an operating staff consisting of a superintendent, engineers, and clerical personnel. Since the pressuring operations were begun, the bottom-hole pressure and gas-oil ratio tests have indicated a trend towards a maintenance or improvement of these factors. The average bottom-hole-pressure curve for the field began to level off in March 1942, and this condition has been maintained to such an extent that operators,

previously estimating 4500 brls./acre, now believe recovery will be in the neighbourhood of 10,000 brls./acre.

The Loco Hills Field is described, together with some of its history and organization.

The most recent survey taken, in January 1943, shows a gain on reserve pressure on twenty-four wells over the previous survey of September 1942. In October 1941, when the plant was put in operation, there were twenty-seven pumping wells in the field. During 1942 only two additional wells were placed on the pump. These two wells were making a small amount of water. Several of the pumping wells have shown an increase in production, and it is the general opinion of many of the operators that, without repressuring, many more wells would have been pumping by the end of 1942.

A. H. N.

747.* Systematic Measures Would Increase Production of Old Shallow Wells. J. Schmer. *Oil Wkly*, 26.4.43, 109 (8), 33.—To increase the production from old shallow wells certain instructions are given. (1) Increase or restore the gas pressure in all wells through injecting compressed gas or air in a few carefully selected input wells. (2) Clean, systematically, well after well, starting with the oldest and lowest producing wells, in the manner prescribed in the paper, which involves pulling the pump, cleaning the sand-face with a tool, and heating the formation by hot oil or steam. (3) If the results, after applying all the above measures, are not satisfactory, shoot the oil sandstone, but only if this formation is "free" (below the casing), or if the casing can be moved higher without much difficulty and without danger of opening the water. The results are often sensational, and are well worth trying. Some wells have increased their production 5000% with these methods. (4) In the event that shooting was not successful or was impossible to apply for technical reasons, deepen the well after consulting an experienced geologist who is familiar with this terrain. (5) If production does not increase, salvage casing and drill new wells.

A. H. N.

748. Patents on Production. A. Boynton. U.S.P. 2,314,868, 30.3.43. Appl. 8.12.39. Flowing device, tubing and casing-flow for gas-lift.

A. Boynton. U.S.P. 2,314,869, 30.3.43. Appl. 8.12.39. Differential stage-lift flow-device for gas-lifting of liquids.

H. M. Stevenson. U.S.P. 2,315,023, 30.3.43. Appl. 10.6.39. Water-drain for floating roof tanks.

J. H. McKean and E. K. McKean. U.S.P. 2,315,069, 30.3.43. Appl. 17.4.40. Scraper for removing paraffin deposits from the interior of a conduit.

S. Bullum. U.S.P. 2,315,152, 30.3.43. Appl. 14.10.40. Pump-pull rod adjuster for pumping-wells.

A. Germany. U.S.P. 2,315,414, 30.3.43. Appl. 8.7.41. Sucker rod coupling using overlapping pins and a sleeve.

J. C. Luccous. U.S.P. 2,315,437, 30.3.43. Appl. 27.11.41. Perforator for well-pipes using a knife.

A. M. Baudy. U.S.P. 2,316,216, 13.4.43. Appl. 16.11.40. Apparatus for taking samples of fluid from wells.

B. Henderson. U.S.P. 2,316,429, 13.4.43. Appl. 7.4.41. Inverted cylinder pumping unit for oil-wells.

L. Trager. U.S.P. 2,316,492, 13.4.43. Appl. 26.8.41. Fluid-meter of the nutsting type.

R. Tipton. U.S.P. 2,316,494, 13.4.43. Appl. 12.5.41. Oil-well pump-controller where the prime mover is an electric motor.

H. T. Kennedy. U.S.P. 2,316,596, 13.4.43. Appl. 4.11.38. Shorting wells for increasing their productivity.

P. M. Evans. U.S.P. 2,316,679, 13.4.43. Appl. 22.12.41. Coupling device for well apparatus such as pumps.

R. R. Thompson and W. D. Mounce. U.S.P. 2,316,728, 13.4.43. Appl. 17.10.40. Gun perforator for wells.

A. H. N.

Synthetic Products.

749.* **Properties of Rubber Solutions and Gels.** M. L. Huggins. *Industr. Engng Chem.*, 1943, 35, 216.—From published experimental work and thermodynamic equations, a series of constants have been calculated for various natural and synthetic rubbers and a large number of solvents, which enable the molecular weight to be determined from osmotic pressure and cryoscopic data. J. W. H.

Refining and Refinery Plant.

750. **A Method by Which Refining Plants May Accumulate Scrap Metals Using Sound Business Principles.** G. M. Dent. *Refiner*, March 1943, 22 (3), 65-67.—A tally system is described. The economics of salvage are also discussed. Estimates of the value of materials taken into the salvage yard are based on the percentage of probable stores valuation which will be assigned to the material on completion of reconditioning. An arbitrary standard "percentage of original value" of 80% for all reconditonal material delivered into stock is used, with the following exceptions: (a) New material broken or damaged during installation and sent to the salvage yard for repair is returned to stock at 100% of original value. (b) Pipe and fittings under 2 ins. in size and bolts and nuts and similar small material are returned to stock at 100% of new value. (c) Materials which cannot be reconditioned to meet specifications of the service for which they were originally purchased and used, but can be substituted in other services, the requirements of which are not so exacting, are returned to stock at 80% of the original value of materials for which they can be substituted when reconditioned, and not at 80% of their own original value. Examples are furnace tubes which are removed due to the walls having reached the minimum thickness allowed for furnaces, but which can be used further as a substitute for standard pipe- or 150-lb. steel valves which can be reconditioned for 125-lb. cast-iron service, but are not suitable for further use in services where 150-lb. steel is required. A. H. N.

