

Chapter 2

Classical Flammability Theories

With the expectation of establishing a fundamental flammability theory, the primary factor that determines the flammability limit is the competition between the rate of heat generation, which is controlled by the rate of reaction and the heat of reaction for the limit mixture, and the external rate of heat loss by the flame [7]. Many theoretical developments are performed to determine the controlling factor, which may be the heat loss and some aerodynamic effects. Here are a few efforts toward this goal.

1. Daniell [23] analytically established a minimum tube radius for flame propagation by analyzing the heat loss through the wall.
2. Flammability limits are explained as the instability to small disturbance from the steady state [24].
3. Flames are governed by a multiple eigenvalue problem [25, 26].
4. Flammability limits are explained in terms of kinetic properties of the mixture [27].
5. Limit appears at the composition at which the flame becomes unstable to a change in the curvature or extent or form of the flame front (Convective effects [28]).
6. Spalding [29], Mayer [30] and Berlad and Yang [31] have developed a uni-dimensional flame theory and implied that the radiation loss produces a fundamental limit.
7. According to Lewis and von Elbe [32], the flame propagation in a diverging flow results in that the burned gas moves parallel to the flame and this the cause of convection-induced heat loss from the flame into the cold mixture.
8. Heat loss and chain termination are simultaneously important at these limits [33].
9. The extinction limit occurs as a result of flame temperature reduction when the rate of radiative loss becomes substantial compared with the rate of combustion heat release [34].

They all stress a certain feature interrupting the flame propagation. However, the major mechanism for heat transfer, mass transfer, is not given sufficient attention. Only when the flame temperature has dropped near its critical threshold, the above

mechanisms began to play a role. In addition, there are also several conflicting views on the controlling factors. For example, radiation losses represent a small proportion of the total losses, which has been shown by Egerton and Powerling [35] using silvered and blackened tubes. Linnett [28] proposed that the limits obtained in tubes (even the widest ones) are not fundamental. Since there are so many factors controlling the flame propagation process, a consistent flammability theory is difficult to establish. **This is consistent with the fact that flammability is not fundamental to that fuel.** This fact led many researchers to propose empirical rules to manipulate flammability. These empirical rules work for some problems, without the need to know the fundamental difference between flammability and explosibility.

2.1 Empirical Rules on Flammability

2.1.1 Milestone Events on Flammability Theory

Since the pioneering experimental work by Davy in 1816, the first major theoretical breakthrough came with Le Chatelier's empirical rule, which first appeared in 1891 [36]. During a systematic study on diluents and flame temperature, Coward et al. [37] first applied Le Chatelier's rule in its present form. Burgess-Wheeler [6] tried to establish a thermal balance for flammability limits with the concept of flame temperature. The comprehensive flammability data were reported in a series of BOM Bulletins, the most famous one is the last version [4], which appeared in 1952. In 1965, Zabetakis [43] compiled and published latest data for flammability limits, auto-ignition, and burning-rate data for more than 200 combustible gases and vapors in air and other oxidants, as well as of empirical rules and graphs that can be used to predict similar data for thousands of other combustibles under a variety of environmental conditions. His report is the bible on flammability, still in use today. His work remains the core document for supplying flammability information, showing the fact that there is little progress on flammability theory after him. In a series of reports (first appeared in 1975), Hertzberg [38–40] tried to establish an in-depth view on flammability theory, however, his theory is far from engineering applications and left small impact in a computer age. With the development of computer technologies, a detail chemical analysis has been applied for predicting the flammability behavior [41], however, engineering applications are still relying heavily on the empirical Le Chatelier's rule or modified Burgess-Wheeler's law for estimations. Without a fundamental theory, it is difficult to provide an overview of flammability theories, especially when the testing principles behind data are also not well received.

2.1.2 Energy Dependence

It was long recognized that the calorific value of the paraffin is the sole determining factor in calculating the relative lower limits of inflammation of mixture of each with air. Le Chatelier and Boudouard [42] observed that the heat of combustion per unit volume of limit mixtures with air for alkanes was approximately a constant at lower limits, an empirical finding later confirmed by numerous researchers. Out of the simple energy balance at lower flammability limit, Burgess and Wheeler [6] further proposed the principles in deriving the temperature dependence of flammability limits. For the first time, they suggested “the heat liberated by a mole of a lean limit mixture is nearly constant for many combustible-air-mixture at ordinary temperature and pressure”, out of which developed the Law of Burgess and Wheeler [43]. That is, the calorific values of the pure paraffin hydrocarbons times their lower limits of inflammability were a constant and that a lower-limit mixture of any of the paraffin hydrocarbons with air on combustion liberates the same amount of heat. White [44] confirmed that the lower limit for downward propagation of flame was approximately inversely proportional to the net calorific value of the vapor used. Jones [9] further concluded that the primary factor that determines the flammability limit is the competition between the rate of heat generation, which is controlled by the rate of reaction and the heat of reaction for the limit mixture, and the external rate of heat flow by the flame. However, such an energy balance was not established and applied properly, probably due to the ternary nature of a mixture.

Based on the observation that the amount of heat contained in the products of combustion of any given layer is just sufficient to raise to its ignition-temperature for the layer adjacent, Burgess and Wheeler [6] established

$$x_L \cdot \Delta H_C = K \quad (2.1)$$

where x_L is the percentage of combustible in the low limit mixture, ΔH_C is the net heat of combustion of the fuel and roughly as ~ 10.5 kCal/mol. Most existing correlations follow this format to estimate the mixture flammability [17]. It is called “K-constant” method [45], which holds for paraffin up to pentane. Note the original Burgess Wheeler’s law [6] used $K = 1059$ for methane. Spakowski [46] used $K = 1040$ to make his simplification. Hanley [47] proposed $K = 1120$, while Ramiro et al. [17] proposed $K = 1042$. They all belong to the “K-constant” method. The scattering of data shows the uncertainty in flammability measurement.

However, earlier researchers, including Burgess and Wheeler, noticed that K is not a constant for some fuels and more heat is required to maintain the combustion of the higher hydrocarbons. The value K increases as the paraffin series is ascended and there is therefore an increase in flame temperature for C_p shows only a relatively small change. The values increase asymptotically to about 1600 K where the effect of dissociation begins to become appreciable [5]. Britton [48] later concludes,

“K Constant” method implies a constant flame temperature at the LFL. White [44] and Zabetakis et al. [49] further proposed

$$x_L \cdot \Delta H_C + \Delta H = K \quad (2.2)$$

where ΔH is the fraction of energy absorbed by ambient air.

