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Environmental Capability of Liquid Lubricants

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The purpose of this paper is to provide in compact form as complete as possible an array of the methods available for predicting the properties of liquid lubricants from their structural formulas. These methods carry with them the ability to design lubricants by forecasting the results of changing the structure. In a more general way, they serve to map out the ultimate limits to which liquid lubricants can cope with extremely hostile environments.

The methods are arranged roughly in the order of their rigor from thermodynamic properties through empirical physical properties to chemical properties. As far as possible, these discussions have been kept on a common basis, using group contributions to solubility parameters, even at the sacrifice of rigor and precision, to show how adjustment of one property affects all the other interactions with the environment.

1. INTRODUCTION

THE HISTORY OF LIQUID LUBRICANTS is essentially that of a battle against increasingly hostile environments. Five years ago the author (ref. 1) prepared figures 1 and 2 to show that we had already encountered the worst that the universe had to offer, and there is no reason now to change that statement. What has changed enough to justify reopening the subject is our increased competence in dealing with the same problems.

Figure 1 shows the physical situation reduced to two variables, temperature and pressure. These are the two main forces that control three of the most vital properties of every liquid lubricant, its viscosity and the endpoints of its liquid range at which it solidifies or evaporates. The means used to deal with this class of stresses include mainly the thermodynamic properties, or those that can be predicted from complete knowledge of the intermolecular forces within the lubricant.

Figure 2 shows the chemical stresses to which lubricants are subject. Temperature again appears as one of the three axes, but this time in its role as the principal accelerator of chemical reactions, usually with the rate

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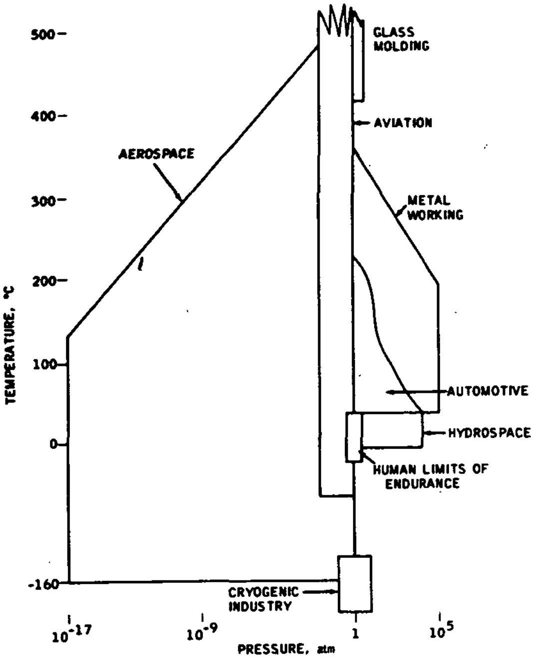

FIGURE 1.—The physical lubrication environment.

doubling for every 10° C rise, but sometimes with very different exponents. The radiation axis represents another form of energy. Infrared (IR) is exactly equivalent to heat, but as the wavelength decreases, ionization and free radical formation become increasingly important side effects. Molecular scission starts to become important at X-ray wavelengths and at gamma-ray energies dominates the reactions. However, all these processes have their thermal equivalents, so these two axes are, to some extent, redundant. The oxidizing power axis, on the other hand, conceals a hidden factor because it represents the partial pressure of oxygen, or its equivalent in some other element or compound. The necessity for such an axis is relatively recent. Until the coming of the aerospace age, such matters were of interest only to a few engineers in chemical industry.

Thus, the two variables in figure 1 also create problems in figure 2, but the means for dealing with them must be chemical rather than thermodynamic. At this point, the author must insist on excluding chemical thermodynamics as a phrase, because its use would lead to confusion with the purely physical aspects related to figure 1. Those chemical effects sometimes classified as thermodynamic will be discussed in terms of kinetics.

Another factor not explicitly included in figure 2 might be broadly classified as catalytic effects. These include those of humidity and bearing metals, and most especially those associated with freshly sheared metal

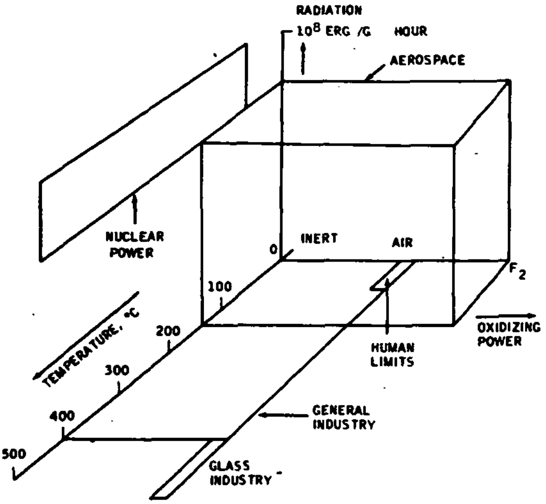

FIGURE 2.—The chemical lubrication environment.

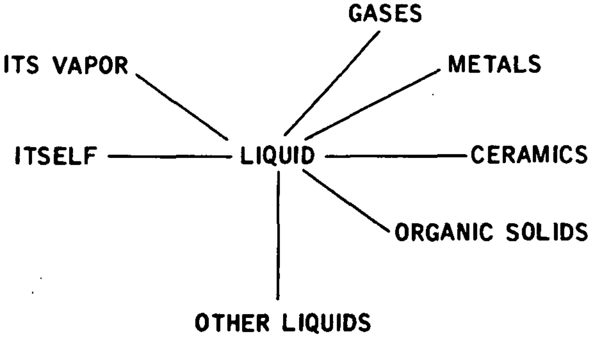

FIGURE 3.—The interactions of a liquid.

surfaces. Unfortunately, while these enter primarily into the oxidation axis, they also contribute to thermal degradation and so must be dealt with twice.

A third set of factors is shown in figure 3, which outlines the physical interactions of a liquid with its material environment. While these are seldom as drastic as the effects in figures 1 and 2, they are by no means trivial. The implications of figure 3 are discussed in more detail in section 2.2.

To discuss the effects of the environmental extremes on lubrication, it is necessary to go into considerable detail about their effects on lubricant properties. Most of the lubrication problems normally encountered result from the lubricant's being too thick, too thin, evaporated, burnt off, nonwetting, etc., and so are lubricant failures. The direct effects of the environment on the lubrication process are subtle enough to often be masked by these gross problems, and even now are we only beginning to be able to study them directly. If in the following discussion properties tend to overwhelm processes, this is merely an indication of the incomplete state of our knowledge.

Table 1 shows the various properties of any liquid lubricant, arranged in the order of their predictability. It is the plan of this paper to go through this list down to "corrosion," which Dr. Rowe will handle, discussing each property in terms of its relation to chemical structure. While these discussions progress from rigorous to quite empirical, it will be seen that all these properties are basically predictable. In addition, there are many relationships among the properties that are predictable, which should clarify the fact that certain combinations of properties are very difficult to achieve. Where feasible, the degree of control that these predictive methods provide over interactions with the environment will be indicated. Finally, an example of how one might use this approach to improve aircraft performance is lightly sketched in.

2. THERMODYNAMIC PROPERTIES OF LIQUID LUBRICANTS

It may be safely said that for the first few thousand years of lubricant technology, the thermodynamic properties of the lubricants in use were irrelevant to the problem, as technology slid along on the natural fats and oils. Until petroleum oils became available, there was little choice; olive oil was outstanding for its freedom from odor and its good stability, with fish oil near the other end of the spectrum. These differ from each other, and even from the stiffest tallow, only in the degree of unsaturation, which has only a minor effect on thermodynamic properties.

Petroleum lubricants were not exactly a welcome addition to this close-knit little family. Aside from having an unlimited variety of viscosities, relative freedom from gum formation, and freezing points as low as then desired, these hydrocarbons had little to offer. The natural ester lubricants were far superior in viscosity-temperature coefficient, volatility, and film strength under boundary lubrication conditions. The real reasons for these differences were slow to develop. The explanation offered was that the natural esters had oiliness, which really means "we don't know why, but we'd use olive oil if your hydrocarbons weren't so *cheap.*"

In the end, the answers came from the chemical engineers, whose need for thermodynamic data was tied to the design of distillation and other separation equipment. This activity covers both the chemical and petroleum industries, but it was in the latter that the most rapid strides were made because of the large incentives in spite of the complexity of the problem. The chemists had, by analysis and synthesis, proved the existence of various individual compounds in mineral oil. Meanwhile, the engineers

TABLE 1.—*Classes of Lubricant Properties*

Class	Property	Environmental application
Thermodynamic	Heat of vaporization	Manufacture
	Density and expansivity	Essentially all
	Bulk modulus	High pressure, hydraulic response
	Vapor pressure	High temperature and/or vacuum
	Miscibility	Compatibility—additives and seals
	Gas solubility	Cavitation, compressors
Empirical	Heat capacity	Heat transfer
	Thermal conductivity	Heat transfer
	Freezing point	Storage and starting
	Viscosity and viscosity index	Hydrodynamic lubrication
	Work of adhesion	Boundary lubrication
Chemical	Thermal stability	Inert atmospheres
	Radiation stability	Powerplants, aerospace
	Oxidation stability	Ordinary atmospheres
	Flammability	Air, from low to high pressure
	Corrosion	Metals
Contamination	Color and color stability	Storage and use
	Foaming	Gears and circulation
	Demulsibility	Water
	Rust prevention	Metals and humidity

were compiling charts for whole families of compounds. At this point, J. H. Hildebrand (ref. 2) began to serve as a link between the two groups. After some contributions on correlating heat of vaporization, he concentrated on the mathematical structure, which, in the writer's opinion, is the key to all the physical interactions of liquids with their environment.

This mathematical structure is the set of equations that describe the cohesive energy ΔE_v as the heat of vaporization per mole ΔH_v, minus the work to expand the vapor to infinite volume $P\Delta V$. By this definition, the cohesive energy provides an exact measure of the intermolecular forces that prevent a liquid from quietly expanding into a gas because the energy is the integral of force times distance. If divided by Avogadro's number, it would give the energy per molecule, but a more practical unit can be obtained by dividing by the molar volume to obtain the cohesive energy density $\Delta E_v/V$. An even more useful unit is the square root of $\Delta E_v/V$, the solubility parameter δ. Assuming that the perfect-gas law holds for the vapor,

$$\delta^2=\frac{\Delta H_v-RT}{V} \tag{1}$$

This deceptively simple-looking formula contains the potential for predicting, when expanded as discussed in detail below, the thermodynamic properties of all lubricants from olive oil through synthetics so new that they are represented only by a scrawl on a tablecloth.

Meanwhile, the chemists had achieved a comparable insight. After many years of patient and frustrating analysis and synthesis of lubricant-sized hydrocarbons; they were suddenly relieved of this burden by the development of three new tools. Chromatography, both liquid and gas phase, permits separations into fractions of any detail desired. Mass spectroscopy provides details of the rings and chains, and nuclear magnetic resonance counts the terminal (CH_3) groups. What was only recently the work of years by highly skilled groups is now routinely surpassed by high school graduates.

The kinds of help to be had from these two groups are shown in table 1. While there are still loose ends enough to provide some job security, it is evident that the tools are ready to solve most present and anticipated problems.

2.1 Types of Cohesive Energy

Hildebrand's work (ref. 2) was specifically limited to liquids held together by London forces, sometimes called dispersion forces because of their relation to the refractive dispersion of light. They arise because each atom consists of electrons orbiting around a central positively charged nucleus. The moving negative charges create an electromagnetic field, which attracts all atoms to one another regardless of direction. The nature of the atoms and their assembly into molecules affect the size of the London force but not its existence.

Hildebrand's greatest contribution, published almost simultaneously by Scatchard, was that an equivalent $\Delta E_v/V$ between dissimilar molecules could be approximated by the product of their solubility parameters. This permitted the chemical engineers' tables and charts of the heats of vaporization of hydrocarbon families to be converted into energies of interaction with any sort of matter that is also held together solely by London forces. This limitation is extremely important, as the vast majority of materials are also held together by other forces. Two of these, the Keesom forces due to permanent dipoles and the donor-acceptor (H-bond) forces typified by hydrogen bonding, are discussed below. There are at least two others, less well understood. They are the ionic and metallic forces, which are not exactly within the scope of this paper.

2.1.1 The London Component of Cohesive Energy

In the many liquids that are held together by a combination of London, Keesom, and H-bond forces, it is not feasible to make a direct measurement of the London forces alone. Blanks (ref. 3) used the principle of corresponding states to arrive at a pragmatic solution to this problem by taking as a model a hydrocarbon of similar shape and the same molar volume. All such compounds must have the same heat of vaporization if measured at the same reduced temperature T_R; that is, the ratio of the actual to the critical temperature T_c in absolute degrees. A chart, developed by Blanks (ref. 3) but in expanded form, is shown in figure 4. It performs the entire calculation to obtain the London portion of the solubility parameter δ_D at 25° C, the usual reference temperature.

The most frequent problem in using figure 4 is how to obtain T_c values. These can be calculated from the Lyderson constants in table 2, provided the boiling point T_b at 1 atm is known, by

$$T_b/T_c = 0.567 + \Sigma\Delta T - (\Sigma\Delta T)^2 \tag{2}$$

2.1.2 The Keesom Dipole Component of Cohesive Energy

The Keesom forces arise from the fact that in many molecules the positive and negative charges are not evenly distributed. As a result, the molecule is subject to a torque when placed in an electrostatic field, which is usually reported as the dipole moment μ, and measured in Debyes. The electric field may arise from another molecule of the same type, or another type, rather than from a measuring instrument. This situation was analyzed by Keesom, but a more satisfactory solution was reached by Böttcher, who also used the dielectric constant ϵ and refractive index n of the liquid:

$$\delta_P{}^2 = \frac{12108(\epsilon-1)(n^2+2)\mu^2}{V^2(2\epsilon+n^2)} \tag{3}$$

Beerbower and Dickey (ref. 4) give a much simplified, but less precise, empirical equation

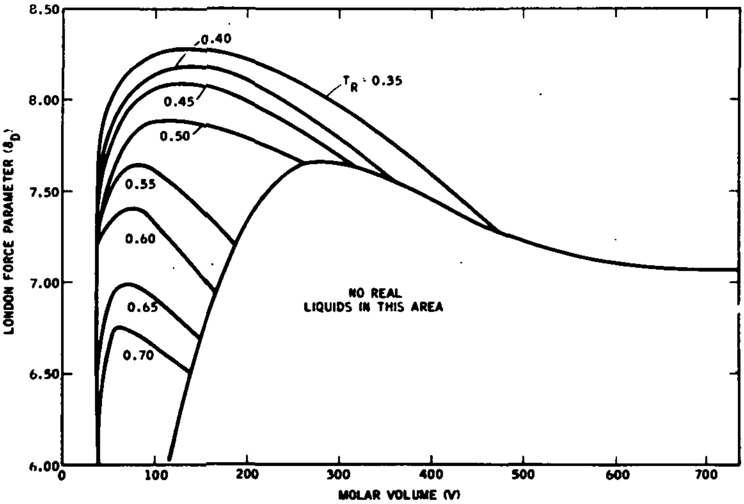

FIGURE 4.—Homomorph chart for noncyclic compounds.

TABLE 2.—*Group Contributions to Total and Partial Solubility Parameters*

Functional group	Molecular weight M, g/mol	Molar volume V, cm^3/mol	Bondi volume V_w cm^3/mol	Total parameter[c] $V\delta$, (cal×cc)$^{0.5}$/mol		Polar parameter $V\delta_P$, (cal×cc)$^{0.5}$/mol	H-bond parameter $V\delta_H{}^2$, cal/mol		Lyderson increments[d]		
				Aliphatic	Aromatic		Aliphatic	Aromatic	ΔT nonring	ΔT ring	ΔVc
CH_3—	15	34.2	13.67	148.3	-------	0	0	0	0.020	--------	55
$>CH_2$	14	16.15	10.23	131.5	-------	0	0	0	.020	0.013	55
$>CH—$	13	0	6.78	86.0	-------	0	0	0	.012	.012	51
$>C<$	12	−14.2	3.33	32.0	-------	0	0	0	.000	−.007	41
H—	1	[a] 14.7	[a] 3.5	--------	-------	[a] 0	[a] 0	[a] 0	--------	--------	------
CH_2=olefin	14	26.5	11.94	126.5	-------	[a] 25	[a] 150	--------------	.018	--------	45
—CH=olefin	13	11.8	8.47	121.5	117.3	[a] 25	[a] 150	--------------	.018	.011	45
=C=olefin	12	0	[a] 5.01	84.5	98.1	[a] 25	[a] 150	--------------	.000	.011	36
Phenyl	77	74.7	45.84	--------	795.4	[b] 50±25	--------------	[b] 50±50	--------	.066	221
C–5 ring (sat.)	0	14.2	--------	21.0	-------	0	0	--------------	--------	--------	------
C–6 ring	0	12.1	--------	−23.4	Same	0	0	--------------	--------	--------	------
Para substitution	0	0	--------	--------	40.3	0	0	0	--------	--------	------
—F	19	17.5	[a] 5.8	41.3	Same	[b] 225±25	~0	~0	.018	--------	18
—Cl	35.5	25.3	[a] 12.0	205.1	161.0	300±100	[b] 100±20	[b] 100±20	.017	--------	49
=Cl_2 twin	71	50.6	[a] 24.0	342.7	-------	175±25	[b] 165±10	[b] 180±10	.034	--------	98
—Br	80	29.1	[a] 14.6	257.9	205.6	300±25	500±100	500±100	.010	--------	[b] 70

—I	127	[b] 32.2	[a] 19.6	[b] 320	270 [b]	[b] 325±25	[b] 1000±200	--------	.012	--------	[b] 95
—O—ether	16	3.6	[a] 3.5	115.0	Same	200±50	[c] 1150±300	[b] [c] 1250±300	.021	.014	20
CO ketone	28	10.7	11.7	263.0	Same	390±15	[c] 800±250	[b] 400±125	.040	.033	60
—COO—ester	44	8.2	15.2	326.6	Same	250±25	1250±150	[b] 800±150	.047	--------	80
—CN	26	[b] 20.5	14.7	354.6	Same	525±50	[c] 500±200	[b] 550±200	.060	--------	[b] 80
—NO_2	46	[b] 19.9	16.8	--------	--------	500±50	[c] 400±50	[b] 400±50	.055	--------	[b] 78
—NH_2 amine	16	[b] 19.0	[a] 10.54	226.6	Same	[b] 300±100	[d] 1350±200	[c] [d] 2250±200	.031	--------	28
NH amine	15	[b] 3.6	[a] 8.08	180.0	Same	100±15	750±200	--------	.031	.024	37
—OH alcohol	17	[a] 10.5	[a] 8.04	225.8	171.0	250±30	[d] 4650±400	--------	.082	--------	[b] 18
—OH phenol	17	--------	--------	--------	--------	--------	--------	4650±500	.031	--------	[b] 3
$(—OH)_n$	17*n*	--------	--------	--------	--------	*n*(170±25)	*n*(4650±400)	[b] *n*(4650±400)	--------	--------	--------
—COOH	45	[b] 23.5	--------	276.1	Same	220±10	2750±250	[b] 2250±250	.085	--------	80
—PO_4	95	[b] 33	25.8	[b] 660	--------	950±400	2500±800	--------	--------	--------	--------
CO_3 cyclic	60	[b] 34.2	--------	[b] 600	--------	[b] 725±25	[b] 380±50	--------	--------	--------	--------
—NH_2 amide	16	[b] 25.1	--------	326.9	Same	500±25	2700±550	--------	--------	--------	--------

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[a] Varies according to adjacent group energies.

