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Chemical Thermodynamics and Flame Temperatures and Equilibrium and the general explosive and oxidation properties of the fuel

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Abstract

This research discusses in the first part the basic chemical thermodynamics and flame temperatures for combustion analysis. Reaction temperatures, free energy, and equilibrium constants are entered and then applied to analyze the chemical equilibrium composition and steady flame temperature of fuels for fuel oxidizer mixtures. The effects of mixture stoichiometric ratio and pressure on flame temperature and composition are discussed along with practical considerations. In the second part of the research, branching chain reactions and explosion criteria are presented. The explosive limits and oxidizing properties of hydrogen and carbon monoxide are described first, as they are simple fuels and intermediates formed during hydrocarbon oxidation. . The high-temperature oxidation mechanisms of aldehydes, methane, aliphatic hydrocarbons, alcohols, biofuels, and aromatic hydrocarbons are discussed. Finally, a brief analysis of the supercritical effects on hydrocarbon oxidation is presented.

Key words: Thermodynamics, Flame Temperatures, Equilibrium, Explosive Oxidation, Fuel

1. Introduction

Thermodynamics, or thermodynamics, is a science that studies the relationship between temperature, work, and energy, and their relationship to energy, radiation, and the physical properties of matter. It is a branch of physics that focuses on the transfer of energy with the accompanying changes in heat and work. As for when energy transfer occurs during chemical reactions, the science that studies this condition is called chemical thermodynamics. The equilibrium product temperature and composition are critical characteristics for evaluating combustion systems. If 100% of the heat produced by the reaction is used to raise the product temperature, this temperature is known as the adiabatic flame temperature. Because temperature and gas composition are important in combustion concerns, it is appropriate to learn those areas of chemical thermodynamics that deal with these issues. This research will focus on basic chemical thermodynamics and flame temperatures for combustion analysis, describing explosion limits and general oxidation properties of fuels [29].

2. Chemical Thermodynamics and Flame Temperatures

2.1 Heats of reaction and formation

All chemical processes involve the absorption or evolution of energy, which commonly appears as heat. This quantity of heat—and hence the temperature and product composition—can be calculated using very simple methods. The internal energy of a material can be calculated using spectroscopic data and statistical computations. The internal energy of a particular substance is discovered to be temperature, pressure, and state dependent, and to be independent of the mechanisms by which the condition is reached. Similarly, the change in internal energy, ΔE, of a system caused by any physical change or chemical reaction is determined only by the system's starting and final states. The overall change in internal energy is the same whether the energy is developed as heat, energy, or work [1].

If a flow reaction occurs with small changes in kinetic and potential energy and no additional work beyond that necessary for the flow, the heat generated is equal to the system's rise in enthalpy [2].

$$Q = \Delta H$$

where Q is the heat added and H is the enthalpy. For a nonflow reaction proceeding at constant pressure, the heat added is also equal to the gain in enthalpy

$$Q = \Delta H$$

and if heat evolved,

$$Q = -\Delta H$$

The majority of thermochemical calculations are performed for closed thermodynamic systems, and stoichiometry is most simply stated in terms of molar amounts found using statistical calculations. It is advisable to use mass quantities when dealing with compressible flow issues that require working with open thermodynamic systems.

The change in energy or heat content associated with a specific chemical reaction at some specified temperature, when each of the reactants and products is in an acceptable standard state, is one of the most crucial thermodynamic facts to understand about the reaction. This shift is referred to as the energy or the heat of reaction at the specified temperature.

The standard state denotes the existence of an aggregate reference state for each state. The ideal gaseous state at atmospheric pressure at each temperature is the thermodynamic standard reference condition for gases. The ideal gaseous state is the situation of isolated molecules that have no interactions and follow the perfect gas equation of state. The actual state of a substance at a pressure of 1 atm is the usual reference state for pure liquids and solids at a particular temperature. Understanding this notion of the standard reference state is critical for examining the scenario of high-temperature combustion with a significant mole fraction of a condensed phase, such as a metal oxide.

The thermodynamic symbol that represents the property of the substance in the standard state at a given temperature is written, for example, as H_T° , E_T° , etc., where the “degree sign” superscript ° specifies the standard state, and the subscript T the specific temperature. Statistical calculations actually permit the determination of $E_T — E_0$, which is the energy content at a given temperature referred to the energy content at 0 K. For 1 mol in the ideal gaseous state,

$$PV = RT \quad (1)$$

$$H^\circ = E^\circ + (PV)^\circ = E^\circ + RT \quad (2)$$

which at 0 K reduces to

$$H_0^\circ = E_0^\circ \qquad (3)$$

Thus the heat content at any temperature referred to the heat or energy content at 0 K is known a

$$(H^\circ - H_0^\circ) = (E^\circ - E_0^\circ) + RT = (E^\circ - E_0^\circ) + PV \quad (4)$$

The value (E° - E0°) is determined from the spectral information and is actually the energy in the internal (electronic, vibrational, and rotational) and external (translational) degrees of freedom of the molecule. Enthalpy (H° - H0°) only has meaning when there is a group of particles involved, for example a mole; Hence the ability of a group of molecules with internal energy to do photovoltaic work. In this sense, then, a single molecule can have internal energy, but not enthalpy. As mentioned, using a small icon indicates the values based on mass. Since ame temperatures are calculated for a closed thermodynamic system, molar conservation is not required, working on a molar basis is most appropriate. In the case of propagating or reacting flows through nozzles, mass conservation is a requirement for an adequate solution; Thus when considering these systems a per unit mass basis is used for thermochemical properties [29].

