

Computation of Some Physical Properties of Lubricating Oils at High Pressures

I. Density

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From a survey of available data on the density of fluid lubricants as a function of pressure and temperature, the following empirical equation has been derived:

$$\rho = \rho_0(1 + ap - bp^2)$$

ρ is the density at a given pressure (gage) p and temperature t ; ρ_0 is the corresponding density at atmospheric pressure. The constants a and b are evaluated over a temperature range extending from 20° to 220°F and the density equation is valid over a pressure range of 50,000 lb./in.². While the equation was derived from data on mineral oils it has been found to hold equally well for animal, vegetable, and fish oils. The variation of density with pressure is independent of the nature of the oil.

order to compute the thermodynamic characteristics of an oil at high pressure it is necessary that the specific volume or density be known as a function of temperature and pressure. However, in problems of lubrication design it is necessary to convert from the dynamic to the kinematic coefficient of viscosity, and vice versa. In order to do this at high pressures the densities must be known over the range of pressures involved. It is the purpose of this paper to present a practical means for calculating densities over a pressure range up to 50,000 lb./in.² at temperatures between 20 and 220°F. These densities of pressure and temperature are those commonly encountered in many problems of lubrication in the fields of engineering and physics, and although data could be obtained readily at higher pressures, provided the temperature was also raised so that the oil would remain fluid, the investigation would become one of academic interest rather than of practical importance.

Densities of five petroleum lubricants have been measured by Hyde¹ at 104°F over a pressure range of 25,000 lb./in.². Similar data were obtained on four petroleum oils by Dow² at 77°F, 104°F, and 167°F at pressures up to 50,000 lb./in.². Dow and Fenske³ obtained data on an oil

¹ Hyde, Proc. Roy. Soc. A97, 240 (1920).

² Dow, J. Wash. Acad. Sci. 24, 516 (1934).

³ Dow and M. R. Fenske, Ind. and Eng. Chem. 27, 1000 (1935).

at 104°F and 167°F at pressures up to 50,000 lb./in.², and then fractionated the oil into narrow-boiling cuts and obtained data on ten of these cuts.

The striking result of all these investigations is the fact that, within the range of experimental error, all of the oils have the same compressibility. Thus the oils studied in Europe by Hyde, who used the moving piston type of apparatus to make his measurements, showed the same behavior in this respect as the oils studied in this country by Dow who used the sylphon apparatus. Furthermore, the work of Dow included extreme types of oils such as a typical Pennsylvania oil which is noted for its high paraffinicity and low temperature coefficient of viscosity, and a typical Gulf Coast oil which is characterized by the fact that it contains large amounts of naphthenic and aromatic types of molecules and has a relatively high temperature coefficient of viscosity. The work of Dow and Fenske, moreover, shows that the generality in regard to compressibility may be extended to narrow-boiling fractions which vary considerably in boiling point and molecular weight. This insensitivity of compressibility, within the range of experimental error, among the wide variety of oils studied is strikingly different from other properties that have been studied under pressure, as, for example, viscosity.⁴

From an experimental standpoint, therefore,

⁴ R. B. Dow, J. App. Phys. 8, 367 (1937).



Electrocardiogram. (a) Cathode ray record. (b) Ink writer record.

same voltage give the same

amplitude linearity characteristic, is shown in Fig. 8. At very large amplitudes a hysteresis effect similar to that of ferromagnetic materials. This introduces an appreciable error in the measurements encountered in biological work.

Electrocardiograms

Therefore, probably the best test recorder is comparison of the trace with a known wave form of the same period. Electrocardiograms recorded in biological work, and a wide range of comparisons have been used to check the instrument. Fig. 9 shows the electrocardiogram, as recorded by the cathode ray at a and by the ink

CONCLUSIONS AND ACKNOWLEDGMENT

The use of an ink-writing oscillograph in the recording of biophysical analysis of the electromechanical element is simplified by designing a critical network. From the amplitude-frequency, and time constants can be calculated. While this method has been proved by inserting a known waveform, it cannot be achieved by a piezoelectric device because of the low efficiency of coupling, greater than obtainable in a crystal.