751. **Seal-Oil Systems for Refinery Centrifugal Pumps.** I. Taylor. *Refiner*, March 1943, 22 (3), 68-72.—In a centrifugal pump the principal parts of a mechanical seal are the two ring-shaped seal-faces which both encircle the shaft side by side, as two rings on a finger. When the pump is running, one ring is rotated by the shaft against the other, which is stationary—a construction somewhat similar to a single-collar thrust-bearing, but without appreciable thrust. These rings or collars and other parts are so positioned in the packing box that the only possibility of liquid escaping through the box would be by a separation of the seal-faces. But this must not happen, so the two rubbing seal-face surfaces are constantly held together, sometimes by hydraulic pressure, sometimes by a coil-spring or a set of small springs arranged to press one of the rings against the other axially. Springs are used to prevent the formation of any gap between the seal-faces while the pump is stopped, and to help prevent separation which might occur due to end-play or whipping of the shaft while running. In some cases the springs rotate with the shaft, holding the rotating collar axially against the stationary collar. (The latter often serves also as the pump-throat bushing or as the packing-box gland.) In other instances, stationary springs may press the non-rotating collar against the rotating one which is locked on the shaft. In either case there must be provision for a slight amount of axial sliding of one of the seal-ring collars to maintain the closure constantly. To prevent any liquid from leaking past the seal through this joint of sliding, it is the practice to arrange the sliding member with a single ring of rubber or neoprene, or sometimes a metal "piston ring," to act as a flexible gasket. Lubrication is usually required, and the lubricant is called "seal oil."

The following is a list of the various sealing methods frequently used for centrifugal pumps in refinery services: (1) Several compressible packing rings, divided into two sections by a lantern ring (sometimes called a water-seal cage), which permits introduction of a lubricant near the centre of the packing space. (2) Compressible packing rings and lantern ring, the same as arrangement No. 1, plus a special connection to a labyrinth-type throat bushing or pressure-reducing device at the inner end of the box, to permit either—(a) *Bleeding out* a small amount of liquid from the pump to a lower

pressure (to reduce pressure on the packing rings), or (b) *Injection* of a different liquid from the outside (so that packing rings will not be subjected to the liquid being pumped). (3) Single mechanical seal, usually having the rotating unit inside the box and surrounded by the liquid being pumped. Sometimes arranged with a groove in the stationary-seal face for introduction of a lubricant to the seal faces only. (4) Double mechanical seal, with both rotating units inside the box surrounded by a lubricating seal oil, the seal oil maintained at a pressure slightly higher than the internal pump pressure which acts at the packing-box throat bushing. Each type is illustrated and discussed in some detail.

The replacement of packing by double mechanical seal in centrifugal pumps necessitates the purchase of such a considerable amount of additional special equipment that a refiner might question the advisability. However, mechanical seals that have given very fine service for three or four years are still running, and have operated almost continuously with a leakage of only $\frac{1}{4}$ pint/24 hrs./packing box, after "wearing-in." This is very satisfactory progress, justifying their use and showing that much has been accomplished towards eliminating some of the trouble, expense, hazard, and unsightliness which go with the use of packing.

A. H. N.

752. Automotive Engines Adapted to Water Pump Drives. Anon. *Refiner*, March 1943, 22 (3), 73-75.—The paper describes the conversion of used truck and bus engines to stationary engines used to pump water for cooling-tower purposes. Support bases were made of channel steel. Connecting each engine to its pump was done with a conventional flexible coupling eliminating the original clutch and gear-box of the bus engine. A short stub-shaft, the size in diameter to match the companion section of the flexible coupling, was welded to a circular plate of heavy steel trimmed to fit in the depression in the centre of the flywheel and bolted to that member of the engine and the crankshaft flange with adequate cap screws. The stub-shaft and flange welded to it was placed in a jib to obtain the necessary straightness, and afterwards faced in a lathe for finishing. The remainder of the connecting job resolved itself into routine mechanics, and was done in the same manner as that accomplished with any other power drive. The exhaust manifold was changed into a water-jacketed unit.

A. H. N.

753. Protective Lighting of Oil Refineries. R. M. Swetland. *Refiner*, March 1943, 22 (3), 77-79.—The paper deals with lighting of refineries where no permanent blackout is imposed, although rapid emergency blackout is contemplated. The principal objectives of protective lighting for oil refineries are: (1) To assure adequate visibility and convenience to guards under the most adverse weather conditions, (2) to assure this visibility despite possible intermittent lamp outages, and (3) to assure maximum discouragement to the would-be intruder. There are two generally accepted and proven methods by which refineries may be lighted efficiently for night protection. By the use of boundary-fence lighting, or through the use of area lighting. The physical make-up of the refinery and its daily working schedule are usually deciding factors in the final choice of the most effective protective-lighting system. If the plant areas are enclosed by a boundary fence with little or no plant activity at night, fence lighting should constitute an effective solution to the problem. Whether or not a boundary fence exists, properly engineered area flood-lighting will offer satisfactory night-time protection against illegal entry to the property, and will serve the additional purpose of allowing efficient operation of the plant at night. The design of such systems is briefly studied.

A. H. N.

754. Compressor Maintenance. Anon. *Refiner*, March 1943, 22 (3), 80-84.—Detailed description is given of the appropriate precautions to be taken and practices to be adopted in the maintenance of compressors to yield efficient working for maximum periods. Starting of new or old overhauled compressors is discussed in full. Systems of inspection are recommended. Lubrication is studied. As many as three different types of oil may be required by a reciprocating compressor, one type for the compressor cylinders, another for the bearings of the driving gear, and a third for the power cylinders, provided the source of power is steam, diesel, or gas engine. Oil intended for compressors of the single-acting trunk piston type must be suitable for both the

compressor cylinders and the running gear, and must be of the type known as compressor-cylinder oil with specifications suitable for the particular machine. Double-acting piston-type compressors, in which the frame, running parts and the compressor cylinders are completely separated, require cylinder oil for the compressor cylinders and crankcase or bearing oil for the running gear. Specifications for oils for the compressor and the steam cylinder are given.

Centrifugal compressors and exhausters require bearing lubrication only, and in overhung units with no bearings of their own only the driving mechanism is lubricated. Ball or roller type anti-friction bearings on small pedestal or multi-stage units require grease or oil in the usual manner. Larger and higher speed units generally have pressure-lubricated sleeve bearings.

The maintenance of auxiliary equipment, *e.g.* piping, coolers, valves, etc., is discussed.

A. H. N.

755. The Stabilization of Crude Oil. Part II. F. L. Kallam. *Refiner*, March 1943, **22** (3), 89-94.—The review of stabilization by years begun in Part I is continued in this part of the paper, beginning with 1937 and ending with 1942. The conclusion reached is that it is obvious that crude-oil stabilization has made some progress during the past sixteen years, but the record indicates that the oil industry has yet failed to grasp fully the economic possibilities of the process. This is to say that complete understanding is still lacking as to the benefit resulting from controlled evaporation brought about by means of fractionation. It is necessary to realize first that only through fractionation is it possible to remove from the oil the light undesirable fractions and still retain all of the heavier and desirable constituents. In accomplishing this retention by fractionation it is usually possible to increase both the volume and the gravity of the oil sold without increasing the evaporation tendency in the lease tanks. This follows from the fact that in controlled removal of the light hydrocarbons, the percentage of the remaining heavier fractions can be increased without disturbing or changing the value of the vapour pressure of the original oil.