Along with the thermal theory, a chain reaction was proposed to explain the thermal phenomena on flame propagation ([35, 50]). Out of the chain reaction theory, it was proposed that some species have more radicals produced in a flame. However, these promoters appeared in the gas ahead of the flame have little specific influence on propagation limits. It is further concluded that the main criterion for inflammation is the maintenance of a sufficient rate of reaction and heat release in the flame, providing thereby sufficient active radicals to inflame the entering gases.

By examining the “K Constant” method, three important outcomes are proposed [48], the modified Burgess-Wheeler law for estimating the temperature dependence, the “Jones’ Rule” or “Lloyd’s Rule” for predicting LFLs of paraffin hydrocarbons, and most important of all, the Le Chatelier Rule for estimating the flammable limits of mixtures of fuels whose individual LFLs are known. This method is the central principle guiding the experimental and theoretical work for the past 100 years. Most of the “hot wire” combustible-gas indicators operate on this principle directly [48].

2.1.3 Temperature Dependence

The most important parameter affecting the flammability limits is temperature, since an increase in initial temperature leads to a widening of the flammable range [43].

Experimentally, White [44] showed that both limits are affected fairly uniformly. There are several researches on the temperature dependence, using hydrogen [51], low temperature of methane [52], toluene [53], upper explosion limit of lower alkanes and alkenes [54], mixtures of gases [55], $\text{NH}_3\text{--H}_2\text{--N}_2$ –air mixtures [56], pure liquids [57], etc. Their experiments have confirmed that the flammability limits and the initial temperature are related linearly. An important error in experiments can be due to the slow oxidation in the heated vessel before it starts burning.

Rowley et al. [58] summarized the following methods for estimating temperature dependence. Out of the assumption on $x_L \cdot \Delta H_C = K$, the original Burgess-Wheeler Law was expressed as

$$x_L \cdot \Delta H_C = 100 \cdot c_p \cdot T \quad (2.3)$$

where c_p is the specific heat at constant volume of air.

Later the temperature difference was expressed as the enthalpy ratio.

$$\frac{x_L(T)}{x_L(T_0)} = 1 - \frac{\bar{c}_{p, fuel-air-mixture}}{x_L(T_0) \cdot (-\Delta H_C)} (T - T_0) \quad (2.4)$$

Zabetakis [43] further simplified this dependence into a simple constant linear dependence, which is widely adopted in any safety-related textbooks.

$$\frac{x_L}{x_{L,0}} = 1 - \frac{0.75}{x_{L,0} \cdot \Delta H_C} \cdot (T - T_0) = 1 - 0.000721 \cdot (T - T_0) \quad (2.5)$$

The second method is proposed by Britton and Frurip [59], which simplifies the temperature dependence as a linear temperature dependence

$$\frac{x_L(T)}{x_L(T_0)} = \frac{T_{AFT} - T}{T_{AFT} - T_0} = 1 - \frac{T - T_0}{T_{AFT} - T_0} \quad (2.6)$$

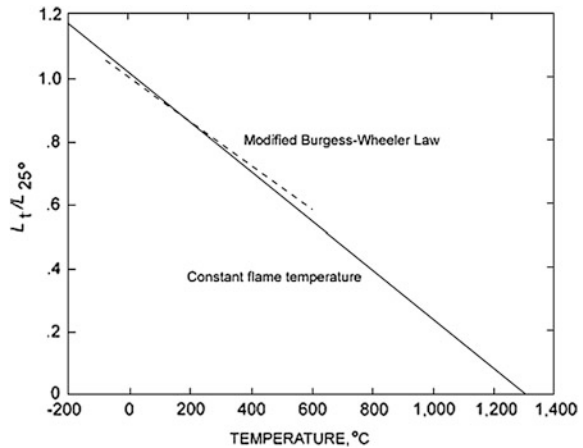
where T_{AFT} is the adiabatic flame temperature for ignition and flame spread to take place.

Finally, Catoire and Naudet [60] developed an empirical correlation with a simple temperature dependence as

$$x_L(T) = 519.957 \cdot X^{0.70936} \cdot n_C^{-0.197} \cdot T^{-0.51536} \quad (2.7)$$

However, they are all related to the energy balance for the background air (temperature or enthalpy). Among them, the modified Burgess-Wheeler Law is well known and widely used in estimating temperature-modified limits. A comparison with experimental data shows there is still some discrepancy between theory and reality (Fig. 2.1). The missing part is the contribution of the fuel, though small, generally ignored in most correlations.

Fig. 2.1 Effect of temperature on L_f/L_{25} ratio of paraffin hydrocarbons in air at atmospheric pressure [43]



Empirically, the temperature dependence is assumed be linear and expressed as the percentage drop per 100 K temperature drop. Zabetakis et al. [49] have found that the lower limits of hydrocarbons decrease linearly by about 8 % for 100 °C rise in temperature. This is consistent with the decrease of net enthalpy rise of back-ground air. Using the propane data of Kondo et al. [61], the experimental decrease per 100 °C is found to be 8.64 %.

This linear temperature dependence applies only if the reaction is complete, the flame temperature is constant, and no disassociation occurs during preheating. Upper limits also increase linearly with temperature but only if the combustion is normal. If a rise in temperature tends to cause cool flames, the flammable range cannot be predicted reliably. With an increase in temperature the low composition area of normal flames disappears while the cool flame region is extending the envelope beyond the normal range [49].

2.1.4 Chemistry Dependence

Since a rigorous theory based on fundamental principles is not established, a lot of empirical rules or correlations were proposed for estimation purpose. Among them, the most famous one is Jone's rule or Lloyd's rule.

Jones [9] first observed that at any specified temperature, the ratio of the lower limit to the amount of combustible needed for stoichiometric reaction, is approximately constant. He further proposed several constants corresponding to families of fuels respectively (see Table 2.1).

Jones' rule assumes ratios of the lower limits of the individual constituents to the amount of oxygen required for theoretical perfect combustion are about the same, however, this is true only within a family of fuels. Under a similar reasoning, Shimy [62] used the number of carbon atoms in the molecule as the variable to correlate flammability limits within a family of fuels with limited success. If the fuel mixture came from a same family, the limits of mixtures of the constituents may be determined rather accurately by Jones' rule.