The best frequency response is equivalent. The best test is a comparison of records with the known potential. Such comparisons with the instrument demonstrate my gratitude to Dr. J. H. Van Vleet for his assistance in the theoretical portion, and to Dr. R. W. Gerard for his help in the practical portion.

the available density data for oils at high pressure appear to be adequate for present needs. The fact that all of the oils studied show the same compressibility indicates the desirability of constructing standard density-pressure curves. The practical means adopted by the writers to express these curves in a form convenient for calculation of density at high pressure is an empirical equation that reproduces the standard curves that were drawn as averages of the experimental data. Interpolation and extrapolation were used, as explained later, to amplify and extend the range of usefulness of the equation.

DETAILS OF COMPUTATION

The pressure-density data of Hyde,¹ Dow,² and Dow and Fenske³ were plotted on graph paper of large enough scale that the coordinates of any point could be read to four significant figures. To facilitate computation, density ratios ρ/ρ_0 were plotted against pressure. ρ is the density in g/cm³ at any fixed temperature and pressure and ρ_0 is the corresponding density at the same temperature and atmospheric pressure. Temperature is expressed in degrees Fahrenheit and pressure in pounds per square inch gage. Curves were constructed for temperatures of 77°, 104° and 167°F. They were found to have the same general shape as those obtained by Bridgman⁵ for many pure liquids; i.e., the density increases quite rapidly as pressure is first applied but at a slower rate at higher pressures. For example, in the case of oils at 104°F the density increases by about 5.3 percent for the first 15,000 lb./in.² but only by an additional 3.2 percent for the next 15,000 lb./in.².

The distribution of points with reference to the curves is of importance in determining the relative precision of the data. The three studies gave density values for twenty oils at various temperatures and pressures. Four of the oils had been studied at all three temperatures, five at 104° only, and eleven at 104° and 167°F. It is evident that the data are not enough for a critical study of accuracy by the method of least squares. Consequently, curves were drawn in such a way that they passed through the averages of all the plotted points. At 77° the maximum

¹ P. W. Bridgman, Proc. Am. Acad. A & S 66, 185 (1931).

deviation of any point from the average was 0.1 percent; at 167°, 0.7 percent; and at 104°F, the most representative since data from all three studies were available, 0.9 percent.

Table I illustrates the distribution of the

TABLE I. Density ratios of twenty oils at 10,650 lb./in.² and 104°F.

OIL	OBSERVER	DENSITY RATIO ρ/ρ_0
1	Dow and Fenske	1.035
2	Dow	1.035
3	Dow	1.037
4	Dow	1.037
5	Dow	1.037
6	Dow and Fenske	1.037
7	Dow and Fenske	1.037
8	Dow and Fenske	1.038
9	Dow and Fenske	1.038
10	Dow and Fenske	1.038
11	Dow and Fenske	1.038
12	Hyde	1.039
13	Dow and Fenske	1.039
14	Hyde	1.040
15	Dow and Fenske	1.040
16	Dow and Fenske	1.040
17	Hyde	1.041
18	Hyde	1.042
19	Dow and Fenske	1.043
20	Hyde	1.045
Average		1.039

densities measured at 10,650 lb./in.² for a temperature of 104°F. Three investigators, working with twenty different oils, are represented by the data. The arithmetic average is seen to be 1.039 as compared with 1.040 obtained graphically, indicating that the graphic method of averaging is sufficiently accurate. The average deviation from the mean of a single observation is seen to be ± 0.002 and the percentage deviation of the mean is ± 0.04 .

The absolute error involved in the measurements is probably somewhat greater than the precision might seem to indicate. Both the piston displacement and the siphon methods of measuring volume change are quite complicated in comparison with the simple and accurate method of weighing with a specific gravity bottle at atmospheric pressure. Furthermore, the measurement of the absolute pressure in the system introduces errors which are not involved in ordinary atmospheric gravity determinations. Bridgman⁵ indicates that the absolute error involved in the measurement of density under pressure might generally be expected to be 2 or 3

