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Flammability Properties of Hydrocarbon Solutions in Air

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Work on the interrelations of the flammability properties of *n*-alkanes in air has been extended to both vapor and liquid fuel mixtures. By application of Raoult's and Dalton's laws governing vapor pressure and composition above a solution of two or more liquid hydrocarbons to Le Chatelier's rule governing the flammability limits of vapor mixtures, equations have been derived which make it possible to predict overall flammability properties of mixtures from the properties and proportions of the individual components. The properties which were studied include: lower and upper flammability limits, heat of combustion, stoichiometric concentration, flash point, and flammability index ("explosiveness"). Experimentally determined flash points of multicomponent solutions were in good agreement with the calculated values, confirming the point that hydrocarbon solutions follow the above laws, and also confirming the concept of flash point as that temperature at which the vapor concentration above a liquid is equal to that at its lower flammability limit. The derived equations demonstrate why vapor pressure of individual constituents plays a more important role than concentration on the overall flammability properties of liquid solutions, and that a very small amount of a highly volatile contaminant in a relatively nonflammable fuel may make it flammable.

As a result of improper preparation, contamination, or other reasons, less volatile liquid combustibles may sometimes contain small quantities of highly volatile flammable components which can significantly influence the overall flammability properties of the mixture. It would be useful to be able to predict these and relate the effects quantitatively. Some physical properties of liquid solutions, such as density, are generally proportional to the properties and concentrations of the individual components. Combustion, on the other hand, occurs in the vapor phase; hence flammability is a function of vapor concentration above the liquid. Therefore, combustion depends not only on the flammability properties and concentrations (both vapor and liquid), but also to a marked degree on the vapor pressures of the individual components of the solution.

From the standpoint of fire hazard in the storage and handling of flammable liquids and fuels, more knowledge is needed concerning the flammability properties of multicomponent liquid mixtures. The flammability properties to be discussed are lower and upper flammability limits, heat of combustion, stoichiometric concentration (for complete oxidation), flash point, and flammability index.

PRINCIPLES INVOLVED

Le Chatelier's rule governing the flammability limits of vapor mixtures (*16*) and the useful rearrangement of this formula by Coward et al. (*9*) have been known for a long time. These equations, summarized by Coward and Jones (*10*) and more recently by Zabetakis (*22*), have been found to be applicable to hydrocarbon vapor mixtures (*10, 19, 22*) for both lower and upper flammability limits (*9, 13, 18*).

For liquid solutions, it is necessary to determine the vapor composition above the liquid before application of Le Chatelier's rule. Since hydrocarbon solutions do not deviate appreciably from Raoult's Law (*17, 22*), a combination of Raoult's and Dalton's laws govern vapor pressure and composition above a solution of two or more liquids. This treatment has been applied to lower flammability limits of liquid solutions containing methyl ethyl ketone and tetrahydrofuran by Zabetakis et al. (*23*). Zabetakis (*22*) also reported its application to flammability limits of two-component liquid hydrocarbon mixtures. Empirical formulas making use of certain of these concepts for calculating flash points of complex mixtures and blends were reported by Thiele (*20*), Butler et al. (*8*), and Mullins (*18*).

As a continuation of previous work at this laboratory on the interrelations of the flammability properties of the *n*-alkanes in air (*1*), it was decided to extend some of the derived relationships to both vapor and liquid hydrocarbon mixtures in order to predict overall flammability properties from the properties and proportions of the individual components.

LIMITATIONS

The present discussion will be limited to liquid and vapor hydrocarbon fuels, excluding droplets and mists, in air at atmospheric pressure. It will be assumed that the vapor is in equilibrium with the liquid at a given temperature, and that

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vapor–air mixtures are uniform throughout. For multicomponent liquid solutions, the derivations will be limited to substances which obey Raoult's law. Except where otherwise stated, flammability limits, related properties, and vapor pressures are at 25°C.

CHOICE OF HANDLING OF LITERATURE DATA

As a rule, a generalized approach will be taken, and symbols, rather than specific data will be employed. Multicomponent solutions will be considered, but to illustrate some of the relationships, binary mixture systems are given with solutions of *n*-alkanes in *n*-undecane as examples. Specific flammability data, where given, have been calculated from averaged literature data by means of the relationships described previously (*1*). Vapor pressure data and relationships are from standard sources (*2, 11, 15*).