From the determination of the heat of reaction, Q_p will depend on the temperature T at which the reaction is evaluated and the enthalpy content. The heat of reaction at one temperature T0 can be related to that at another temperature T_1. According to the First Law of Thermodynamics, the heat changes that precede from reactants at temperature T_0 to products at temperature T_1, by either path A or path B must be the same. Path A raises the reactants from temperature T_0 to T_1, and reacts at T_1. Path B reacts at T_0 and raises the products from T_0 to T_1.

2.2 Free energy and the equilibrium constants

The combined form of the first and second principles of thermodynamics determines the requirement for equilibrium; that is,

$$dE = TdS — PdV \qquad (5)$$

where S is the entropy. In the absence of gravitational, electrical, and surface forces, this condition applies to any change affecting a system of constant mass. However, by adding mass to the system, the energy content may be adjusted. Consider the contribution to the energy of the system on adding one molecule i to be μ_i. The introduction of a small number dn_i of the same type contributes a gain in energy of the system of $\mu_i dn_i$. All the possible reversible increases in the energy of the system due to each type of molecule i can be summed to give

$$dE = TdS — PdV + \sum_i \mu_i dn_i \qquad (6)$$

It is apparent from the definition of enthalpy H and the introduction of the concept of the Gibbs free energy G

$$G \div H — TS \qquad (7)$$

that

$$dH = TdS + VdP + \sum_i \mu_i dn_i \qquad (8)$$

and

$$dG = —SdT + VdP + \sum_i \mu_i dn_i \qquad (9)$$

where μ_i is called the chemical potential or the partial molar free energy.

Recall that P and T are intensive properties that are independent of the size of mass of the system, whereas E, H, G, and S (as well as V and n) are extensive properties that increase in proportion to mass or size.

The equilibrium requirement is that the system's entropy has a maximum value for all feasible configurations that are consistent with constant energy and volume. If the entropy of a system with constant volume and energy is at its maximum, the system is at equilibrium; hence, any shift from the equilibrium state results in dS being zero. As a result of Eq. (6), the condition for equilibrium is

$$\sum \mu_i dn_i = 0 \qquad (10)$$

Because this attribute is significant in reacting systems, the idea of chemical potential is presented here. In this context, a reaction progresses in the direction of decreasing chemical potential, achieving equilibrium only when the potential of the reactants equals the potential of the products [12]. When dealing with ideal gases, there are no forces of contact between the molecules until at the time of reaction; hence, each gas behaves as if it were alone in a container. Let G denote the total free energy of a product combination.

$$G = \sum n_i G_i \, , \;\; i = \mathrm{A, B, \ldots, R, S} \ldots \qquad (11)$$

$$\boldsymbol{G(P, T) = H(T) - TS(P, T)} \qquad \mathbf{(12)}$$

Subtracting the last two equations, one obtains

$$G - G^\circ = (H - H^\circ) - T(S - S^\circ) \qquad (13)$$

Since H is not a function of pressure, $H - H^\circ$ must be zero, and then

$$G - G^\circ = -T(S - S^\circ) \qquad (14)$$

An expression can now be written for the total free energy of a gas mixture. In this case P is the partial pressure P_i of a particular gaseous component and obviously has the following relationship to the total pressure P:

$$pi = \left(\frac{ni}{\sum_i ni}\right) p \qquad (15)$$

where $(n_i / \sum_i n_i)$ is the mole fraction of gaseous species i in the mixture. Equation (15) thus becomes

$$G(T, P) = \sum n_i \{G_i^\circ + RT \ln(p_i / p_0)\} \qquad (16)$$

By the definition of the stoichiometric coefficients,

$$dn_i \sim a_i , dn_i = ka_i \qquad (17)$$

where k is a proportionality constant. Hence

$$\sum_i G_i^\circ dn_i = k\{aG_A^\circ + bG_B^\circ + \cdots - rG_R^\circ - sG_S^\circ \cdots\} \ (18)$$

Similarly, the proportionality constant k will appear as a multiplier in the second term of Eq. (18).