Lloyd [63] generalized Jones' rule into one universal constant, which is widely cited as "**Lloyd's Rule**"

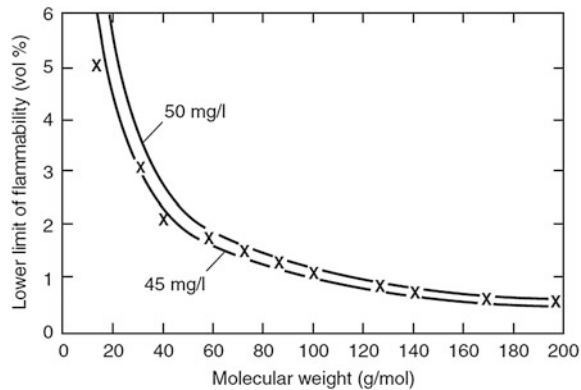
$$x_L = 0.55 \cdot x_{st} = \frac{0.55}{1 + 4.773 \cdot C_O} \quad (2.8)$$

$$x_U = 3.5 \cdot x_{st} \quad (2.9)$$

Table 2.1 Typical values for x_L/x_{st} in Jones' rule

Methane	0.52	Methyl chloride	0.67
Ethane	0.57	Ethyl chloride	0.61
Propane	0.59	Propyl chloride	0.61

Fig. 2.2 Effect of molecular weight on lower limits of flammability of alkanes at 25 °C [64]



At room temperature and atmospheric or reduced pressure, the lower limits of flammability for most of the paraffin hydrocarbon series fall in the range from 45 to 50 mg combustible vapor per liter of air at standard conditions [43], which is corresponding to a limiting oxygen concentration of 0.11 in the mixture [17]. That means 45–50 mg of combustible vapor is sufficient to raise the temperature of one liter mixture from ambient to the critical flame temperature, which is another empirical rule used in industry ([64], see Fig. 2.2).

Other researchers also tried to establish the empirical relationship between LFL and UFL. White [44] found that the corresponding upper limit is roughly 3.5 times the lower limit. Spakowski [65] found that the upper limits were 7.1 times the lower limit. Zabetakis [43] proposes a square-root relationship, which has been used in the experimental work of Kondo [61].

$$x_U = 6.5\sqrt{x_L} = 4.8\sqrt{x_{st}} \quad (2.10)$$

2.1.5 Fuel Dependence

When multiple fuels are involved, Le Chatelier's Rule is the only tool for predicting mixture flammability. Originally, Le Chatelier [36] stated, "if we have, say, separate limit combustible air mixtures and mix them, then this mixture will also be a limit mixture", or a mixture of limit fuels is still a limit mixture. This statement was expressed as

$$\frac{x_1}{x_{L,1}} + \frac{x_2}{x_{L,2}} = 1 \quad (2.11)$$

where x_1, x_2 are the fuel concentrations in a mixture; $x_{L,1}, x_{L,2}$ are their individual flammable limits in air. It was Coward et al. [37] who extended Le Chatelier's rule into its present form (see Eqs. 4.22 and 4.23).

Le Chatelier's Rule is a useful approximation and implies that several combustibles do not influence each other's behavior in a limit mixture. It holds well for combustibles of the same character and even for gases with such different physical properties as hydrogen and methane [35]. White [44] found that for a binary mixture, the approximation is generally better for lower than for upper limits, and better for downward propagation than for propagation upwards. For mixtures that contain combustibles readily exhibiting pre-flame or cool flame combustion, the law does not hold. He also found that the law does not hold strictly for hydrogen-ethylene-air mixtures, acetylene-hydrogen-air mixtures, hydrogen sulfide-methane-air mixtures, and mixtures containing carbon disulfide. Also, in tests on some chlorinated hydrocarbons, Coward and Jones [4] found that the law did not hold for methane-dichloroethylene-air mixtures, and it was also found that the law was only approximately correct for mixtures of methyl and ethyl chlorides. It is therefore apparent that this mixture law cannot be applied indiscriminately, but must first be proved to hold for the gases being investigated [9].

Mashuga et al. [66] identified the assumptions in deriving Le Chatelier's rule,

1. the product heat capacities are constant;
2. the number of moles of gas is constant;
3. the combustion kinetics of the pure species are independent and unchanged by the presence of other combustible species;
4. the adiabatic temperature rise at the flammability limit is the same for all species.

Here assumption No. 3 and 4 are more important than the first two. No. 4 allows all species to compare with each other, while No. 3 allows them to be additive in terms of energy conservation. The major concern is whether fuels are synergistic or antagonistic to each other. Hydrogen is a typical example. In theory, due to its lower flame temperature and high diffusivity on flame structure, hydrogen will have a synergistic effect on other fuels. In reality, hydrogen is a common fuel and there is no specific limit in applying Le Chatelier's Rule for estimation purpose. The No. 1 assumption on constant heat capacities of combustion products can be dropped if scaled by a universal species [15].

White [44] further proposed the assumption that the ignition temperature of a gas mixture at concentrations similar to those present in a lower-limit mixture does not vary much with the concentration of the flammable gas. This temperature is constant no matter what is the initial fuel temperature, which paved the way for later theoretical work on temperature dependence. This assumption is widely found in most theoretical work, even implicitly used in deriving Le Chatelier's rule [66].

Generally, there are two types of methods to use Le Chatelier's rule covering diluents in a mixture. The popular method is grouping a fuel with a diluent into a pseudo fuel, and then Le Chatelier's Rule can be applied to pseudo-fuels only. So the diluted flammability diagram was used to compensate the inability of Le Chatelier's mixture law in dealing with diluents [67, 68]. A case study is provided by Heffington [69] on the flammability of CO₂-diluted fuels. Another estimation method is to determine the equivalency between gases for a mixture. Fuels are scaled by methane, inert gases are scaled by Nitrogen, and oxidizing gases are

scaled by oxygen. By summing up each fuel/diluent/oxygen terms, the fuel and oxidizing potentials are determined and compared to determine the flammable state of a mixture [70, 71].

2.1.6 Pressure Dependence

An increase in pressure has little effect on the lower limit, though the upper limit may be widened; the extent of the reaction at the flame front is affected [5]. Based on the experimental data on natural gas (85–95 % methane and 15–5 % ethane) from Jones et al. [72], Zabetakis [43] suggested that the limits vary linearly with the logarithm of the initial pressure. That is

$$\begin{aligned}x_L &= 4.9 - 0.71 \log P(\text{atm}) \\x_U &= 14.1 + 20.4 \log P(\text{atm})\end{aligned}\tag{2.12}$$

With a standard error of estimate of 0.53 vol pct for x_L and 1.51 vol pct for x_U .

Figure 2.3 shows the flammability change according to high pressure. Lower flammability limits change little, since lower limits are controlled mainly by (the heat release of) fuel. Upper limits are changed significantly, which is related to the flame structure and combustion kinetics. In this specific area, experimental data are still limited.