FLAMMABILITY LIMITS OF VAPOR–AIR MIXTURES

Le Chatelier's rule (*16*) for a flammable vapor–air mixture of two or more components is

$$\sum_i (C_i/L_i) = 1 \tag{1}$$

where C is the actual vapor concentration, L the concentration at the lower flammability limit (both expressed in percent by volume), and the subscript i refers to the property in question of a general component, i. The equation, which is a simple additive relationship, states that for a mixture of gases to be at the lower flammable limit, the sum of the ratios of the actual concentration to that at the lower flammability limit for each constituent is equal to unity. By simple algebraic rearrangement, Coward et al. (*9*) derived a useful form of Le Chatelier's rule

$$1/L_M = \sum_i (y_i/L_i) \tag{2}$$

where y is the mole fraction of a given fuel component in the total fuel vapor on an "air-free" basis, and the subscript M refers to the overall property of the mixture. Equation 2 expresses the lower flammability limit of the flammable vapor or gas mixture as a function of the sum of the ratios of the proportion of each component to that of its lower flammability limit.

Analogous expressions (*9, 13, 18*) can be used for the upper flammability limit U

$$\sum_i (C_i/U_i) = 1 \tag{3}$$

$$1/U_M = \sum_i (y_i/U_i) \tag{4}$$

STOICHIOMETRIC CONCENTRATIONS OF VAPOR–AIR MIXTURES

A similar expression for stoichiometric concentration (assuming complete combustion to carbon dioxide and water) can be derived with the aid of previously derived relationships (*1*):

$$1/C_{s,M} = \sum_i (y_i/C_{s,i}) \tag{5}$$

MOLAR HEAT OF COMBUSTION OF VAPOR–AIR MIXTURES

Le Chatelier's rule, developed from experimental considerations (*16*), can also be derived from molar heat of combustion (ΔH_m) concepts. It can be shown readily from energy considerations of a gas mixture that

$$\Delta H_{m,M} = \sum_i (y_i \Delta H_{m,i}) \tag{6}$$

But as has been discussed previously (*1*), for most hydrocarbons the molar heat of combustion is proportional to the reciprocal of the lower flammability limit. For hydrocarbons in general the constants of proportionality are approximately equal (*13*). Thus, $1/L$ can be substituted in Equation 6, which, on canceling out the constants, becomes Equation 2. This equation is a form of Le Chatelier's rule.

VAPOR MIXTURES CONTAINING TWO FUEL COMPONENTS

For fuel–air mixtures containing only two fuel components, A and B, Equations 1 and 2 become

$$C_A/L_A + C_B/L_B = 1 \tag{7}$$

and

$$1/L_M = y_A/L_A + y_B/L_B \tag{8}$$

Equation 7, on rearrangement becomes

$$C_B = L_B - (L_B/L_A)C_A \tag{9}$$

Thus, for a lower limit mixture, a plot of C_B as a function of C_A is a straight line. Similarly, Equation 8 may be rearranged and substituting $(1 - y_B)$ for y_A (the sum of the mole fractions is unity), Equation 8 becomes

$$1/L_M = (1/L_B - 1/L_A)y_B + 1/L_A \tag{10}$$

Equation 10 is likewise linear. Thus, for a two-component fuel vapor–air mixture, for which the individual flammability limits are known constants, Equations 9 and 10 become simple linear equations useful for calculating or plotting concentrations of limit mixtures. Analogous equations may be derived for the other flammability properties.

FLAMMABILITY INDEX OF VAPOR–AIR MIXTURES

Another useful flammability property, which can be measured readily for a given fuel vapor–air mixture, has been referred to by various terms "percent explosiveness" (*12*), "explosivity," or "percent of the lower exploive limit." It is actually a measure of potential flammability hazard rather than "explosiveness" as such. For this reason, the term "flammability index" is suggested as a more meaningful description of this property and will be used here. This property is an expression of the fraction, or ratio, of the actual concentration of fuel vapor to that at its lower flammability limit. The fractions may be expressed as a decimal or percentage of volume concentrations; but the former, based on unity rather than 100, is simpler and will be used as a basis of flammability units in the present discussion. If, at a given temperature, C_i is the volume concentration of a given fuel vapor in air and L_i is its lower flammability limit (% v/v), then its flammability index E_i is defined

$$E_i = C_i/L_i \tag{11}$$

Thus, if the fuel-vapor concentration in a given air-fuel mixture is equal to the concentration at its lower flammability limit ($C_i = L_i$), the flammability index is unity ($E_i = 1$). If E_i is equal to or greater than unity, the mixture is flammable, provided it is not so large as to exceed the upper flammability limit value. If E_i is less than unity, the mixture is nonflammable. Le Chatelier's rule (Equation 1) is therefore a sum of ratios which are actually flammability indices. Thus, Equation 1 becomes

$$E_M = \sum_i E_i = 1 \qquad (12)$$

Therefore, the flammability index of a mixture is equal to the sum of the indices of the components. From Equation 12 it can also be shown that air mixtures of different hydrocarbons at their lower limits, if mixed in any proportions, will give rise to mixtures which are also at their lower limits (*10*).

