Part II

Flammability Properties of Hydrocarbon Fuels

Interrelations of Flammability Properties of n-Alkanes in Air

WILBUR A. AFFENS
U. S. Naval Research Laboratory, Washington, D. C.

By a systematic study of literature data, mathematical equations have been derived which describe the interrelationships of flammability and other related properties of the n-alkanes. The properties which have been correlated are: lower and upper flammability limits, flash point, vapor pressure (at the flash point), boiling point, stoichiometric concentration, heat of combustion, molecular weight, and carbon number. Good agreement was found between average literature data and values calculated by the derived equations. From a given flammability property, by use of the derived equations, it is possible to predict the other properties, as well as the relative magnitudes of changes in these properties as a result of a change in the given property.

THE FLAMMABILITY PROPERTIES of hydrocarbon fuels and similar petroleum derivatives are of considerable concern to workers who handle these flammable liquids and gases since understanding these properties helps make it possible to recognize and predict hazardous situations, and to take proper steps to eliminate them.

Numerous flammability properties exist which may be measured experimentally such as flash point, fire point, heat of combustion, flammability limits, spontaneous ignition temperature, explosiveness, ignition energy, and vapor pressure. Many flammability interrelationships have been reported for pure hydrocarbons and fuel mixtures. For example, several workers (3, 4, 6, 9, 10, 12, 20) found linear relationships between the net molar heat of combustion and the reciprocal of the lower flammability limit. Spakowski (20) derived empirical relationships of lower and upper flammability limits with molecular weights and heats of combustion. Based on theoretical principles, Solov'ev and Baratov (19) derived a linear expression for the reciprocal of the lower flammability limit as a function of the number of carbon atoms which they confirmed experimentally for alkanes, alcohols, acetates, and formates. Zabetakis, Scott, and Jones (24) reported that the lower flammability limit (expressed as milligrams of combustible per liter of air,

NTP) is fairly constant for a wide variety of hydrocarbon compounds. Linear relationships between flash points and boiling points were reported for distillate mixtures by Butler et al. (5) and for pure hydrocarbons by Gwinn (13). Relationships between flash point, vapor pressure, molecular weight, and lower flammability limit were reported by Butler and coworkers (5) and by Mullins (15, 16) for mixtures of hydrocarbons and fuels, respectively. Thiele (21) derived an equation for calculating flash points of blends from that of the individual components.

Although the hydrocarbon and fuel literature is well stocked with flammability data, there is a great need for a clearer understanding of the meaning and significance of individual data, and the quantitative interrelationships among them. Such knowledge can supply information for fuel evaluation in engine performance or fire-safety studies; can elucidate fundamental processes of hydrocarbon oxidation, ignition, and combustion; and can be of assistance in data evaluation to detect experimental or other errors resulting from variations in method and techniques, or from other sources.

This laboratory has been especially interested in jet fuels for many years. These fuels consist almost entirely of hydrocarbon mixtures of normal, branched chain, and cyclic

paraffins and lesser amounts of aromatic and unsaturated hydrocarbons (4). Since paraffins and cycloparaffins are very similar in most of their properties, and together make up 75 to 90% of most aircraft fuels (4), a study of the n-alkanes, if fruitful, might be extended to other hydrocarbons and actual fuel mixtures, such as jet fuels in air and other atmospheres. Thus, the purpose of this preliminary study was to discover whether useful interrelationships of the flammability and related properties of the n-alkanes in air exist.

The various equations for the interrelationships of the combustion and related properties of hydrocarbon mixtures and fuels which have been reported are limited in scope, are only partly interrelated, and in most cases are only approximations. This is an additional reason for studying a homologous series of pure compounds, such as the n-alkanes, to determine whether more exact interrelationships might be discovered which perhaps would be masked by a diversity of compounds in complex mixtures.

Because of its large structural dependence (1) as compared to other flammability properties, spontaneous ingition was not included at this time.