The problem of whether or not to stabilize the crude oil calls for very careful engineering study, with the overall interests of the company kept foremost in mind. It is apparent that the subject of oil and gas separation is not one to be decided by any one department or individual, but rather by its relationship and importance to the entire project of oil and gas production. Every problem of crude-oil stabilization must be solved for the particular oil and gas characteristics of the field considered. The question of temperatures and pressures of separation are involved, to say the least, and are further complicated by the allied subject of stages to be employed. The final selection will be governed by the field conditions, methods of production and the physical characteristics of the oil and gas. About the only generalization possible is that one separation should be conducted at the highest optimum pressure. This will permit economic venting of the ethane and lighter materials from the oil with the minimum loss of desirable and valuable hydrocarbons.

Under certain field conditions, the installation of a crude-oil stabilizer unit can be arranged to eliminate the necessity of a natural-gasoline plant. In most cases, however, the crude-oil stabilizer will fit conveniently into an existing operation involving the conventional gasoline plant. It should always be remembered that one of the advantages of the crude-oil stabilizer is that it results in the saving of gas-compressor capacity. This results from the fact that vapours removed from the crude oil in the stabilizer are made available at a higher pressure than would be the case if they were released in the ordinary low-pressure trap or at the lease tanks. Producing stabilized oil into lease-tanks does away with weathering losses and automatically eliminates the need for any form of vapour-recovery system. Similar savings will result at all tank farms and in handling through the pipe-line and the refinery.

In fields where the oil production is accompanied by hydrogen sulphide, the crude-oil stabilizer will serve as an excellent scrubber and economic remover of this corrosive agent. Likewise, by adequate design, the stabilizer can lend itself to the problem of dehydration of the oil and the removal of salts and other sediments. A. H. N.

756.* Bead Catalyst. Anon. *Nat. Petrol. News*, 17.3.43, **35** (11), 18.—The production of a new synthetic catalyst in the form of small translucent spherical particles is announced. The new material is claimed to increase yields by 13-30% and to produce

such an improvement in octane number that the available power output of an aero engine is increased by 23–35%. The catalyst is claimed to be robust and to possess exceptional catalytic activity with little loss in practice. Existing plants are said to be easily adapted for the use of "beads."
H. G.

757. Method of Design of Steel Stacks and Foundation. S. Levine. *Refiner*, April 1943, **22** (4), 116–117.—A typical problem, which the author had to solve in practice, is presented, and the steps taken in solving it are summarized.
A. H. N.

758. Effective Treating for a Small Plant. Anon. *Refiner*, April 1943, **22** (4), 118–119.—Solution of treating problems in the small refining plant are difficult to accomplish for the reason that research and laboratory facilities are not comparable with those of the larger plants. The method used in one of the small plants of the west coast came into use through trial-and-error progress, so that now caustic washing of cracked distillate is employed in two stages, the first for the removal of H_2S and the reduction of mercaptan content in the second. The caustic solution of this second stage also serves to wash the vapour charge to the polymerization plant for H_2S reduction. The plant output is doctor sweetened. The treating method is of continuous operation with treating solutions regenerated. The plant is described and illustrated.
A. H. N.

759. Caustic in Vapour Stream Halts Corrosion. Anon. *Refiner*, April 1943, **22** (4), 123.—When excessive corrosion was found in the vapour line from the dephlegmator and in condensers in one of the west coast natural gasoline plants, investigation established that the cause was acidity in the vapour stream and its resulting condensate. The fact that in refining it is common practice to introduce alkaline solutions into vapour lines at many points, was in part responsible for the selection of a caustic injection as a means of neutralizing the destruction of sulphur compounds in this instance. The major problem was in the method introducing the solution. Because of the lack of desirable equipment, such as a proportioning pump or other force-feed appliance, recourse was taken to the method used in plants involving a blow-case, such as is seen in refiners manufacturing various grades of distillates and lubricating stocks. The system should, obviously, be as simply made as practicable, so that workers not familiar with gasoline-plant operation who might replace those inducted into the armed forces, might readily grasp the significance of the process and operate it without involved calculations and frequent manual manipulation.
A. H. N.

The process is described.

A. H. N.

Chemistry and Physics of Hydrocarbons.

760.* Vapour-Liquid Equilibrium of Methylcyclopentane-Benzene and other Binary Aromatic Systems. J. Griswold and E. E. Ludwig. *Industr. Engng Chem.*, 1943, **35**, 117.—Boiling point, relative volatility, and vapour-liquid equilibrium data are presented for the binary mixture methylcyclopentane-benzene. These data show that the mixture deviates appreciably from Raoult's Law and that a minimum boiling-point azeotrope occurs at 71.5° C. containing 90 mol.-% methylcyclopentane. A discussion of the results of other workers shows that benzene forms an azeotrope with cyclohexane of boiling point 70° C. containing 50 mol.-% benzene, and that, although no azeotrope of benzene with *n*-hexane has been proved, it is probable that one exists having a boiling point only 0.1° C. below the boiling point of *n*-hexane containing approximately 3% benzene. No azeotropes of toluene with methylcyclohexane, *n*-heptane or *n*-octane are formed, but the relative volatilities decrease abnormally as the compositions approach the pure low-boiling compound.

These deviations from Raoult's Law explain the failure of good fractionation equipment to resolve six- and seven-carbon petroleum fractions into pure components when aromatics are present.
J. W. H.

761.* Solubility of Hydrogen in *n*-Butane. E. E. Nelson and W. S. Bonnell. *Industr. Engng Chem.*, 1943, **35**, 204.—The solubility of hydrogen in *n*-butane has been determined over the temperature range 24–116° C. and at pressures up to 100 atoms

Full details of the experimental technique employed are given, and from a plot of the bubble-point pressure against temperature it is shown that a minimum occurs for mixtures containing 3-4% hydrogen. The significance of this result is to indicate the existence of a region of isobaric retrograde recondensation at temperatures far below the critical region of the mixtures.
J. W. H.