For lower-than-ambient pressure, the flammable range is little changed until a certain lower pressure threshold is achieved. Then the flammable zone shrink to nil, consistent with our intuition that vacuum will not support ignition or flame propagation. Lewis and Von Elbe [32] produced a pressure-modified flammable zone in Fig. 2.4.

Fig. 2.3 Variation of flammability limits due to high pressure

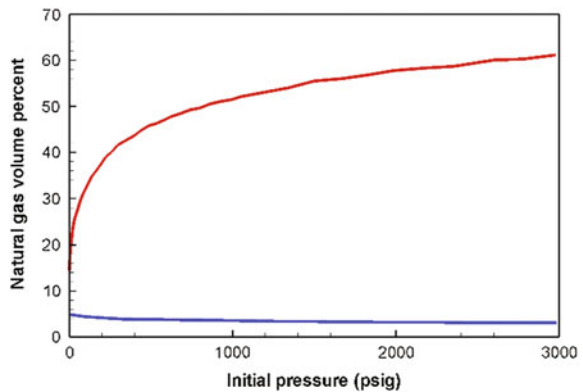
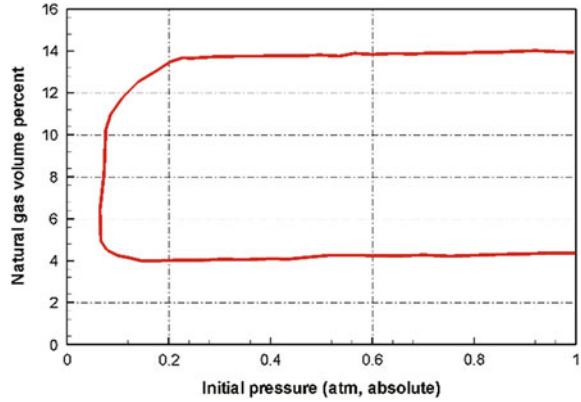


Fig. 2.4 Variation of flammable zone due to low pressure



2.2 Correlations for Flammability

Based on the above principles, several correlations were proposed for estimating the flammability of a fuel or a mixture. They are falling into two categories, fuel-based or oxygen-based. The former is based on the heat of combustion (of the fuel), while the latter is based on the stoichiometric oxygen number, or oxygen calorimetry. Heat of combustion is a property related to the combustion process, or related to the ignitability of the fuel. Oxygen calorimetry is a property related to oxygen, or a property of the background air, or the explosibility. This fact itself shows the energy background for flammability is rather ambiguous and complex.

Let us check the fuel-based correlations in Table 2.2. From the modified Burgess-Wheeler's law, Hanley [47] proposed $X_L = \frac{11.2}{\Delta H_c (\text{kcal/mol})}$ for LFL, while $X_L = \frac{43.54}{\Delta H_c}$ is proposed by Spakowski [73]. These are slight variations of Burgess-Wheeler's law, which implicitly assumed that any fuel releases same amount of energy at lower limits. This is an oversimplification, since the information on diluent and oxygen are completely ignored, not consistent with the fact that the flammability is a function of local oxygen and diluent. More refinement is proposed to improve the prediction, such as the polynomial correlation proposed by Shieh [74] and Suzuki [75]. They are proposed based on a small set of data, so their applicable range is limited.

Table 2.2 List of energy-based LFL correlations [17]

	Correlation for LFL	Average error in estimation
Hanley	$X_L = \frac{11.2}{\Delta H_c (\text{kcal/mol})}$	0.119
Spakowski	$X_L = \frac{43.54}{\Delta H_c}$	0.069
Shieh	$x_L = 1145 \cdot \Delta H_c^{-0.8} - 0.38$	0.076
Suzuki	$x_L = -3.4 \cdot \Delta H_c^{-1} + 0.569 \cdot \Delta H_c + 0.0538 \cdot \Delta H_c^2 + 1.8$	n/a

Table 2.3 List of oxygen-based LFL correlations [17]

	Original correlation	Average error in estimation
Jones' rule/Lloyd's rule/Zabetakis [43]	$X_L = 0.55 \cdot x_{st} = \frac{0.55}{1 + 4.773 \cdot C_O}$	0.108
Britton [48]	$X_L = \frac{10}{C_O}$	0.070
Pintar [76]	$X_L = 0.512 \cdot x_{st} = \frac{0.512}{1 + 4.773 \cdot C_O}$	0.085
Hilado [81] (CHO compounds only)	$X_L = 0.537 \cdot x_{st} = \frac{0.537}{1 + 4.773 \cdot C_O}$	0.125
Monakhov [78]	$X_L = \frac{1}{4.679 + 8.684 \cdot C_O}$	0.077
Beyler [64] ($\phi = 0.5$)	$X_L = \frac{1}{1 + 9.546 \cdot C_O}$	0.094
Donaldson et al. [80]	$X_L = \frac{1}{5.2114 + 8.2069 \cdot C_O}$	0.091

Since flammability is the ability of background air to support flame propagation, a more reasonable choice for correlation is the stoichiometric oxygen number, or oxygen/fuel stoichiometric molar ratio. A list of correlations on this parameters is provided in Table 2.3. From Jones' rule, $X_L = 0.55 \cdot x_{st} = \frac{0.55}{1+4.773 \cdot C_O}$ is listed as an approximation of lower flammability limits. Britton [48] proposed a simpler form as $X_L = \frac{10}{C_O}$. Pintar [76] and Hilado [77] refined the correlation coefficients for a specific family of hydrocarbons. Monakhov [78], Beyler [79] and Donaldson et al. [80] realized that $x_L \cdot C_O$ is not a constant, so a constant is reserved in the denominator. This is consistent with the modified “k-constant” rule ($x_L \cdot \Delta H_C + \Delta H = K$). As we will see later in Sect. 4.4, $x_L \cdot \Delta H_C = K$ applies for ignitability, while $\lambda_2 \cdot \frac{\Delta H_C}{C_O} = K$ applies for explosibility. The difference is that the inerting contribution from the fuel is ignored in the former while the oxygen-based energy release is more dominant at critical limits.

For upper limits, no energy-based correlations are proposed, consistent with the fact that the upper limits are oxygen-limited. The fuel mainly plays the role as a diluent, while the availability of oxygen and oxygen calorimetry dominate the flame propagation process. Due to the scattering of experimental data, all correlations are rough at predicting upper limits. Details of their performance can be found in Table 2.4, with a prediction error identified in [17].