Figure 1. Boiling point and heat combustion vs. carbon number for n-alkanes

VARIATION WITH CARBON NUMBERS

The orderly variation of the physical properties of the n-alkanes with molecular weight or carbon number has been well demonstrated, and is applicable to the flammability properties as well (19, 20). In general, this has been the basis of the technique which has been employed in the present work to derive the mathematical equations which describe the interrelationships of the properties of the n-alkanes. For each property, average literature data were plotted against carbon number, n, and equations were derived to describe these relationships. The constants of the equations were calculated from the data by the method of least squares (7).

In the case of molecular weight, $\bar{M}$, which, of course, is a primary relationship and is not derived from literature data, $\bar{M}$ itself is a direct linear function of n.

$$\bar{M} = 14.027n + 2.0160 \tag{1}$$

The equation for boiling point $(t_B, \, ^\circ C.)$ is

$$(t_B + 293.2)^2 = 21{,}580n \tag{2}$$

The indirect expression $(t_B + 293.2)^2$ is a linear function of n. In the case of molar heat of combustion (ΔH_m), the equation is

$$\Delta H_m = 146.91n + 47.496 \tag{3}$$

Equations 2 and 3 are plotted as straight line graphs in Figure 1, and averaged literature data (2, 8) are superimposed on the graphs for comparison. The agreement with the literature data is good for t_B, and very good for ΔH_m.

Since Equations 1 through 3 are each functions of n, they may be treated as simultaneous equations. For example, the relationship of boiling point or heat of combustion to molecular weight, or to each other may be readily obtained.

CHOICE AND HANDLING OF LITERATURE DATA

Since wide variations were often found in the literature data for specific properties of individual compounds, judicious choices were made. The basis of choice in general was rejecting data whose deviation was excessive using standard statistical techniques (7), and maintaining uniformity where necessary in the choice of experimental methods employed to obtain the data. Arithemetic means of the
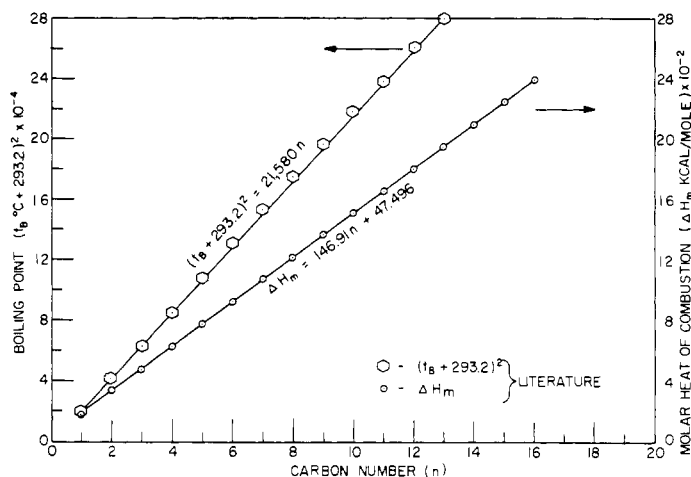
selected literature data were calculated. The method of least squares which was applied to the average literature data to calculate the constants of the mathematical equations thus served as a second averaging step.

Data from ethane through n-hexadecane were included in this study. As a general rule, methane did not fall in line with the other members of the n-alkane series and it was necessary in most cases to omit it. Methane data were not used in the derivation of the various equations.

FLAMMABILITY LIMITS AND STOICHIOMETRIC CONCENTRATIONS

Flammability limits have been defined in rather precise terms (6). The experimental values for these limits, however, depend on the method and the nature of the apparatus employed—e.g., the direction of flame propagation. For consistency literature flammability data used in this work are based on a vertical tube apparatus for upward propagation, which is the technique most generally used (6). In general, limits in this work are expressed as per cent by volume, and are in air at room temperature. For the alkanes n-nonane and above, lower flammability limit literature data were obained at elevated temperatures and were extrapolated to 25° C. using Equation 9. The upper limit literature data (n-octane and above) were determined at temperatures above room temperature or at reduced pressures or both. No attempts were made to extrapolate these data since the corrections involved would be small compared to the other errors involved in upper limit data (21, 24).