EFFECT OF TEMPERATURE ON FLAMMABILITY LIMITS OF VAPOR–AIR MIXTURES

Flammability limits of hydrocarbons do not vary significantly with moderate changes in temperature (*10*), but over a wide temperature range a correction for this variation must be made. The lower flammability limit of a hydrocarbon vapor–air mixture decreases approximately linearly with increasing temperature (*10, 22*). An expression for the ratio of the lower limit at a temperature, t, relative to that at room temperature (25°C) is given by Zabetakis (*22*) and can be put in the form

$$L_t/L_{25} = 1.02 - 0.000721\,t \qquad (13)$$

where L_{25} and L_t are the lower flammability limits of a given hydrocarbon at 25°C and t°C, respectively. It will be convenient to write Equation 13 in the form

$$L_t = QL_{25} \qquad (14)$$

where Q is the lower flammability limit temperature correction factor,

$$Q = 1.02 - 0.000721\,t \qquad (15)$$

The question of the flammability limits of a multicomponent vapor–air limit mixture is treated by application of the temperature correction factor, Equation 14, to the rearranged Le Chatelier's formula (Equation 2). At any temperature t, Equation 2 becomes

$$1/L_{t,M} = \sum_i (y_i/L_{t,i}) \qquad (16)$$

Substituting for L_t (Equation 14) in Equation 16 and factoring out $1/Q$, we get

$$1/L_{t,M} = \sum_i (y_i/QL_{25}) = (1/Q)\sum_i (y_i/L_{25}) \qquad (17)$$

Substituting $1/L_M$ (Equation 2) for its equivalent in Equation 17 and rearranging give

$$L_{t,M} = QL_{25,M} \qquad (18)$$

Equation 18 for mixtures is equivalent to Equation 14, and therefore the variation of the flammability limits of a multicomponent hydrocarbon mixture with temperature is the same as that of a single hydrocarbon.

The same relationships which have been demonstrated for lower flammability limits also apply to upper limits (*10, 14, 19*).

VAPOR COMPOSITION ABOVE LIQUID SOLUTION

The flammability properties of a liquid hydrocarbon depend on the composition of the vapor–air mixture above the liquid. For a multicomponent mixture, the vapor composition is a function of the concentration and vapor pressure of the individual components. If vapor–liquid equilibrium is assumed, it is possible to estimate the vapor–air composition above a liquid mixture. Since hydrocarbon solutions obey Raoult's law (*17, 22*), the vapor composition above a solution of hydrocarbons at constant temperature may be determined by a combination of Dalton's and Raoult's laws, i.e.,

$$y_i = p_i'/p_M = x_i p_i / \sum_i (x_i p_i) \qquad (19)$$

where y_i has been previously defined (Equation 2), p_i is the vapor pressure (atmospheres) of the pure liquid component, i, and p_i', its partial pressure, x_i is its liquid concentration (mole fraction), and the denominator is the total vapor pressure, p_M.

The conventional textbook example of this ideal solution relationship for a two-component liquid solution usually plots the partial and total vapor pressures against concentration for liquids of relatively similar vapor pressures. In the case of binary liquid mixtures of two components of widely different vapor pressures, however, the general shape of the graph is highly distorted from that of the textbook case. Such a plot is shown in Figure 1 for a solution of n-octane and n-undecane. The graph demonstrates that the total vapor pressure of a liquid solution of volatile and relatively nonvolatile components is approximately equivalent to the partial pressure of the more volatile constituents. This relationship has an important bearing on vapor composition and the flammability properties of liquid solutions.

FLAMMABILITY LIMITS OF LIQUID SOLUTIONS

In this discussion, the flammability limits of a liquid fuel are understood to be based on the flammability limits of its vapor in equilibrium with the liquid at a given temperature, and not on the totally evaporated liquid. In the relatively simple case of a pure liquid hydrocarbon, its vapor is a single component and therefore the flammability limits of the vapor determine the limits of the liquid. Multicomponent liquid fuels, on the other hand, are more complex in that the relative proportions of the individual hydrocarbon vapors in equilibrium with the liquid at a given temperature generally are not the same as in the liquid phase. The composition of the hydrocarbon vapor mixture is what determines the flammability limits of the liquid. Treating the total hydrocarbon vapors as a single entity, the minimum concentration in air of such a hydrocarbon vapor mixture which can propagate a flame is defined as the lower flammability limit, and the maximum concentration is the upper limit.