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⁵ National B
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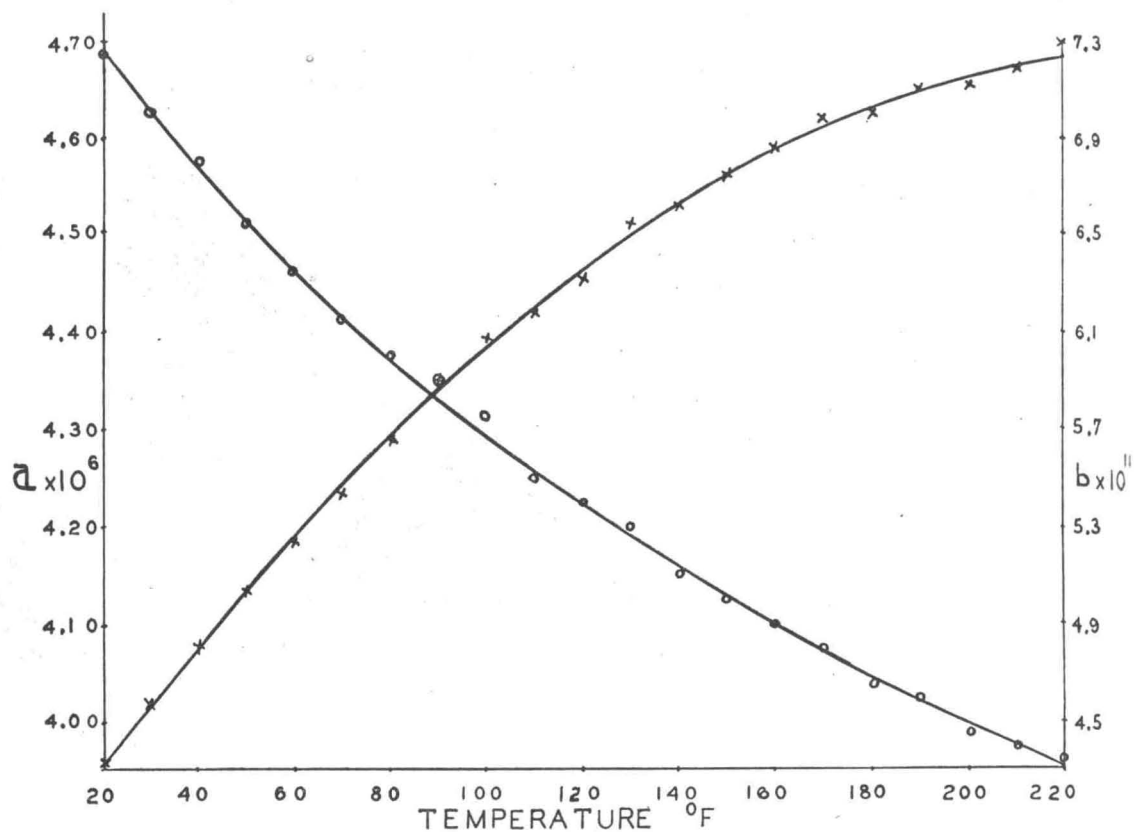


FIG. 1. Calculated values of a and b as functions of temperature; ax, bo .

from values read from smooth curves through these plots.

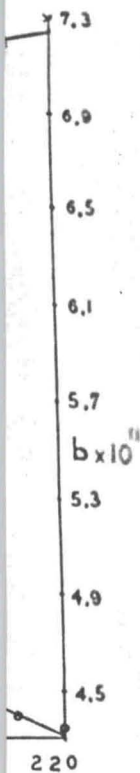
If the density of an oil is known at atmospheric pressure and it is desired to calculate its density at some other pressure, it is only necessary to refer to the values of a and b of Table II at the temperature under consideration and make the calculation by means of Eq. (1). If the known atmospheric density is at a temperature different from that required in the final answer, the atmospheric density is first adjusted to the desired temperature by means of one of the methods already known to the petroleum industry, as, for example, the National Bureau of Standards tables⁶ referred to already.

DISCUSSION

It is the belief of the writers that the system developed in this paper offers the best means so far described for the calculation of density of lubricating oils at various pressures from their

known densities at atmospheric pressure. Taking all of the possible sources of error, discussed in a previous section, into account, it is believed that the error in any density computed by this system is not above 3 to 5 percent.