Applying a technique similar to that employed with boiling point and heat of combustion to the lower (L) and upper (U) flammability limits, the following equations were derived:

$$1/L = 0.1347n + 0.04353 \tag{4}$$

$$1/U = 0.01337n + 0.05151 \tag{5}$$

$$1/C_s = 0.07160n + 0.03387 \tag{6}$$

The stoichiometric concentration, C_s, which is included for comparison, assumes complete combustion to carbon dioxide and water.

Plots of the reciprocal functions (Equations 4 through 6) are shown in Figure 2. As before, the curves represent calculated values, and the points shown are averager literature values.

In general, except for methane, there was good agreement between literature and calculated values for both lower and upper flammability limits as is also shown in Table I. Agreement between calculated and averaged literature data is better for L than for U. The literature data for upper flammability limits were in relatively poor agreement among themselves, and less available. and therefore, the derived equation for U (Equation 5) may be less reliable.

It is now possible to derive our first flammability interrelationship. Simultaneous solution of the equations for molar heat of combustion, and lower flammability limit (Equations 3 and 4) shows that their product is constant.

$$L\Delta H_m = 1091 \tag{7}$$

This is in agreement with the findings of others (6, 9, 10, 12, 19, 20). A plot of the reciprocal of L vs. δH_m (Figure 3) is linear and goes through the origin. It shows good agreement with average literature values with an average relative error of $\pm 2.1\%$.

The next important interrelationship is that of the lower and upper flammability limits obtained from Equations 4 and 5.

$$1/U = 0.0993(1/L) + 0.0472 \tag{8}$$

A plot of the reciprocal of L vs. reciprocal of U is shown in Figure 4. Averaged literature data are in fair agreement with the calculated values.

Analogous flammability interrelationships may also be calculated for other combinations of these properties by use of the above equations.

LOWER FLAMMABILITY LIMITS AND TEMPERATURE

Flammability limits do not vary significantly with moderate changes in temperature (6, 23). However, when comparing data from wide ranges of temperature, the variation of flammability limits with temperature must also be taken into account. As pointed out by Coward and Jones (6), there is an inverse relationship between the lower flammability limit and temperature, so that the limit decreases approximately linearly with temperature. Combining the findings of Zabetakis, Scott, and Jones (24) and White (23), an average quantitative relationship between lower limit and temperature for the n-alkanes was derived which was used in certain of these calculations. The equation for the lower flammability limit, L_t at a given temperature t °C. as a function of the limit L at 25° C. and t, is as follows:

$$L_t = 1.02L \ (1 - 7.75 \times 10^{-4} \ T) \tag{9}$$

Thus, knowing the flammability limit at room temperature, or about 25° C. (L), the limit at any temperature, t, can be calculated. The equation predicts an approximately 8% decrease in L_t with a temperature rise of 100° C. This equation is approximate, and is based on average values for several hydrocarbons. However, since the temperature correction is small, it does not introduce a serious error in the calculations.

FLASH POINT

There are many definitions of flash point, most of them based on the experimental method of determining it, but a more fundamental definition which is sometimes used by workers in this field (22) defines flash point as "the minimum temperature at which sufficient vapor is released by a liquid or solid to form a flammable vapor-air mixture at one atmsophere pressure." In other words, flash point is that temperature at which the vapor pressure of the fuel (in atmospheres) is equivalent to the concentration at the lower flammability limit (mole fraction or its equivalent, $L\%$ v./v. $\times 10^{-2}$). Thus, within this meaning, the intersec-