2.3 Flame temperature calculations

1. Analysis

Given that several moles of product develop for every mole of reactant fuel, the sum of the molar temperatures of the products will be much more than the sum of the molar heats of the reactants; that is,

$$\sum n_i (\Delta H_f^\circ)_i >> \sum n_j (\Delta H_f^\circ)_j$$

As a result, it appears that the flame temperature is governed not by the specific reactants, but solely by the atomic ratios and atoms injected. It is the atoms that determine what products will form. Only ozone and acetylene have sufficiently high positive molar temperatures of production to generate a noteworthy fluctuation (increase) in flame temperature. Ammonia has a negative heat of formation, which lowers the final flame temperature.

Nitric oxide has a low ionization potential and may ionize at flame temperatures. Many additional products would have to be examined for a typical composite solid propellant including C-H-O-N-Cl-Al. In reality, if all viable goods for this system are listed, the answer becomes more complicated, necessitating the employment of modern computers and codes for precise results. However, understanding thermodynamic equilibrium constants and kinetics allows one to rule out many potential product species. Concerns about emissions from power plants have heightened interest in specific goods with concentrations of less than 1%, even though such concentrations have no discernible effect on temperature. Nitric oxide (NO) is the primary contaminant of concern in this regard [5].

One determines n_C from the equation for N_C. Because the reaction between the reactants and products is irreversible, only the products exist in the system being studied. As a result, if the reactants were H_2 and O_2, H_2 and O_2 would also show on the product side. When dealing with equilibrium reactions, the molar amounts of the reactants H_2 and O2 are ignored. They are predetermined or known quantities. The concentrations of H_2 and O_2 in the resultant combination would be unknown. Even if it is evident, this argument should be considered carefully. It is a primary cause of mistake in first-hand attempts to tackle flame temperature difficulties .There are several mathematical methodologies for solving these equations numerically [4, 6, 7].

To explicitly solve for the temperature T2 and the product composition, mass balance equations, (μ — α) nonlinear equilibrium equations, and an energy equation in which one of the unknowns T2 is not even explicitly present must be considered. Because numerical processes are utilized on computers to address the problem, thermodynamic functions are represented in terms of power series with regard to temperature. In the general iterative technique, the equilibrium state for the product composition is first determined at an originally assumed temperature and pressure, and then the energy equation is checked to see whether it is satisfied.

Chemical equilibrium is often characterized by one of two comparable formulations: equilibrium constants or free energy minimization. It is more convenient to work with equilibrium constants for basic situations like finding the decomposition temperature of a mono propellant with few exhaust products or investigating the fluctuation of a particular species with temperature or pressure. For complicated situations, whether using equilibrium constants or free energy minimization, the issue simplifies to the same amount of interactive equations. When using equilibrium constants, however, one encounters more computational bookkeeping, numerical difficulties with the use of components, difficulty testing for the presence of some condensed species, and difficulty extending the generalized methods to conditions that require nonideal equations of state [4, 6, 8].

Any of numerous thermodynamic functions, such as the minimization of the Gibbs or Helmholtz free energy or the maximizing of entropy, can be used to express the condition for equilibrium. If temperature and pressure are used to define a thermodynamic state, the Gibbs free energy is most readily reduced since temperature and pressure are its natural variables. Similarly, if the thermodynamic state is defined by temperature and volume (density), the Helmholtz free energy is most effectively decreased [4]. The adaptable computer program of Gordon and McBride [4], which uses the minimization of the Gibbs free energy methodology and a descent Newton-Raphson method to solve the equations repeatedly, is the most often used strategy for temperature and composition estimates, as indicated. Ref. [7] shows a similar approach for solving the equations when equilibrium constants are employed.

2. Practical Considerations

The computation of flame temperature is simply the answer to a chemical equilibrium issue. Reynolds [8] has devised a more adaptable approach to the problem. This technique use theory to connect mole fractions of different species to values known as element potentials:

Each independent atom in the system has one element potential, and these element potentials, together with the number of moles in each phase, are the only variables that must be modified for the solution. In huge issues, the number of variables is significantly lower than the number of species; hence far fewer variables must be changed [8]. Stanjan [8] is a simple application that can be run on even the most basic systems. Both techniques, like the Gordon-McBride program, make use of the JANAF thermochemical database [1]. The CHEMKIN software package also includes an equilibrium code based on Stanjan [8].

In combustion calculations, the primary goal is to determine the temperature fluctuation as a function of the oxidizer-to-fuel ratio. As a result, it is common to treat the number of moles of fuel as 1 and the number of moles of oxidizer as provided by the oxidizer/fuel ratio when addressing flame temperature issues. As a result, the reactant coefficients are 1 and a quantity that is generally more than 1.

Plots of flame temperature vs oxidizer/fuel ratio peak around the stoichiometric mixture ratio, often on the fuel-rich side of stoichiometric (as will be explained later). When a system is overoxidized, the excess oxygen must be heated to the product temperature, which causes the product temperature to deviate from the stoichiometric value. If there is insufficient oxidizer present—that is, the system is underoxidized—there is insufficient oxygen to burn all of the carbon and hydrogen to their most oxidized form, therefore the energy released is reduced and the temperature falls. The flame temperature is represented as a function of the equivalency ratio, which is defined as the fuel/oxidizer ratio divided by the stoichiometric fuel/oxidizer ratio. The equivalence ratio is given the symbol φ. For fuel-rich systems, there is more than the stoichiometric amount of fuel, and $\varphi > 1$, for overoxidized, or fuel-lean systems, $\varphi < 1$. Obviously, at the stoichiometric concentration, $\varphi = 1$. Because most combustion systems employ air as the oxidizer, being able to easily measure the flame temperature of any fuel with air at any equivalency ratio is useful [29].