762.* Liquid-Vapour Equilibrium Compositions in Hydrogen Chloride-*n*-Butane System. J. H. Ottenweller, C. Holloway, and W. Weinrich. *Industr. Engng Chem.*, 1943, **35**, 207.—The equilibrium liquid and vapour composition of the system hydrogen chloride-*n*-butane has been determined over the temperature range 70-180° F. and at pressures up to 550 p.s.i. Complete details of the experimental and analytical technique are given, and the data are presented in the form of bubble and dew-point curves and in the form of K-values at constant temperature. The data indicates that this system is in general agreement with Raoult's Law over the range investigated. On the basis of similarity between this system and the hydrogen chloride-propane system the data have been extrapolated up to pressures of 1000 p.s.i. At pressures above 600 p.s.i. it is shown that retrograde vapourization can occur on isothermal compression.
J. W. H.

763.* Surface Tension of Methane-Propane Mixtures. C. F. Weinaug and D. L. Katz. *Industr. Engng Chem.*, 1943, **35**, 239.—The surface tension of mixtures of methane and propane have been determined over the temperature range 5-194° F. and at pressures from 40 to 1500 p.s.i. A description of the experimental techniques employed are given, and the results have been correlated in graphical form, which reproduces the data to within 0.1 dyne/sq. cm. It is shown that in the critical region liquids have very low surface tensions.
J. W. H.

764.* Vapour-Liquid Equilibria of Close-Boiling Hydrocarbons. J. Griswold. *Industr. Engng Chem.*, 1943, **35**, 247.—Re-examination of the vapour-liquid equilibria of the systems *n*-heptane-methylcyclohexane has shown that this mixture may not be assumed to be ideal, and that the previously accepted value of 1.07 for the relative volatility must be revised to 1.083. The basis of the revision of this value is the verification of Bromiley and Quiggle experimental equilibrium data, which had been rejected by Beatty and Calingaert. The basis of the experimental technique employed for this verification was the determination of the relative volatility by means of a fractionating column containing a known number of theoretical plates as tested with other mixtures. By this method the relative volatility of the binary mixture *n*-heptane-isooctane has been determined, and found to be 1.023. This method is of great value in determining the relative volatility of closely boiling mixtures. It is concluded that ideality is only reached between two compounds of the same homologous series.
J. W. H.

765. Chemical Notations. P. H. Faust. *Refiner*, March 1943, **22** (3), 85-86.—An extremely elementary treatment of structural formulæ of hydrocarbons is presented.
A. H. N.

766. Some Physical Properties of Butadiene and Styrene. L. A. Wood and C. F. Higgins. *Refiner*, March 1943, **22** (3), 87-88.—Both the properties and the sources of information are given for 1:3-butadiene and styrene. The properties are given in metric and British engineering units. The following properties are tabulated: molecular weight, normal boiling point, freezing point, vapour density (for 1:3-butadiene only) and liquid density at different temperatures, thermal expansion, vapour pressure, and a formula for calculating it at various temperatures, rate of change of boiling point with pressure, latent heat of vaporization, heat of fusion, heat of formation of vapour and of combustion (for 1:3-butadiene only), specific heat, refractive index, rate of change of refractive index with temperature (for styrene only), dimensions of unit cell of crystalline 1:3-butadiene, surface tension of styrene and limits of flame propagation for both.
A. H. N.

767. Petroleum as a Source of the Aromatic Hydrocarbons. A. W. Trusty. *Refiner*, April 1943, **22** (4), 95-99.—Production of aromatics from coal is first discussed, and this is followed by a concise report on the occurrence of aromatics in petroleum.

Scarcely any aromatic hydrocarbons are found in natural gases. Small amounts begin to appear in the lighter liquid fractions from crude oils, and the aromatic content of the heavier fractions of a naphthenic-base crude oil increases considerably in volume. Rarely can a crude oil be found with sufficient aromatics present to justify commercial separation. For the production of aromatics from petroleum sources, it is necessary to use some thermal- or catalytic-cracking process. The most thorough investigation of the hydrocarbon constituents of a crude oil probably was the work done by the Bureau of Mines in A.P.I. Project No. 6. The amount of aromatic hydrocarbons present in Oklahoma crude oil is shown—benzene, 0.08%; toluene, 0.30%; *o*-xylene, 0.04%; *o*-xylene, 0.12%; *m*-xylene, 0.12%; ethyl benzene, 0.03%.

Bureau of Mines preliminary work on East Texas naphtha showed the following aromatic content: Benzene, 0.04%; toluene, 0.46%; ethylbenzene, 0.14%; *n*-propylbenzene, 0.04%; xylenes, 0.56%. Canadian workers have investigated the aromatic content of two Canadian crude oils, and found the following: benzene, 0.28 and 0.32; toluene, 1.07 and 2.00; and xylene and ethylbenzene, 1.45 and 2.50 respectively.

The following table is reproduced from a paper by Garner and Evans:—

Crude Oil.	Yield of Gasoline.	Benzene.	Toluene.	Xylene.	Total Aromatics up to 32° F.
Seminole, Okla.	36	0.1	0.6	1.5	2.2
Grosny, Russia	13	0.4	1.4	2.0	3.8
Mexican	10	0.5	1.5	3.0	5.0
Panuco	3	0.7	1.9	4.0	6.6
Venezuelan	7	0.9	1.5	3.7	6.1
Colombian	20	0.2	0.8	1.3	2.3
California	20	0.6	2.4	3.7	6.7
Persian	30	1.5	4.5	5.1	11.1
Heavy Smackover, Ark..	—	0.15	0.4	1.5	2.05
Roumanian	—	1.8	3.6	4.2	9.6
Borneo	—	7.0	14.0	15.0	36.0

The rest of the paper deals with chemical methods used for preparing aromatics and with their uses in synthetic rubber, explosives, etc. A. H. N.

768. Some Uses of Infra-Red Spectroscopy for Hydrocarbon Analysis. R. R. Brattain. *Refiner*, April 1943, 22 (4), 104–110. *Paper presented before California Natural Gas Association.*—Three different types of energy change within a molecule give rise to its spectrum. Changes in the electronic energy of a molecule cause either emission or absorption of radiation in the ultra-violet or visible regions. Examples of this, often used for analytical purposes, are the absorption bands of aromatic compounds in the 2400–2700 Å. range. Absorption in the ultra-violet region can be and is being used as a powerful analytical tool. However, paraffins and mono-olefins do not have characteristic absorptions, caused by electronic energy changes, in a wave-length region easily accessible. Practically all of their absorption is at shorter wave-lengths than 2000 Å. and, consequently, they cannot be studied unless vacuum spectrographs, either prism or grating, are used.