[b] Based on too few data to be reliable.

[c] Unpublished IR data included in correlation.

[d] Data from reference 10 corrected to 25° C and $V\delta_P^2$ subtracted. (For important steric shielding effects, see tables 7.6 and 7.7, p. 205, ref. 10.)

[e] "Base value" of 135.1 must be added to $\Sigma\ V\delta$.

[f] "Base value" of 40 must be added to $\Sigma\ \Delta V c$.

$$\delta_P \simeq \frac{18.3\mu}{V^{0.5}} \tag{4}$$

Equation (3) is not applicable to alcohols (ref. 5), but equation (4) fits them as closely as it does other compounds.

2.1.3 The Hydrogen-Bond Type of Components of Cohesive Energy

Hansen (ref. 5) designated the remainder of the energy as hydrogen bonding, but it is now recognized that it includes other forces. These are all similar enough to permit lumping them as the H-bond CED, which can be obtained by difference

$$\delta_H{}^2 = \delta^2 - \delta_D{}^2 - \delta_P{}^2 \tag{5}$$

This has resulted in a considerable number of values, consistent with each other but less satisfying than would be values obtained by independent measurements. The best known means for quantifying the H-bond is that of Gordy and Stanford, in which a small amount of a donor material is added to the pure liquid. A typical probe is methyl deuteroxide, CH_3OD. The change in O—D spacing is measured by IR spectroscopy. Unfortunately, this yields only a relative value, as each probe liquid requires a separate factor for conversion of the shift in wave number to absolute units. A second problem is selection of a baseline condition for the unperturbed probe molecule. While vapor phase readings would seem ideal, a dilute solution in a purely London-bonded liquid has experimental advantages.

Bagley (ref. 6) has recently described an experimental method that offers new help. By measurement of the internal pressure, he was able to obtain values for the sum of the London and Keesom cohesive energy densities, which removes some of the uncertainty from equation (3).

Table 2 lists values for the contributions of a number of groups to V, δ, δ_P, and δ_H. The δ and δ_P values follow the form set by Small (ref. 7), who showed that the best correlations could be obtained by

$$\delta = \frac{\Sigma(V\delta)_i}{V} \tag{6}$$

The actual $V\delta$ values shown are those of Hoy (ref. 8), who used a much larger data bank than Small. The $V\delta_P$ values were compiled from the experimental results of Hansen (ref. 5) and Beerbower and Dickey (ref. 4) and the tabulated dipole moments of McClellan (ref. 9).

The H-bond energies follow a different pattern. Both theoretically and from the uncertainties computed by both methods, these correlate best on a cohesive energy ($V\delta_H{}^2$) basis. The values shown are again from references 4 and 5, with some additional data from Bondi (ref. 10) and unpublished work by Beerbower and Elliott,[1] using an improved Gordy technique.

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[1] Beerbower, A.; and Elliott, J. J.: Unpublished data, 1969.

Because the contributions of δ_P and δ_H to ΔE_V have these different forms, accurate group contributions to δ_D are not easily tabulated. If the boiling point is not known, equation (2) cannot be used, and δ_D is best calculated by differences, as in equation (5).

It must be emphasized that the methods in this paper are not the best ones for precise calculations, nor are they the most soundly grounded in modern theory. They were selected on the basis of providing easy recognition of the roles of V and the three intermolecular forces in controlling liquid properties. They are also easily used for rough calculations, but caution must be exercised lest the oversimplifications spoil the result. These are most apparent in the V column, which should only be used when no better means are at hand.

What is available to those interested in serious pursuit of this branch of materials science is five books, authored by three physical chemists and three chemical engineers. Significantly, it is difficult to be sure in which of these disciplines any given author was trained, as all of them have tended to break down the fences.

Hildebrand and Scott began this process with a book, now in its third edition (ref. 2), which concentrates on solubility. The approach is semirigorous, with a number of approximations that are justified on pragmatic grounds. Their second book (ref. 11) is more rigorous and explores the consequences of the simplifying assumptions.

Bondi (ref. 10) is the third physical chemist of this team. His book appeared slightly after the second edition of Reid and Sherwood (ref. 12), and there was an effort on both sides to avoid overlap and conflict. Bondi's coverage of organic solids and glasses is unique and goes far beyond Hildebrand's interest in solids mainly as solutes. Reid and Sherwood ignore solids and are stronger on gases than the others, including liquid-gas interfaces.

Prausnitz' (ref. 13) approach is probably the most rigorous; he concentrates on those matters to which the corresponding states principle applies. Writing later, he was able to unify many points made by the others. He does not attempt to include solids or any interfacial phenomena.

The problem encountered on V is typical of those arising from different reference states chosen by these authors. Hildebrand tends to concentrate on 25° C and 1 atm; Bondi on 0° K; and the others on the critical point (T_c, P_c). In the case of V, the 25° C value creates a problem because group contributions to volume have consistent values only at points that are thermodynamically definable, such as 0° K, T_b, T_c, and probably T_g (the glass transition temperature). Bondi's V_w and the Lyderson ΔV_c from Reid and Sherwood are shown in table 2, but getting to 25° C from either or both of them is too complex. One minor complication is that, while $V_w = \Sigma V_{wi}$, $V_c = \Sigma \Delta V_{ci} + 40$. Fortunately, experimental values of V are so easily available that the problem rarely arises.

2.2 The Interactions of Liquids With Their Environment

The environmental capability of a liquid can be expressed in terms of its interactions. This may seem artificial and clumsy to those accustomed to another approach, but it has the potential of viewing all the limitations on a comparable basis rather than the customary hodgepodge of "flash, pour, seal-swell, and Ryder load." The possible interactions of a liquid are covered by the diagram in figure 3. The logical entry point is the simplest possible interaction, that of the liquid against itself under the influences of temperature and pressure.

2.2.1 Density

It is obviously ridiculous to predict the density of a liquid, which is available, because it is much easier to measure it. Traditionally, this is the first measurement any synthesist makes on a new product, which shows good intuition, because this leads to one of the key thermodynamic parameters, V. To reconstruct a density ρ at 25° C or predict that for a planned lubricant, calculate

$$\rho=\frac{\Sigma M_i}{\Sigma N_i V_i} \tag{7}$$

where ΣM_i is the molecular weight and $\Sigma N_i V_i$ is the sum of the group contributions to volume in table 2. Bondi (ref. 10), Reid and Sherwood (ref. 12), and Prausnitz (ref. 13) all provide more elegant solutions to this, but they are relatively complicated.

A very rough idea of the effect of each functional group on density can be obtained by dividing M by V, except for $V=0$ or less. A better way is suggested by some work by Bondi, who was frustrated by lack of V_c and T_c data and took another route (ref. 10):

$$\rho=\frac{MT_R}{V_c}+\frac{0.74M(1-T_R)}{V_w} \tag{8}$$

where 0.74 is the packing density at 0° K and T_R is that for the complete molecule at 25° C.

The results may seem rather trivial, as most chemists can recite from memory the effect on density of adding CH_3, F, I, or NO_2 to a molecule, but it is gratifying to see the success of this patched-together model.

2.2.2 Thermal Expansion

Unfortunately, table 2 is limited to the standard reference temperature of 25° C and hence provides no direct means for quantifying the expansion coefficient ($\alpha\equiv d(\ln V)/dT\equiv -d(\ln \rho)/dT$): Bondi (ref. 10) cites Wall and Krigbaum's equation

$$\alpha\simeq\frac{R}{\Delta H_v} \tag{9}$$

which may be computed from table 2 by the built-up equation

$$\alpha \simeq \frac{R}{RT + (\Sigma V \delta_i)^2 / \Sigma V_i} \tag{10}$$

Bondi points out that α is widely but incorrectly believed to be constant with temperature. Actually, it is $\rho\alpha (= d\rho/dT)$ that is constant with temperature, so this may be more a useful property to compute. Differentiating equation (8),

$$\frac{d\rho}{dT} = \left(\frac{1}{V_c} - \frac{0.74}{V_w} \right) \frac{M}{T_c} \tag{11}$$

which gives some insight into the contributions of various groups. To design a lubricant for minimum expansivity requires maximizing T_c, which agrees with petroleum experience. Selection of groups to minimize the rest of equation (11) is less clear, especially since such changes affect T_c.

Thermal expansion is not very sensitive to structure; as implied in equation (10), the three sources of CED all participate equally and the situation is usually dominated by δ_D and V. The latter alone is sufficient if $\delta_p \simeq \delta_H \simeq 0$, as shown by the fact that the American Society for Testing and Materials (ASTM) (ref. 14) tabulation requires entry only of ρ at 60° F for any petroleum fraction.

2.2.3 Bulk Modulus

Wright (ref. 15) has provided a comparable model for the bulk modulus and its reciprocal, the isothermal compressibility, of petroleum fractions. He was able to show that the isothermal secant bulk modulus B_T, representing total change in volume between 0 and test pressure P, is a function only of pressure and density at test temperature and 1 atm. As noted in section 2.2.2, the density at any temperature may be obtained from the density at 60° F or any other reference temperature. Thus,

$$B_T \equiv \frac{P\rho}{\rho - \rho_0} = f(P, \rho) \tag{12}$$

where $f(P, \rho)$ is defined by figures 5 and 6.

The isothermal tangent bulk modulus K_T is defined as the rate of change of pressure with fractional volume

$$K_T = \frac{-V\, dP}{dV} \tag{13}$$

This can be approximated by the rule that K_T at any pressure equals B_T at half that pressure, though Wright gives a more accurate procedure (ref. 15).

Problems arise when nonpetroleum liquids are considered, but these are largely associated with long chains or with hydrogen bonds. Bondi (ref. 10) provides a special equation for polymers, but Wright found that small concentrations of polymer need not be taken into account so the Bondi equation is needed only for oils that are mostly polymeric; i.e., silicones.

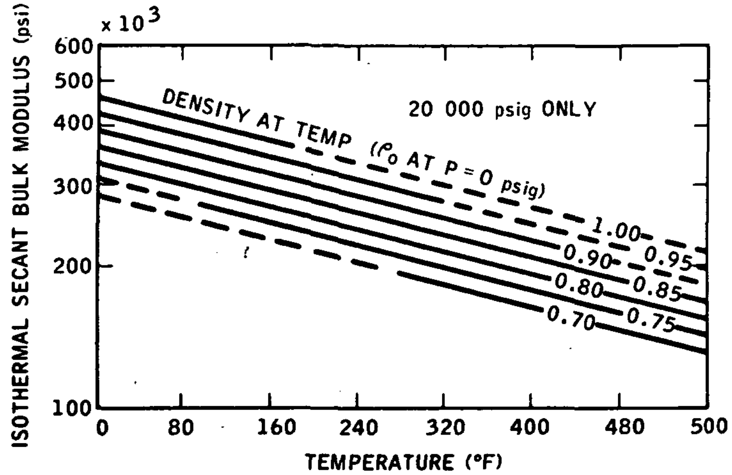
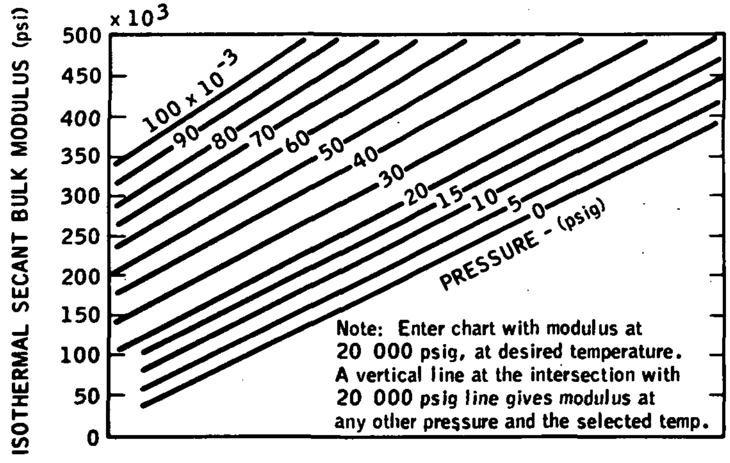


FIGURE 5.—Isothermal secant bulk modulus at 20 000 psig.



Note: Enter chart with modulus at 20 000 psig, at desired temperature. A vertical line at the intersection with 20 000 psig line gives modulus at any other pressure and the selected temp.

FIGURE 6.—Isothermal secant bulk modulus at any pressure.

Bagley (ref. 6) has recently shown that Hansen's H-bond energy is measured by the difference

$$\delta_H{}^2 = \frac{\Delta E_v}{V} - T\left(\frac{\partial P}{\partial T}\right)_V + P \qquad (14)$$

where $(\partial P/\partial T)_V$ is the thermal pressure coefficient at constant volume. This is equal to αK_T and $\Delta E_v/V = \delta_D{}^2 + \delta_P{}^2 + \delta_H{}^2$, so by combining and rearranging,

$$-K_T=\frac{P+\delta_D^2+\delta_P^2}{\alpha T} \tag{15}$$

This equation indicates that the H-bond energy contributes to K_T only through its effect on α. The reason for this appears to lie in the increase of the degree of polymerization of alcohols under pressure.

The most complex of the family is the isentropic or adiabatic bulk modulus K_s. While the isothermal versions are useful only when the pressure is applied slowly, as in high-pressure reactors or deep-sea exploration, K_s relates to the speed of sound U_s in the liquid by

$$K_s=\rho U_s^2 \tag{16}$$

For this reason it is useful in predicting the response time of hydraulic systems where a signal must travel some distance. It is interesting to note that the only bulk modulus ever recognized by ASTM (ref. 16) is K_s. Because designers tend to demand B_T values, which the chemists have laboriously computed from U_s, and then use B_T to recompute U_s, it appears that there is more waste motion in the information circuit than in the hydraulic loop.

The definition of K_s is

$$\frac{1}{K_s}=\frac{1}{K_T}+\frac{T(d\rho/dT)^2}{\rho^3 C_p} \tag{17}$$

where C_p is the heat capacity of the liquid at constant pressure. This reintroduces some structural effects that will be dealt with in section 3.

2.2.4 Vapor Pressure

The absolute value of the vapor pressure may be obtained from table 2, but only by way of some other vaporization properties that are of equally great interest. As a start, the three parameters δ, δ_P, and δ_H and V should be computed. From these, δ_D is obtained by difference, and can be converted into T_c by means of figure 4 if this property is desired. The more useful T_b can be obtained from an equation derived from Burrell (ref. 17)

$$T_b=25\sqrt{563+0.080(3542+V\delta^2-V\delta_H^2)}-593 \tag{18}$$

unless T_b is available from experiment or literature. For lubricants other than petroleum, such information is very rare. For other methods, see Somayajulu (ref. 18).

This leads to a solution of the Clapeyron equation

$$\frac{d(\ln P_v)}{dT}=\frac{\Delta H_v}{T\Delta V_v}\simeq\frac{V\delta_D^2+V\delta_P^2+V\delta_H^2+RT}{RT^2} \tag{19}$$

By converting ΔH_v at 25° C from table 2 to that at T_b, the resulting Antoine equation is

$$\ln P_v = \frac{B}{T_b - C} - \frac{B}{T - C} \tag{20}$$

where

$$B = \frac{V\delta^2 + RT}{0.95R}\left(\frac{T_c - 273.2}{T_c - T_b}\right)^{0.38}\left(\frac{T_b - C}{T_b}\right)^2 \tag{21}$$

$$C = 0.19T_b - 18 \tag{22}$$

and P_v is the vapor pressure in atmospheres, as adapted from Reid and Sherwood (ref. 12).

Equation (20) provides a good computation model but is too complicated to be the basis for discussion of the separate effects of V and the partial parameters. The general picture may be seen by consideration of equations (18) and (19). These may be combined into an Antoine plot of $\ln P_v$ versus $1/T$, as in figure 7. Equation (18) shows that the boiling point is raised by increasing V, δ_D, and δ_P, but not by increasing δ_H. This may be

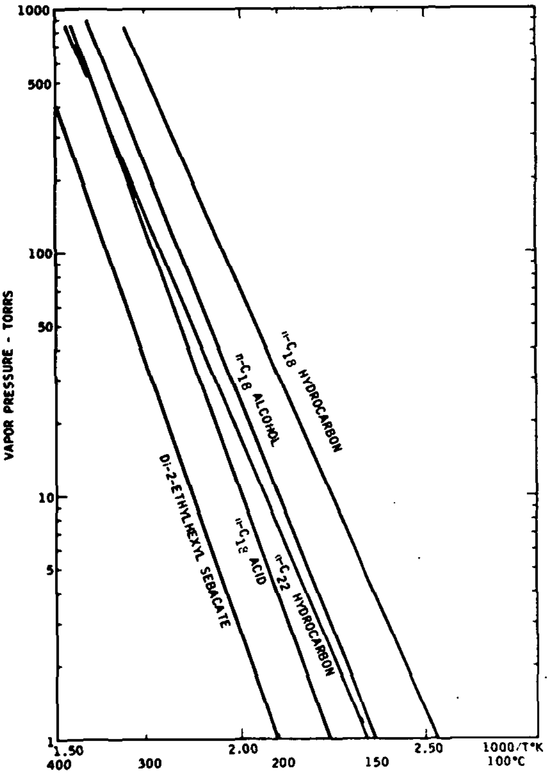


FIGURE 7.—Antoine chart for various prototype lube compounds.

an oversimplification, as it is based on Burrell's empirical corrections: "for alcohols add 1.4, for esters add 0.6, and for ketones boiling under 100° C add 0.5" to δ values calculated from T_b. For $V=100$ and $\delta_D^2+\delta_P^2=100$, these corrections average about the same as the $V\delta_H^2$ values in table 2. Thus, δ_H fails to contribute to T_b just as it does not contribute to bulk modulus.