Substituting for y_i (Equation 19) in Equation 2, we get the

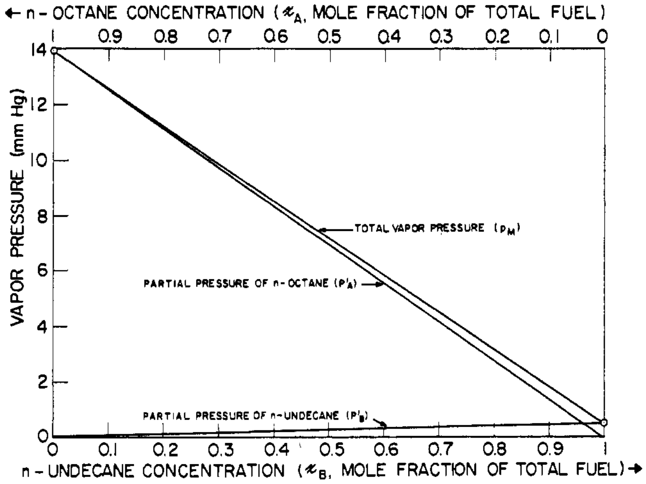

Figure 1. Vapor pressure vs. concentration of binary liquid solutions of *n*-octane and *n*-undecane at 25°C

equivalent equations for liquid solutions at constant temperature

$$1/L_M = \sum_i(x_i p_i/L_i)/\sum_i(x_i p_i) \quad (20)$$

or for a binary solution

$$1/L_M = (x_A p_A/L_A + x_B p_B/L_B)/(x_A p_A + x_B p_B) \quad (21)$$

This is plotted in Figure 2 for three separate solutions of *n*-hexane, *n*-octane, and *n*-decane each in *n*-undecane at 25°C. The curves in Figure 2 also demonstrate the relatively large influence of the more volatile constituent. Analogous equations apply to upper flammability limits, stoichiometric concentrations and molar heat of combustion.

FLAMMABILITY INDEX OF LIQUID SOLUTIONS

The flammability index of a liquid fuel, which is a temperature dependent property, is the ratio of the actual concentration of hydrocarbon vapors in the vapor–air mixture in equilibrium with the liquid to that at its lower flammability limit, at an arbitrary temperature, *t*, usually 51.7°C (125°F) for specification test purposes (*12*). The above discussion on flammability limits of liquid hydrocarbon fuel mixtures also applies to flammability index since these two flammability properties are closely related.

The flammability index of a multicomponent hydrocarbon mixture is given by

$$E_M = C_M/L_M = \sum_i(C_i)/L_M \quad (22)$$

where C_M is the total hydrocarbon concentration in air, and is equal to the sum of the concentrations of those of the individual components (C_i). The equilibrium vapor concentration in percent by volume C_i of a particular component of a liquid solution in the vapor space above the liquid at constant temperature is

$$C_i = 100\, x_i p_i \quad (23)$$

where p_i is in atmospheres.

Substituting the values of C_i from Equation 23 and of L_M from Equation 20 in Equation 22, and simplifying, we get

$$E_M = \sum_i(100\, x_i p_i/L_i) \quad (24)$$

But, the flammability index of the vapors above a pure liquid component, E_i, at constant temperature is

$$E_i = 100\,(p_i/L_i) \quad (25)$$

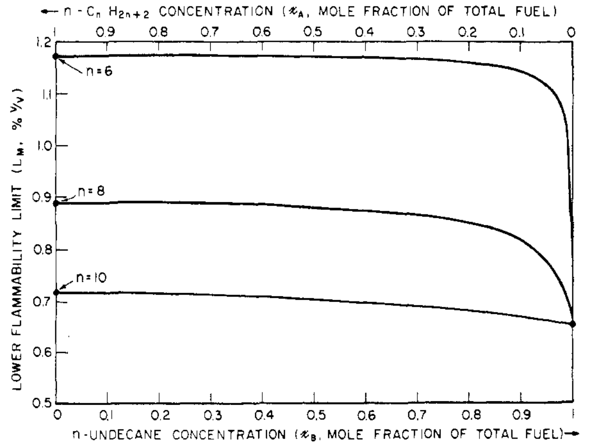

Figure 2. Calculated lower flammability limits of binary liquid solutions of *n*-alkanes and *n*-undecane in air