2.3 ISO10156 Method for Predicting Mixture Flammability

Currently, the professional method to deal with multiple fuels and diluents is provided in ISO10156 [70], which contains the testing method and calculation methods for mixture flammability. The calculation method uses flammability limit data and so-called Tci values of flammable gases and vapors for inputs. These data

Table 2.4 List of oxygen-based UFL correlations [17]

	Original correlation	Average error in estimation
Zabetakis [43]	$x_U = 3.3 \cdot x_{st} = \frac{3.3}{1 + 4.773 \cdot C_O}$	1.227
Pintar [76]	$x_U = 3.8 \cdot x_{st} = \frac{3.8}{1 + 4.773 \cdot C_O}$	2.345
Monakhov [78]	$\begin{cases} x_U = \frac{1}{0.56 + 1.55 \cdot C_O}, & \text{for } C_O \leq 7.5 \\ x_U = \frac{1}{6.554 + 0.768 \cdot C_O}, & \text{for } C_O > 7.5 \end{cases}$	0.289
Donaldson et al. [80]	$x_U = \frac{1}{1.2773 + 1.213 \cdot C_O}$	0.303
Beyler [64] ($\phi = 3.0$)	$x_U = \frac{1}{1.0 + 1.591 \cdot C_O}$	0.182

are mostly taken from the database CHEMSAFE that contains recommended safety characteristics for flammable gases, liquids and dusts.

The T_{ci} values are taken under atmospheric conditions with air as an oxidizer, which is also called the maximum permissible flammable gas concentration (MXC). MXC is the largest fraction of the flammable gas for which this gas mixture cannot be ignited, irrespective of the amount of flammable gas being added [70]. As we will see later (in Chap. 5), MXC is a concept of ignitability, equivalent to LFC or OSFC in the literature. In contrast, the coefficients of equivalency relative to nitrogen (K value) must be calculated using several flammable-inert gas system. The K value for the mixture is calculated as

$$K_{ij} = \frac{MXC_{ij} \cdot \left(\frac{100}{T_{ci}} - 1 \right)}{(100 - MXC_{ij})} \quad (2.13)$$

where i is the index of the flammable gas and j is the index of the inert gas, different from Nitrogen which is used in the flammable/inert/air mixture. Table 2.5 lists coefficient of equivalency (K_i) for some common diluents, which are close to the concept of Quenching Potential to be introduced in next chapter. Table 2.6 lists T_{ci} values for common flammable gases, which is another name for LFC or OSFC for nitrogen inertion, to be introduced and discussed in Chap. 5.

Table 2.5 Coefficient of equivalency (K_i), or nitrogen-equivalency

Gas	N ₂	CO ₂	He	Ar	Ne	Kr	Xe	SO ₂	SF ₆	CF ₄
K_i	1	1.5	0.5	0.5	0.5	0.5	0.5	1.5	1.5	1.5

Table 2.6 T_{ci} for flammable gases, or the limiting fuel concentration for nitrogen-inerting

Gas	H ₂	CO	Methane	Ethane	Butanes	Ethylene	Propane	Propene's	Acetylene	n-Hexane
T_{ci}	5.7	20	8.7	7.6	5.7	6	6	6.5	4	3.5

The mixture has to be classified as FLAMMABLE if

$$\sum_{i=1}^n A_i \left(\frac{100}{T_{C_i}} - 1 \right) \leq \sum_{k=1}^p B_k K_k \quad (2.14)$$

where

A_i Mole fraction of the flammable component I in the mixture in mol%

n Number of flammable components

B_k Mole fraction of the inert component k in the mixture in mol%

p Number of inert components

K_k Nitrogen equivalence coefficient of the inert component

T_{C_i} Threshold for flammability of the flammable component I in the mixture with nitrogen

The physical meaning of Eq. 2.14 is the fuel-needed diluent (nitrogen, left-hand side) should be less than existing diluent (nitrogen, right-hand side) to keep the mixture non-flammable.

A variation of Eq. 2.13 is supplied [70] as

$$\frac{1}{MXC_{mixture}} = \frac{\left(\frac{100}{T_{C_i}} - 1 \right)}{B_{K1} \times K_{K1} + B_{K2} \times K_{K2}} + 1 \quad (2.15)$$

Which can be used to find the critical fuel concentrations in response to multiple diluents.

2.4 Flammability Diagrams

The flammability problem of a mixture is difficult, since it typically involves three components with dual functions in a combustion reaction. Fuel is not only a source of energy, but also a heat absorber during the ignition process. Oxygen is not only a source of energy (together with fuel), but also a heat absorber affecting the flame temperature. Only nitrogen is a typical diluent, without any heating role involved. Because of such a ternary combustion system, the concept of flammability is difficult to present without the help of a flammability diagram. However, various diagrams are proposed to demonstrate the inerting and diluting process, all with some limitations over the past century. Depending on its application field and purpose, there are four diagrams are typically used in industry.

2.4.1 Standard Flammability Diagram

The first diagram is called standard flammability diagram, which uses the combination of diluent/fuel to describe the state of a mixture. Since the diluent concentration is serving as a major input variable, it is commonly used to compare the agent effectiveness, in chapters of suppression theory [82]. It is also used in flammability theory, to demonstrate the role of a diluent on changing flammable envelopes [64]. For practical safe handling of gases, since the concentration measurement is not convenient as the volume measurement (nitrogen concentration is derived from oxygen measurement, not directly measured), the diluted diagram is used instead of the standard diagram, which can be converted to each other easily. The critical nose point in a standard flammability diagram is the inertion point, which tells the Minimal Inerting Concentration (MIC) (shown in Fig. 2.5). Most of flammability data in Zabetakis' BOM Bulletin [43] are presented in this form, while it provides less information as compared to other diagrams.

2.4.2 Diluted Flammability Diagram

Using the diluent/fuel ratio and the diluent/fuel fraction as inputs, we have a diluted flammability diagram. Its original purpose is to pair a fuel and a diluent into a pseudo fuel, then Le Chatelier's rule can be applied to a mixture of pseudo fuels [83, 84]. As Le Chatelier's rule is the only hand-calculation tool in industry, and the industry prefers the volume measurement in dilution, diluted flammability diagram gains a special position on safe handling of flammable gases.