Spectra caused by changes in the rotational energies of molecules appear in the far infra-red. This region, the short wave-length limit of which is usually taken as 30 μ , is not used for analysis because the experimental technique is too difficult.

The spectral region which is discussed in this paper is referred to as the near infra-red, and extends from 2 μ to 30 μ . The actual analyses discussed only make use of absorption between 3 μ and 15 μ , but the methods and instruments described could be used to 30 μ with slight modifications. Molecular spectra in this region are caused by changes in the vibrational energy. The particular wave-lengths or frequencies of radiation which a molecule absorbs are determined by the masses of the atoms forming the molecule, the forces between the atoms, and their relative positions. For the simpler molecules it is thus possible to correlate completely the absorption bands in this region with the normal vibrations of the molecule considered as a dynamical

system. Such calculations are most useful when infra-red spectra are being used for purposes other than analysis.

The above facts can be re-stated in a form which indicates more explicitly what may be expected when using near infra-red spectra as the basis of analysis. In general the spectra of two molecules will be different when any of the three following conditions exist: (1) The molecules contain different atoms (methane and chloromethane). (2) The molecules contain the same atoms but the bonds between them are different (butane and butylene). (3) The molecules contain the same atoms held together by the same forces, but the atoms are in different relative positions (*n*-butane and *iso*-butane).

The paper discusses these points in some detail with typical illustrations.

A. H. N.

Analysis and Testing.

769. The Ultraviolet Absorption Spectra of Aromatic Hydrocarbons. R. N. Jones. *Chemical Reviews*, 1943, **32**, 1-46.—References to the absorption spectra of 370 aromatic hydrocarbons are given, and the influence of the structural factors on the absorption spectra are discussed. The spectrum of the benzene molecule is much more susceptible to the influence of substituents than that of the polynuclear aromatics. The individual effects of the introduction of alkyl, alicyclic, and aryl derivatives on the absorption spectrum of a given aromatic nucleus are discussed.

J. W. H.

770. The Penetrometer Method for Determining the Flow Properties of High Viscosity Fluids. W. W. Pendleton. *J. Appl. Phys.*, April 1943, **14** (4), 170-180.—A review of the literature has shown that there was no reliable method of measuring the flow properties of fluids in the range of viscosity 10^6 - 10^{12} poises where the flow is "generally viscous." The theory of the penetrometer has been developed in this paper to a point where absolute viscosities may be determined both for viscous flow (viscosity independent of rate of shear) and generally viscous flow (viscosity dependent on rate of shear). The new penetrometer method was checked (1) with the capillary viscometer for viscous flow using coal tar pitch, and (2) with the revised axially moving cylinder method for generally viscous flow using a high melting blown asphalt. For any one temperature, the flow properties of a generally viscous material are defined by the straight line relationship between log shearing stress and log rate of shear. From this relationship viscosity may be calculated at any desired rate of shear. The slope of this line is required in the calculation of rate of shear both for the penetrometer method and for any other type of standard viscometer method. An independent means for observing was developed for the penetrometer and for the moving cylinder method. It is shown that earlier formulæ for standard instruments based on viscous flow are invalid when applied to fluids showing generally viscous flow properties. The power function law relating shearing stress and rate of shear has been found to hold for the asphalt studied over the range of rate of shear from 10^{-5} to 10 reciprocal seconds. In addition to speed of operation and precision, the penetrometer has the advantages of minimizing the elastic effects and reproducibility without extensive heat treatment and preworking. Entire shearing stress-rate of shear curves can be determined with one load and one penetration using a succession of time intervals.

A. H. N.

Special Products.

771.* Peace-Time Values from a War Technology. G. Egloff. *J. Inst. Petrol.*, May 1943, **29** (233), 135-145. *Paper presented before War-Time Marketing Conference, American Management Association.*—The paper deals with a number of subjects varying from improvements in treating the wounded and consequent reduction in death-rate of combatants to synthetic rubber and plastics.

A. H. N.

BOOK REVIEW.

Emulsions and Foams. By S. Berkman and G. Egloff. Pp. viii + 591. Reinhold Publishing Corp., New York, 1941.

Whilst the title of this book indicates a discussion of a generic nature, the authors quickly reveal—even in the preface—that it deals to a large extent more specifically with emulsions and foams of petroleum than those of other types. The book is divided into two main sections: (1) theoretical, and (2) practical knowledge of emulsions and foams. Theory is afforded 150 pages and practice 400 pages. This ratio of 1 : 2.6, however, is not truly representative; the theoretical section is a thorough and painstaking compilation of reports on practical laboratory experiments. The book is, indeed, a good summary of the practical knowledge about petroleum emulsions and foams. It is difficult to see how a theory of emulsions or foams or any other branch of colloidal science can be worked out in full with our present meagre knowledge of the liquid state. Until the theory of liquids is evolved and tested with a similar degree of success as has already attended the kinetic theory of gases, we cannot hope to have better knowledge than the findings of different laboratories. These findings are often contradictory, and sometimes inexplicable; the correlating fundamentals behind the findings are unknown. Hence, despite the great efforts the authors make in splitting the first chapter into two main sections on emulsions and foams, and further sub-divisions dealing with effects of different properties (*e.g.* surface tension, viscosity, etc.), in order to elucidate the fundamental nature and behaviour of emulsions and foams, yet pages sometimes follow pages in puzzling contradictions, paragraphs disprove statements established in previous paragraphs, and even sentences throw doubts on preceding sentences. This is not due to any fault of the authors; merely the present state of knowledge regarding “the cloudy science” of colloids is to a large extent fog-bound. Indeed, the authors clear the view, to a certain extent, by summarizing the results of these studies at the end of each section, indicating the most probable correlation between observed facts and theory. Thus Chapter I forms an exhaustive summary of laboratory research, sub-divided into separate compartments, and finally integrated by a shrewd summary. The section on emulsions is appended by 296 and on foams by seventy-three references to the literature.

Chapter I is probably the most important to the student of emulsions and foams, and hence one or two minor criticisms might be excused. The first is that the treatment is in certain respects elementary. Thus equations like those of Einstein, Stokes, Gibbs and others are given in their final—and sometimes the approximate—forms without a critical study of derivations and limitations. Viscosity is treated as a constant in systems where it changes with changing conditions of stress and strain. The second is that the data collected from the literature are reported in many cases too impartially. This results in apparent or real contradictions being reported with no guidance to the student except in the short summary at the end of the section as to which line he should follow. Again, certain results which have been doubted subsequent to their publications may be reported with a stronger sense of conviction than they deserve. It is, of course, understood that both these criticisms are matters of opinion rather than condemnatory facts, but they are given in the belief that the otherwise excellent Chapter I loses a little in value due to these shortcomings.