The slope is predicted by equation (19) to increase with V and all three partial parameters. As this equation is only valid at the temperature (25° C) for which these four numbers are listed, and all four vary in different ways with temperature (ref. 19), it is unwise to draw detailed conclusions from figure 7. However, it is clear that using hydrogen bonding to control the vapor pressure of lubricants will be the least effective of the four possible ways.

The same reasoning applies to the evaporation rates. As shown by Coburn (ref. 21) and formalized in ASTM method D 2878, these two methods of expressing volatility are interchangeable, with due allowance for molecular weight.

2.2.5 Miscibility and Seal Swelling

The problem of solubility in nonelectrolytes was Hildebrand's principal target. While not properly an environmental problem, the compatibility of base stocks with one another and with the many additives included in finished lubricants should be briefly mentioned. This can be predicted by appropriate modification of Hildebrand's miscibility criterion (ref. 2), in which the entropy of mixing is equated to the heat of mixing. A further simplification can be made by assuming that the maximum temperature for miscibility T_M comes at 50 percent by volume of each component (1 and 2),

$$T_M=\frac{[(\delta_{D1}-\delta_{D2})^2+0.25(\delta_{P1}-\delta_{P2})^2+0.25(\delta_{H1}-\delta_{H2})^2](V_1+V_2)}{4R} \tag{23}$$

The 0.25 factors were empirically determined by Hansen (ref. 5) for a wide variety of solvents, polymers, and surfactants.

This work was applied by Beerbower and Dickey to the swelling of elastomeric seals (ref. 4). The equation for this phenomenon is a little different, as the restraint against infinite swelling is due to cross-linking of the polymer rather than entropy. As the volume increase Q approaches that at which all the slack is taken out of the polymer chains between cross-links Q_e, the work of swelling increases exponentially. Hence,

$$\log\frac{Q_e}{Q}=\beta V_1[(\delta_{D1}-\delta_{D2})^2+a(\delta_{P1}-\delta_{P2})^2+a(\delta_{H1}-\delta_{H2})^2] \tag{24}$$

where β is a factor depending on the elastomer and 1 and 2 refer to lubricant and elastomer, respectively. For vulcanized polyisoprene, $\beta V_1=0.08$

and $a=0.19$; the latter may simply represent a minor deviation from Hansen's 0.25.

One complication is that many elastomers are block copolymers or blended polymers that have been covulcanized. This results in having two sets of values for the partial parameters of the elastomer. In such cases, a graphical analysis must be substituted for equation (24).

2.2.6 Gas Solubility

The measurement of gas solubility has generated a surprising amount of literature in the past few years, especially in view of the fact that Prausnitz and Shair published an excellent predictive method (ref. 20) 10 years ago. In effect, their model required two steps. First, the gas was condensed to a hypothetical liquid at 25° C, which is actually far above its critical point, and 1 atm. This was then blended with the solvent in a manner analogous to equation (23). The basic method was limited to regular solutions in which for both gas and liquid $\delta=\delta_D$. Special methods were shown for polar gases, polar liquids, pairs forming temporary compounds, i.e., CO_2+H_2O, and for the light gases requiring substantial quantum-mechanics corrections, e.g., He, H_2, and Ne.

A special adaptation of this method to lubricants has been made and is awaiting publication as an ASTM method.[2] It differs from the original only in uisng δ_D for the lubricant, rather than δ, on the basis that the gases of interest are nonpolar. The basic equation is

$$\frac{1}{x_2}=\frac{f_2^L}{f_2^G}\exp\frac{V_2(\delta_{D1}-\delta_2)^2}{RT} \tag{25}$$

where x_2 is mole fraction of solute gas; f_2^G is the fugacity of pure gas, equal to pressure in most cases; δ_2 is the solubility parameter of the hypothetical liquid (table 3).

Prausnitz provided a chart for estimating f_2^L, the fugacity of the hypothetical liquid, from P_c and T_R of the gas. For computation, this was fitted with two empirical equations:

For $T_R\leqslant 2.6$,

$$\log\frac{f_2^L}{P_c}=12.353T_R-8.494T_R^2+2.723T_R^3-0.3357T_R^4-6.3931 \tag{26}$$

For $T_R>2.6$,

$$\log\frac{f_2^L}{P_c}=0.5160T_R-0.1012T_R^2+0.1724 \tag{27}$$

Table 3 also lists V and δ_D parameters for some lubricants in which the nitrogen solubility has been successfully predicted by equation (25). The

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[2] Proposed Method for Estimation of Solubility of Gases in Nonpetroleum Liquids. Amer. Soc. Testing Mater., to be published.

TABLE 3.—*Liquid Volumes and Solubility Parameters for Gases and Liquids at 25° C*

Substance	V, cm^3/g-mol	δ, (cal/cc)$^{1/2}$
N_2	32.4	2.58
CO	32.1	3.13
O_2	33.0	4.0
Ar	57.1	5.33
CH_4	52	5.68
CO_2	55	6.0
Kr	65	6.4
C_2H_4	65	6.6
C_2H_6	70	6.6
Rn	70	8.83
Cl_2	74	8.7
Di-2-ethylhexyl adipate	399	7.4
Di-2-ethylhexyl sebacate	465	7.0
Trimethylol propane ester	477	7.2
Pentaerythritol ester	539	7.3
Di-2-ethylhexyl phthalate	377	8.1
Poly-(C_2F_3Cl)	[a] 770	7.0
Polyphenyl ether (4 ring)	373	10.0
Polyphenyl ether (5 ring)	430	10.0
Dimethyl siloxane	[a] 345	5.9
Methylphenyl siloxane	[a] 600	7.0

[a] These values are to be used regardless of the molecular weight.

volumes are needed to convert x_2 to more useful units. It should be noted that V values for polymers are to be used regardless of the molecular weight. These purely empirical values are based on the concept that the gas molecule can only interact with a certain volume of the polymer molecule. A sounder approach, based on the entropy of mixing, is under development.

3. EMPIRICAL PROPERTIES

There are a number of properties listed in table 1 that are dependent on intermolecular interactions but which do not fall into the neat pattern so far discussed. They are purely physical but depend on details of structure to such a degree as to eliminate all hope of a rigorous solution. Even for pure compounds, the task would be sizable, and for mixtures it would be hopelessly complex. As a compromise, empirical methods have grown up, most of which follow essentially thermodynamic models with adjustable parameters.

3.1 Heat Capacity

Thermodynamics denotes the amount of heat needed to raise the temperature of a mole of liquid 1° at constant volume, C_V, as being fairly accessible to rigorous treatment. However, the heat capacity at constant pressure C_p is almost universally the value desired, and it is more difficult to evaluate, although

$$C_p - C_V = TVK_T\alpha^2 \tag{28}$$

This relationship, combining the uncertainties of C_V, K_T, and α, is not very precise. Bondi (ref. 10) gives a detailed analysis of the various oscillations and rotations involved in C_V. This includes a table of dipole orientation energies similar to table 2 in general nature, but by no means compatible with it, and a table of group contributions to the heat capacity of the ideal vapor. Table 4 shows some group contributions to C_p (ref. 10). From these, it is possible to deduce that δ_P always makes a substantial contribution to C_V and hence to C_p, while the contribution of δ_H is less noticeable. Since Bondi lists nine methods, ranging from crude to quite precise, there does not seem to be much justification for further work, but if anyone desires to do so, C_p could probably be computed from table 2. ASTM D 2766 provides a standard method for ΔC_p (ref. 21).

TABLE 4.—*Group Contributions to Heat Capacity at 20° C*

Group	Contribution, cal/g-mol-°K
H— (formic acid and formates)	3.55
CH_3—	9.9
—CH_2—	6.3
\ —C—H /	5.4
—COOH	19.1
—COO— (esters)	14.5
\ C=O /	14.7
—CN	13.9
—OH	11.0
—NH_2	15.2
—Cl	8.6
—Br	3.7
—NO_2	15.3
—O— (ethers)	8.4
—S—	10.6
C_6H_5—	30.5

3.2 Thermal Conductivity

There is much less theoretical background on thermal conductivity in liquids, though Reid and Sherwood (ref. 12) cite several good models for gases. Bondi (ref. 10) devotes an entire chapter to liquids but is not able to establish a simple general rule. This arises from the fact that nonassociated liquids can transfer heat only by interchange of translational and rotational energies, while associated, i.e., H-bonded, liquids have what amounts to a parallel pathway in which the heat of association is also being transferred by an essentially independent mechanism.

For nonassociated liquids, the dense-gas correlation cited by Reid and Sherwood (ref. 12) could be used, but it involves several properties that are not readily accessible. Bondi adapts this idea to his special reduced parameters and arrives at a linear equation with two empirical constants

$$\lambda=\frac{3.20\times10^{-20}}{V_w^{2/3}}\left(\frac{E^\circ}{M}\right)^{1/2}-\frac{8.70\times10^{-20}cRT}{V_w^{2/3}(E^\circ M)^{1/2}} \tag{29}$$

where V_w is the van der Waals volume, E° is the standard energy of vaporization at $V=1.70\ V_w$, and $c=1/3$ of external degrees of freedom.

Values of V_w can be built up from table 2. The variable E° is not listed in table 2 but is roughly proportional to $V\delta^2$, and c may be taken as 2 for rigid molecules and somewhat higher for elongated ones.

Equation (29) establishes linearity of λ with T, at least up to about $T=0.9T_b$, where the well-known anomalies surrounding T_c begin to appear. This is a very valuable contribution, as the literature contains a great deal of questionable data. Jamieson and Tudhope (ref. 21) surveyed the matter up to 1963 and found about one-third of the values to be outside the ±5-percent limits they considered borderline for acceptability. This did not include screening against equation (29), but "consistency of data" was one of their five criteria. Hopefully, the new ASTM D 2717 Method (ref. 21) will help to avoid generating further erroneous data.

The decision as to when equation (29) is not applicable involves three criteria including $T>0.9T_b$. For aliphatics of $T_b<100^\circ$ C (up to octane), special constants are required. These two points are academic to the lubrication engineer. The problem of flexible molecules responsible for the T_b anomaly also causes trouble in certain elongated lubricant molecules. Of these, polyphenyl ethers are especially troublesome, with a reversal of slope reported (ref. 23). Other data obtained by the method used have not been very precise, so there is room for doubt here. A special formula, developed for polymer melts, is suggested for such cases as long-chain esters, silicones, etc.

The third criterion, deciding when a liquid is sufficiently associated to justify addition of a nonlinear term, can be satisfied by three subcriteria, all of which must be met: The alternate path must be by H-bonds; the association must be 20 to 80 mol percent; and in our symbols, $V\delta_h^2>2RT$.

On this basis, any experimental data on liquids other than water, glycerol, glycol, etc., that is nonlinear with temperature must be considered suspect.

Bondi considers one empirical model worthy of reference (ref. 24), but it is too complex to offer any insight into the roles of δ and M. In general, it may be said that λ shows the responses forecast by the two terms in equation (29), with due allowance for the fact that the first term will be about twice the second at $T_R \simeq 0.5$, a typical situation for lubricants. This is because the first term represents λ at $V = 1.70V_w$, and the difference at T_c will be λ for the vapor. As a result, the response to δ is positive but not very strong, while the response to M is negative and fairly strong.

The temperature dependence $d\lambda/dT$ is dominated by dV/dT, and tends to parallel it, though this is by no means evident by differentiating equation (29). Bondi offers the empirical relationship

$$\left(\frac{\partial \ln \lambda}{\partial T}\right)_p = 1.35 - 2.7\alpha \tag{30}$$

which implies that $d\lambda/dT$ becomes negative at low temperatures. This has been verified experimentally. He also cites

$$\left(\frac{\partial \ln \lambda}{\partial P}\right)_T \simeq \frac{2.15}{K_T} \tag{31}$$

as empirically correct though not in agreement with theory.

3.3 Freezing Point

Surely the most frustrating of all these semithermodynamic properties is the freezing point T_m. It has a clear-cut basis in that

$$T_m = \frac{\Delta H_m}{\Delta S_m} \tag{32}$$

where ΔH_m is the heat of fusion, and ΔS_m is the entropy of fusion.

As Bondi points out, ΔH_m is roughly proportional to the heat of sublimation ΔH_s, which equals the sum $\Delta H_v + \Delta H_m$. Thus, the first problem lies in evaluating ΔS_m, which "is essentially a function of the number of different positions a molecule can occupy in the liquid as compared to the solid state. Hence, ΔS_m is small for spherical rigid molecules and large for anisometric flexible molecules," and T_m responds inversely. He proceeds to establish a set of rules, rather intricate but logically consistent, for various types of nonpolar molecules ranging from the simplest diatomic gases up through the complications of linear molecules of high flexibility.

Before discussing these rules, it seems wise to review briefly the concept of entropy, which seems to become less understood with each passing year. Not only was it poorly taught in the 1930's and 1940's, resulting in lapses of memory, but it has also grown in breadth and depth since then. The simplest concept is of a well-insulated gearbox, which receives 20 J of work on the input shaft in a brief period and delivers only 19 J from the output shaft. Where is the missing joule? It is still in the box, as frictional heat, but no longer available because it is now 0.239 cal at essentially ambient temperature T. The change in entropy, $\Delta S = 0.239/T$, is a standardized measure of its unavailability.

From the gearbox to a steam engine that takes in 0.478 cal of heat at high temperature T' and produces 1 J of work is a rather large step, but not a great strain on logic. The byproduct is the same, 0.239 cal of unavailable energy at ambient temperature T, and again $\Delta S = 0.239/T$. In current terminology 0.478 cal of enthalpy (ΔH) has become 1 J of free energy (ΔG) and 0.239 cal entropic energy ($T\Delta S$).

The next step is not so easy to accept, but the logic is perfect. The gearbox is an irreversible process, while the steam engine is reversible, except for frictional losses. Both have their counterparts on the molecular scale. As an irreversible process, consider mixing two kinds of molecules, different in size, shape, or both. This might be compared to a macroscale process such as buttering bread, easier to do than to undo. The result can be expressed as a change in entropy of mixing, the use of which is discussed below.

The reversible process, however, is the real source of a whole set of relations such as equation (32), covering entropy of vaporization and surface formation as well as freezing or fusion.

Returning to Bondi's rules, the first is that all first-order crystalline transitions must be included in the melting process, and $\Delta S_{m,\mathrm{tr}}$ is so defined. The second is that ΔS_m consists of two parts; $\Delta S_m{}^v$ is due to change in volume, and $\Delta S_m{}^j$ to fusion at constant volume. He avoids the term "configurational entropy of fusion" for the latter, as it popularly implies (wrongly) that this portion is calculated by molecular theories.

$$\Delta S_m{}^v = \alpha K_0 \, \Delta V_m \tag{33}$$

where K_0 is K_T at zero pressure. Subtraction of this from $\Delta S_{m,\mathrm{tr}}$ permits examination of $\Delta S_m{}^j$ alone.

A lengthy process of analysis results in the equations in table 5, which need be entered only with the number of carbon atoms per molecule N_c to yield $\Delta S_{m,\mathrm{tr}}$. All the constants are empirical, and some are more trustworthy than others, but at least a solid base has been provided. The next step is to introduce the effect of certain groups within the nonpolar structure, and Bondi goes through olefins, noncondensed aromatics, and tetraalkyl metals.

The strong dipole interactions have the effect of reducing hindrance to internal rotation and simultaneously hindering external rotation, so the net effect must be obtained. Using a homomorph approach more direct than that discussed above, Bondi simply subtracts ΔS_m for a specific

TABLE 5.—*Equations Relating the Total Entropy of Fusion of Long-Chain Compounds to the Number of Carbon Atoms per Molecule* [a]

Homologous series[b]	Formula
n-Paraffins (N_c = even)	$\Sigma\Delta S_{m,\mathrm{tr}}/R=0.80+1.33N_c$
n-Paraffins (N_c = odd)	$\Sigma\Delta S_{m,\mathrm{tr}}/R=1.10+1.18N_c$
2-Methyl-*n*-alkanes	$\Sigma\Delta S_{m,\mathrm{tr}}/R=-1.24+1.2N_c+20/N_c^2$
2,2-Dimethyl-*n*-alkanes	$\Sigma\Delta S_{m,\mathrm{tr}}/R=-6.26+1.33N_c+83/N_c^2$
n-Alkyl-cyclopentane	$\Sigma\Delta S_{m,\mathrm{tr}}/R=-5.1+1.30N_c+131/N_c^2$
n-Alkyl-cyclohexane	$\Sigma\Delta S_{m,\mathrm{tr}}/R=-6.3+1.45N_c+56/N_c^2$
n-Alkyl-benzene[c]	$\Sigma\Delta S_{m,\mathrm{tr}}/R=-5.6+1.18N_c+100/N_c^2$
n-Alkane thiols (N_c = even)	$\Sigma\Delta S_{m,\mathrm{tr}}/R=3.3+1.2N_c$
n-Alkane thiols (N_c = odd)	$\Sigma\Delta S_{m,\mathrm{tr}}/R=3.90+1.33N_c$
n-Alkyl bromide (N_c = odd)	$\Sigma\Delta S_{m,\mathrm{tr}}/R=2.4+1.38N_c+0.54/N_c^2$
n-Alkanoic acid (N_c = even)	$\Sigma\Delta S_{m,\mathrm{tr}}/R=-2.56+1.33N_c+36/N_c^2$
n-Alkanoic acid (N_c = odd, >5)	$\Sigma\Delta S_{m,\mathrm{tr}}/R=-2.7+1.25N_c$
Na-*n*-alkanoates (N_c = even)	$\Sigma\Delta S_{m,\mathrm{tr}}/R=-6.6+1.35N_c$

[a] Generally not valid for the first 2 members of the series.