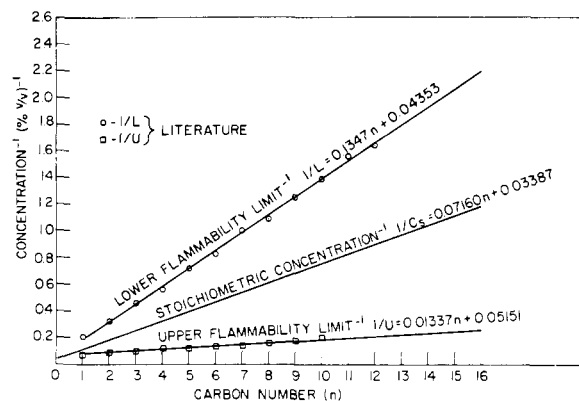Figure 2. Flammability limits vs. carbon number for n-alkanes

Table I. n-Alkanes—Flammability Limits vs. Carbon Number

Carbon No., n	Lower Limit (l, %v./v.)		Upper Limit (U, %v./v.)	
	Lit. av.[a]	Calcd.[b]	Lit. av.[a]	Calcd.[c]
1	5.0	5.6	14.8	15.4
2	3.0	3.2	13.2	12.8
3	2.2	2.2	10.4	10.9
4	1.8	1.7	9.3	9.5
5	1.4	1.4	8.4	8.4
6	1.2	1.2	7.8	7.6
7	1.0	1.0	7.1	6.9
8	0.92	0.89	6.5	6.3
9	0.80	0.80	6.0	5.8
10	0.72	0.72	5.0	5.4
11	0.64	0.66	...	5.0
12	0.61	0.60	...	4.7
13	...	0.56	...	4.4
14	...	0.52	...	4.2
15	...	0.48	...	4.0
16	...	0.46	...	3.8

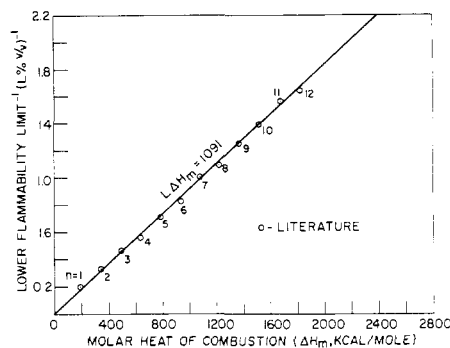[a] Refs. 3, 6, 9, 11, 18, 20, 24. [b] Equation 4. [c] Equation 5.

Figure 3. Lower flammability limit vs. heat of combustion for n-alkanes

tion of the vapor pressure and the lower flammability limit curves, both plotted against temperature, should be the temperature at the flash point. This technique was used for deriving equations rather than averaging literature data in which there was relatively poor agreement. A theoretical plot, similar to a diagram by Van Dolah, and coworkers (22), which demonstrates this concept is shown in Figure 5. The flammable and nonflammable zones are indicated. The vapor pressure-temperature curve intersects the lower flammability limit-temperature curve at point A. The analogous intersection of the upper flammability limit-temperature and vapor pressure-temperature curves is shown at point B. Though this point is of interest, it will
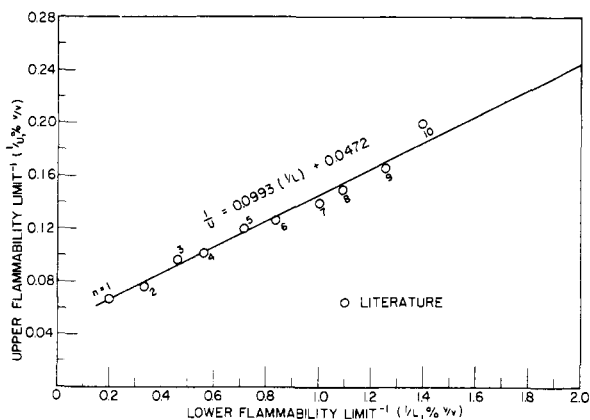
Figure 4. Upper vs. lower flammability limits for n-alkanes

not be covered here. The flash point (t_F) and the corresponding vapor pressure (p_F) are indicated by temperature and pressure coordinates at the intersection A.