Substituting the value of E_i from Equation 25 in Equation 24 gives us

$$E_M = \sum_i(x_i E_i) \quad (26)$$

By analogy with the total pressure–partial pressure relationships of liquid solutions, it is seen that the "total" flammability index (E_M) is equal to the sum of the "partial" flammability indices (E_i')

$$E_M = \sum_i E_i' = \sum_i(x_i E_i) \quad (27)$$

For a two-component solution, Equation 26 becomes

$$E_M = x_A E_A + x_B E_B \quad (28)$$

which, on elimination of x_A (the sum of the mole fractions x_A and x_B is unity), develops into

$$E_M = E_A - (E_A - E_B)x_B \quad (29)$$

A plot of E_M vs. x_B (Equation 29) is linear, as illustrated in Figure 3, which shows the flammability indices (at 125°F or 51.7°C) of several binary solutions of *n*-alkanes in *n*-undecane vs. the concentration of *n*-undecane. The temperature is that of a standard test method (*12*). Both vapor pressure and flammability limits were calculated at 125°F to obtain the

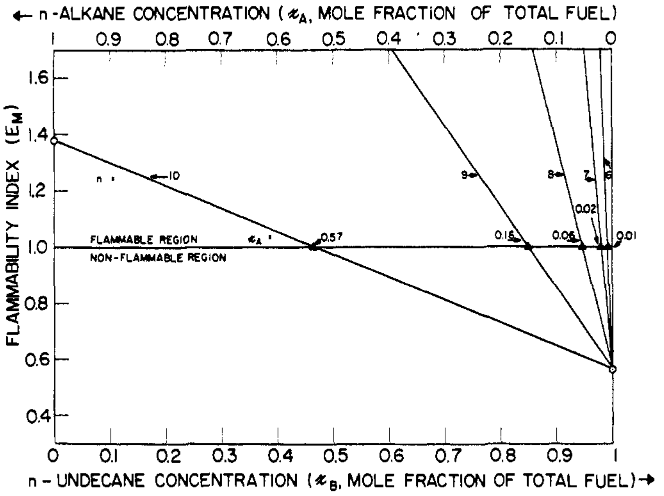

Figure 3. Flammability indices (explosiveness) of binary liquid solutions of *n*-alkanes and *n*-undecane in air at 125°F (51.7°C)

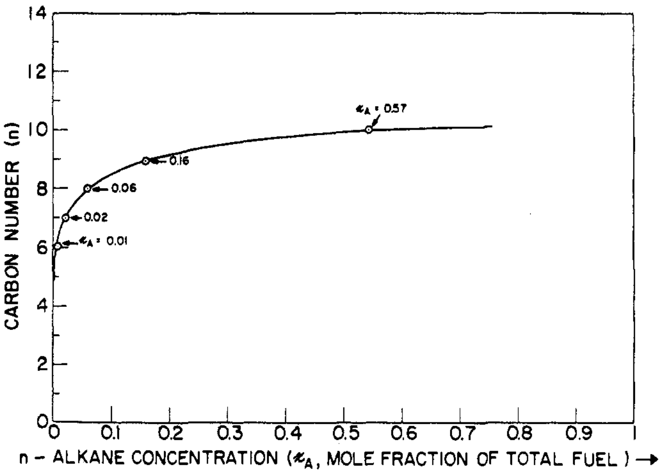

Figure 4. Flammable concentrations vs. carbon number of binary liquid solutions of alkanes and *n*-undecane in air at 125°F (51.7°C)

flammability indices. The horizontal line at E_M, equal to unity, delineates flammable from nonflammable solutions, and the *n*-alkane concentrations (x_A) needed to make *n*-undecane flammable at 51.7°C are indicated. A plot of x_A vs. carbon number is indicated in Figure 4. The two figures demonstrate that at higher vapor pressure, increasingly smaller concentrations of volatile components are required to make the relatively nonvolatile *n*-undecane, flammable.

FLASH POINT

Fundamentally, the flash point of a flammable liquid is the minimum temperature at which its vapor pressure is sufficient to form a flammable vapor–air mixture at 1-atm pressure (*1, 18, 21*). In other words, it is that temperature at which the equilibrium vapor composition above the liquid is equivalent to that at its lower flammability limit. Flash point is thus the same as the lower flammability temperature limit. There are actually two flash points, a lower flash point, t_L, and an upper flash point, t_U, corrsponding to the lower and upper flammability temperature limits. The unmodified expression "flash point," as is usually the custom, refers to the lower flash point. Experimentally determined, flash points depend to a high degree on the type of apparatus and the method used for its determination—e.g., such items as "closed" or "open" cup and rate of heating. From the experimental viewpoint, flash point may be defined as "the temperature to which the product must be heated under the specified conditions of the method to give off sufficient vapor to form a mixture with air that can be ignited momentarily by a specified flame" (*7*).