[b] The available data for 1-alkenes and 1-alkanols are too irregular (and probably unreliable) for representation.

[c] The datum for ethylbenzene is appreciably higher than predicted by this equation.

TABLE 6.—*Entropy of Fusion Correction Due to the Presence of Polar Groups* [a] [b]

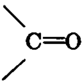
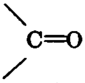
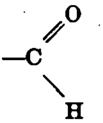
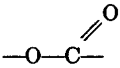
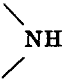
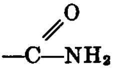
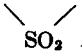
Polar group	Functional group	Correction [c]
Aliphatic ether	—O—	[d] −0.5 ±0.1
Aliphatic thioether:		
n-alkyl	—S—	[e] −1.0 ±0.5
sec-alkyl		
one		0.85±0.2
both	—S—	1.0
t-alkyl	—S—	−0.3 ±0.2
Aliphatic and diaromatic ketone		−1.5 ±0.1
Quinone		−0.7 ±2
Aliphatic aldehyde		0.8 ±0.3

TABLE 6.—*Entropy of Fusion Correction Due to the Presence of Polar Groups*[a, b]—Concluded

Polar group	Functional group	Correction[c]
Aliphatic ester	 $-O-C(=O)-$	
Aliphatic alcohol	One OH group per molecule	−1.2 ±0.2
Aliphatic primary amine	$-NH_2$	0.9 ±0.3
Aromatic amine (unhindered)[f]	$-NH_2$	0.3
Aliphatic and aromatic secondary amine	 $>NH$	−0.9 ±0.1
Monocyano alkane	$-C\equiv N$	0.7 ±0.2
Dicyano alkane	$-C\equiv N$	−1.8 ±0.1
Alkane amide	 $-C(=O)-NH_2$	−0.5 ±0.1
Alkane thiols	—SH (N_c = even)	1.0 ±0.2
	(N_c = odd)	1.8 ±0.1
Secondary alkane thiols	—SH	0.25±0.15
Tertiary alkane thiols	—SH	1.2 ±0.5
Dialkyl disulfide	—SS—	−1.2
Dialkyl or diaryl sulfone	$-SO_2-$	3.3 ±0.3
Heterocyclic sulfone	 $>SO_2$	−1.4

[a] Weighted to emphasize extrapolation toward $N_c>3$.
[b] For details on haloalkanes, see table 6.20, ref. 10.
[c] In units of *R*.
[d] This is the most common value; a range *trans* −1.4 (vinyl and ethyl ether) to +0.2 (1,4-dioxane) is found with lesser frequency.
[e] Very irregular.
[f] Hindered primary amine = −0.9.

homomorph from that of the compound. There is no need for T_R, as both are measured at their melting points. His corrections for polar and H-bond groups are shown in table 6.

Obviously, this system has a few loose ends, and Bondi discusses them very frankly. The reader is advised not to plunge into calculations without reading his work thoroughly. One major gap, for the present purposes, is that he presumes T_m to be known and hence does not undertake to predict ΔH_m. As pointed out at the beginning of this section, it tends to parallel ΔH_v, so hope for a solution from δ_D, δ_P, and δ_H is not unreasonable.

If the freezing points of pure compounds are difficult to predict, it might appear that those of mixtures would be nearly impossible to handle. Actually, the problem is relatively easy, and the van't Hoff equation, which first appeared in 1887, requires only minor adjustments to solve many cases, if the higher of the two freezing points is known. This is because mixed freezing points depend on the relatively well-understood solubility phenomena.

In lubricants, three types of cases commonly arise: (1) miscible liquids depositing immiscible crystals, (2) miscible liquids depositing "solid solution" crystals, and (3) miscible liquids depositing addition compounds. If the liquids separate before freezing, there are several other cases but these will not be considered.

For case 1, Hildebrand gives

$$-\ln x_2=\frac{\Delta H_{m2}(T_{m2}-T)}{RT_{m2}T}+\frac{V_2\phi_1{}^2(\delta_2-\delta_1)^2}{RT}+\phi_1\left(1-\frac{V_2}{V_1}\right) \tag{34}$$

where x_2 is the mole fraction of the solid in solution.

The first term is the entropy of fusion of the solid ΔS_{m2}, adjusted to the actual temperature T but with the terms involving the change in heat capacity on fusion ΔC_p omitted as an approximation. Near $x_2=0$, $\phi \simeq 1$ and the temperature gradient dT/dx_2 depends primarily on ΔS_{m2} and secondarily on the nonideality correction $V_2(\delta_2-\delta_1)^2$. A third dependence is on the entropy of mixing $\phi_1\ [1-(V_2/V_1)]$. To summarize, the effect of a small addition of a high-melting component on the first crystal formation, i.e., cloud point, is minimized by it having a small ΔS_{m2} and by close matching of δ_D, δ_P, δ_H, and V.

The eutectic temperature T_e may be estimated by simultaneous solution of the pair of equations

$$\ln(1-x_2)_e=\frac{\Delta S_{m1}}{R}\left(\frac{T_{m1}}{T_e}-1\right) \tag{35}$$

$$\ln(x_2)_e=\frac{\Delta S_{m2}}{R}\left(\frac{T_{m2}}{T_e}-1\right) \tag{36}$$

While petroleum lubricants are usually so nearly ideal mixtures that eutectics are not significant, substantial lowering of the freezing point of synthetics by blending is a common practice; e.g., mixed terphenyls.

3.4 Viscosity and Viscosity Index

Early work on correlating viscosity with structure was frustrating, and so were attempts at a purely thermodynamic approach. It has only recently become evident that part of the trouble was the lucky accident that so much data was fitted so well by the completely empirical ASTM (or Walther) equation

$$\log\log\left(\frac{\eta}{\rho+0.6}\right)=m\log\left(\frac{1}{T}\right)+k \tag{37}$$

where η is the viscosity in centipoises and η/ρ is the kinematic viscosity in centistokes. (The term "absolute" is controversial, as is the European term "dynamic," so in this paper "viscosity" without any adjective will be used for centipoises.) This form of equation has no logical connection with the thermodynamics of flow, but its widespread use in the form of the ASTM D 341 charts (ref. 21) will make it hard to displace.

Appeldoorn (ref. 25) reviewed the situation on empirical relationships, and concluded that Roelands' version (refs. 26 and 27) may prove even more satisfactory in fitting a wide range of lubricants. It covers the variation not only with temperature but also with pressure, and in addition shows a correlation against the percentage of total carbon atoms in aromatic C_A and naphthenic C_N rings. His general equation is

$$\log \eta = \frac{A_0}{T^x} + C\frac{P^v}{T^x} + DP^v + B_0 \tag{38}$$

where A_0 and B_0 are empirical constants characteristic of the liquid, $C = A_0/P_p{}^v$, $D = (B_0 - \log \eta_p)/P_p{}^v$, P_p is the pole pressure at which all the lines converge, and η_p is the viscosity at this pole.

The relation to composition is limited to petroleum products and uses a number of empirical constants. However, it is worthy of reporting here as an example of what can be done on a less than fundamental basis. Roelands (ref. 26) illustrates this for the pressure part of the equation by

$$\log (y - 0.890) = 0.00855(C_A + 1.5C_N) - 1.930 \tag{39}$$

$$P_p = 500 \frac{500}{(C_A + C_N + 27.5)^{1/v}} \tag{40}$$

$$\log \eta_p = \frac{-114}{C_A + 1.5C_N + 27.5} \tag{41}$$

No method for computing x is given because Roelands found that a constant value of $x = 3.5$ gives very satisfactory results for the oils studied, even at pressures up to 3000 atm.

Despite the sweeping generality of the Roelands equation, it still has little relation to thermodynamics. Bondi (ref. 10) points out that a more logical form was proposed 50 years ago by Vogel, though he could not at that time give any physical meaning to its three adjustable parameters. Various efforts since then have brought it to the form

$$\ln \frac{\eta}{\rho} = \ln \frac{A + E'}{T - T_0} \tag{42}$$

where A is an empirical constant depending on the liquid, E' is the energy of activation independent of temperature, and T_0 is the reference temperature, related to the glass transition T_g.

While this has a better foundation than equation (38), its application to petroleum is less well worked out. Bondi (ref. 28) made a vigorous effort to relate viscosity to molecular structure by means of equation (42). Though he met with considerable success above T_b, the region between T_g and T_b proved to be relatively difficult. The best correlating parameter was the reduced form of the equilibrium glass transition temperature, $5cRT_0/E°$, but the relationship between T_0 and T_g remains incompletely resolved. If N_c is greater than 15 and the molecules are aliphatic or cyclic with unbranched side-chain lengths of more than 4 atoms per chain, then T_0 is about $0.8T_g$. To quote, "Even that covers a range and can be related only very approximately to currently known structure parameters, primarily the number of external degrees of freedom per unit volume." In addition, hydrogen bonding presents special problems that will have to wait for better data. Of course, the reader can pick out a good many semiquantitative rules from his analysis, and in his book (ref. 10) these are made more accessible. Thus, anyone wishing to design a lubricant from first principles will get a good deal of help but not quantitative predictions.

Appeldoorn (ref. 25) offers a few suggestions on the effects of structure on the temperature and pressure coefficients: "Straight-chain, flexible molecules have low coefficients; bulky, branched and rigid molecules have high coefficients." He cites extensive studies in this area, in addition to reference 28.

In view of the lack of success of many sophisticated attempts to produce a unified structural explanation of viscosity, it is evident that the final model will have to be complex, nearly to the point of being useless. Viscosity is affected by both the intermolecular forces of section 2 and every possible sort of intramolecular force so far considered.

The problem of blending, as with freezing point, was solved long ago. Almost any model will do; the Walther function [$\log \log (\eta/\rho+0.6)$] gives quite good results, and Bondi's partly completed $5cRT_0/E°$ functions also can be used satisfactorily. Even the viscosity loss due to dissolved gas has been successfully predicted (ref. 29).

3.5 Work of Adhesion to Metals

The ability of a lubricant to resist being wiped off the bearing is obviously important. This is usually described in terms of contact angle (ref. 30), which is unfortunate as most lubricants show zero contact angle on the surfaces they are to lubricate. Except for some rare cases of autophobic liquids that cannot spread on their own monolayers, liquids which ball up on the surface are generally nonlubricants. Even worse, it is frequently stated that all solids on which a given liquid shows a contact angle of 0° have the same work of adhesion to it, because this work is calculated for nonwetting liquids as $\gamma_1(1+\cos\theta)$, where γ_1 is the surface free energy of the liquid and θ the contact angle. The fallacy of using this expression for wetting liquids was exposed long ago by Philipoff (ref. 31) and more recently by Gans (ref. 30). Their method for estimating the work of adhesion by extrapolation from contact angles of nonwetting liquids is shown in figure 8. The results must be used with some caution as the data were obtained by Bernett and Zisman (ref. 32), on metals that had been polished under water and hence were both oxidized and hydrated. However, they do compare favorably with older data obtained in vacuum.

Means for estimating γ_l from table 2 was published by Beerbower (ref. 40) who showed that for most organic liquids,

$$\gamma_l = 0.0715 V^{1/3} \left[\delta_D^2 + 0.632(\delta_P^2 + \delta_H^2)\right] \tag{43}$$

where 0.0715 includes the fraction of bonds cut by the liquid surface slicing across the octahedral space occupied, on a time-averaged basis, by a liquid molecule. This can be broken up into the partial free energies required for the Fowkes model of wetting (ref. 34), though there is some lack of numerical agreement on

$$\gamma_l^d \simeq 0.0715 V^{1/3} \delta_D^2 \tag{44}$$

Fowkes' polar surface tension corresponds roughly to

$$\gamma_l^p \simeq 0.0451 V^{1/3} (\delta_P^2 + \delta_H^2) \tag{45}$$

but might well be further subdivided. Corresponding values for the bear-

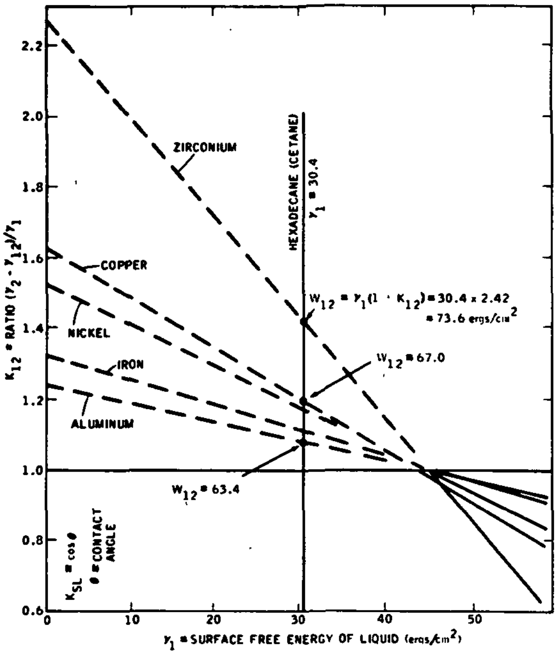


FIGURE 8.—Zisman-Gans plot of wetting power of organic liquids on metals (at relative humidity of 0.6 percent).

ing surface, $\gamma_2{}^d$ and $\gamma_2{}^p$, are difficult to obtain and impracticable to precompute. However, his equation for the work of adhesion W_{12} has yielded the useful information

$$W_{12}=2[\sqrt{\gamma_1{}^d\gamma_2{}^d}+\sqrt{\gamma_1{}^p\gamma_2{}^p}] \tag{46}$$

A different approach was taken by Hansen (ref. 35) who plotted δ_p and δ_H of a number of probe liquids on the surface and drew a circular contour line through all those just wetting. A further adaptation of this, to drawing the circle through borderline coefficients of friction, was worked out for polyethylene at various levels of surface sulfonation (ref. 36). This method of plotting gives a center of interaction located at δ_{D2}, δ_{P2}, and δ_{H2} and hence may be used in a work of adhesion:

$$W_{12}\propto 0.0715(\delta_{D1}\delta_{D2}+a\ \delta_{P1}\delta_{P2}+a\ \delta_{H1}\delta_{H2}) \tag{47}$$

Presumably this should eventually include the correction for molar volume disparity,

$$\Phi=\frac{4(V_1V_2)^{1/3}}{(V_1{}^{1/3}+V_2{}^{1/3})^2} \tag{48}$$

by Good (ref. 37), who prefers to build up his own equivalent of table 2 from other parameters and is very cautious about his ability to predict works of adhesion at solid-liquid interfaces.

Zadumkin (refs. 38 and 39) attempts to simplify the whole problem to essentially electrostatic attraction:

$$W_{12}=B\,\frac{\epsilon-1}{\epsilon+1} \tag{49}$$

where B is a constant for any given metal that is proportional to its contact potential against a hydrocarbon. His supporting evidence on liquid gallium and mercury looks favorable, though some nonconforming data are discarded on the basis of "impure liquids." He probably has justification for this screening, as such impurities taint the whole history of interfacial energies. The writer has shown (ref. 33) that B must vary with temperature to avoid a second-law violation and used equation (49) to explain the formation of multilayers of stearic acid (ref. 41) but has some reservations about describing a liquid with ϵ alone.

Despite the fragmentary state of this phase of the work, it appears that high values of V, δ_D, probably δ_P, and perhaps δ_H will lead to high values of W_{12}. Presumably this will at last quantify lubricity, where this is used as the modern equivalent of oiliness. Other usage of this word implies that chemical reactions are involved (see secs. 4.1.3 and 4.2.4) so still more parameters will be needed to eliminate that controversial word.

Up until recently, it has been taken for granted that high W_{12} values are an unmitigated blessing, but Rounds (refs. 42 and 43) has shown that some additives that enhance boundary lubrication can have adverse effects on ball bearing fatigue. Unfortunately, his tests were conducted without controlling the humidity. High humidity promotes fatigue, presumably through hydrogen embrittlement (ref. 44), so Rounds' case is incomplete, but there is another reason to believe his conclusion is correct. The standard Griffith equation for the minimum force L_0 to propagate a crack of length l in a solid is

$$L_0^2 \propto \frac{E\gamma_2}{l} \tag{50}$$

where E is the Young's modulus and γ_2 the surface free energy of the solid. For submerged solids, $\gamma_{12}(=\gamma_1+\gamma_2-W_{12})$ must replace γ_2, tending to lower L_0. Data on crystalline materials certainly bear this out (ref. 45), while data on glass usually take the opposite trend, quite unexpectedly, since equation (50) was basically derived from glassy concepts. It is to be hoped that some way around this conflict of interest can be found, but for the moment it appears that increasing W_{12} to protect gears, etc., entails some risk of decreasing L_0 on ball bearings in the same housing.

4. CHEMICAL PROPERTIES

In comparison with the abundant work of the materials sciences people, the crop of prediction methods from those studying chemical interactions with the environment seems scanty. However, it must be remembered that there are a limited number of chemical reactions that can be expected from lubricants, except those used in the chemical process industries which are outside the scope of this paper. The reactions which have been sufficiently studied to justify inclusion are thermal and radiation decomposition, hydroperoxide oxidation, oxidative dehydrogenation, flash and explosivity, autogenous ignition, and corrosion. Each of these categories must be subdivided into catalytic and noncatalytic, but not all of these subdivisions can be discussed in any meaningful way.

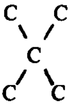
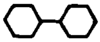
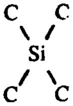
4.1 Thermal Decomposition

As implied in the above list, thermal decomposition will be discussed as it takes place under inert atmospheric conditions. The careless use of the term "thermal stability" to mean "catalytic oxidation and corrosion resistance at elevated temperatures" is a deplorable instance of language pollution. The reaction is basically homogeneous when noncatalytic; the effects when catalyzed are more difficult to classify. Radiation is handled simply as a special case of thermal stability.