Furthermore, as the size of most hydrocarbon fuel molecules grows, so does their negative heat of production. As a result, fuels with negative temperatures of production similar to carbon dioxide are feasible. So it appears that heat emission would be limited. Hydrocarbon heats of formation range from 227.1 kJ/mol for acetylene to —456.3 kJ/mol for n-ercosane ($C_{20}H_{42}$). However, the more carbon atoms there are in a hydrocarbon fuel, the more moles of CO_2, H_2O, and, of course, and their generated dissociation.

As a result, even though a fuel has a high negative heat of creation, it can produce several moles of combustion products while maintaining a low flame temperature. Then, in order to assess the contribution of the heat of formation of the fuel to the flame temperature, the heat of formation should be examined on a unit mass basis rather than a molar basis. Taking this into account, nearly every hydrocarbon fuel has a heat of formation between —1.5 and 1.0 kcal/g. In reality, the majority range from —2.1 to +2.1 kcal/g. The two exceptions are acetylene and methyl acetylene, which have values of 2.90 and 4.65 kcal/g, respectively.

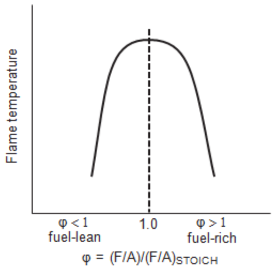


Figure 1: Variation of flame temperature with equivalence ratio φ.

When studying the flame temperatures of fuels in air, it is clear that the equivalency ratio has the greatest influence on flame temperature. The H/C ratio, which controls the ratio of water vapor, CO_2, and their generated dissociation products, is almost as important. Because the temperatures of formation per unit mass of olefins vary little and the H/C ratio is the same for all, flame temperature varies little among the monoolefins. The maximum temperature for acetylene-air peaks, for example, at a value of $\varphi = 1.3$ (see Table 1).

The H/C ratio has a greater effect in rich systems. One can attribute this trend to the fact that there is less nitrogen in the rich cases as well as to a greater effect of the mean specific heat of the combustion products. For richer systems the mean specific heat of the product composition is lower owing to the preponderance of the diatomic molecules CO and H_2 in comparison to the triatomic molecules CO_2 and H2O. The molar specific temperatures of diatomic molecules are lower than those of triatomic ones. The lower the mean specific heat of the product mixture for a given enthalpy content of reactants, the higher the final flame temperature. The greater the H/C ratios for a given chemical enthalpy content of reactants, the higher the temperature. This impact is partly caused by the lower specific heat of water and its dissociation products compared to CO_2, as well as the higher endothermicity of CO_2 dissociation. As one progress to higher energetic reactants, CO_2 dissociation rises and the discrepancies narrow. For many fuels, the temperature does not peak at the stoichiometric value at the greatest reaction enthalpies, but, as stated, between $\varphi = 1.0$ and 1.1 owing to lower mean specific heats of the richer products [9].

TABLE 1 Approximate Flame Temperatures of Various Stoichiometric Mixtures, Initial Temperature 298 K

Fuel	Oxidizer	Pressure (atm)	Temperature (K)
Acetylene	Air	1	2600[a]
Acetylene	Oxygen	1	3410[b]
Carbon monoxide	Air	1	2400
Carbon monoxide	Oxygen	1	3220
Heptane	Air	1	2290
Heptane	Oxygen	1	3100
Hydrogen	Air	1	2400
Hydrogen	Oxygen	1	3080
Methane	Air	1	2210
Methane	Air	20	2270
Methane	Oxygen	1	3030
Methane	Oxygen	20	3460

[A] This MAXIMUM exists AT $\varphi = 1.3$.

[b] This MAXIMUM exists AT $\varphi = 1.7$.

The dissociation of water is so thorough at the greatest temperatures and reaction enthalpies that the system does not profit from the heat of creation of the combustion product water. There is still a benefit from heat or CO production, the primary dissociation product of CO_2, therefore the lower the H/C ratio, the greater the temperature. Thus, at equivalence ratios close to unity and extremely high energy content, the lower the H/C ratio, and the higherthe temperature; the H/C curves overlap. When the pressure in a combustion system is increased, the quantity of dissociation reduces and the temperature rises. This remark is closely related to Le Chatelier's premise.