Actual pairs of curves were plotted for each of the n-alkanes up to a carbon number of 15 for both vapor pressure and lower flammability limit against temperature. The vapor pressure–temperature data were obtained from the literature $(8, 14)$. The lower flammability limit curves were obtained from calculated values of L and L_t from Equations 4 and 9. The points of intersection of all the pairs of curves for the 15 n-alkanes are shown as small circles in Figure 6 along with averaged literature flash point values (large crossed circles) superimposed on a plot of calculated p_F vs. t_F values from the equation.

$$(t_F + 277.3)^2 p_F = 741.7 \tag{10}$$

Equation 10 was derived by least squares treatment of the points of intersection of the graphs.

In a similar manner, using the t_F and p_F values obtained from the graphs rather than averaged literature data, but using the same technique as employed for equations 2 through 6, the following two equations were derived which give t_F and p_F as functions of n,

$$(t_F + 277.3)^2 = 10,410n \tag{11}$$

$$1/p_F = 14.04n \tag{12}$$

Plots of these equations are shown in Figure 7.

A comparison of averaged literature data with values derived both from the graphs and by calculation (Equations 11 and 12) is given in Table II. Examination of the data in Figures 6 and 7 and Table II show rather good agreement for flash point data, and fair agreement for vapor pressure at the flash point, except for methane. The relatively poor agreement for p_F in certain cases, particularly for n-hexane, tri-, and tetradecane appears to be the result of discrepancies in the literature flashpoint data for these hydrocarbons. The literature flash point temperatures of -23, 79, and $103°$ C. respectively for these three compounds as shown in Table II, are apparently out of line with the other n-alkanes, and this suggests a need to recheck these experimental values. Because of the logarithmic relationship between vapor pressure and temperature $(8, 14)$, small errors in t_F result in relatively large errors in p_F. The derived literature p_F values for n-hexane, tri-, and tetradecane, 0.015, 0.003, and 0.006 atm., respectively, are obviously in serious error, and have not been included in the graphs (Figures 6 and 7).

From Equations 11 and 12, and the previously derived equations, interrelationships of the flash point properties, t_F and p_F, and other properties may be derived. For example, the interesting relationship between vapor pressure at the flash point, and molecular weight may be derived from Equations 1 and 12.

$$p_F (\bar{M} - 2.016) = 1.000 \tag{13}$$

The reciprocal molecular weight data in Table II are also presented to illustrate this relationship. This relationship is in accord with the results of Mullins $(15, 16)$ for fuel mixtures.

The relationship between flash point and boiling point may be derived from Equations 2 and 11.