4.1.1 Noncatalytic Thermal Stability

This is commonly measured in the isoteniscope, recently standardized as ASTM D 2879. Table 7 shows some typical results. Strictly speaking, only the decomposition point column relates to D 2879, which defines this as

TABLE 7.—*Effect of Chemical Structure on Thermal Stability*

Weakest links	Activation energy, kcal/mol	Decomposition point, °C
CH_2—CH_2	57.6	350
	67.6	330
	65	455
CH_2—CH_2—O—CO—CH_2	45.0	275
CF_2—CF_2—O—CO—CF_2	60	310
	65.7	350

the temperature T_D at which the rate of pressure increase $(\Delta P/\Delta\theta)$ is equivalent to 500 torr in 10 hr.

The activation energy is obtained by continuing the test beyond the decomposition point, as described in the appendix of the ASTM method. The slope of the plot is then converted to an apparent activation energy (E') by the Arrhenius equation

$$\ln \frac{\Delta P}{\Delta\theta} = \ln A' - \frac{E'}{RT} \tag{51}$$

where A' is proportional to the frequency factor or Arrhenius constant.

Blake (ref. 46) has done a great deal of work to elucidate the effects of various structures on A and E, with the specific objective of designing more thermally stable molecules. A molecule tends to fail at its weakest link, so those containing combinations of the groups shown have the lowest T_D values possible. If two groups fail at nearly the same T_D, the D 2879 result tends to be blurred. Several general rules supplement table 7.

(1) Branched chains tend to be less stable than straight ones, due to steric crowding and the production of relatively stable free radicals.
(2) Aromatic C—H and C—C bonds are strengthened by resonance.
(3) Ordinary esters fail by a special mechanism in which the β-hydrogen of the alcohol attacks the C═O group to form a quasi-6-member ring, which decomposes to olefin and acid. Esters without β-hydro-

gen are not subject to this and show T_D values as high as the corresponding hydrocarbons.

(4) Cyclohexane rings are more stable than alkane chains and may even surpass aromatic rings.
(5) Ether groups decompose to an alkane and an aldehyde or ketone, but unsubstituted aromatic ethers cannot follow this route and so resemble polyphenyls.
(6) Even one methyl group is enough to destabilize the polyphenyl ethers, by about 65° C, and multiple substitutions cause further decrease due to more decomposition sites.
(7) NH groups fail by a low-energy path, but in $N—CH_3$, etc., this is blocked.

Work by Klaus (ref. 47) added another rule,

(8) Polymers with an all-carbon backbone have a sort of "zipper" structure and revert to monomer or dimer at about 275° C. Oligomers tend to follow the same path, and hydrogenation does not "lock the zipper."

When the 455° C limit of the polyphenyls is passed, lifetime lubrication ceases to be feasible. However, as implied in figure 1, glass molding at 480° C on the mold and 1000° C on the glass is being lubricated. More recently, continuous casting of steel at 200° C on the mold and 1200° C on the steel has been added. These jobs depend upon rapid renewal of the lubricant film, and the fact that the E values are low enough to fit the cycle time. For glass, this is about 1 sec, and the lubricant has a safety factor of 20 or more.

4.1.2 Radiation Stability

The effect of radiation, as briefly mentioned above, resembles a rather special form of thermal decomposition. A high-energy (0.5 to 10×10^6 eV) photon or particle enters the liquid. If a single atom absorbed all this, it would acquire kinetic energy equivalent to about 10^{10} degrees Celsius. Such total absorption is rare, and energy transfers often run about 1 percent per atom struck. The secondary radiation from a primary impact is considerably milder, ranging down to very-short-wavelength ultraviolet. Each impact, according to the Compton principle, tends to produce two photons or electrons of about half the incoming energy so that near the end of the process, the original photon might have generated 10^6 more photons, each of about 1 eV. After that, chemical action ceases and the photons end as entropic heat.

Regardless of the type of molecule involved, the first 10^4 or more impacts will tend to rip out the hydrogen or carbon atom struck, leaving an ionized gap. It makes a great difference which is struck in terms of subsequent events. Hydrogen removal merely creates a free radical and some hydrogen gas, but striking a carbon causes scission if a linear molecule is involved. The two fragments are also radicals; they may cool off to olefin or combine into tar. If air is present, they may initiate autocatalytic oxidation reactions. The products are thus different from those of thermal cracking, which tends to generate one olefin and one saturate.

Cyclic molecules tend to be more resistant, as the two hot ends are kept together and healing can take place. In aromatics, there is additional protection because the ring is elastic enough to store moderate energy long enough to dissipate it without scission.

There is no threshold below which radiation damage is completely healed. In general, the integrated dose in ergs per grams is a true measure of the damage regardless of whether initiated by a high- or low-energy photon or electron. However, the measurability of the damage tends to increase more or less exponentially with the integrated dose. Thus, a linear molecule often shows little or no detectable damage at 10^8 erg/gm and yet is distinctly degraded at 10^9 erg/gm, while an aromatic would show the same effects at about 100 times the dose.

As in a thermal decomposition, the weak parts of a molecule fail first, and alkylated aromatics tend to show the response of the alkyl groups. However, there are no special traps such as the β-hydrogen or zipper polymers to be feared.

4.1.3 Catalytic Thermal Decomposition

Lubricants seldom encounter catalytic cracking in the ordinary sense because oxides and silicates require temperatures of 400° C or more. However, some interactions with metals are now becoming recognized as a factor in lubricant failure, and these fall within the complex discipline known as catalysis. Blake (ref. 46) conducted tests with 52100 steel present and noted a loss of 35° to 60° C in T_D for three esters. Klaus (ref. 47) has done a great deal of this work, using the MIL–H–27601A stainless steel pressure cylinder, with balls of M–10 tool steel, 52100 steel, and naval bronze which have been HCl washed and dried. His work tends to confirm that catalysts decrease T_D for esters but shows little difference from the D 2879 all-glass method on well-refined hydrocarbons.

An interesting further analysis can be made of his data on a more or less homologous series of five superrefined oils of various molecular weights. He analyzed the data on a constant frequency constant A of 10^{13}, but if instead it is analyzed on the basis of a constant E value of 63 000 cal/mol (the mean of the data), A becomes a function of the molar volume V so that

$$\ln \frac{\Delta P}{\Delta \theta} = 49.2 + 0.0014V - \frac{63\,000}{RT} \tag{52}$$

This indicates that frequency of scission per unit volume is the variable, and hence that large molecules are less stable than small ones. This will be further considered in section 4.4.

There is a special feature of the lubrication process that may bring out effects not ordinarily observed. It is the vigorous wiping action that not only exposes fresh surfaces, but goes further and activates them with dislocations. The effect of freshly cut metal is not at all like that of the usual metal specimen that is isolated from the oil by a layer of hydrated oxides.

Two phenomena are known to take place. With aliphatic hydrocarbons, the primary process is dehydrogenation (ref. 48). This may take two, four, or even more hydrogen atoms away from the molecule, leaving a multiradical that tends to polymerize. The hydrogen soaks into the metal; it may contribute to hydrogen embrittlement and fatigue failure, though only on the harder steels (ref. 49). Under some conditions, the dehydrogenation is so complete as to form a cementite (Fe_3C) layer on the metal surface (ref. 50).

Aromatic hydrocarbons follow a different path, according to Goldblatt (ref. 51). The primary process is electron acceptance to form anionic radicals. These may discharge their energy to aliphatic molecules, leading to polymer formation; be quenched by O_2, H_2O, or heteroatom organic impurities, or combine with the metal to form unstable compounds that later dump the metal as semicolloidal wear debris.

Due to the newness of these concepts, no predictions can be made as to the interactions of nonhydrocarbon molecules, except that many of them would fall in the category of quenching agents for the anionic radicals.

The effect of polymer may sometimes be helpful, as discussed below, but it can also, and more often, form harmful deposits (ref. 52). Carbide formation certainly is not beneficial, as Fe_3C is quite brittle and abrasive.

No catalytic effects of metals have been reported in radiation decomposition. This may be partly due to the fact that metals resemble radiation in their effects and even emit electrons similar to β-particles from freshly deformed surfaces. The effects would thus be simply additive rather than catalytic.

4.2 Oxidation Phenomena

As mentioned above, there are several oxidation processes, most of which must be considered from both noncatalytic and catalytic viewpoints. The two processes that take place without flame should be considered separately from the others, as they tend to overlap for a certain temperature interval.

4.2.1 The Hydroperoxide Reaction Without Catalyst

The phenomenon of low-temperature oxidation of aliphatic structures (ref. 53) has been so well studied that only token mention will be made of this process. The typical result of a series of reactions is represented by

$$R\text{—}CH_3+1.5O_2\rightarrow R\text{—}CH_2OOH+O\rightarrow R\text{—}COOH+H_2O \qquad (53)$$

Side reactions on CH_2 groups produce ketones, and aldehydes may also be formed. The resulting mixture has a fruity odor that is quite characteristic.

4.2.2 The Catalyzed Hydroperoxide Reaction

While thermal stability tests run in inert vessels can usually be correlated with the more realistic catalyzed situations, this is by no means true of oxidation. One reason is that catalysis of thermal decomposition takes place mainly at the metal surface. This heterogeneous catalysis involves only a few steps. Oxidation depends quite heavily on homogeneous catalysis, in which dissolved metal is the main accelerating factor. This type of reaction is basically simpler, but many complications arise in the processes of dissolving the metal and then losing it again into sludge. In a classic paper, Thompson (ref. 54) studied the interaction of copper with transformer oils and air. The results of seven series of increasingly sophisticated experiments could be correlated into one line by a corresponding-test-conditions principle. This is less basic than the corresponding states of section 2, but it served to unify about 80 points, some of which represented means of as many as 36 separate determinations, from several laboratories. Other tests in which he deviated from corresponding conditions fall off the line in the appropriate direction. The correlating equation is

$$\log A_S=1.15 \log A_I-0.31 \qquad (54)$$

where A_I is the acidity or sludge due to solid metal catalyst in 164 hr at 100° C and A_S, that due to 5 ppm of dissolved copper in 164 hr or to 5 ppm Cu+5 ppm Fe in 48 hr, at 110° C.

All Thompson's oils were without additives but contained varying amounts of aromatics and heteroatom compounds. It is probably safe to say that his conclusion is generally valid, and hence that the rate of oxidation is directly proportional to the amount of metal in solution at any instant. It should be possible to write a model equation based on rate of solution and rate of loss of metal as sludge, both as functions of the acidity already produced, but that is outside the scope of the paper.

When antioxidants, metal deactivators, and other additives are used, as is almost always the case, except in electrical oils, modelmaking would require more terms and is hardly worth trying. It is probable that the interaction terms would dominate the result, which leads to a very important point: Tests run without appropriate additives and environment are worse than useless.

The ranking of metals as catalysts for this reaction is based on their ability to alternate between two valence states, thus serving as a very active link in a chain reaction. Copper is at the top of the list, by any of the many criteria; cobalt, manganese, iron, and lead follow in about that order, based on equal concentrations in solution. These effects are subject to great variations due both to the lubricant composition and the surface condition of the metal. Alloys may behave as if composed of 100 percent of the catalytic metal in some cases (Cu in monel), or proportionate response (Cu in brass), or totally concealed (Fe in 300 series stainless steel). The responses seem to follow the Gibbs principle of the surface of a mixture presenting the composition that minimizes the free energy of the system. However, there does not seem to have been any detailed study of this. This situation is complicated by the three kinds of freezing noted just above equation (34), metals being especially prone to form addition compounds.

The effects of temperature and pressure are readily predictable if done on an induction period basis. This is illustrated in figure 9, where the behavior of a pure compound, an uninhibited petroleum oil, two oils A and B with antioxidants, and an inhibited oil with catalyst are illustrated at the same temperature *T*. The induction period θ_i is the vital parameter. The dangerous fallacy of testing to a constant time is shown by oils A and B. If examined at θ_1 or at θ_2, oil A will be given the better rating, but actually oil B is superior if the oxidation level A_1 represents the point at which serious metal damage starts, usually the widely accepted rejection criterion of 2.0 mg KOH per gram of oil neutralization number. Thompson was fortunate that he was using uninhibited oils, as his sampling was too infrequent to give accurate values of either θ_i or the time to reach A_1.

If a suitable test method is used, such as ASTM D 943 (iron and copper

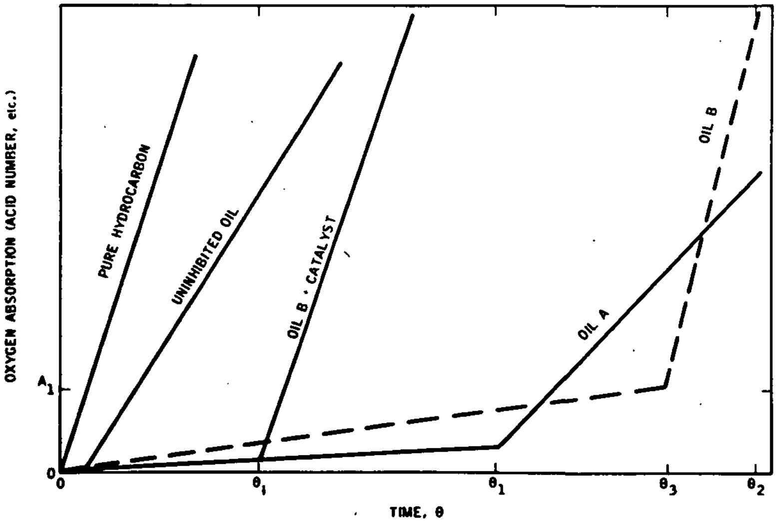


FIGURE 9.—Idealized oxidation models.

catalysts, water, oxygen at 1 atm, and 95° C) or ASTM D 2272 (copper catalyst, water, oxygen at 14.3 atm, and 150° C), θ values are acquired for A_1, which may be taken as an approximation of θ_i. There are a great deal of data, not yet properly assembled, which show that θ_i is inversely proportional to the partial pressure of oxygen and follows an Arrhenius equation, doubling for every 10° C decrease in temperature. Combining these, the induction period at T_2 and P_0 is

$$\theta_i = \theta_0 \frac{0.210}{P_0} \exp\left[-33\,500\left(\frac{1}{RT_1} - \frac{1}{RT_2}\right)\right] \tag{55}$$

where θ_0 is the induction period at T_1 in air and P_0 is the partial pressure of oxygen.

Not much can be offered in the way of correlations with chemical structure. The above discussion was based on typical petroleum lubricants, more or less well refined. There is no distinction among normal, iso, and cycloparaffins in this respect, but aromatics require special attention. Those with one ring must be further subdivided into those that include a hydrogen in the benzylic position and others. The others behave like the aliphatics, but the benzylic groups are extremely difficult to inhibit and tend to poison any mixture in which they constitute even a few percent. The fused-ring aromatics tend to have inhibitive properties, in addition to having inherent oxidation resistance unless heavily alkylated. The heteroatom molecules are so many and complex that they have still not been classified in this way, but it appears that some are oxidation catalysts, others are inhibitors, and many are neither. The same applies to synthetic lubricant molecules, past, present, and future. The chain-linked aromatic hydrocarbons and ethers share many of the properties of the fused-ring type. Perfluoro compounds are, of course, free from the hydroperoxide reaction but have troubles all of their own.

4.2.3 Dehydro-Oxidation Without Catalyst

A second oxidation process competes with the hydroperoxide mechanism. It may be typified by

$$4R-\text{H}+\text{O}_2=4R^*+2\text{H}_2\text{O}=2R\text{—}R+2\text{H}_2\text{O} \tag{56}$$

and might be loosely described as a combination of thermal decomposition, with oxygen as the catalyst, followed by prompt oxidation of the hydrogen. The free radicals can discharge their energies in all the usual ways but tend most frequently to end by polymerizing, first to thickened oil, and then to sludge. A great deal can be learned about this reaction from the asphalt industry, where products are customarily thickened by air blowing at 225° C. It is hard to draw any sharp line between the hydroperoxide and this free radical mechanism, but the former may be considered dominant from 25° to 175° C, and the latter above 215° C.

This is not the place to discuss additives, but it should be mentioned that the phenols and aromatic amines that are so effective at lower temperatures often become substantial contributors to high-temperature sludge. These peroxide destroyers seem especially prone to dehydrogenation. The radical-quenching inhibitors are a much more miscellaneous collection of chemicals.

4.2.4 Catalytic Dehydro-Oxidation

Predictably, the metal catalysts tend to reinforce and extend the temperature range of this reaction. When the metal is freshly deformed, this mechanism can prevail even at 25° C. Because the catalysis is heterogeneous, the free radicals tend to deposit on the metal in the form of polymers, just as under inert conditions. However, the process in the presence of oxygen is many times faster than without, and the results are extremely common. On the harmful side is a series of films known as lacquer, varnish, and coke, formed at increasing temperatures. What forms at relatively low temperatures is a material originally known as friction polymer. It was first recognized and named by Hermance and Egan (ref. 55), who found it on noble-metal electrical contacts as a high-resistance deposit. Subsequent work has shown that a related surface resin can be beneficial in lubrication (refs. 33 and 51). Because it forms in the vicinity of wear spots as a thick liquid that subsequently polymerizes to a resin, perhaps "wear oligomer" would have been an appropriate name, but "surface resin" appears quite descriptive. It is believed to alleviate wear by filling in the antiasperities, which causes increased hydrodynamic lift and relieves the load on the asperities. It has long been recognized that successful break-in sometimes involves a sort of "glaze"; this is now believed to be surface resin at its hardest and best.

The composition of this material has been reported by Fein and Kreuz (ref. 56) and confirmed in our laboratory. It contains a substantial amount of oxygen as CO and CO—O groups and up to 3 percent of nitrogen. As the latter must have come from the air, and as even pure aromatics are split into aliphatic chains, it is evident that very high energy is involved.