The other four chapters deal with the practical knowledge of emulsions. Chapters II and III discuss the practical, or industrial, processes of emulsification and demulsification respectively. The treatment is exhaustive, severely technological (the patent literature is very well represented), and almost entirely devoted to petroleum emulsions. The subjects are treated under the usual headings, but with great thoroughness—Chapter II has 443 and Chapter III 658 references to scientific and patent literature. The sub-division of the complex subject of demulsification into the various systems used shows much thought and is all that can be desired.

Chapter IV deals with two important branches of useful petroleum emulsions; the first section treats in some detail asphalt and bitumen emulsions; the second, lubricants and lubricating emulsions. In discussing a subject like asphalt and

bitumen emulsions in only half a chapter, instead of a whole volume, it is an extremely difficult problem to decide what to include and what to reject, and, having decided that, to determine how far each item can be studied. Yet the authors manage in 48 pages to give a concise and clear exposition of the main problems, criteria and tests connected with bituminous emulsions. The treatment is rather empirical, but most of our knowledge about the subject treated is empirical.

The preceding remarks apply equally well to the second section of the chapter, dealing with lubrication. In a very small space the authors manage to present a good picture of the multitudinous aspects of lubrication—oiliness is discussed in a single page with another page dealing with tests for oiliness—yet sufficient is said to indicate to the student the path along which he must tread. "The fact that the principles of adsorption at phase boundaries apply not only to emulsions but to lubricants indicates a parallelism between emulsification and lubrication." This is the introductory sentence to the study, and it partly explains why lubrication should be included in a book on emulsions and foams. It must be pointed out that the study is mainly confined to boundary lubrication when lubricants, other than emulsions, are discussed. Yet there is a feeling that a page here and there simply does not fit into the scheme of "emulsions and foams"—*e.g.*, studies on compressibility and tensile strengths of lubricating oils. Further, if lubrication is to be discussed because of the influence of surface phenomena on the matter, then surely greases should have been studied. On the whole, the reviewer is of the opinion that this section of Chapter IV could be rewritten with advantage by confining the studies strictly to emulsions in lubrication.

Whilst Chapters II, III and IV are probably the most important to the practising engineer, Chapters I and V must form the greatest interest to the research worker. Chapter V deals with the examination of emulsions. Important tests are discussed in sufficient detail—anyone who attempted to evaluate accurately the water content of heterogeneous systems containing hydrocarbons and soaps will agree that the apparently lengthy 11-page discussion of this subject is not at all too long. Similarly the tests for surface phenomena could, if any change were required, be a little more detailed. Electrical properties are well catered for too. Only viscosity has been treated rather arbitrarily. It is true that its effects on emulsion formation and stability and on foams is secondary, nevertheless the omission of any detailed reference to fundamental methods of measuring viscosity is probably a mistake. The U-tube viscometer is merely referred to, whilst rotating viscometers are not even mentioned. Space is given instead to illustrating the Saybolt, the Engler and the Redwood viscometers. Again, the "Appendix" to the chapter deals with subjects which are not connected with emulsions or foams: origin of petroleum and certain A.S.T.M. and I.P. Standard tests of petroleum, including such items as the carbon residue and sulphur determinations. As anyone who intends to perform these tests will naturally refer to the A.S.T.M. handbook or to "Standard Methods for Testing Petroleum and its Products" for details, it is felt that the pages used on illustrating these standard tests could be better used to describe the non-standard methods of measuring viscosity, surface and interfacial tensions in greater detail. Nevertheless, sampling and testing emulsions are truly well described and illustrated.

The volume is well bound, in a serviceable size, and extremely few errors could be detected. The most important of these is in the formulæ for dynamic surface tension, page 496. The book is heartily recommended.

ALFRED H. NISSAN.

BOOKS RECEIVED.

British Standard No. 1099 : 1943.—Small Fusion-Welded Steel Air Receivers. Pp. 21. British Standards Institution, 28, Victoria Street, London, S.W.1. Price 2s. net.

This specification forms part of a series of British Standards for Steel Air Receivers.

British Standard No. 1101 : 1943.—Pressure Paint Containers. Pp. 23. British Standards Institution, 28, Victoria Street, London, S.W.1. Price 2s. net.

This specification forms one of a series of British Standards for Pressure Vessels.

American Society for Testing Materials. Proceedings of the Forty-fifth Annual Meeting. Vol. XLII, 1942. Committee Reports and Technical Papers. Pp. 1217. American Society for Testing Materials, 260, South Broad Street, Philadelphia, Pa., U.S.A.

The Production Authorities Guide. Ministry of Production, June, 1943. Pp. 20. H.M. Stationery Office, York House, Kingsway, London, W.C.2. Price 4d. net.

This guide shows at a glance which is the Authority responsible for the production of manufactured products that are not obviously the concern of a single Government Department.

Institution of Chemical Engineers. Transactions. Vol. 19. 1941. Pp. 100. Institution of Chemical Engineers, 56, Victoria Street, London, S.W.1.

Iron and Steel Institute, Journal. Vol. 146, No. 2. 1942. Proceedings, 1p to 504p. Survey of Literature, 1A to 233A. Iron and Steel Institute, 4, Grosvenor Gardens, London, S.W.1.

Among the sixteen papers presented at the Autumn Meeting of the Institute, the following may be mentioned as being of interest to the petroleum industry :

Tests on the Corrosion of Buried Ferrous Metals. (J. C. Hudson, T. A. Banfield, and H. A. Holden.)

A Study of some Soluble Inhibitors with Special Reference to Heat Transfer and Water Line Attack. (R. S. Thornhill and U. R. Evans.)

Journal of the Engineering Society, University College, University of London. Pp. 60. University College, London, at University College, Singleton Park, Swansea, South Wales.



INSTITUTE NOTES.

AUGUST, 1943.

NEW MEMBERS.

The following elections have been made by the Council in accordance with the By-Laws, Sect. IV, para. 7.

Elections are subject to confirmation in accordance with the By-Laws, Sect. IV, paras. 9 and 10.

As Fellows.

BASS, Ernest Leon	ROSENFELD, Ludwig
ERNSTE, Jan Willem	SCHNABEL, Fred
MEULEN, Hubert Ter	WANDY CZ, Damian
MITCHELL, John	WINDEBANK, Charles Stanley
RIDLER, Kenneth Edgar William	

Transferred to Fellows.