From the flammable envelope, two critical lines can be derived, MMR (Maximum Molar (diluent/fuel) Ratio) and MMF (Maximum allowable fuel Mixture Fraction), which provides a rectangular boundary encompassing the flammable envelope. Note, MMR and MMF may not be taken from a same point on

Fig. 2.5 Methane in standard flammability diagram

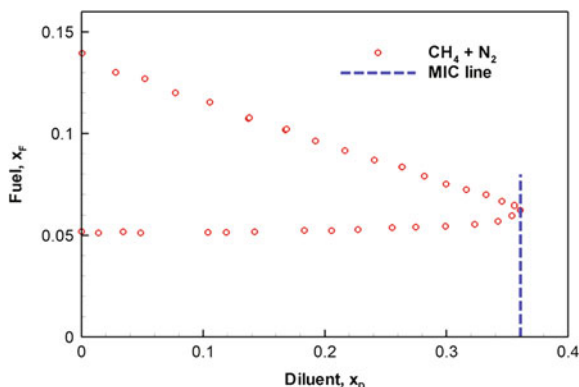
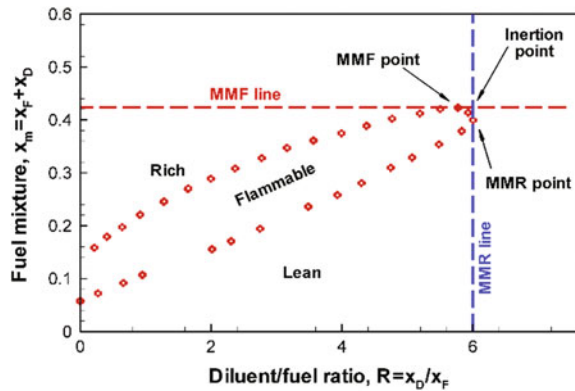


Fig. 2.6 Methane in diluted flammability diagram



the envelope. Theoretically, there is only one inertion point, while in experiments, there is a maximum MMF (inertion) point and a maximum MMR (dilution) point, on MMF and MMR lines respectively (as shown in Fig. 2.6). In this perspective, the inertion point in an experimental flammability diagram is fictitious.

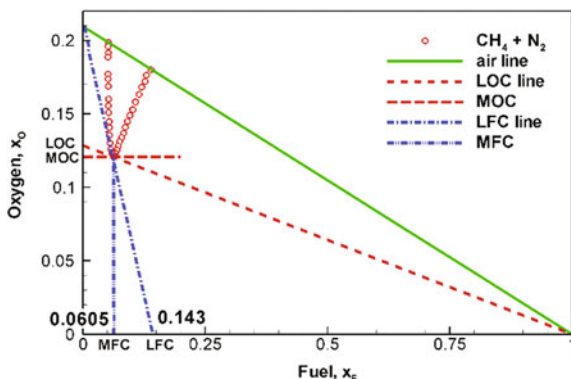
However, this fictitious inertion point provides valuable information (MMR and MMF) on explosibility and ignitability for other critical points, so this diagram is fundamental to any flammability related operations.

2.4.3 Explosive Triangle Diagram

When multiple diluents are included in a mixture, such as gases from a mine fire, the flammable state of such a mixture is difficult to present in any diagrams with a definite axis on diluent. Instead, Coward explosive triangle was proposed to use the oxygen level in the mixture, avoiding the complexity induced by multiple diluents [68]. If drawing a line from the 100 % fuel point, tangent to the experimental flammable envelope, this is called LOC line (Limiting Oxygen Concentration) with a cross point on Oxygen axis as LOC point. Similarly drawing a straight line from the normal air (20.95 % O_2 + 79.05 % N_2) point tangent to the flammable envelope, this is called LFC (Liming Fuel Concentration) line. The cross point on fuel axis is called LFC point. In practice, the iso-oxygen line tangent to the envelope is called MOC (Minimum allowable Oxygen Concentration to support flame propagation), while the fuel concentration at the tangent point of LFC line on flammable envelope is called Minimum Fuel Concentration (MFC).

If the background air is inerted by a diluent to LOC point, the evaporation/addition of fuel will move this point from LOC to MOC along the LOC line. If a fuel stream is already diluted by a diluent to its LFC point, then mixing with air will decrease this fuel concentration further from LFC to MFC along the LFC line. In theory, LFC and LOC are better and fundamental critical targets of inertion.

Fig. 2.7 Methane in coward explosive triangle diagram



In practice, MOC and LFC are recommended for safe-operation (dilution or purge) targets (as shown in Fig. 2.7).

When dealing with a complex mixture, such as the gases from a burning mine fire, various fuels are lumped into a fuel equivalent (usually methane), while contributions of diluents will be lumped into an oxygen limit, plotted in the diagram as the nose point. Various schemes are proposed to perform the conversion more effectively [85]. However, the fundamental theory behind such a conversion is provided in Chap. 7.

2.4.4 Ternary Flammability Diagram

The major problem of a diluted flammability diagram is that it is difficult to demonstrate the dilution and purge processes (not a straight line), as composite parameters are used. A ternary flammability diagram was proposed [43] and gained a popular position in industry for guiding dilution and purge operations. The advantage of a ternary diagram is that all data are directly readable and oxygen-enriched atmosphere is allowed, while the disadvantages is that a conversion scheme is needed to plot the data. Crowl [86] listed some engineering rules to use this diagram better. Another disadvantage of this diagram is that oxygen only occupies 1/5 of air, so a large part of domain is useless if we are dealing with fuels burning in air. How to make use of space more effectively is a skill requiring special training.

Starting with the 100 % fuel point, draw a line tangent to the flammable envelope, it is called the LOC line. If an iso-oxygen line is tangent to the flammable envelope, this is called the MOC line. Starting with the air point (21 % O₂ and 79 % N₂), draw a line tangent to the flammable envelope, which is called the LFC line. If an iso-fuel line is tangent to the flammable envelope, this is called the MFC line. These four lines are demonstrated in Fig. 2.8. Again, MFC point and MOC point may not be a same point, though both are representing the inertion point.

2.5 Problems and Solutions

2.5.1 ISO10156 Method

Problem 2.1 T_{Ci} method

A gaseous mixture of 7 % of hydrogen in CO_2 , is it flammable in air? [71]

Solution:

K_k , Nitrogen equivalency of CO_2 , is 1.5.

Therefore 93 % CO_2 is equivalent to 93×1.5 or 139.5 % nitrogen.

Normalized hydrogen concentration is $x_{H_2} = \frac{7}{7+139.5} = 4.78\%$. The T_{Ci} value of Hydrogen is $5.7 > 4.78$, therefore the mixture is not flammable.

Problem 2.2 T_{Ci} method for multiple fuels.

A mixture has methane/propane (20:80 mol%) altogether 5.6 %. The rest is nitrogen. Is it flammable in air?