Of course, the impact is strongest at the stoichiometric air-fuel mixture ratio, where the quantity of dissociation is largest. The pressure influence on temperature is negligible in a system with little dissociation. As one progress to a very lean operation, the temperatures and degree of dissociation are very low in comparison to the stoichiometric values; hence, the temperature rise caused by an increase in pressure is likewise quite tiny. Many experimental setups in which nitrogen may perform certain reactions use artificial air systems that replace nitrogen on a mole-for-mole basis with argon. Because of its lower specific heat as a monotomic gas, argon absorbs far less of the heat of reaction in this situation, resulting in substantially greater system temperatures. Of course, the opposite is true when nitrogen is substituted by a triatomic molecule such as carbon dioxide [10].

3. Explosive and general oxidation properties of the fuel

3.1 Explosion limits and oxidation characteristics of hydrogen

The study of explosion limits yielded several early advances to the knowledge of hydrogen-oxygen oxidation reactions. Many detailed treatises on the hydrogen-oxygen reaction have been produced, with special emphasis on the influence of walls on radical annihilation (a chain termination step) [11]. Such effects are not significant in the combustion processes of concern here.

Hydrogen flames in air or oxygen emit little or no visible radiation, with the radiation that is seen being caused by trace contaminants. However, significant levels of OH may be detected in the UV portion of the spectrum. In stoichiometric flames, the highest temperature achieved in air is around 2400 K and 3100 K in oxygen. The burnt gas composition in air is 95-97% water, with the radicals H, O, and OH accounting for roughly one-quarter of the remaining [13]. Below 675 K, almost no reactions occur in static systems, while over 850 K, explosion happens spontaneously in modest pressure ranges. The explosive state is reduced at very high pressures due to a third-order chain termination reaction.

It is now critical to emphasize the following elements in order to avoid any misunderstanding with previously held notions and specific themes to be discussed later. The explosive limits are not the same as the flammability limits. Explosion limits are the pressure-temperature boundaries that separate the slow and rapid reaction areas for a specific fuel-oxidizer combination ratio. Flammability limits indicate the lean and rich fuel-oxidizer mixture ratios beyond which no flame will spread at a given temperature and pressure. Remember that for a flame to spread, quick reflexes are required.

At typical circumstances, a stoichiometric mixture of H_2 and O_2 will support a flame because an ignition source initially puts a local mixture into the explosive regime, and the established flame then warms new mixture to explosive temperatures via diffusion. As a result, in the early stages of any flame, the fuel-air combination may follow a low-temperature stable reaction system, whereas in the later stages, it may follow an explosive reaction system. This is crucial, especially in hydrocarbon combustion, since certain pollutant-causing chemicals are generated at low temperatures.

The explosive limits of a stoichiometric combination of hydrogen and oxygen are depicted in Figure 3. Many distinct mixing ratios have explosion limitations. The point X on Fig. 3 represents the circumstances (773 K; 1 atm) given in Fig. 2 at the beginning of this chapter. It is now clear that raising or lowering pressure at constant temperature might result in an explosion [29].

Certain general characteristics of this curve can be stated. First, the third limit portion of the curve is as one would expect from simple density considerations. Next, the first, or lower, limit reflects the wall effect and its role in chain destruction. For example, HO2 radicals combine on surfaces to form H_2O and O_2. Although the characteristics of the boundary movement are not fully described, the basic form of the three limits can be explained by credible mechanism ideas. The method in which the reaction is launched to create the boundary shown by the curve in Fig. 3 shows, as previously hinted, that the explosion is a branching chain phenomena in and of itself. To understand the boundaries, one must explore various branching chain processes. Thermal processes are mostly explored, rather than photolytic mechanisms. Because hydrogen has lower dissociation energy than oxygen, the initiation can be linked to hydrogen dissociation. Only a few radicals are required to start the explosion at the temperature range of interest, which is around 675 K.

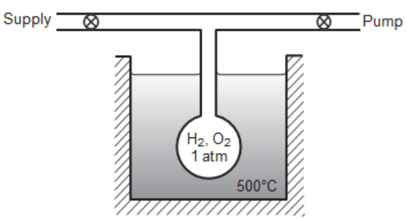


Figure 2: Experimental configuration for the determination of H2-O2 explosion limits.

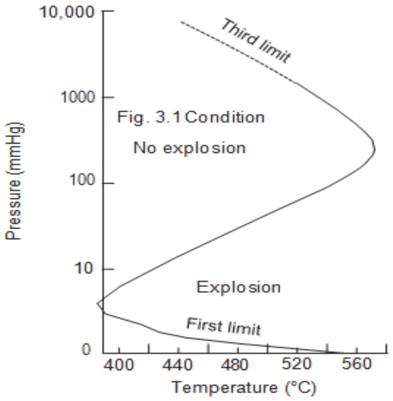


Figure 3: Explosion limits of a stoichiometric H_2-O_2 mixture (after Ref. [11]).

It is critical to note that, depending on the temperature and pressure of interest, not all H_2-O_2 reactions must be included. It should also be noted that each of these reactions is a pair of forward and backward reactions; however, as the reactions are stated, many of the backward reactions may be omitted. Remember that the backward rate constant may be calculated using the forward rate constant and the reaction system's equilibrium constant [29].