CHAPMAN, Stanley Herbert	MOORE, Harold
FLEMING, Peter	OCKENDEN, Maurice Albion
FLETCHER, Robert Mason	PLEETH, Samuel John Warren
FORSTER, Walter Leslie	

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BATTYE, John	MATTHEWS, Charles
BISHOP, Henry John	MULHERN, John
CHAPMAN, George Norman	NOBLE, George
CHRISTIAN, John Bell	PEPPER, Albert Cecil
COE, Frederick Henry	RICHARDS, Alan Roy
CROSS, David Thomas	RUMBLE, Victor Horace
FINNIGAN, Peter Francis	SHARP, William Robert
FRANKEL, Paul Herzberg	WIGZELL, Albert Orsborn
GOSSLING, Percy William	WILDING, John Sherley
HUMPHREY, Kenneth Ernest	

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BLOWERS, Frank Frederick	KING, Stanley
BUTCHER, Kenneth Leopold	MACKINDER, Richard
CHAPMAN, Stanley Frank	McEWEN, George Charles
CHARLESWORTH, Percy Allan	MOON, Sydney Edward Allen
CURRAN, Bernard Reginald	NEUBALD, Walter Noel Selby
FISHER, John William	PATMAN, Frederick John
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HARKESS, John Mackay	ROY, Clarke
IVEY, Terence	SIMPKIN, Francis Ronald
JACOBS, Thomas Henry	STEPHENS, Francis Edward

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GOTTESMAN, Manfred	GRUNBERG, Leander
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BOWES, Emmerson	SHELDON, James Hervev
FAULKNER, Brian Alex	SUGDEN, Walter
HUGGINS, Leonard John	

CANDIDATES FOR ADMISSION.

The following have applied for admission to the Institute. In accordance with the By-Laws, the proposals will not be considered until the lapse of at least one month after the publication of this *Journal*, during which time any Fellow, Member, or Associate Member may communicate by letter to the Secretary, for the confidential information of the Council, any particulars he may possess respecting the qualifications or suitability of the candidate.

The object of this information is to assist the Council in grading the candidate according to the class of membership.

The names of candidates' proposers and seconders are given in parentheses.

COWELL, Leonard Herbert, Assistant Chemist, Petroleum Board. (*Edward L. Gent ; T. C. R. Baker.*)

DUSSEK, Alan James, Managing Director, Dussek Bitumen & Taroleum, Ltd. (*E. R. Hatt ; Prof. F. H. Garner.*)

MCCARTHY, William Charles Frederick, Buying Manager, Sterns, Ltd. (*A. L. Read ; Walter Kay.*)

TETLOW, Norman, Mechanical Engineer, Mather & Platt, Ltd. (*H. A. Hammick ; E. A. Satchell.*)

WALLACH, Herbert Lewis, Director, Sterns, Ltd. (*A. L. Read ; Walter Kay.*)

Application for Transfer.

DRAPER, Philip, Mechanical Engineer. (*John A. Oriel ; J. S. Jackson.*)

FORTHCOMING MEETING.

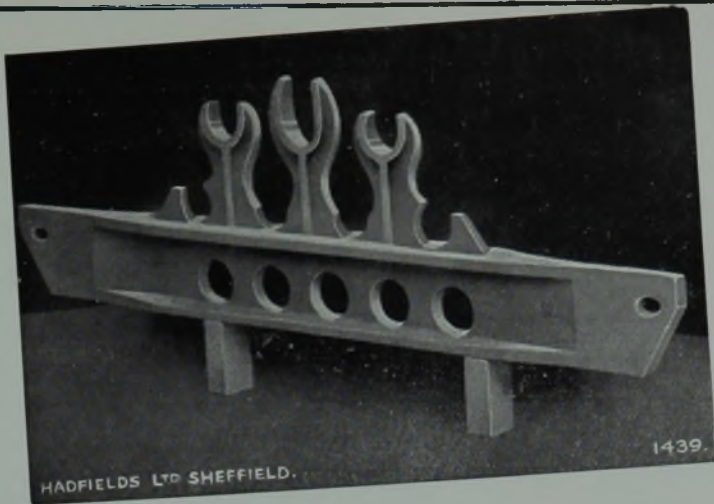
On the 30th September, 1943, Dr. P. H. Frankel will read a paper on "Oil Transport and Post-War Reconstruction in Europe."