Time has not permitted an extensive investigation of the effects of changing metallurgy on the beneficial results of surface resin. However, the original data (ref. 55), plus some confirmatory work by Dietrich and Honrath-Barkhausen (ref. 57), have been analyzed. Two steps were taken that may startle the catalyst workers, but which seem justified. Based on some correlations by Bond (ref. 58), it was assumed that the A constant in equation (51) was independent of the metal and that the activation energy E was a function of γ_2, the surface free energy of the metal. The resulting correlation is shown in figure 10 and in the equation

$$\log r = 7.3 \times 10^{-7} \gamma_2 RT - 6.85 \qquad (57)$$

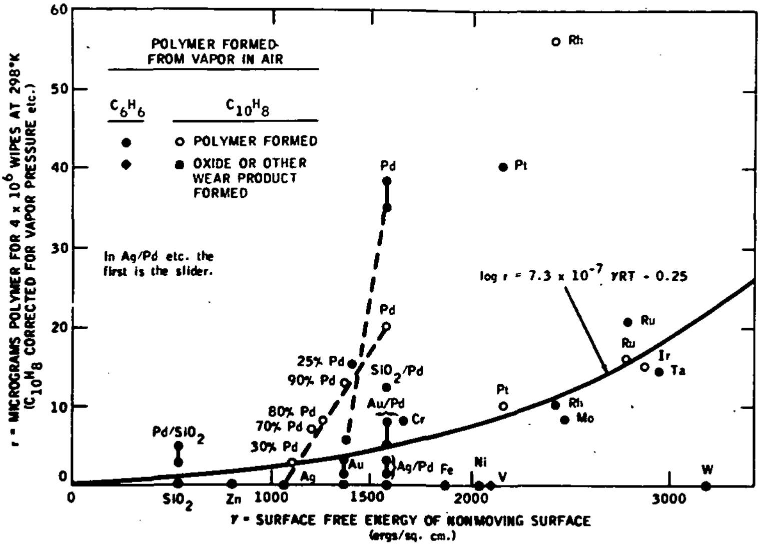


Figure 10.—Correlation between polymer formation and surface free energy.

where r is the rate of polymer formation in μg per wipe of the contacts. It is somewhat presumptuous to include T, as all the data were obtained at 25° C, but analogy to the much simpler reactions cataloged by Bond tends to justify this step.

The bulk oil also undergoes polymerization, just as happens without catalyst. While there are many other points of difference, it may be postulated that the clearest postreaction distinction between the hydroperoxide and dehydro reactions is that the main result of the former is acidity, and the latter, viscosity increase. Sludge may arise from secondary reactions in either case. If, as frequently happens, acidity and viscosity increase together, mixed modes are to be suspected.

Structuring to resist catalytic dehydro-oxidation is difficult because all hydrocarbons are subject to it. Perfluorination or the use of free radical trapping additives appear to be the best routes available.

4.2.5 Catalytic Oxidation With Radiation

There is little to add since the previous publication (ref. 1), so figure 11 is reproduced from it without change. The technique was a modification of ASTM D 943, run without water to permit the use of higher temperatures than the standard 95° C. Results from the latter may be entered at the point marked by "+" to estimate the combined effects of temperature and radiation. Two points are made in figure 11, the first being the way that radiation rate and temperature may be interchanged one for the other. The second is that lubricants are insensitive to radiation doses that

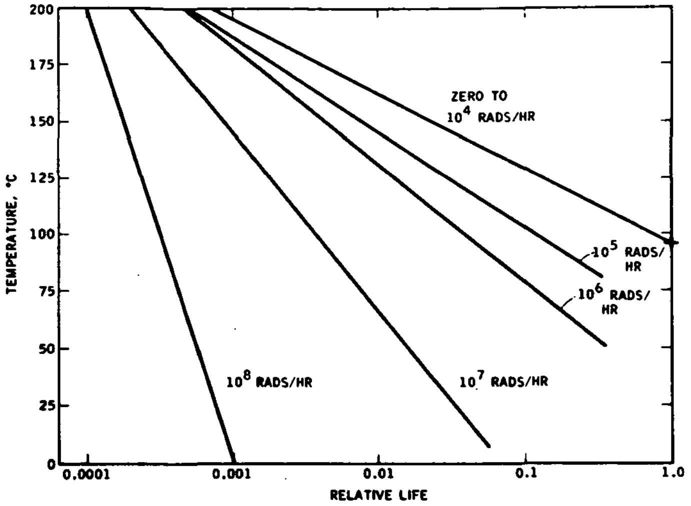


FIGURE 11.—Effects of radiation and temperature on life of turbine oils.

would kill a human in about 30 sec, so in any part of a powerplant visited by personnel special lubricants are not required.

4.2.6 Effects of Water and Humidity

The ubiquitous presence of moisture makes it hard to find cases in which it is absent, especially because it is a primary product of oxidation by both equations (53) and (56). However, it has long been known that there is a difference between dry and liquid H_2O present, especially in the presence of catalytic metals. It may be presumed that water serves several roles, one of which is to facilitate solution of the metal into the homogeneous catalyst situation. Very recently, Vaessen and de Gee (ref. 59) have thrown some light on the intermediate situation by pointing out that each metal has a critical relative humidity (RH) above which it or its corrosion products maintain a film of liquid water. This would help to account for some anomalies that have been only vaguely reported. Much more work is needed in this 50- to 95-percent RH area.

4.3 Flashpoint and Explosivity

Work by Affens (refs. 60 and 61) has shown that the various flashpoints have a rational basis. However, his data are limited to fuels, and no comparable correlations have been published on lubricants. Some years ago, the writer (ref. 62) undertook to establish the relations among the ASTM D 1160 distillation under reduced pressure, the vapor pressure, and the ASTM D 972 evaporation rate. The literature search uncovered work by Dreisbach (ref. 63), who had already correlated the Cleveland open cup flashpoint by ASTM D 92 with vapor pressure for a number of classes of compounds, as shown in table 8. With this encouragement, the writer then proceeded to correlate the D 92 flashpoint T_F and D 1160 temperature for 5 percent distilled at 10-torr pressure T_{b5} on a total of 50 lubricating oil base stocks. Flashpoints ranging from 190° to 580° F were successfully included in the equation

$$T_F = 0.924T_{b5} + 9.62 \tag{58}$$

with a correlation coefficient of 0.996. This gives an equivalent reproducibility of prediction of 26° F, compared with the single-test reproducibility of 30° F (ref. 21). As a result of these three separate studies, a few rules can be laid down with considerable confidence:

(1) The flashpoint (D 92) of lubricating oils comes at the temperature for 5 percent distilled at 10-torr pressure.
(2) This is essentially as predicted by Dreisbach, so his other values in table 8 should apply to lubricants.
(3) Raoult's law blending, as discussed by Affens, gives good predictions for the 10-torr temperature, and hence the flashpoint, for hydrocarbons.
(4) The lower flammability limit F_L and the flashpoint are two expressions of the same phenomenon.

TABLE 8.—*Estimation of Flashpoints*

Family	Formula	Vapor pressure at flashpoint (torrs)	Accuracy
Benzenes with saturated side chains	C_nH_{2n-6}	8	Close
Benzenes with unsaturated side chains	C_nH_{2n-8}		
Alkylchlorobenzenes	$C_nH_{2n-7}Cl$	10	Very close
Dichlorobenzenes	$C_nH_{2n-8}Cl_2$	25	Very close
Monochlorobenzene	$C_nH_{2n-7}Cl$	16	Exact
Naphthalenes	C_nH_{2n-12}	10	Close
Phenylethyl alcohols	$C_nH_{2n-6}O$	13	Close
Phenols	$C_nH_{2n-6}O$	10	Close
Aromatic amines	$C_nH_{2n-5}N$	8	Close
Aliphatic hydrocarbons	C_nH_{2n+2}	6 to 10	Approximate
Aliphatic alcohols (C_1 to C_5)	$C_nH_{2n+2}O$	40	Approximate
Aliphatic alcohols (t–C_5 and C_6)	$C_nH_{2n+2}O$	15	Approximate
Aliphatic ketones	$C_nH_{2n}O$	10	Very close
Aliphatic esters (T_b<80° C)	$C_nH_{2n}O_2$	40	Approximate
Aliphatic esters (T_b=80 to 120° C)	$C_nH_{2n}O_2$	25	Approximate

(5) The fire point by D 92 corresponds to 20 torr at 5 percent evaporated on lubricating oils. There is reason to hope that this correlation is as good as that on flash, allowing for the difference in standard deviations of testing (ref. 21).

(6) The upper flammability limit F_U is estimated, on a similar basis to that used by Affens, to represent 6 percent (volume or mole) of vapor in the space above the liquid. At 1 atm, $P_v = 45$ torr for this condition.

In regard to rule (3), the reader must be warned that any blends not essentially all hydrocarbon may show very marked deviations from Raoult's law. In such cases, both Hildebrand (ref. 2) and Prausnitz (ref. 13) give methods for calculating the fugacities from the V and δ values. However, many of the worst deviations come from blends involving alcohols, where flashpoints up to 15° F below that of the lower component have been observed. Fortunately, alcohols are not often major components in lubricant blends. If they are required, three-parameter equations must be used.

Rule (4) requires some consideration of the four flashpoint methods, because it can strictly be true of only one. Affens gave this matter a great deal of thought and selected the Tag closed cup (ASTM D 56). This is eminently logical and proper, but bad news to the lubrication engineer who thinks only in terms of D 92. As implied in rule (1), D 92 correlates with the vapor pressure at 5 percent off. This is the reason that many years of study have never produced a valid correlation of the closed cup tests D 56 and D 93, with the open cup tests D 92 and D 1310. Pure compounds may generate one correlation line, but mixtures must generate a whole series of lines whose spacing is a function of the initial slope of the distillation curve $dT_b/d\phi$, where ϕ is the volume fraction evaporated. However, since most of the loss takes place in the last few minutes of heating, while P_v is between 0.25 P_F and P_F, the vapor pressure for flashing, and the evaporation rate $d\phi/d\theta$ for a given geometry and ventilation is proportional to $P_v\theta$, the lines should be parallel.

This being the case, the writer has found that inquiries as to P_v and the flammability limits are best handled with dual answers. The questioner is asked to decide between the closed system regime, in which all vapor is retained, and the open system in which 2 to 5 percent of weathering off may be anticipated. Almost all engineers have expressed their need for open system data, though a number have also collected the other just for information. This is gratifying, because most lubricant test methods relate to open system, including the open cup flash and fire tests, ASTM D 972 evaporation and D 1160 distillation. The latter specifically forbids collecting data before 5 percent has distilled and references an article in which initial boiling points by D 1160 were shown to be highly inaccurate. Our problems clearly are different from those of the fuel and solvents people, who seem to need closed system data. The only closed system methods designed to provide both fuel and lubricant data are ASTM D 93 flashpoint by Pensky-Marten closed cup and D 2879, vapor pressure by isoteniscope.

In view of this reference, coupled with the much greater capability of the lubricant makers to supply open system data, the writer decided to limit this discussion to flammability limits as measured by D 92, D 972, D 1160, and D 2878. This is the philosophy expressed in rules (4) and (6), which cover the flammability limits at 1 atm. The effect of changing air pressure can readily be computed. The two vapor pressures are first converted to mole fractions by dividing by 760 torr; the lower limit, $x_L = 0.013$, and the upper limit, $x_U = 0.060$. These are then multiplied by the prevailing pressure to yield the two pressures, P_L and P_U, which are converted to temperatures by equation (20) or, more simply, by a Maxwell chart (ref. 64) that expresses the same facts. The results are shown in figure 12.

These correlations are based on the premise that the lubricant maintains its chemical integrity. If this is not true, due to oxidation or thermal decomposition, other rules apply. When T_D is reached, $F_U \simeq T_D$.

4.4 Autogenous Ignition

Several different ignition phenomena may be grouped under the general term "autogenous," which simply means that no pilot flame is required to touch off a self-sustaining reaction. These phenomena are only related to that extent, as they proceed by very different mechanisms.

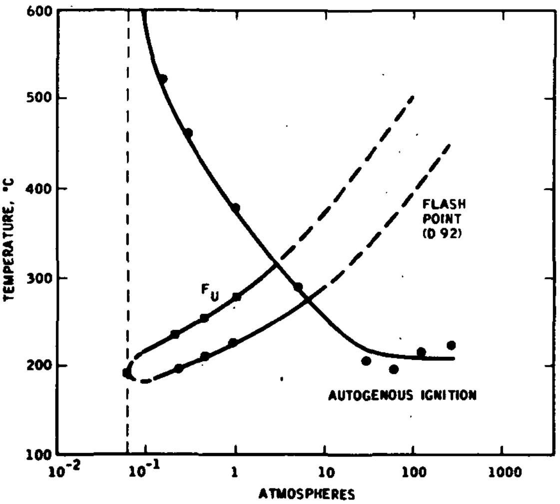


FIGURE 12.—Effect of air pressure on turbine oil.

4.4.1 Spontaneous Combustion

There seems to be some degree of confusion over the old problem of oily rags that, left too long in a heap, have been known to heat up and burst into flame with disastrous results. The problem is real, but much of the concern is not necessary as this reaction is quite specific to paintmaking oils such as tung and linseed, which are characterized by conjugated double bonds. This phenomenon was intensively studied many years ago, and a method developed for measuring the heating tendency. The Mackey test, now out of print, involved soaking a wad of cotton in the suspected oil, wrapping it around a thermometer bulb and passing a stream of oxygen past it. If no spontaneous rise took place from room temperature, the whole apparatus was slowly warmed until it started or 100° C was reached. No oil that would be classed as a lubricant ever failed the Mackey test; but the supposition that rags saturated with lubricants are dangerous certainly contributes to better housekeeping.

4.4.2 Autoignition Temperature

A second phenomenon, which does involve hydrocarbons, is a serious concern to both fuel and lubricant experts. This takes the form of a flame arising, without any source, when an oil is injected into a heated vessel containing air. Affens (ref. 65) did a good deal to elucidate the effects of structure on the autoignition temperature (AIT) of fuels.

His results may be summarized by listing the factors favoring resistance to autoignition: decreasing chain length, addition of methyl groups and branching, alicyclic rather than straight chain, aromatic better than alicyclic, and freedom from side chains on aromatics.

This list has a good deal in common with the results in section 4.1. Except for addition of methyl groups and branching, which clashes with Blake's list but was not found to be important by Klaus, these effects are precisely what one would expect if autoignition is preceded by thermal decomposition. Unfortunately, it is difficult to compare Affens' data on C_6 to C_{10} *n*-alkanes with equation (51); but his increase of 20° to 25° C in AIT over that range of molar volumes is quite in line.

While there are undoubtedly similar structural effects in lubricants, they tend to be mingled in a confusing way in such large molecules. As a general observation, there seems to be a fair degree of correlation with thermal decomposition temperature, so the AIT tends to be about 40° C above the result of ASTM D 2879. This may not be applicable to all types of lubricants, but it would indicate that decomposition is a necessary first step on mineral oil. As a result, the AIT's of most well-refined petroleum lubricants tend to cluster around 375° C. Higher molecular weight oils tend to be a little lower. Synthetics vary so much that discussion of structures and mechanisms will be omitted.

The technique for AIT has long been ASTM D 286, using a small quartz flask. This was replaced by an improved version, D 2155, in 1966. Both of these methods have been criticized because of wall effects, known and suspected, due to the use of small flasks. A new method, D 2883, called the reaction threshold temperature (RTT), was introduced in 1970. It uses a much larger (1000 cm^3) flask, which may be stainless steel to permit running RTT at up to 10 atm. It is too soon to state whether the improvements anticipated will all be realized.

Previous work at pressures other than 1 atm has largely been done by Zabetakis (ref. 66). Some of his data, on a typical steam turbine oil, are shown in figure 12 along with the flammability envelope on the same oil. While Zabetakis drew this particular curve with minimum at about 70 atm and justified this on the basis that *n*-propyl nitrate also shows a minimum (ref. 67), all of his other data show a regular decrease of AIT with increasing pressure.

4.4.3 Impact Sensitivity

A rather specialized oxidation mechanism is associated with aerospace, where liquid oxidizers are commonly handled in equipment, some of which must be lubricated. The test consists of submerging a standard volume of lubricant in the oxidizer and dropping a 20-lb weight on it. The maximum height for no reactions from 20 drops is known as the threshold in ASTM D 2512, originally limited to liquid oxygen, but now extended to include liquid fluorine, nitrogen tetroxide, etc. A different philosophy is expressed in appendix III of D–2—1969, in which the reaction intensity is measured at a standard drop height of 43.3 in.

All hydrocarbons and many other synthetics fail these tests, and little has been learned about structural effects in the perhalogenated lubricants that pass. It is not likely that any correlations with other oxidation tests will be possible.

5. STRETCHING THE ENVIRONMENTAL CAPABILITY OF LIQUID LUBRICANTS

The U.S. Air Force recently sponsored two studies on what factors in lubricants represent the main barriers to further improvements in aircraft (refs. 68 and 69). Both came out with essentially the same conclusions, that the weakness lies in thermal and oxidation stability, with an accompanying need for higher AIT. Both studies point out that this could be alleviated by improvements in thermal conductivity and heat capacity, but no amount of improvement in λ and C_p will help enough to avoid higher engine temperatures. Other physical properties were also subject to improvement, but not in any pressing need of it. On the other hand, improvements in stability that adversely affect thermal properties, vapor pressure, viscosity at low temperatures, or density would be of questionable value. Bulk modulus and gas solubility were not specifically considered. Bearing life and gear load capability had to be considered in terms of overall design plus lubricant improvements; significant results were found, but the current state of lubrication theory made it impossible to assign separate credits.