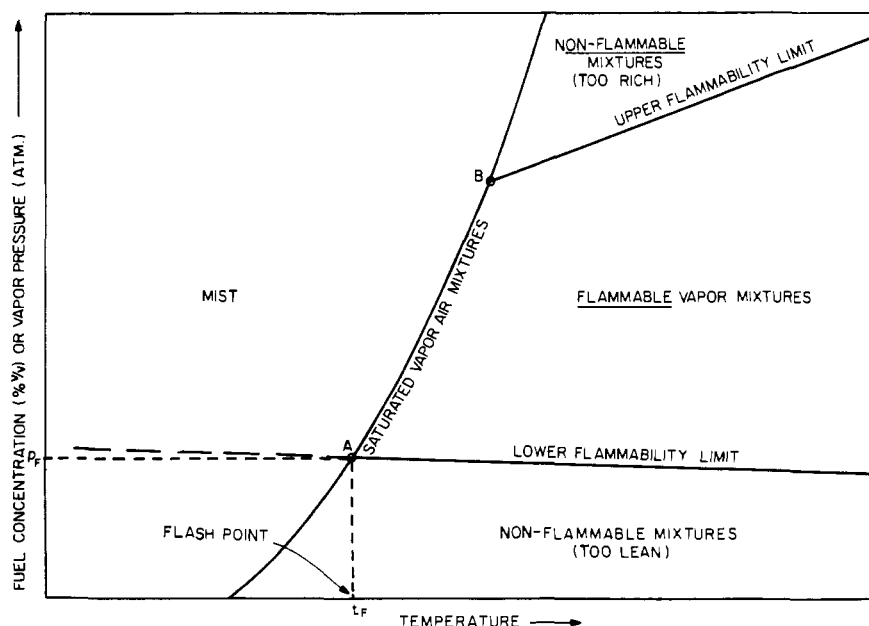$$t_F = 0.6946 \, t_B - 73.7 \tag{14}$$

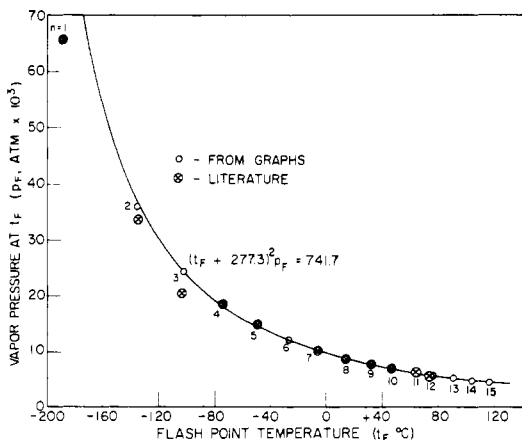Figure 5. Vapor pressure and flammability limits vs. temperature for a typical hydrocarbon fuel-air mixture

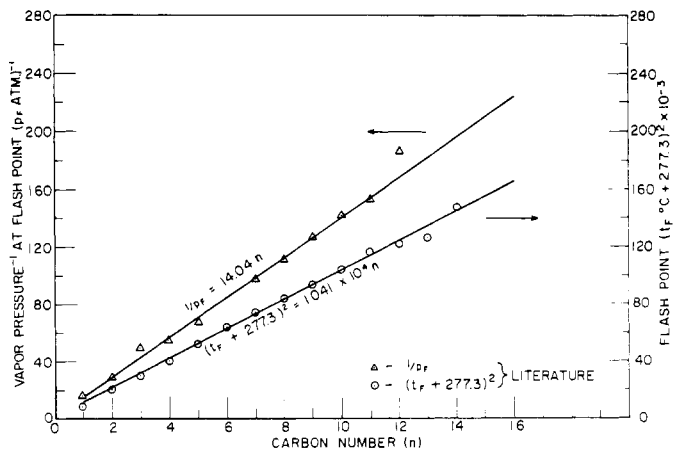Figure 6. Vapor pressure at the flash point vs. flash point for n-alkanes

Figure 7. Vapor pressure at the flash point, and flash point vs. carbon number for n-alkanes

Table II. n-Alkanes—Vapor Pressure at Flash Point and Flash Point vs.
Carbon Number and Reciprocal of Molecular Weight

Carbon No., n	Recip. Mol. Wt. $(1/M)$ $\times 10^3$	Vapor Pres., p_F, atm. $\times 10^3$ at t_F			Flash Point, t_F, °C.		
		Lit. av.[a]	Graph[b]	Calcd.[c]	Lit. av.[d]	Graph[b]	Calcd.[e]
1	62.3	65.8[f]	65.8	71.2	−188[f]	−188	−175
2	33.3	33.5[f]	36.0	35.6	−135[f]	−135	−133
3	22.7	20.5[f]	24.5	23.7	−104[f]	−102	−101
4	17.2	18.5	18.5	17.8	−74	−74	−73
5	13.9	14.9	14.9	13.9	−49	−49	−49
6	11.6	15.1[g]	12.2	11.9	−23	−26	−28
7	10.0	10.3	10.3	10.2	−3	−6	−7
8	8.8	9.0	9.0	8.9	14	13	11
9	7.8	7.9	7.9	7.9	31	31	29
10	7.0	7.0	7.1	7.1	46	47	45
11	6.4	6.5	6.4	6.5	64	62	61
12	5.9	5.4	5.8	5.9	74	76	76
13	5.4	3.0[f,g]	5.3	5.5	79[f]	90	91
14	5.0	6.0[g]	4.9	5.1	107	103	104
15	4.7	...	4.5	4.8	...	...	118
16	4.4	...	...	4.5	...	...	131

[a] p_F derived from literature average flash points, and literature vapor pressure data (8, 14). [b] From intersection vapor pressure and lower flammability limit curves (Figure 7). [c] Equation 12. [d] Ref. (5, 8, 11, 13, 17, and 18). [e] Equation 11. [f] Only one or two values found in literature. [g] Derived literature values of p_F for n-hexane, tri-, and tetradecane appear to be in error. See text.