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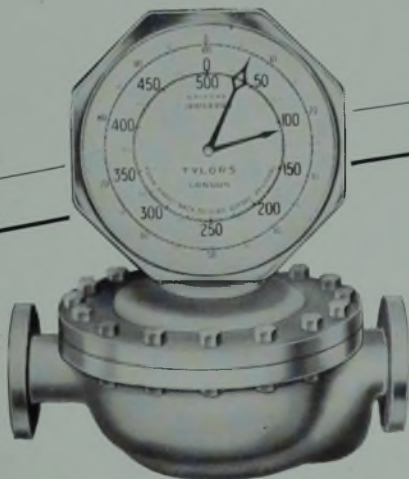
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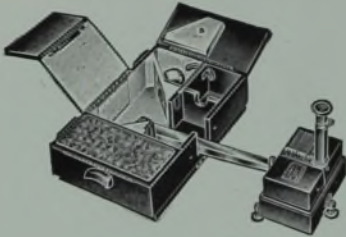
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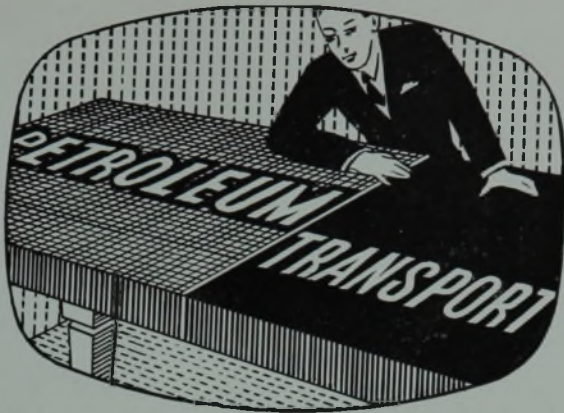
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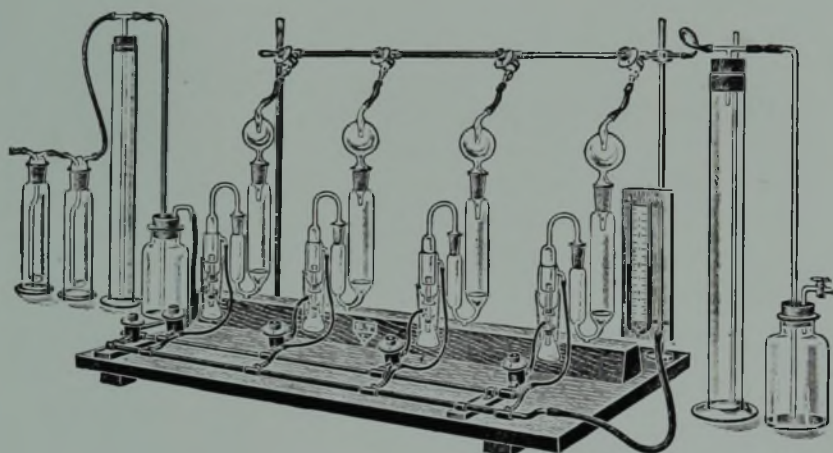
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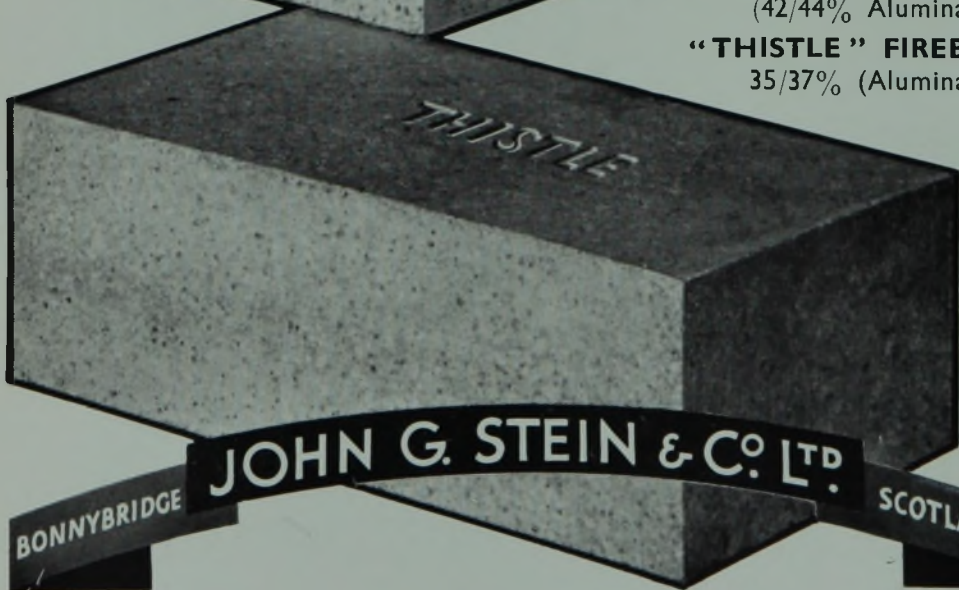
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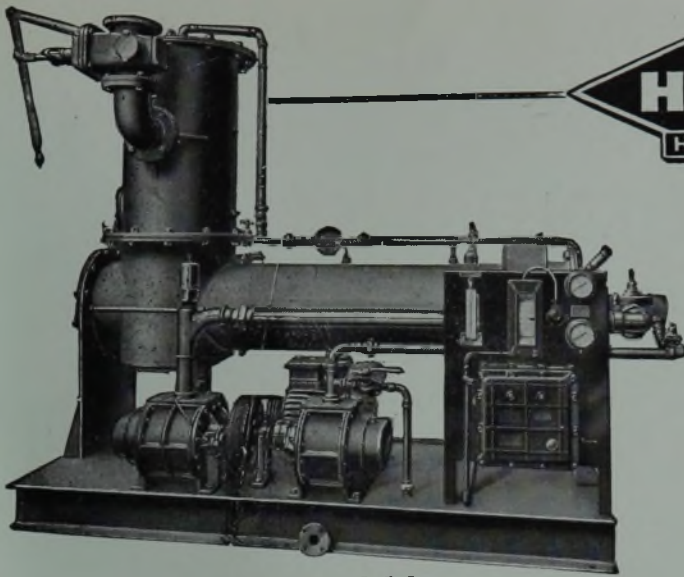


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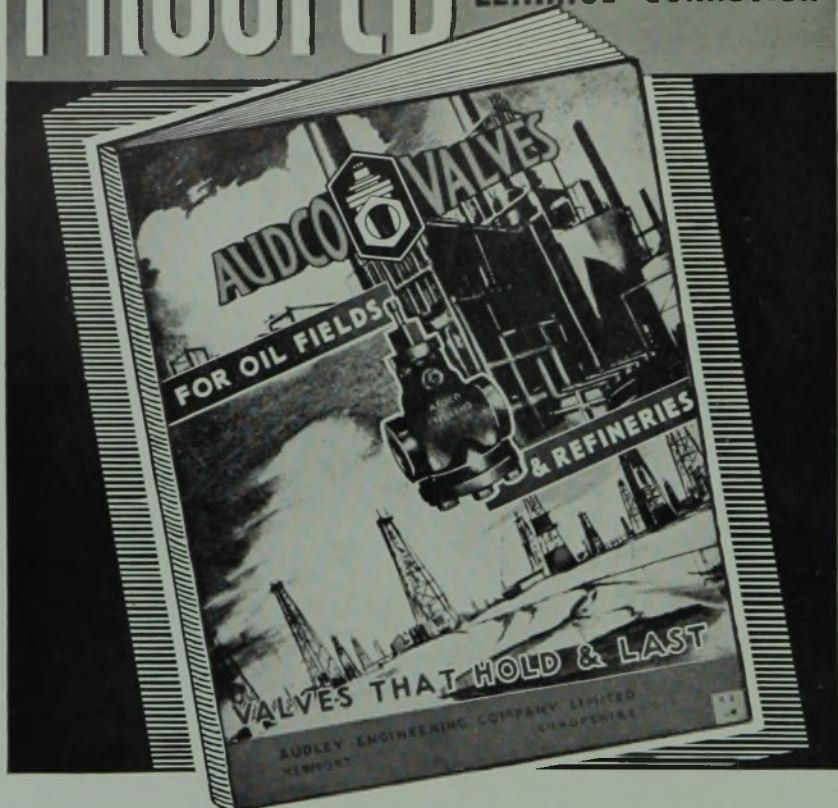
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