Thus, it appears that the burden lies largely on the lubricant manufacturer to increase the thermal decomposition temperature, the AIT, and oxidation resistance. The first two were shown above to be intimately related and probably will have a common solution. The third, viewed as primarily high-temperature oxidation by the free radical mechanism, also shows strong symptoms of being initiated by decomposition. This is indicated best by the resistance of aromatics, as well as other lesser evidence. If this is indeed the case, the problem becomes one of maximizing thermal stability without impairing the physical properties. Obviously, this has been tried hundreds of times, but perhaps new insight into what all the effects are that a given change would produce will aid in planning for a minimum of dead ends. A few guidelines might be—

(1) Low molar volume minimizes the exposure to thermal damage but raises the vapor pressure.
(2) Strong dipoles will lower the vapor pressure, but hydrogen bonds will not.
(3) Dipoles may raise the glass transition temperature T_g a little, but if molar volume is kept low, T_g will approach the freezing point T_m.
(4) Low melting point in such a molecule as described calls for an extraordinary amount of ΔS_m because ΔH_m will be raised by the dipoles.
(5) The presence of hydrogen is highly detrimental, and it should be replaced with fluorines, at least in the most vulnerable positions, plus chlorines to provide polarity.
(6) If the resulting liquid fails to lubricate, interdisciplinary work with metallurgists and bearing designers is strongly recommended.

6. CONCLUSION

It is evident that liquids have solved lubrication problems in the past on a trial-and-error basis solely because they had far greater potential than was realized. The present situation marks the end of such good fortune, and further improvements will depend on thorough ability to predict the interactions in figure 3, lest a fortune be spent in half-blind searching. Help must be drawn from the chemical engineers, the paint and adhesive experts, the ceramicists, the metallurgists, and other materials scientists for the time when an uneasy alliance of organic chemists and mechanical engineers could make progress by trial and error is now ended.

ACKNOWLEDGMENT

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DISCUSSIONS

F. T. Barwell (University College of Swansea, Swansea, England)

While sympathizing to some extent with Mr. Beerbower's view that "the time when an uneasy alliance of organic chemists and mechanical engineers could make progress by trial and error is now ended," one must acknowledge a great deal of achievement attributable to those workers who have overstepped the bounds of their initial discipline and have cooperated with men from other fields of study to develop the subject of tribology. If what the author means is that chemists and engineers must themselves acquire the outlook of tribologists, I must agree with him.

In common with other authors in this symposium, Mr. Beerbower has been set a difficult task of dealing with a specific topic, in his case liquid lubricants, which must however be set within the context of the total tribological system, which embraces the complete machine element as affected by the thermal and dynamic duties imposed thereon. In figure 3 he has resolved this problem by taking the lubricant as his standpoint and considered the manner in which it reacts with other elements of the tribological system. In section 4 the importance of specific reactions with the surfaces are illustrated by the case of friction polymers. These may be beneficial by limiting corrosion and facilitating lubrication or they may be harmful as in microelectrical contacts where tarnish films may inhibit proper functioning. Closely allied to the friction polymers are the degradation products that cause lacquering of engine pistons. Similarly, in a study of the temperature limitations of the lubrication of ball bearings with inner-race-located separators, it was observed that failure was due to polymer-type deposits that were similar in appearance to the lacquering of pistons and piston rings and that eventually filled the space between the separator and the locating land on the inner ring leading to failure. In supplementation therefore of his treatment of the crucial problem in the formulation of liquid lubricants, namely, their thermal and oxidation stability, perhaps Mr. Beerbower would indicate the extent to which basic chemical structure can determine the nature of the degradation products. In the last resort it is the nature of the degradation product that may determine whether or not failure of the mechanism will occur. Solid carbon or polymers are disastrous, whereas a substance that degraded to give off a gaseous decomposition product would be entirely acceptable.

Regarding collaboration between different disciplines, the contribution of Professor Lamb, an electrical engineer, at this symposium is worthy of mention. Most chemists and engineers tend to think in terms of steady-state solutions, whereas the electrical engineer has to face up to transient conditions involving both resistance and reactance, two terms governing effects that are related by a 90° phase lag. Therefore in considering what happens in a tribological contact, particularly under concentrated elastohydrodynamic (EHD) conditions where the time scale is exceedingly short, any elastic or Hookean strains will be in quadrature with the viscous or Newtonian deformations. Therefore the electrical engineer's way of thinking is particularly appropriate. Of course, the introduction of phase considerations may have been fortuitous, arising from electrical methods used in excitation of the crystals in the determination of the appropriate properties rather than from forethought. Nevertheless, the result of the intervention of the electrical engineer has been of considerable benefit. Referring to the paper by Professor Cheng, the conditions of the concentrated contact in a fast-running machine element are so specific that it is virtually impossible to reproduce them in any other form of laboratory apparatus. Nevertheless, the vibrational method can approach reality more closely than the conventional viscosity measurement using a capillary tube, which is essentially a steady-state experiment.

Recent computer studies on ball bearings operating under EHD conditions have indicated that variation in the pressure-viscosity index may be of critical importance. Have we any indications as to how this quantity may be determined by chemical structure?

Mr. Beerbower has spoken of pollution of language and in this connection I would like to comment about the tendency to use the word "lubricity" for "oiliness." The difficulty with both these terms is that they imply a specific property of lubricants rather than their tendency, which may differ in different circumstances, to react with surfaces. In any case, the dictionary definition of the word "lubricity" should be sufficient to cause its use to be avoided by anyone seriously interested in good terminology.

Am I correct in concluding from Mr. Beerbower's lecture that the synthesis of viscous liquid lubricants for use at 300° C and above is going to elude us so, if and when we must operate tribological systems at higher temperatures, designers must employ externally or internally pressurized bearings operating on gas or process fluids?

K. L. Berkey (Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio)

Rather than go into a discussion of the ins and outs of lubricant properties and capabilities, which the author has already accomplished quite nicely, I felt that a short discussion of predicted future military aircraft engine lubrication requirements would be in order. Guidance from the propulsion side of the house has been rather sparse. There have been various studies on future aircraft propulsion needs. However, these have been lamentably lacking in details on lubrication requirements. The two Air Force studies cited by Beerbower have given some guidance, but still fall short of a complete picture. Currently, studies are underway to define lubrication requirements for the next two decades. These studies will also consider fuels, engines, and aircraft requirements to attain high-performance mission profiles.

Figure 13 shows past history and predicts future lubricants based on current knowledge. It looks like esters may take us to 500° F bulk oil temperatures at best. Some people draw this line at 450° F. Polyphenyl ethers can go to 650° F, at least for short-term operation. The perfluorinated materials show promise of up to 700° F operation in aircraft turbines if their corrosion problems can be solved. Above 700° F, materials other than currently known organics will be required. Gases, solid lubricants, and inorganic materials are likely candidates. Let me point out that lubrication capability will be required for most or all temperature plateaus at levels of about 75° F apart. This will be necessitated by the varying mission aircraft that are expected to be developed during the next decade.

I agree with the author that the day of economically solving future lubrication needs by trial and error is past. The capability to design lubricants as well as their applications must be developed. As indicated by the author, great strides are being made toward this end.

D. H. Buckley (NASA Lewis Research Center, Cleveland, Ohio)

The three-sentence conclusion presented in this paper very succinctly and aptly states our present position not only with regard to liquid lubricants, but applies to our position with respect to lubrication in general.

The importance of the elements and the interaction of the elements referred to in figure 3 of the author's paper cannot be overstressed. As indicated by this paper, all too frequently in the past, the organic chemist has

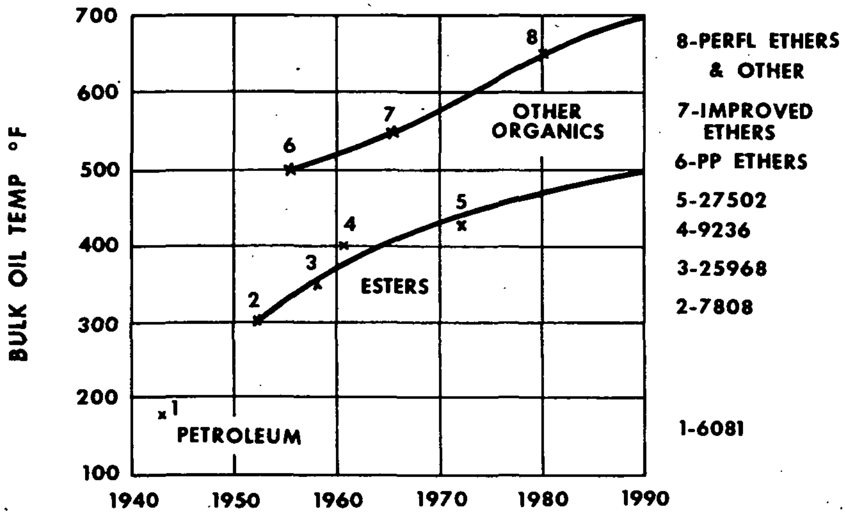

FIGURE 13.—Turbine engine lubricant trends.

been concerned with tailoring molecules to give physical properties of one kind or another that are somehow better than the presently used lubricants. At the same time the mechanical engineer, finding that frequently the organic chemist cannot predict the behavior of a specific lubricant in a particular system, has had to resort to the trial-and-error technique referred to by the author.

For the organic chemist, the mechanical engineer, and the balance of us in the field of tribology to better understand lubricant performance, liquid or otherwise, in a particular system, we must all come to a better understanding of the respective roles played by the elements in figure 3 and their interactions. This is imperative.

We all know that the friction coefficient for a typical bearing steel in air can be reduced from approximately 0.5 to 0.1 when a boundary lubricant is applied to its surface. This is a fivefold reduction in friction. Yet, the interaction of the oxygen from that same air environment with that same steel in the clean state can reduce its friction coefficient from well over 100 to the 0.5 we started to reduce with our liquid lubricant. With Nature's own lubricant, the oxide, the friction coefficient is decreased 200-fold. Even when a liquid lubricant is present on a surface, it contains large quantities of dissolved oxygen and water vapor that can alone or by interaction with other active species present influence friction and wear. Have we ever, outside of vacuum experiments, ruled out the role played by oxygen and water vapor in the lubricating properties we think we are measuring for a particular liquid lubricant?

It would appear that stepwise studies are in order. First, we must come to appreciate the interaction of the environment with the metals we wish to lubricate. Second, we should understand the interaction of the liquid lubricant with the environment. And third, we should study the interaction of all three components. It would appear that this is the way and the only way we will be able to understand the lubrication system.

In the author's discussion of catalytic thermal decomposition and oxidation phenomena, brief mention is made of the role played by the metals being lubricated in these processes. All too often insufficient attention is paid to the surface to be lubricated. The reaction products formed from the interaction of the lubricant or the environment, or both, with the surface to be lubricated can vary markedly with the metal or alloy.

It very frequently happens that when we think of chemical interactions with such materials as copper alloys, we think of reactions with copper, steels, reactions with iron, etc. Even in basic studies, bulk properties are frequently used to predict surface behavior. The surface of a metal or alloy does not have the same properties as the bulk material. The surface may, and frequently does, not even have the same composition as the bulk alloy.

Recent studies in our laboratory indicate, for example, that small concentrations of aluminum in copper can undergo equilibrium segregation to the alloy surface. The segregation can be temperature or strain initiated. With a few atomic percent aluminum in copper, the surface layer consists entirely of aluminum atoms that have popped out onto the surface. The number of aluminum atoms in this outermost layer is one-third that of the total atoms contained in the first subsurface layer (one-third monolayer coverage). With respect to adhesion, the alloy behaves as if it were elemental aluminum rather than copper.

Similar studies with iron-aluminum alloys indicate segregation of aluminum to the surface during sliding friction experiments. In dry sliding this segregation of aluminum to the alloy surface resulted in increased friction and adhesive wear. With stearic acid in hexadecane present on the surface as a lubricant, a lower concentration of stearic acid was needed to achieve effective boundary lubrication than was necessary for iron because of the greater chemical reactivity of the aluminum and its segregation to the surface with sliding.

The segregation of silicon to the surface of iron-cobalt-silicon alloys has also been observed in lubrication studies. These segregation observations all indicate that the true surface of an alloy should be considered in studies of liquid lubricant interaction with metal surfaces. The surfaces may not at all be what we think they are.

Another important interaction from the author's figure 3 and one not touched upon by him is the effect of the liquid lubricant on the mechanical properties of the surface to be lubricated or the Rehbinder effect. Through the years many researchers have made mention of this effect with respect to lubrication. In recent years we have seen the presence of such materials as stearic acid influence the plasticity of lithium fluoride, calcium fluoride, and zinc single-crystal surfaces during sliding. Not only can the lubricant present on a surface influence plastic deformation, but in the case of zinc, it affects the modes as well. The effect of a lubricant in determining whether a metal surface deforms by twinning or slip can be very significant in such observations as fatigue behavior.

The author, in his discussion of wetting, cites the work of Zadumkin with gallium and mercury. Extreme care must be taken with reference to the wetting of surfaces by gallium. Since gallium will react chemically with nearly all metals, and a wide variety of other surfaces as well, any wetting studies with this metal are apt to be relatively meaningless.

In a discussion of hydrogen embrittlement of steels, the author uses the Griffith equation for crack propagation. Griffith originally postulated his equation to predict crack propagation in amorphous glass. It is difficult to see how the equation can be applied to the propagation of cracks in steels during bearing fatigue. Crystallinity, grain boundaries, and inclusions would seem to exert an influence on crack growth and the rate of growth in steels.

The author, with reference to dehydrogenation of aliphatic hydrocarbons, indicates that the hydrogen soaks into the metal, resulting in hydrogen embrittlement. One can understand the dehydrogenation process resulting in the formation of cementite on a ferrous surface because the carbon is a solid and remains on the surface after dehydrogenation. The liberated hydrogen is, however, a gas and would be expected to pass into the environment rather than into the metal. One wonders what the evidence is for it soaking into the metal. It certainly cannot be any measurements involving surface brittleness.

Mention is made to the fact that the resultant carbide formation from dehydrogenation is detrimental. Is this always true? Carburization is frequently employed to improve surface wear resistance.

In concluding, this discusser found that the author attempted to cover many topics, giving each a cursory treatment. While the title and subject of the paper were relatively broad, the author should have selected a few less topics and given those selected for incorporation a more in-depth and thorough treatment. For example, the very important concept of the influence of water and humidity were discussed in only a short paragraph in the paper. This topic could have been expanded at the expense of deleting such topics as seal swelling.

B. W. Hotten (Chevron Research Co., Richmond, Calif.)

The link made by the author between the prooxidative power of metals and their ability to alternate between two valence states reflects conventional opinion, but it is a weak link in the chain of evidence. Everyone who has measured the oxidation rate of lubricating greases gelled with Li^+, Na^+, Ca^{2+}, Ba^{2+}, etc., soaps knows that metals with static valence are also powerful oxidation catalysts (ref. 70). Even when a catalytic metal is potentially varivalent, as Fe^{3+} in Fe^{3+} naphthenate (also in hemoglobin), it probably retains the higher valency under oxidizing conditions. A more general mechanism for metallic oxidation catalysis may be by coordination of O_2 with the metal cation. The most prooxidative of the statovalent metals listed, Li^+ in the alkali metal family and Ca^{2+} in the alkaline earth family, also have the highest charge density and greatest coordinating power for electron donors. The varivalent metals usually studied as oxidation catalysts have even stronger coordinating power through their available *d* orbitals.

G. Salomon (Central Laboratory, TNO, Delft, The Netherlands)

The thermodynamical classification of lubricant properties given by the author will be of great help to physical chemists, who have to deal with lubrication technology. The discusser proposes to extend and slightly modify some of these concepts.

Molecular Interactions.—The discusser applied Langmuir's principle of independent surface action with some success to the interpretation of ring-closure reaction more than 30 years ago (ref. 71). Since that time the discusser and his associates have used the now conventional molecular models in the study of molecular interactions of polymer systems, thus avoiding more complex theories. (See also Zisman, ref. 72.)

Gas-Polymer and Gas-Oil Interactions.—The low gas permeability of polyisobutylene was explained in terms of CED by Van Amerongen (ref. 73). In a recent study the discusser found that the solubility of He, N_2, O_2, and CO_2 in natural rubber (ref. 73) and in the oils compiled and measured by the author (ref. 29) are almost identical. Solubility of the same gases in oils of lower aromaticity, estimated by the discusser, was much higher, in good agreement with predictions (table 3). Diffusion constants for gas-oil and gas-polyisoprene systems are also very similar. Structural comparisons are easier to perform with polymers (ref. 73) than with oils.

For prediction of gas entrainment in and gas transport through oils, actually two sets of data are required: the thermodynamic equilibrium solubilities and diffusivities and the time-dependent stability or instability of finely dispersed gas bubbles. The former depend on the bulk properties of the liquid, the latter on the concentration of surface active impurities. By comparing the ratio of inert gas permeability, for example, He to Ar or H_2 to N_2, in pure gum rubbers and in oils, separation of molecular and surface chemical parameters could be achieved.

Liquid-Polymer Interactions.—Technical service groups of lubricant and paint industries have to cope with a great variety of solubility problems. These involve an almost unlimited combination of liquid-polymer systems. Though extension of the well-founded solubility theory (refs. 11 and 74) as proposed by Hansen (refs. 5 and 35) is based on experiments with dirty surfaces and of questionable (ref. 72) theoretical value, these experiments are certainly useful for rapid interpolation. However, extrapolation to specific systems, such as nitrile rubbers with liquid amines or nitrile rubbers with CX_3H halides, is difficult to perform with either equation (5), (23), or (24). As such combinations can pose a problem, e.g., in seal technology, swelling measurements (refs. 75 and 76) in series of liquids with incrementally changing chemical structures (ref. 71) have been performed.

The Surface of Metals and Lubricity.—The discusser agrees with the author that the work of adhesion is one of the parameters needed in the analysis of the term "lubricity." However, the discusser fails to understand how the extrapolations suggested by Gans (ref. 30) can add to the original conclusions of Bernett and Zisman (ref. 32), more particularly when these are taken in conjunction with other data of high-energy surfaces at 0.6 percent *RH* (ref. 72). The Naval Research Laboratory data describe the γ_c value of a partial monolayer of water. The existence of this layer is also evident from UHV work on the wetting of silica by CH_2I_2 (ref. 77). If the extrapolation in figure 8 has a physical meaning, it describes differences in the ease of removing residual water from metal oxides. The conclusions of Zisman (and not of Gans) are in excellent agreement with those of Groszek, given in his paper presented at this symposium. In many practical cases, differences in the reversible heat of adhesion to metal oxide surfaces will be leveled out by traces of water, as shown by Zisman and by Groszek.