Equation 14 is in good agreement with that derived by Butler et. al. (5) for a wide variety of hydrocarbon compounds where the slope and intercept are 0.683 and 71.7 (changed to centigrade), respectively.
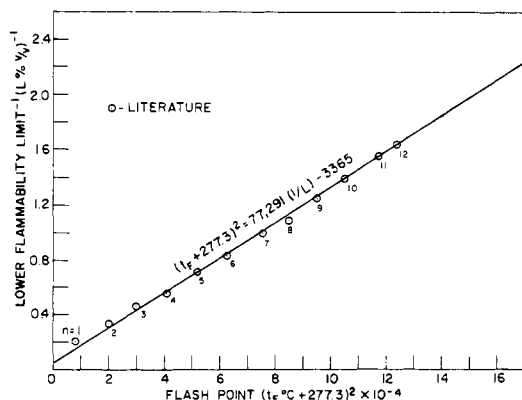
The very important relationship between flash point and lower flammability limit may be derived from Equations 4 and 11.

$$(t_F + 277.3)^2 = 77{,}291(1/L) - 3365 \tag{15}$$

This relationship is plotted in Figure 8, and literature data are included for comparison.

Figure 8. Flash point vs. lower flammability limit for n-alkanes

LITERATURE CITED

(1) Affens, W.A., Johnson, J.E., Carhart, H.W., J. CHEM. ENG. DATA 6, 613 (1961).
(2) American Institute of Physics Handbook, McGraw-Hill, New York, 1963.
(3) Barnett, H.C., Hibbard, R.R., Natl. Advisory Comm. Aeronautics, Rept. 1300, 1957.
(4) Barnett, H.C., Hibbard, R.R., Natl. Advisory Comm. Aeronautics, Tech. Note 3276, August 1956.
(5) Butler, R.M., Cooke, G.M., Lukk, G.G., Jameson, B.G., Ind. Eng. Chem. 48, 808 (1956).
(6) Coward, H.F., Jones, G.W., U. S. Bur. Mines, Bull. No. 503, 1952.

(7) Crumpler, T.B., Yoe, J.H., "Chemical Computations and Errors," p. 220, Wiley, New York, 1940.
(8) Dreisbach, R.R., *Advan. Chem. Ser.* **22**, 1959.
(9) Durbin, E.J., *Aeron. Eng. Rev.* **16**, 58 (1957).
(10) Egerton, A., Powling, J., *Proc. Roy. Soc. (London), Ser. A.* **193**, 172 (1948).
(11) Factory Mutual Engr. Div., Norwood, Mass., Loss Prevention Bull. No. **36.10**, 1950.
(12) Goto, R., Nikki, M., *Bull. Inst. Chem. Res. Kyoto Univ.* **28**, 68 (1952).
(13) Gwinn, S.H., Phillips Petrol. Co., Research Division Rept. **1736-57R**, March 1957.
(14) Jordan, T.E., "Vapor Pressure of Organic Compounds," Interscience, New York, 1954.
(15) Mullins, B.P., Combustion Researches and Reviews, AGARDograph 15, pp. 55-75, Butterworths, London, 1957.
(16) Mullins, B.P., Penner, S.S., "Explosion, Detonation, Flammability and Ignition," Part II, Chap. 11 AGARD, Pergammon Press, New York, 1959.