Solution:

T_{Ci} values of methane and propane are retrieved from Table 2.6 as 8.7 and 3.7 respectively. K_k for nitrogen is 1 by definition. B_k for nitrogen is given as $1 - 5.6\% = 94.4\%$. $A_{\text{methane}} = 20\% \times 5.6\% = 1.12\text{ mol}\%$, $A_{\text{propane}} = 80\% \times 5.6\% = 4.48\text{ mol}\%$. So we have

$$\sum_{i=1}^n A_i \left(\frac{100}{T_{Ci}} - 1 \right) = \left[1.12 \times \left(\frac{100}{8.7} - 1 \right) + 4.48 \times \left(\frac{100}{3.7} - 1 \right) \right] = 128.35\% \leq \sum_{k=1}^p B_k K_k = 1 \times 94.4\%$$

Since the inequality is not fulfilled, the mixture is not fully diluted, or is classified as FLAMMABLE.

Problem 2.3 T_{Ci} method for multiple diluents

A mixture has a methane fraction of 16.4 %. The rest is carbon dioxide/nitrogen (70:30). Is it flammable in air?

Solution:

T_{Ci} value of methane is retrieved from Table 2.6 as 8.7.

The limiting fuel fraction, MXC is computed from

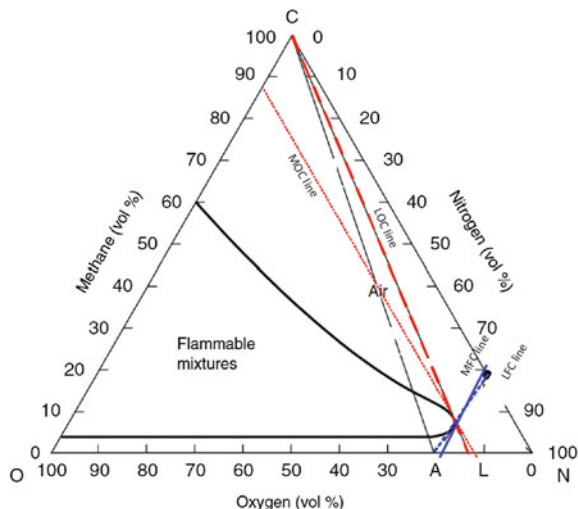
$$\frac{1}{MXC_{\text{mixture}}} = \frac{\left(\frac{100}{T_{Ci}} - 1 \right)}{B_{K1} \times K_{K1} + B_{K2} \times K_{K2}} + 1 = \frac{\left(\frac{100}{8.7} - 1 \right)}{0.7 \times 1.5 + 0.3 \times 1} + 1 = 8.77$$

So the limiting fuel fraction is

$$MXC = \frac{1}{8.77} = 11.4\% < 16.4\%$$

So this mixture is non-flammable.

Fig. 2.8 Methane in a ternary flammability diagram



Problem 2.4 T_{Ci} method for multiple fuels and multiple diluents

A flammable mixture has 2 % Hydrogen, 8 % methane, 65 % Helium, and 25 % Argon, is it flammable in air? [71]

Solution:

Using nitrogen-equivalent coefficients K_k , this mixture is equivalent to 2 % H_2 + 8 % CH_4 + 0.55×25 % Ar + 0.9×65 % He = 2 % H_2 + 8 % CH_4 + 13.8 % N_2 + 58.5 % N_2 = 82.3 %

Rescale the mixture by $100/82.3 = 1.215$, we have the mixture as 2.43 % H_2 + 9.73 % CH_4 + $(58.5 + 13.8) \times 1.213$ % N_2

Here T_{Ci} for hydrogen and methane is 5.7 and 8.7 respectively.

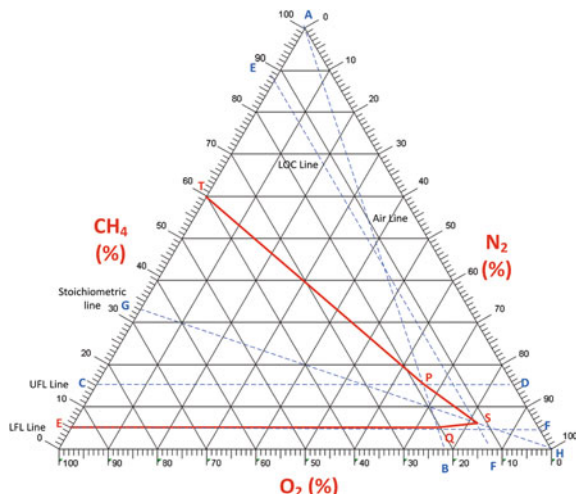
$$\sum_{i=1}^n A_i \left(\frac{100}{T_{Ci}} - 1 \right) = \left[2 \times \left(\frac{100}{5.7} - 1 \right) + 8 \times \left(\frac{100}{8.7} - 1 \right) \right] = 118.3 \% \leq \sum_{k=1}^p B_k K_k = 0.55 \times 25 \% + 0.9 \times 65 \% = 75.25$$

Since the above inequality does not hold true, the criterion for a non-flammable gas mixture is not fulfilled and this particular gas mixture is considered flammable.

2.5.2 Operations in a Ternary Diagram

Problem 2.3 Use 5 points (MOC = 12 %, LFL(O_2) = 5 %, UFL(O_2) = 61 %, LFL (air) = 5 %, UFL(air) = 15 %) to reconstruct the flammable envelope of methane (Fig. 2.9).

Fig. 2.9 5-pts to determine the flammable zone for methane



Solution:

- Step 1. Plot $\text{UFL}(\text{O}_2) = 60\%$ and $\text{LFL}(\text{O}_2) = 5\%$ in fuel axis as Point T/E respectively.
- Step 2. Use nitrogen concentration of 79% in air (point B), draw an airline AB.
- Step 3. Use $\text{UFL}(\text{air}) = 15\%$ to draw an UFL line CD, crossing the airline AB with point P.
- Step 4. Use $\text{LFL}(\text{air}) = 5\%$ to draw a LFL line EF, crossing the airline AB with point Q.
- Step 5. Find the stoichiometric value through the balanced equation, $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + \text{H}_2\text{O}$, so the stoichiometric fraction of methane in methane/oxygen mixture is $1/(1 + 2) = 0.33$. Connect point G ($33\% \text{CH}_4$) with H, is the stoichiometric line GH.
- Step 6. Use $\text{MOC} = 12\%$ to draw an LOC line EF, crossing the stoichiometric line GH with point S.

Now in Fig. 2.9, the triangle PQS is the flammable envelope in air, while the polygon TPSQE is the flammable envelope of methane.