The term "fire point" is used to define the temperature at which the product will burn continuously under the same prescribed conditions and is determined in an open-cup-type (open to the atmosphere) apparatus. In general, closed cup flash points are lower and more reliable than those obtained by open cup methods. This might be expected since the vapors in a closed cup apparatus are likely to be closer to equilibrium than those in an open cup where diffusion to the outside can occur.

For solutions of two or more flammable liquids, the problem of defining these concepts is more complex. For solutions, the lower flash point temperature is that temperature at which the vapor pressure of each of the flammable volatile components is such that the composition of the vapor–air mixture above the liquid is flammable in accordance with Le Chatelier's rule. In the discussion up to this point, the various flammability functions were assumed to be at constant temperature, and (except for flammability index) this temperature was generally at 25°C. The concept of flash point brings in temperature as an additional variable. The object will be to express the flash point of a multicomponent solution ($t_{L,M}$) as a function of the flash points ($t_{L,i}$) and concentations (x_i) of the individual components of the solution.

For a flammable multicomponent liquid solution at its flash point temperature, $t_{L,M}$, by application of Le Chatelier's rule, Equation 24, becomes

$$E_M = \sum_i (100\, x_i p_{t,i}/L_{t,i}) = 1 \tag{30}$$

where $p_{t,i}$ and $L_{t,i}$ are the vapor pressure and lower flammability limit values, respectively, of each component at the flash point temperature of the solution ($t_{L,M}$).

Substituting for the value of $L_{t,i}$ from Equation 13 and rearranging, we get

$$\sum_i (100\, x_i p_{t,i}/L_{25,i}) = 1.02 - 0.000721\, t_{L,M} \tag{31}$$

For a solution of pure hydrocarbon components of known concentrations (x_i), if we assume that the lower flammability limits of each fuel component at 25°C are also known, it is then necessary to know the vapor pressures as functions of temperature for each component, ($p_{t,i}$), to solve Equation 31 for the flash point temperature ($t_{L,M}$). Vapor pressure–temperature data for the hydrocarbons are readily available (*2, 11, 15*). For purposes of this work, the familiar Antoine-type equation (*11*) was a useful and good approximation:

$$\log p_{t,i} = m_i/(t_{L,M} + a) + b_i \tag{32}$$

where b_i, m_i, and a are constants varying from hydrocarbon to hydrocarbon. In general, a value of 230 was a good approximation for the constant a, for the *n*-alkanes. The values of b_i and m_i may be estimated from the literature (*2, 11, 15*). With values of b_i and m_i known for each fuel component, solution of Equation 31 for $t_{L,M}$ can be attempted with the aid of Equation 32. For approximate purposes, this solution can be done graphically by the following elementary treatment:

From Equation 31, let

$$Y = \sum_i (x_i p_{t,i}/L_{25,i}) - 1.02 + 0.000721\, t_{L,M} \tag{33}$$

The solution involves finding its roots ($Y = 0$) which can be done graphically by plotting Y vs. $t_{L,M}$ at various values of $t_{L,M}$. For each $t_{L,M}$, the value of $p_{t,i}$ in Equation 32 is determined and substitution of this value in Equation 33 for each component yields the solution for Y. However, it would be more useful to express $t_{L,M}$ as a function of the flash points of the individual pure components ($t_{L,i}$) than as a function of the lower limits. This transformation was done by algebraic manipulation which is summarized here.

For a pure liquid hydrocarbon at its flash point ($t_{L,i}$), Equation 31 on rearranging becomes

$$100\, p_{L,i}/L_{25,i} = 1.02 - 0.000721\, t_{L,i} \tag{34}$$

where $p_{L,i}$ is the vapor pressure at $t_{L,i}$.