3.2 Explosion limits and oxidation characteristics of carbon monoxide

The inclusion of any hydrogen-containing contaminant confounded early experimental studies on the oxidation of carbon monoxide. The rate of CO oxidation is significantly faster in the presence of species such as water than in the "bone-dry" state. It is critical to understand that even little amounts of hydrogen, on the scale of 20 ppm, will significantly boost the rate of CO oxidation [15]. The "wet" carbon monoxide situation refers to the manner in which hydrogen-containing molecules are present.

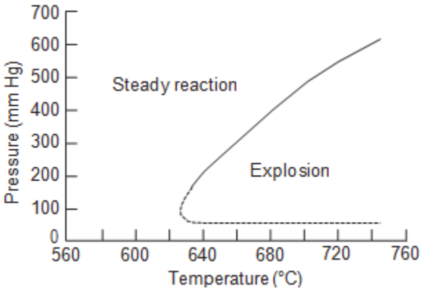


Figure 4: Explosion limits of a $CO-O_2$ mixture (after Ref. [11]).

$CO + OH \rightarrow CO_2 + H$ (19)

In most actual systems, CO oxidation will undoubtedly take place via this so-called moist pathway. However, considering the potential pathways for dry CO oxidation is instructive. Once again, the idea is to think about the explosion boundaries of a stoichiometric, dry CO-O2 combination. However, neither the explosive limits nor their repeatability are well defined, owing to the fact that the level of dryness in the several trials used to determine the limits may not be the same. As a result, typical explosion limits for dry CO would be as shown in Fig. 4.

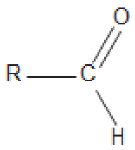
Figure 4 shows that the low-pressure ignition of CO-O2 is characterized by an explosion peninsula similar to that of H_2-O_2. Outside this peninsula, there is often a pale-blue radiance, the limits of which may also be established. A third limit has not been identified, and if it exists, it is far higher than 1 atm.

Certain broad properties of the defining curve in Fig. 4 may be indicated, as in the case of H_2-O_2 limitations. The lower limit satisfies all of the wall destruction requirements of a chain propagating species. Experiment has thoroughly established the impacts of vessel diameter, surface character, and condition [11].

The reverse of reaction (19) has no effect until the system has equilibrated, at which point the two coefficients $\partial \ln Y_{CO}/\partial \ln k_{44f}$ and $\partial \ln Y_{CO}/\partial \ln k_{44b}$ are equal in magnitude and opposite in sense. At equilibrium, these reactions are microscopically balanced, and therefore the net effect of perturbing both rate constants simultaneously and equally is zero. However, a perturbation of the ratio ($k_{44f}/k_{44b} = K_{44}$) has the largest effect of any parameter on the CO equilibrium concentration [29].

3.3 The oxidation of aldehydes

The CO is formed from the reaction of aldehydes with their acetyl (and formyl) radicals, RCO. Because the same sort of conversion occurs at high temperatures, it is necessary to understand the aldehyde conversion process before contemplating high-temperature hydrocarbon oxidation strategies. As shown, aldehydes have the structure



where R is either an organic radical or a hydrogen atom and $H\dot{C}O$ formyl radical. The initiation step for the high-temperature oxidation of aldehydes is the thermolysis reaction

$$RCHO + M \rightarrow R\dot{C}O + H + M \qquad (20)$$

The CH bond in the formyl group is the weakest of all CH bonds in the molecule and is the one predominantly broken. The R-C bond is substantially stronger than this CH bond, so cleavage of this bond as an initiation step need not be considered. As before, at lower temperatures, high pressures, and under lean conditions, the abstraction initiation step must be considered. Hydrogen-labeling studies have shown conclusively that the formyl H is the one abstracted—a finding consistent with the bond energies.

$$RCHO + O_2 \rightarrow R\dot{C}O + HO_2 \quad (21)$$

An organic group R is physically much larger than an H atom, so the radical RCO is much more unstable than HCO, which would arise if R were a hydrogen atom. Thus one needs to consider only the decomposition of RCO in combustion systems; that is,

$$R\dot{C}O + M \rightarrow \dot{R} + CO + M \; (22)$$

Similarly, HCO decomposes via

$$HCO + M \rightarrow H + CO + M \qquad (23)$$

but under the usual conditions, the following abstraction reaction must play some small part in the process:

$$HCO + O_2 \rightarrow CO + HO_2 \quad (24)$$

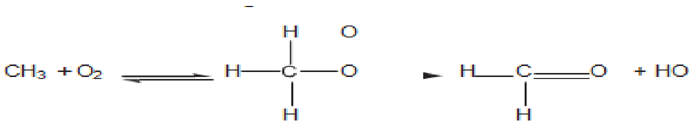
The existence of the HO_2 radical also helps at high pressures via HCO + $HO_2 \rightarrow H_2O_2$ + CO, however HO2 is the least effective of the OH, O, and H radicals. Formyl radicals react quickly with OH, O, and H radicals. However, because radical concentrations are substantially lower than those of stable reactants and intermediates, formyl reactions involving these radicals are regarded as negligible in comparison to other formyl reactions.