2.5.3 Reading a Ternary Diagram

Problem 2.5 There is a methane mixture composed of 50% methane, 40% O_2 and 10% Nitrogen.

- a. Is this mixture flammable?
- b. If this mixture is flammable, how to make it non-flammable by adding nitrogen for inertion?

- c. If the original mixture is 100 mol, how much nitrogen is needed?
- d. If all mixture is held in a compartment of 100 m³, how much nitrogen is needed to purge the compartment, so the mixture is not flammable (out-of-envelope, non-flammable/explosive, non-ignitable)?

Solution:

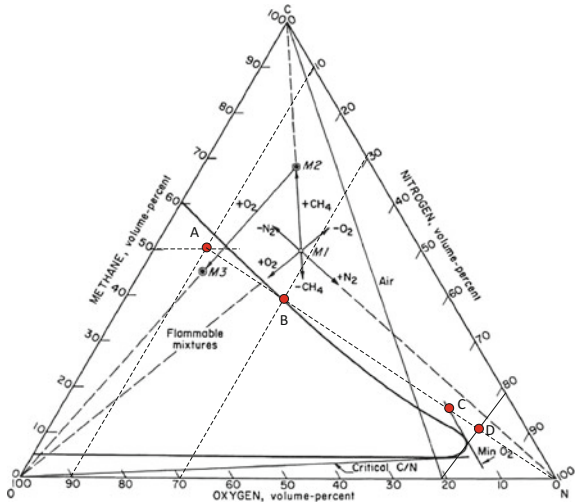
- (a) By plotting the composition of the mixture in the ternary diagram (point A), the mixture composition point falls within the flammable envelope, so it is flammable.
- (b) Connecting composition point A with Nitrogen point, we have a straight dilution line, crossing the flammable boundary at point B. So in order to get the mixture non-flammable, the nitrogen should be increased from 10 to 30 %.
- (c) Originally, there are 10 mol of nitrogen in the mixture, assume y mole is to be added, then

$$30\% = \frac{10 + y}{100 + y} \rightarrow y = 28.6 \text{ mol}$$

That means the system will be non-flammable if added with 28.6 mol of nitrogen.

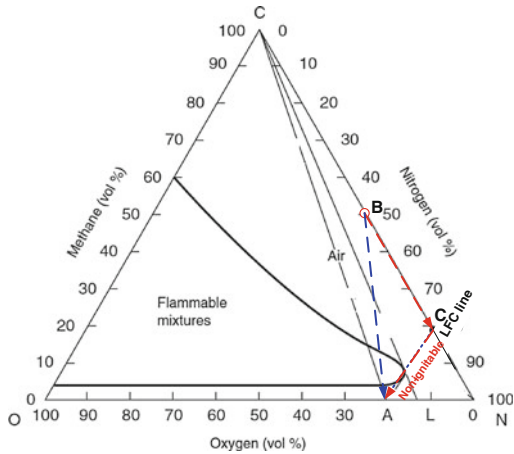
- (d) From the diagram (Fig. 2.10), the out-of-flammable zone state is reached if the fuel concentration is dropped from 50 to 40 % (point B), so the purge requirement is $V_{N_2} = -V_0 \cdot \ln\left(\frac{x_F}{x_{F,0}}\right) = -100 \times \ln\left(\frac{0.4}{0.5}\right) = 22.3 \text{ m}^3$. That means 22.3 m³ of nitrogen will be introduced into the compartment, so the fuel concentration will be dropped to 40 %.
- (e) From the diagram (Fig. 2.10), the non-flammable/explosive zone state is reached if the fuel concentration is dropped from 50 to 18 % (point C), so the purge requirement is $V_{N_2} = -V_0 \cdot \ln\left(\frac{x_F}{x_{F,0}}\right) = -100 \times \ln\left(\frac{0.18}{0.5}\right) = 102.2 \text{ m}^3$. That means 102.2 m³ of nitrogen will be introduced into the compartment, so the fuel concentration will be dropped to 18 %.
- (f) From the diagram (Fig. 2.10), the non-ignitable zone state is reached if the fuel concentration is dropped from 50 to 10 % (point D), so the purge requirement is $V_{N_2} = -V_0 \cdot \ln\left(\frac{x_F}{x_{F,0}}\right) = -100 \times \ln\left(\frac{0.1}{0.5}\right) = 160.9 \text{ m}^3$. That means 160.9 m³ of nitrogen will be introduced into the compartment, so the fuel concentration will be dropped to 10 %.

Fig. 2.10 Dilution by nitrogen in methane's flammability diagram



2.5.4 Safe Dilution of a Flammable Gas Mixture

Problem 2.6 A vessel contains a gas mixtures composed of 50 % methane and 50 % nitrogen. If the mixture escapes from the vessel and mixes with air, will it become flammable? How to make it strictly non-flammable during the dilution process?



Solution:

- a. This is a problem of nitrogen dilution to avoid the flammable envelope. The initial dilution status is shown as point B. If released into air, the final status of dilution is pure air (Point A). Line BA shows the necessary mixing process (or the mixing route). In order to reach purely air, the mixing line BA is crossing the flammable zone, so there is a danger of explosion during the mixing process.
- b. In order to avoid the flammable zone during the mixing, a tangent line is drawn passing the air point A, which is called LFC line or dilution line later. The cross point with Nitrogen axis is point C (82 % nitrogen and 18 % methane). That means, the initial mixture has to be diluted to point C (non-ignitable) by nitrogen dilution first, then it can be allowed to be mixed with air without any danger of ignition (or explosion).

2.5.5 Methane Dilution by Air

Problem 2.7 A 1 kg/s flow of methane is being dumped into the atmosphere. How much nitrogen must be mixed with methane to avoid a flammable mixture in the open?

Solution:

From the previous ternary diagram, the inertion is realized through diluting the mixture from 100 % methane to 18 % methane with addition of 82 % of Nitrogen. So the nitrogen molar flow rate is

$$\dot{n}_{N_2} = \left(\frac{\dot{m}_{CH_4}}{MW_{CH_4}} \right) \cdot \left(\frac{C_{N_2}}{C_{CH_4}} \right) = \frac{1000 \text{ g/s}}{16 \text{ g/mol}} \cdot \frac{82 \%}{18 \%} = 285 \text{ mol/s}$$

$$\dot{m}_{N_2} = \dot{n}_{N_2} \cdot MW_{N_2} = 285 \text{ mol/s} \times 28 \text{ g/mol} = 7970 \text{ g/s} = 7.97 \text{ kg/s}$$

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