While the density equation, as given above, was derived from data on mineral oils, it is of interest to note that it has been found to hold equally well, using the same table of values for the constants a and b , for animal, vegetable, and fish oils, insofar as there are data available. Hyde¹ obtained data at one temperature for castor oil, trotter oil, rape oil, and sperm oil. Dow² obtained data at three temperatures for lard oil and sperm oil. Using the atmospheric densities reported by these investigators for the oils, a number of density computations were made at various pressures and temperatures using Eq. (1). The values so obtained were then compared with the experimental values reported by Hyde and Dow. For ten such calculations made, the equation reproduced the experimental



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APPLIED PHYSICS

to within 0.5 percent in nine cases, and to
 1.0 percent in all cases. While the data are
 sufficient to show definitely that the method
 calculating densities developed in this paper is
 applicable to these other types of oils, there
 seems to be good indication that it is.
 Two thermodynamic quantities of interest, the
 thermal compressibility and the thermal ex-
 pansion, can be calculated from the data of this
 paper. The compressibility can be obtained by
 differentiation of the density equation at the
 temperature corresponding to the constants a
 and b , and, if computed at two pressures, shows
 a normal decrease with increase of pressure. On

the other hand, if the compressibility is calculated
 at two temperatures, it will be found to increase
 with temperature. The thermal expansivity can
 be calculated by applying the density equation at
 two temperatures at constant pressure. If compu-
 tations are made at two pressures it will be found
 that the expansivity decreases also with increase
 of pressure. In regard to these derived quantities
 it should be noted that they cannot be calculated
 to an accuracy claimed for the basic density data.
 However, this lack of accuracy becomes im-
 portant only at the lowest pressures where
 possible inaccuracy in measuring pressure by
 means of the manganin coil is recognized.

An X-Ray Method of Determining Rates of Diffusion in the Solid State

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gold and copper were simultaneously deposited in
 vacuum by vaporization on a plate of glass, the copper
 being deposited at a uniform rate while the gold was
 deposited in one hundred stratified layers in the copper
 by alternately raising and lowering the temperature of
 a benzene vaporizing trough containing the boiling
 liquid. The translucent deposit so formed had a total
 thickness of about 10,000A and hence an average inter-
 layer distance of 100A. In an especially constructed x-ray
 diffractometer selective diffraction of Mo K radiation from
 the stratified films was observed corresponding to the
 regularly imposed periodicity of the stratification and the
 intensity of this diffracted image relative to the direct
 beam was found to fall off with time so as to indicate a
 "lifetime" for the stratified structure of about two days.
 This suggests a general method for the study of average
 rates of diffusion and the determination of diffusion coef-
 ficients of solids in solids by utilizing the decay of such
 stratified films. Simple theoretical considerations indicate
 that such an artificial stratification should, through the

action of diffusion alone, rapidly and automatically lose
 the higher Fourier harmonics of its periodic density dis-
 tribution function and retain the fundamental in such a
 way as to render the determination of the diffusion coef-
 ficient quite accurate. The observed behavior of the dif-
 fracted maxima seem to support these expectations as does
 also the absence of any intensity in higher orders than the
 first. This purification by diffusion probably takes place
 principally during the depositing process itself while the
 temperatures are still quite high. Formulae are derived
 relating the observed rate of decay of the diffracted in-
 tensity, the artificial "grating constant" of the strata, and
 the diffusion coefficient. The method seems especially
 promising for substances and temperatures where diffusion
 is so slow as to be otherwise quite unobservable because
 the diffusion time varies as the square of the distance over
 which atoms must migrate and in this method these
 distances are many orders of magnitude smaller than in
 any other.

I. INTRODUCTION

WHEN the experiments here described were
 started¹ our purpose in trying by con-
 ventional means to produce artificial
 stratification in solids was to produce artificial
 gratings for x-ray diffraction. For a discussion of
 this problem see J. DuMond and J. P. Youtz, *Phys. Rev.* **48**, 703
 (1935) and also for unsuccessful attempts to produce artificial
 gratings see H. Koeppel, *Dissertation Gieszen* 1923,
 and H. Koeppel, *Ann. d. Physik* **5**, 261 (1930).

controlled evaporation in vacuum to produce arti-
 ficially stratified layers of two different substances
 (gold and copper) was to develop, if possible, a
 technique of measuring the absolute wave-length
 of x-rays by a type of diffraction more nearly
 resembling Bragg reflection than is the case in the