R is most likely a methyl radical, and the highest-order aldehydes to occur in high-temperature combustion are acetaldehyde and propionaldehyde. Acetaldehyde is the most common kind. Essentially, the preceding sequence was devised on the assumption that R was a methyl group.

3.4 The oxidation of methane

3.4.1 Low-Temperature Mechanism

Methane has unique oxidation properties that distinguish it from all other hydrocarbons. Bond energy tables demonstrate that the first broken C-H bond in methane requires around 40 kJ more than the others, and certainly more than the C-H bonds in longer-chain hydrocarbons. As a result, it is not unexpected to find a variety of experimental data demonstrating that methane/air (oxygen) mixes are more difficult to ignite than other hydrocarbons. Even oxygen atom assault is sluggish at low temperatures. Indeed, the words total hydrocarbons and reactive hydrocarbons are employed when considering exhaust emissions in terms of contaminants. The distinction between the two names is merely methane, which at atmospheric temperatures interacts so slowly with oxygen atoms that it is called unreactive. It is critical to thoroughly analyze reaction, which progresses [16, 17] through a metastable intermediate complex—the methyl peroxy radical—as follows:



$$CH_3 + O_2 \rightleftharpoons H-\overset{H}{\underset{H}{C}}-\overset{O}{O} \rightarrow H-\underset{H}{C}=O + HO \qquad (25)$$

At lower temperatures, the equilibrium step shifts substantially toward the complex, permitting the production of formaldehyde and hydroxyl radicals. The complex represented in reaction (25) has a well-established structure. Remember that when O2 reacts with the carbon atom in a hydrocarbon radical, it generates a bond angle of roughly 90°. Perhaps more importantly, [16] suggests that at temperatures of 1000 K and beyond, the equilibrium step in reaction (25) changes considerably toward the reactants, preventing the overall process to create formaldehyde and hydroxyl from proceeding. As a result, the fast oxidation of methane at high temperatures would be constrained. This potential should come as no surprise given that a specific response mechanism can alter significantly when temperature and pressure fluctuate [15, 17];

$$CH3 + O_2 \rightarrow CH_2O + OH \quad (26)$$

3.4.2 High-Temperature Mechanism

Many detailed models of methane oxidation at high temperatures have been published [18, 19, 20, 21]. These models are highly sophisticated, including hundreds of reactions. The availability of powerful computers and computer programs, allows for the development of these models, which may be used to forecast flow-reactor outcomes, flame speeds, emissions, and so on, and then compared to appropriate experimental data. Differences between the model and the experiment are utilized to adjust processes and rate constants that are not well established. The goal here is to highlight the major chemical reaction pathways in these complicated models of methane oxidation, just as modern sensitivity analysis [18, 19, 20] according to the particular application of the mechanism. At high temperatures the thermal decomposition of the methane provides the chain initiation step, namely

$$CH_4 + M \rightarrow CH_3 + H + M \quad (27)$$

With the presence of H atoms at high temperature, the endothermic initiated H_2–O_2 branching and propagating scheme proceeds, and a pool of OH, O, and H radicals develops. These radicals, together with HO_2 [which would form if the temperature range were to permit reaction as an initiating step], abstract hydrogen from CH_4 according to

$$CH_4 + X \rightarrow CH_3 + XH \quad (28)$$

where X might be any of the radicals. The radicals OH, O, and H are all fast, with OH being the fastest in general. However, throughout the temperature range of relevance in combustion, these reactions are known to display significant non-Arrhenius temperature behavior. The rate of abstraction by O is normally somewhat quicker than the rate of abstraction by H, although the order can alter depending on the prevailing stoichiometry; for example, in fuel-rich circumstances, the H rate will be faster than the O rate due to the considerably higher hydrogen atom concentrations [29].

The fact that reaction (25) may not occur as described at high temperatures may explain why methane oxidation is sluggish in comparison to other hydrocarbon fuels and why significant amounts of ethane are detected [12] during the methane oxidation process. Because the mechanisms that consume methyl radicals appear to be sluggish, the methyl content rises and ethane develops by easy recombination:

$$CH_3 + CH_3 \rightarrow C_2H_6 \quad (29)$$

As a result, methyl radicals destroy other methyl radicals to produce ethane, which must subsequently be oxidized. The oxidation properties of ethane and higher-order aliphatics differ significantly from those of methane. As a result, in combustion studies, methane should not be utilized to represent hydrocarbon oxidation processes. In general, a third body is not written for reaction (29), since the energy generated by the formation of the new bond can be redistributed by the ethane molecule's multiple internal degrees of freedom.