To simplify matters, substituting Q_M and Q_i for the right sides of Equations 31 and 34, respectively, gives us

$$\sum_i [(100\, x_i p_{t,i}/L_{25,i})] = Q_M \tag{35}$$

$$100\, p_{L,i}/L_{25,i} = Q_i \tag{36}$$

where

$$Q_M = 1.02 - 0.000721\, t_{L,M} \tag{37}$$

and

$$Q_i = 1.02 - 0.000721\, t_{L,i} \tag{38}$$

Dividing Equation 35 by Equation 36 and rearranging give

$$\sum_i [x_i (p_{t,i}/p_{L,i})(Q_i/Q_M)] = 1 \tag{39}$$

The vapor pressure of each hydrocarbon component at its flash point temperature ($\theta_{L,i}$) and that of the solution ($\theta_{L,M}$), respectively, may be calculated from Equation 32, where $\theta = t + 230$

$$\log p_{L,i} = b_i + m_i/\theta_{L,i} \tag{40}$$

$$\log p_{t,i} = b_i + m_i/\theta_{L,M} \tag{41}$$

Subtracting Equation 40 from Equation 41 gives

$$\log (p_{t,i}/p_{L,i}) = m_i(\theta_{L,i} - \theta_{L,M})/\theta_{L,i}\theta_{L,M} \tag{42}$$

Combining Equations 37–39 and the exponential form of Equation 42, using θ for temperature, and rearranging, we get

$$\sum_i [x_i\, 10^a (1642 - \theta_{L,i})/(1642 - \theta_{L,M})] = 1 \tag{43}$$

where

$$a = m_i(\theta_{L,i} - \theta_{L,M})/\theta_{L,i}\theta_{L,M} \tag{44}$$

By means of Equation 43, one may calculate the flash point of a multicomponent hydrocarbon mixture ($\theta_{L,M}$) from the flash points ($\theta_{L,i}$) and concentrations (x_i) of the individual components. This maneuver is based on the assumption that the vapor pressure–temperature relationships are known, and that the system obeys the laws of Raoult, Dalton, and Le Chatelier.

EXPERIMENTAL DETERMINATION OF FLASH POINT

There are numerous methods for the determination of flash point, of which four (*3–6*) are standard in the United States. The flash points of three hydrocarbon samples, and six jet fuel samples were determined by these four methods, and comparative data are given in Table I. With one minor exception (JP-4, jet fuel, No. J-354), the Tag closed cup apparatus (*5*) gave the lowest results. From the point of view of assessing flammability hazard, and from design and experimental considerations, it was decided to use the Tag closed cup apparatus in this work. The hydrocarbons used were obtained from the Phillips Petroleum Co. and were specified to have a minimum purity of 99 mol %.

FLASH POINTS OF PURE *n*-ALKANES

The method for calculating flash point was first tested against some pure hydrocarbons, and the results are given in Table II along with average literature (*1*) and calculated data (*1*) for comparison. The experimental results, although somewhat high, are in good agreement with both the literature average and calculated data.

FLASH POINTS OF MULTICOMPONENT SOLUTIONS

Two series of binary solutions covering the entire concentration ranges of *n*-heptane and *n*-octane, each in *n*-undecane, were tested. The results are plotted against the curves based on Equation 43 and are given in Figure 5. It is seen that experimental results are in excellent agreement with calculated values.

Eight additional multicomponent solutions were prepared from two to six components, and the flash points are shown in Table III. Here also, results are in good agreement with calculated values.

Table I. Comparison of Flash Point Temperatures by Different Methods

Fuel	Flash point temp (t_L, °C) Tag closed cup (*5*)	Pensky-Martens closed cup (*4*)	Tag open cup (*6*)	Cleveland open cup (*3*)
n-C_8H_{18}	15	17	19	31
n-$C_{11}H_{24}$	64	69	71	78
95% (v/v) $C_{11}H_{24}$ + 5% C_8H_{18}	53	57	61	70
JP-4 (Andrews)	−10	−14	−13	−2
JP-4 (No. J-354)	−6	−8	−4	9
JP-5 (No. J-434)	58	60	70	78
JP-5 (No. J-437)	57	62	68	71
JP-5 (No. J-439)	60	61	71	77
JP-5 (No. J-441)	58	60	68	76

Table II. Flash Point Temperatures of Pure *n*-Alkanes

n-C_nH_{2n+2}	Flash point temp of pure n-alkanes (t_L, °C) Calcd (graphical) (*1*)	Lit. av (*1*)	Exptl (Tag closed cup) (*5*)
n = 7	−6	−3	−1
8	13	14	15
9	31	31	33
10	47	46	48
11	62	64	64
12	76	74	79