White (ref. 78) has demonstrated that all metal oxide surfaces rapidly adsorb organic vapors. Schrader has produced similar evidence in elaborating the hydrophilic properties of gold (ref. 72) in UHV (ref. 79). Great differences, however, exist in the rate of desorption from the same surfaces (ref. 78).

The combined evidence cited above points to the following parameter, partly determining the quality of physical lubricity: the ratio between reversible and irreversible adhesion to metal surfaces. Lubricity will increase if certain types of chain molecules are adsorbed and then bonded irreversibly to the metal surface.

The Design of Tribological Experiments.—Figures 1 and 2 of the paper should be placed in front of young researchers, planning a career in four-ball chemistry. The author states in his introduction that our competence in dealing with these problems is gradually increasing. The discusser would like to emphasize that the International Research Group on Wear of Engineering Materials under the auspices of OECD is taking part in this process by way of self-education. A test should be built up in steps of increasing chemical effects.

As pointed out already (see my discussion of Mr. Furby's paper), a distinction should be made between isothermal and adiabatic friction testing. While conventionally the transition to severe wear, scuffing, or seizure is explored (a situation of nearly adiabatic heating), merit rating of lubricants under isothermal conditions needs more attention.

The next step should be a comparison performed in neutral and in oxidizing atmospheres. Many researchers hesitate at this point and for good reasons. Surrounding a friction couple with an argon or a helium atmosphere poses leakage problems, which demand designs beyond the means of many testing laboratories. Further, convenient gas-analytical tools are not always at the disposal of mechanical engineers. However, in our experience, even a "dirty" argon atmosphere with about 0.5 to 1 percent air leaking in, can suffice to show great differences between lubricants. Probably the natural esters discussed by the author would show up as even more superior, if compared with mineral oils in a neutral atmosphere. The ease of formation of irreversible adsorbates and of protective films with the metal is probably greater with unsaturated esters than with hydrocarbons. It would be of great help to have merit ratings of the "lubricity" of natural products in a neutral and dry atmosphere.

The third step, already extensively studied by the author and his colleagues, would then be the influence of moisture. In an early phase of our cooperative effort, we found no systematic trends in the presence of moisture when testing "dry" steel on steel (ref. 80). What we did not know, at that time, is that the adsorption properties of iron oxides are leveled out already by small quantities of water, while according to the author, the condensation of a water film on steel takes place only at very high RH (ref. 81).

C. E. Vest (NASA Goddard Space Flight Center, Greenbelt, Md.)

Mr. Beerbower in his lecture has presented information regarding liquid lubricants related to predicting properties of liquid lubricants from their structural formulas, the ability to design liquid lubricants by forecasting the results of changing their structure, and the ability to map out the ultimate limits to which liquid lubricants can cope with extremely hostile environments. He has shown formulas and the reasoning behind each for determining various properties and their relationship to each other.

The lecture is very interesting to a lubrication technologist in the space applications field, and it has made me more aware of several points that have been bothering me in ball bearing work. The author listed and discussed several properties under "Interactions of Liquid Lubricants With Their Environment." I would appreciate comments by the author on the following questions: What is the effect of changing density upon the lubricant's interaction with the environment, especially fresh new surfaces and oxygen? What effect does the bulk modulus have on the operation of a ball bearing? Would the isothermal tangent bulk modulus be more meaningful to ball bearings? Can vapor pressure be related to cohesive energy? I have read that there is a significant difference in the bulk V_p and the V_p of a monomolecular layer of the same liquid lubricant. In ball bearings wherein the film between the ball and race is very thin, which V_p should be of prime consideration? In considering gas solubility, it is implied that some gases are beneficial with regard to oxidization of a fresh surface but nonbeneficial with regard to breakdown and polymerization of the liquid. In space applications, where we are working in a reduced overall pressure and the liquid becomes degassed, what do you feel would happen if someone decided to use a liquid lubricant with no additives? Viscosity was discussed regarding temperature and pressure. Values are available for the viscosity at various temperatures. What would be the change in viscosity of the lube in a ball bearing at the ball-race interface due to the increase in pressure and temperature? Would the change in viscosity be great enough to consider increasing the bulk viscosity for that application?

In the discussion of adhesion to metals, the contact angle of a good lubricant should be 0 on its own monolayer. In space applications in which zero gravity is a part of the environment, would it not be better to have a small contact angle so that creepage would be reduced? Or would it be best to have an autophobic liquid that spreads on its own monolayer?

The author's discussion of noncatalytic and catalytic reactions with the liquid, its gases, and the contacting surfaces is very enlightening and informative. He shows that some reactions could be beneficial and others nonbeneficial. This would be true especially where the lubrication supply is limited. In a case where boundary lubrication is not of primary concern, but is of concern at startups and stops, it may be beneficial for a free radical and a fresh surface to combine and form an organometallic compound at the fresh surface. Would the author comment on this?

Mr. Beerbower has presented helpful information on the manner in which properties can be predicted, on how structural design can be made to forecast specific results, and on how the ultimate limits to which lubricants can be exposed can be mapped out. Mr. Beerbower also knows from his past experiences many applications by which he could illustrate the effects of each of the property changes. It would be greatly appreciated if he would illustrate a few of these for us.

The author has presented guidelines for consideration in research and development of better lubricants. It would be advisable for the researcher to keep these in mind during his work.

Mr. Beerbower is to be congratulated on a very interesting and informative lecture.

LECTURER'S CLOSURE

In reply to Dr. Barwell, the writer did indeed mean that all of us should drop our special labels and work together as a team. Whether we call it tribology or lubrication engineering, each of us is going to need all the help he can get, and soon.

The point that surface resin is a mixed blessing is certainly an important one. The paper stressed its value in journal bearings, but the same amount of resin is known to be very harmful to rolling-element bearings. It is also apt to be the first stage in the notorious series "lacquer→varnish→coke." The goal should be controlled generation of resin, when, as, and if it is needed, by judicious use of appropriate liquids and metals. Ranking the resin-forming tendency of hydrocarbons has been discussed (ref. 33), but it is much more difficult to devise a ranking scheme in which gaseous products are also predicted. The only sure guide to the latter is that the zipper polymer structure (sec. 4.1.1) always breaks down to low-boiling material with essentially no residue; this has been used for the bearings in annealing tunnel carts. At the other extreme, the complex aromatics found in petroleum residua tend to split into hydrogen and asphalts that soon resemble coke.

The point on viscoelastic phenomena is a good one, in that tribology must adopt ideas from electrical engineering. However, this applies especially to oils formulated with polymers, and rheology as discussed in the paper had to be limited essentially to that of base stocks, where this concept is least useful.

It is to be hoped that tables of the reversible and irreversible energies of surface interactions will soon begin to appear, and that "lubricity" can be turned back to the ever-growing science of pornography.

As Dr. Barwell concluded, there is little hope for organic compounds to stand up to continuous service at 300° C. Possible alternates are discussed in reply to Mr. Berkey.

The pressure-viscosity index is very intimately related to the bulk modulus K for flow depends on the free volume in the liquid and any compression leads to a viscosity increase. Thus, high $(d\eta/dP)$ liquids may be obtained by increasing δ_D and δ_P, as shown in equation (15). Specifically, this would lead to aromatics with functional groups such as polyphenyl ethers, etc.

Mr. Berkey raised the same point as Dr. Barwell on the bad prospects for organic lubricants above about 300° C or 650° F. However, this limitation is based on the practice of exposing the bulk of the lubricant to the temperature. As seen in figure 1, glass molding is routinely lubricated at over 500° C. Actually, the mold is at about 450° C and the glass at 900° C, with the lubricant somewhere in between. A similar pattern is found in continuous steel casting, where the mold is at about 200° C and the steel at 1100° C. The secret of such operations is to regard the lubricant as expendable and use it on a once-through basis. Data on glass molding are available (ref. 82) to show that liquid lubricants can be formulated that far exceed the required lifetime of about 0.25 sec. Application to advanced aircraft will require some ingenuity, as once-through lubrication does not provide the cooling power of bulk lubrication. However, it does seem more promising than the relatively unexplored field of liquid inorganics. Liquid metals have not been very satisfactory. While gas bearings and solid films have their uses, they also have some very harsh limitations.

Mr. Buckley raises the question of the role of dissolved oxygen and water vapor in liquid lubrication. He is right to question whether most of the dry, inert atmosphere experiments reported in the literature really are free from such effects. However, techniques are now being used, in a few laboratories, that give results so different from the conventional data as to encourage belief that these contaminants have been rendered negligible.

Though the point was not stressed in the paper, figure 10 does include two demonstrations of the alloy effect. The two dashed lines represent alloys of palladium with silver and gold. The rates of polymer formation correlated excellently with the surface free energies of the alloys as calculated by Hildebrand's equation (ref. 24, p. 408),

$$\gamma_m = \gamma_2 - \frac{RT}{V_m^{2/3}} \left[\ln (1 - x_3) + x_3 \exp \frac{(\gamma_2 - \gamma_3) V_m^{2/3}}{RT} \right]$$

where γ_m is the surface free energy of the alloy, γ_2 is the surface free energy of palladium, γ_3 is the surface free energy of the other metal, V_m is the molar volume of the alloy, and x_3 is the mole fraction of the other metal.

This expresses the general surfactant tendency of low-γ_3 metals, such as the aluminum so ably demonstrated by Mr. Buckley. Related equations that predict the surface composition are also available, but not the rate of attaining this Gibbs equilibrium. It is a great credit to Mr. Buckley that he has shown how rapidly even solid solutions equilibrate and that probably the sliding stress is a factor in this speed.

The point about the Rehbinder effect was touched on briefly in section 3.5, though not by that name, in the attempt to explain Rounds' (refs. 42 and 43) data by equation (50). The loss of free energy in submerging a solid ($\gamma_2-\gamma_{12}$) should represent the decrease in crack propagating force. As Mr. Buckley points out, this equation does not give accurate predictions in steel, nor in many other situations, but it is still the only mathematical relation available for this problem.

The Zadumkin (refs. 38 and 39) work cited did not relate to the wetting of solids by gallium and mercury, but to the wetting of these liquid metals by organic liquids. He did have to throw out some data because of a change in γ_{12} with time, which he attributed to reaction of gallium with impurities in the liquids. Perhaps the liquids themselves were reacting.

The evidence for hydrogen soaking into steel from a surface reaction is due to Grunberg (ref. 83), who found radioactive hydrogen (tritium) beneath the surface after four-ball tests in the presence of tritiated water. The extension to the hydrogen released from hydrocarbons is by analogy but seems plausible because what is released is not hydrogen gas but hydrogen radical. The latter is well known to cause corrosion embrittlement.

Carbide formation at the surface can be extremely beneficial as casehardening, provided it is not overdone. If carried too far, the case tends to spall away from the soft substrate, and such an effect was intended in the paper.

The author agrees with Mr. Buckley that many topics were given cursory treatment. The intention was to provide a critical review, so that the reader could spend as much time as justified on those references of particular interest to him. This was not done for the effects of humidity and oxygen on lubrication (as opposed to oxidation of the lubricant) because that was considered to be a solid-gas interaction. A review of this interaction is included in the author's recent Army report (ref. 84).

Mr. Hotten certainly has a good point in his statement that statovalent metal soaps definitely accelerate the oxidation of lubricants. The varivalent theory cited is one that has been fairly widely accepted but fails to predict the ranking of even those metals. It would be extremely valuable to have a complete theory that covers both classes of metals, and it is hoped that Mr. Hotten will publish a more complete account of this one.

It seems appropriate at this point to offer an additional reference on the subject of homogeneous versus heterogeneous catalysis. Klaus and Tewksbury (ref. 85) arrived at conclusions similar to those of Thompson (ref. 54) in a much more elegant study.

Dr. Salomon has provided some very interesting light on the relationship of solubilities in the gas-liquid-polymer triad. Having verified that gas-liquid and liquid-polymer solubilities correlate with CED, the author had speculated that gas-polymer interactions would also correlate but lacked the proof that Dr. Salomon provided.

The problems of using the Hansen (ref. 35) surface technique for obtaining thermodynamically useful parameters are as stated by the discusser. A more complete analysis is now available (ref. 84). This also goes into much more detail on the use (and abuse) of the straight-line assumption of Gans (ref. 30) and Bernett (ref. 32) in figure 8. The author's conclusion is essentially the same as that reached by Dr. Salomon, that reversible adsorption is a necessary step in boundary lubrication but does not accomplish much unless irreversible adhesion follows.

As Dr. Salomon states, the contrast of humid air with dry argon is very revealing (ref. 57). We have not found it very difficult to provide special atmospheres, using plastic bags, etc., with enough positive pressure to insure that all leakage is outward. Degassing the lubricant and equipment is more troublesome, but even a modest effort will produce a reasonably inert atmosphere.

Mr. Vest has raised a great many important questions, some of which are beyond the author's ability to answer completely. The following answers are factual as far as is possible, with a minor amount of speculative fill-in.

Density largely controls the solubility of gases, high-density hydrocarbons having low solvency for oxygen but high solvency for water. As a first approximation, high-density liquids have higher works of adhesion on freshly cut metals, but the more important irreversible adhesion is quite dependent on chemistry.

Bulk modulus as such does not affect ball bearing operation, but its tie to pressure-viscosity index might lead to a correlation. Isothermal or adiabatic moduli would be of equal value in this.

Vapor pressure is very strongly related to cohesive energy. As shown in section 2.2.4, it is least responsive to the hydrogen-bonding energy component. The vapor pressure of a monolayer will be greatly dependent on the heat of adsorption ΔH_a from the vapor phase, which must replace ΔH_v in equations (18) and (19):

$$T_{ba}=25\sqrt{563+0.080(2950+\Delta H_a)}-593$$

$$d(\ln P_{va})\ dT=\frac{\Delta H_a}{T\,\Delta V_v}$$

On a solid where $\gamma_l > \gamma_c$, $\Delta H_a < \Delta H_v$ and P_{va} is greater than for the liquid, so no monolayer forms. When $\gamma_l < \gamma_c$, the vapor pressure of the monolayer will be less than for the liquid, and the deviation could be computed from figure 8 if a few assumptions are made (ref. 72). This P_{va} should be used for thin films in ball bearings.

Oxygen solubility controls the rate of deactivation of fresh metal surfaces and hence the rate of radical formation, but oxygen availability in the environment controls the rate of polymer formation. Thus, low oxygen atmospheres tend to reduce the usual benefit from antioxidants to the vanishing point.

Viscosity is lowered by temperature and raised by pressure, so the two tend to offset each other. However, good experience shows that the viscosity for a ball bearing lubricant may be selected on a maximum anticipated temperature basis with no regard for pressure.

For adhesion to metals, figure 8 predicts that all lubricants of $\gamma_l < 44$ should spread to a monolayer on all metals. Surely the discusser has a misprint, as autophobic liquids are those which do not spread on their monolayers. Such liquids are rare, as are those of $\gamma_l > 44$, so the use of barrier films of fluorocompounds painted around the races is a more practical solution to the creepage problem.

Catalytic reactions essentially imply the formation, at least temporarily, of an organometallic compound. These can be very beneficial in the situation the discusser describes. Clearly, some care would be required in selecting the metal and lubricant so as to have controlled catalytic reaction, as the cure can be worse than the disease if applied too generously.

The author had planned to include some numerical examples of the design process, but they proved too lengthy for presentation here.

NOMENCLATURE

Latin

A	Arrhenius preexponential constant; Vogel constant (eq. (42))
a	factor in equation (24)
B	bulk modulus (eq. (12)); contact potential function (eq. (49)); Antoine constant (eqs. (20) and (21))
C	molar heat capacity, cal/mol °K; temperature correction (eqs. (20) and (21)); parameter in Roelands equations (38) to (41)
D	parameter in Roelands equation (38)
d	differential of
E	energy, cal; Young's modulus
F	flammability limit
f	fugacity, atm
G	Gibbs free energy, cal
H	enthalpy, cal

K	bulk modulus (eq. (13)), atm
k	term in equation (34)
L	force, gm
l	length, cm
M	molecular weight, g/mol
N	number of
n	refractive index
P	pressure, atm
R	gas constant, cal/mol °K
r	reaction rate
S	entropy, cal/°K
T	temperature, °K (in section 4.3, °F)
t	temperature, °F
V	molar volume, cm^3/mol
W	work, ergs/cm^2
x	mole fraction

Greek

α	expansivity, (°K)$^{-1}$
β	factor in equation (24); second carbon atom in alcohol
γ	surface free energy, ergs/cm^2
Δ	change in
δ	solubility parameter, hildebrands
∂	partial differential of
ϵ	dielectric constant
θ	time, sec; contact angle
λ	thermal conductivity, J/cm sec °K
μ	dipole moment, debyes
η	viscosity, centipoises
Φ	volume disparity factor
ϕ	volume fraction
ρ	density, gm/cm^3
Σ	sum of

Subscripts

A	aromatic carbons (eqs. (39) to (41))
a	absorption
b	at boiling point
b5	at 5 percent boiling point
c	at critical point; carbon atoms (table 5)
D	London force contribution; decomposition
E	extended viscosity index
e	at equilibrium; eutectic mixture
F	at flashpoint
g	at glass point

H	H-bond contribution
I	insoluble
i	position in summation (eq. (6)); induction period (eq. (55))
L	lower
M	of mixing
m	of melting; after equation (33), of melting and transition
N	naphthenic carbons (eqs. (39) to (41))
O	of oxygen
0	at reference condition
P	polar contribution
p	at constant pressure; at the convergence pole (eqs. (39) to (41))
R	reduced property (actual/critical)
r	of transition
S	soluble
s	isentropic
T	isothermal
tr	transition
U	upper
V	at constant volume
v	of vaporization
w	van der Waals (volume)
1	less dense phase (liquid)
2	more dense phase (solid or liquid)

Superscripts

d	London force contribution (eqs. (44), (45), and (46))
G	gas property
j	due to fusion at constant volume
L	property of hypothetical liquefied gas
$\circ$	Bondi's reduced E at $V/V_w = 1.70$
p	polar and H-bond contribution (eqs. (44), (45), and (46))
v	due to change in volume
x	Roelands' temperature exponent (eqs. (38) to (41))
y	Roelands' pressure exponent (eqs. (38) to (41))
$*$	free radical

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