Brabbs and Brokaw [22] were among the first to propose that the principal oxidation destruction path of methyl radicals should be

$$CH3 + O2 \rightarrow CH3\dot{O} + \dot{O} \qquad (30)$$

Of course, all of the required higher-temperature H2 and CO reaction pathways outlined in earlier sections must be included. Again, whether X is a H atom or an OH radical, the reaction (28) produces molecular hydrogen (H2) or water. As previously noted, the system is not complete since sufficient ethane forms, necessitating consideration of its oxidation route. For example, Warnatz [23, 24] calculated that in atmospheric-pressure methane-air fires, roughly 30% of methyl radicals recombine to generate ethane in lean stoichiometric systems, and up to 80% in fuel-rich systems. In essence, the methane system has two parallel oxidation paths: one by methyl radical oxidation and the other via ethane oxidation. Again, reaction (28) with hydroxyl is quicker than reaction (19), thus CO accumulates early in the methane system; subsequently, when CO concentration rises, it effectively competes with methane for hydroxyl radicals, slowing the fuel consumption rate. The processes of CH_4 oxidation discussed in this section appear to be the most suited, however they are not definite. As the individual stages in the process are examined further, the rate constants for various specific reactions may change.

3.5 The Oxidation of higher order hydrocarbons

3.5.1 Supercritical Effects

Chemical reactions in supercritical conditions are substantially outside the sphere of considerable concern for combustion-related factors. However, a trend to increase the compression ratio of some turbojet engines has raised concerns that the fuel injection line to the combustion chamber could place the fuel in a supercritical state, increasing the possibility of carbon formations such as soot. The concern then becomes whether the pyrolysis of the fuel in the line may result in the creation of PAH (polynuclear aromatic hydrocarbons), which are commonly found in soot chemistry.

Because the general conditions in the devices of concern are not near the critical point, what is important in a process like hydrocarbon decomposition is whether the high density of the fuel constituents affects the decomposition kinetic process in such a way that species other than those found in a subcritical atmosphere appear.

It is clear that the high pressure in the supercritical domain influences not only the density (concentration) of the reactions, but also the diffusivity of the species formed during pyrolysis of crucial intermediates in fuel pyrolysis. Indeed, while contemplating the supercritical regime, one must additionally consider the possibility that the normal state equation will not hold.

Early research on the pyrolysis of the endothermic fuel methylcyclohexane

(MCH) discovered that in the subcritical state, MCH decomposition is scission dominated with little, if any, PAH [25, 26]. Furthermore, while scission processes are still relevant in supercritical circumstances, they are much slower [27]. According to these findings, the pyrolysis process of MCH produces the methylhexedienly radical (MHL) in both subcritical and supercritical circumstances [25, 26]. However, in supercritical conditions, dimethylcyclopentane was discovered to form. The method by which the initial 6-member ring is transformed to a 5-member ring appears to be owing to the phenomena of caging, which is often studied in the literature on supercritical chemical processes.

The creation of a cyclic intermediate is more likely to result in the production of PAH. Thus, once MHL occurs, it can take one of two paths: scission leading to conventional pyrolysis or cyclization due to a mechanism known as caging. The amount of either is determined by the experiment's physical parameters, primarily the density (or pressure). The typical technique for estimating the influence of caging on a chemical reaction process has been to use transition state theory [27]. The rate of production of a product through an intermediate (complex) in competition with the intermediate reforming the starting reactant has been examined in general transition state theory. As a result, scission is viewed as a competitor to caging. The transition state idea differs in that the intermediate does not return to the reactant but instead has two distinct paths to generate separate products. One approach is a scission pathway that results in a general hydrocarbon pyrolysis product, while the other is a caging process that may result in a product that causes fuel line clogging.

Following the general chemical approach [27] to determining the extent of a given route, it is possible to conclude that under supercritical conditions, the extent of fuel fouling (PAH formation) could be determined by the ratio of the collision rate of formation of the new cyclohydrocarbon due to caging to the diffusion rate of the scission products "to get out of the cage". This ratio can be represented by the expression $[vd^2 \exp(—E/RT)/D]$ or $[v \exp(—E/RT)/(D/d^2)]$, where v is the collision frequency ($s^{—1}$), d^2 the collision cross-section, E the activation energy, and D the mass diffusivity (cm^2/s) [27]. The second ratio expression is formulated so that a ratio of characteristic times is presented. This time ratio will be recognized as a Damkohler number [27]. For the pyrolysis process referred to, the caging institutes a bond formation process and thus activation energy does not exist. Then the relevant Damkohler number is $[v/(D/d^2)]$.

The typical small molecule diffusivities for gases range from $10^{—1}$ cm^2/s for gases to $10^{—5}$ cm^2/s for liquids [28]. Under supercritical circumstances, the supercritical fluid is expected to be halfway between the two values. Although supercritical fluids are more comparable to liquids than gases in many ways, their diffusivities are more akin to gases than liquids. As a result, the caging product should grow with pressure, as shown in MCH pyrolysis [26] and maybe in other comparable scenarios involving combustion issues.

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