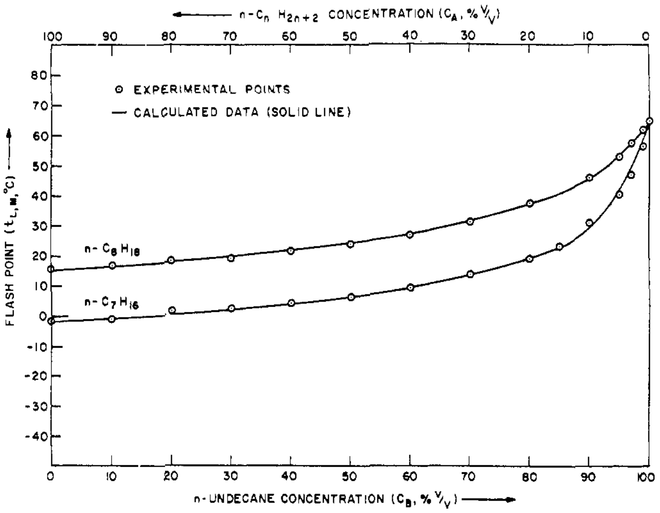

Figure 5. Calculated and experimental flash points of binary liquid solutions of *n*-alkanes and *n*-undecane in air

Table III. Flash Point Temperatures of Multicomponent *n*-Alkane Solutions

n-Alkane [n-$C_nH_{(2n+2)}$] concn (C_i, % v/v) n = 7	8	9	10	11	12	Flash point, $t_{L,M}$(°C) Calcd	Exptl[a]
50	50	...	...	...	...	5	2
33.3	33.3	...	...	33.3	...	10	10
25	15	...	...	60	...	15	14
20	20	...	...	60	...	17	16
5	5	...	...	90	...	37	37
25	...	25	...	25	25	17	15
20	20	20	...	20	20	16	16
15	15	15	15	25	15	20	20

[a] Tag closed cup (*5*).

CONCLUSION

Experimental flash point results are in good agreement with calculated flash points for multicomponent solutions of *n*-alkanes. The data confirm a flash point equation derived from the laws of Dalton, Raoult, and Le Chatelier governing the vapor pressure, composition, and flammability limits of liquid hydrocarbon solutions. The concept that flash point is that temperature at which the vapor concentration above a liquid is equal to that of its lower flammability limit is also shown to be valid. The most important conclusion demonstrated by the derived equations is that a very small amount of highly volatile contaminant in a relatively nonflammable fuel may make it highly flammable. Although precise relationships have been derived about relatively simple solutions of pure hydrocarbons, the concepts they imply are applicable to more complex mixtures such as gasoline, jet and diesel fuels, and the like.

NOMENCLATURE

c = concentration of fuel component by volume in liquid fuel mixture, % v/v
C = concentration of fuel component by volume in vapor–air mixture, % v/v
x = mole fraction of fuel component in liquid fuel mixture
y = mole fraction of fuel component in fuel vapor mixture on an "air-free" basis
p = vapor pressure, atm
p' = xp = partial pressure, atm
t = temperature, °C
θ = $t + 230$
ΔH_m = net molar heat of combustion, kcal/mol
C_s = stoichiometric concentration of fuel component by volume in vapor–air mixture (assuming complete combustion to carbon dioxide and water), % v/v
L = concentration of fuel component by volume in vapor–air mixture at lower flammability limit, % v/v
U = concentration of fuel component by volume in vapor–air mixture at upper flammability limit, % v/v
t_L = flash point, °C
E = C/L = flammability index
E' = xE = partial flammability index
Q = L_t/L = lower flammability limit temperature correction factor

SUBSCRIPTS

t = temperature (if t is specified, use its value as subscript—e.g., L_{25})
L = at flash point
i = general component, i
A, B, etc. = specific component A, B, etc.
M = multicomponent mixture

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Enthalpies of Dilution and Relative Apparent Molal Enthalpies of Aqueous Barium Perchlorate

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Relative apparent molal enthalpies (ϕ_L) were measured at 25°C for barium perchlorate solutions over the concentration range 0.006–5.8m. The data were fitted to a form of the Debye-Hückel equation which leads to reliable extrapolation to $m = 0$.

This study originated in part from specific need for relative apparent molal enthalpies (ϕ_L) for $Ba(ClO_4)_2$ solutions, and also as part of a broader interest in the behavior of ϕ_L with concentration for 2–1 perchlorates free from hydrolysis effects. Jongenburger and Wood (*4*) have reported ϕ_L values for $Mg(ClO_4)_2$ and $Sr(ClO_4)_2$ solutions up to 4.4m. The barium cation is the largest of the series, so should be the least solvated and exhibit the least tendency to hydrolyze. The studies reported here cover the concentration range from 0.006–5.755m, close to saturation.

EXPERIMENTAL

Materials. Five barium perchlorate stock solutions were prepared by slowly adding J. T. Baker Analyzed

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