(17) Phillips Petrol. Co., Bartlesville, Okla., Bull. No. **518**, 5th Ed., 1958.
(18) Phillips Petrol. Co., Bartlesville, Okla., Bull. No. **521**, 1962.
(19) Solov'ev, N.V., Baratov, A.N., *Zhur. Fiz. Khim.* **34**, 1661 (1960); *Russian J. Phys. Chem.* **34**, 793 (1960).
(20) Spakowski, A.E., Natl. Advisory Comm. Aeronautics, Research Memo RM E52H15, Sept. 30, 1952.
(21) Thiele, E.W., *Ind. Eng. Chem.* **19**, 259, (1927).
(22) Van Dolah, R.W., Zabetakis, M.G., Burgess, D.S., Scott, G.S., *U. S. Bur. Mines, Inform. Circ.* **8137**, 1963.
(23) White, A.G., *J. Chem. Soc.* **127**, 672 (1925).
(24) Zabetakis, M.G., Scott, G.S., Jones, G.W., *Ind. Eng. Chem.* **43**, 2120 (1951).

Coefficient of Thermal Expansion

Reduced State Correlation Developed form Ethane PVT Data

CHARLES E. HAMRIN, JR.[1], and GEORGE THODOS
Northwestern University, Evanston, Ill.

PVT data available in the literature for ethane in the gaseous and liquid states have been utilized to develop a reduced state correlation for the dimensionless modulus, βT_c in terms of T_R and P_R. The coefficient of thermal expansion is defined by the thermodynamic relationship, $\beta = (1/V)(\partial V/\partial T)_P$. At low pressures, the modulus βT_c approaches $1/T_R$, which represents ideal gas behavior. For the critical isotherm, this quantity increases rapidly with P_R, becoming infinite at the critical pressure, and steadily decreases for $P_R > 1.0$. The correlation developed in this study is applicable to nonpolar substances having critical compressibility factors comparable to that of ethane, $z_c = 0.285$.

THE coefficient of thermal expansion, β, is a thermodynamic property of gases and liquids, which finds direct application in natural convective heat transfer processes. Heat transfer studies of this type are identified by the dimensionless Grashof number, $Gr = \rho^2 g b^3 \beta \Delta T/\mu^2$. The physical properties ρ and μ included in this modulus have been studied extensively and have been presented in reduced state correlations (*4, 5, 7, 19*). The coefficient of thermal expansion has been presented recently as a reduced state correlation by Damasius and Thodos (*6*), who utilized *PVT* data for argon in the gaseous and liquid states. Their final correlations were presented in terms of the dimensionless quantities, βT_c, T_R, and P_R. In their work, argon was selected as representative of substances which have a simple molecular structure and which are characterized by a critical compressibility factor, $z_c \approx 0.291$. These substances include the monatomic gases argon, krypton, and xenon; the diatomic gases, nitrogen, oxygen, and carbon monoxide; and the hydrocarbon, methane. An extension of this work using ethane as a reference substance has been carried out in this study. Ethane was selected because its molecular structure is more complex than that of argon and also because it has a critical compressibility factor, $z_c = 0.285$.

[1]Present address: Union Carbide Nuclear Division Y-12 Plant, Oak Ridge, Tenn.

REDUCED STATE CORRELATION FOR ETHANE

A comprehensive literature survey made by Phillips and Thodos (*11*) resulted in the development of a reduced density correlation for ethane applicable for the gaseous and liquid regions. Ten references supplied the pertinent *PVT* data for ethane (*1, 2, 3, 8, 9, 10, 15, 16, 18, 20*), which permitted the construction of a reduced density correlation for temperatures up to $T_R = 2.0$ and pressures up to $P_R = 14$. In the original, the correlation includes the basic density data utilized for its development. A reproduction of this ethane reduced density correlation is presented in Figure 1 with the experimental points deleted for the sake of clarity. For the regions of the compressed liquid phase and the dense gaseous phase for which no data are available, the isobars in Figure 1 are presented as dashed lines.

The coefficient of thermal expansion of a pure substance is defined as follows:

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{1}$$

To develop a generalized correlation for this property, Equation 1 can be expressed in terms of the dimensionless parameters of density and temperature as follows: