

Chapter 2: Chemical kinetics and the chemistry of combustion

Objectives

The objectives of this Chapter are:

- To introduce concepts of chemical kinetics.
- To present simplified models for fuel consumption rate.
- To derive simplified models for nitric oxide formation.
- To describe qualitatively the chemistry of hydrocarbon combustion.

Introduction

In chapter 1, we talked about the heat of combustion Q , the mass flux, and we derived governing equations for the species mass fractions and the temperature. To completely close our system of equations that describe a reacting fluid, we need expressions for the rate of reaction \dot{w} . The rate of reaction comes from Chemical Kinetics and is discussed in this Chapter. We will also discuss the basic qualitative features of hydrocarbon combustion and how these are manifested in various applications.

Chemical kinetics

Global and elementary reactions

Chemical reactions occur when molecules of one species collide with molecules of another species and, for some of these collisions, one or more new molecules will be created. The chemical reaction essentially involves a re-distribution of how atoms are bonded together in the molecule. To achieve this, chemical bonds must be broken during the impact (i.e. the molecules must have sufficient kinetic energy) and other bonds must be formed. As the energy of these bonds depends on the nature of the atoms and on geometrical factors, the energy content of the products of the collision may be different from the energy content of the colliding molecules. This is the origin of the heat released (or absorbed) in chemical reactions.

So far, to describe combustion we have been writing reactions like



This is an example of a *global reaction*. What we mean is that the overall process of combustion uses 1 kmol of CH_4 and 2 kmol of O_2 to produce, if complete, 1 kmol of CO_2 and 2 kmol of H_2O . We do not mean that in an actual molecular collision, 1 molecule of methane collides at the same time with 2 molecules of oxygen, to produce 1 molecule of carbon dioxide and 2 molecules of water. This would be impossible to happen because it would involve too many bonds to break (e.g. between C and H in the methane molecule) and too many bonds to form (e.g. between H and O in H_2O). What makes it impossible is that the colliding molecules just cannot have enough kinetic energy to achieve that much bond reshuffling. However, the reactions

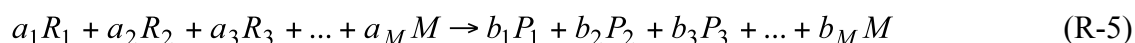


are possible. For example, R-2 involves breaking one C-H bond and forming a O-H one. Reactions R-2 to R-4 are examples of *elementary reactions*, i.e. reactions that can occur during a molecular collision. The overall combustion process follows hundreds or thousands of such elementary reactions and many species and *radicals* appear. By the term “radicals” we mean very reactive unstable molecules like O, H, OH, or CH₃. The series of elementary reactions that describes the overall process is called a *reaction mechanism* or *detailed chemical mechanism*.

The concept of global reaction helps us visualize the overall process and stoichiometry. But it is only when we identify the elementary reactions that we can talk in detail about what really happens inside the flame. A large part of the science of Chemical Kinetics is centred on identifying which elementary reactions are possible under various conditions for various species and to prescribe the *rate*, i.e. how quickly these reactions take place.

The Law of Mass Action

The Law of Mass Action is a very important concept in Chemical Kinetics. It relates how quickly the reaction proceeds as a function of how much reactant is available. It is valid only for elementary reactions. Consider the generic elementary reaction



between reactants R_1, R_2, R_3, \dots , from which products P_1, P_2, P_3, \dots , are formed. M is an example of species that appears on both sides. The rates of reactants consumption and products formation are given by:

$$\begin{aligned} \frac{d[R_1]}{dt} &= -a_1 \omega, & \frac{d[R_2]}{dt} &= -a_2 \omega, & \frac{d[R_3]}{dt} &= -a_3 \omega, \dots \\ \frac{d[P_1]}{dt} &= b_1 \omega, & \frac{d[P_2]}{dt} &= b_2 \omega, & \frac{d[P_3]}{dt} &= b_3 \omega, \dots \\ \frac{d[M]}{dt} &= b_M \omega - a_M \omega \end{aligned} \quad (2.1)$$

with ω being the *reaction rate*

$$\omega = k[R_1]^{a_1} [R_2]^{a_2} [R_3]^{a_3} \dots \quad (2.2)$$

The parameter k is the *reaction rate constant* and $[R_1]$ is the concentration (in kmol/m³) of reactant R_1 etc. Equation (2.1) is a statement of the *stoichiometry* of the reaction: every a_1 kmol of R_1 is joined by a_2 kmol of R_2 , a_3 kmol of R_3 etc., to produce simultaneously b_1 kmol of P_1 , b_2 kmol of P_2 , b_3 kmol of P_3 etc.. So the amount of R_1 that has reacted is related to how much R_2, R_3 etc. have reacted and Eq. (2.1) describes this relationship. If a species M appears in both the reactants and the products, then what multiplies ω is the difference ($b_M - a_M$). If $b_M = a_M$, then M is called a *third body*: it may not be altered, but its presence is crucial for the success of the reaction, as it provides energy to, or takes energy away from, the collision between the reactants.

Equation (2.2) is the Law of Mass Action and states that the reaction rate is proportional to the reactants concentrations, raised to their respective *stoichiometric coefficients* (i.e. a_1, a_2 , etc). The amount of products does not affect ω . The reaction rate constant k is not a function of the reactants concentration and it is specific to the elementary reaction.

The reaction rate constant – a cornerstone of combustion science

The reaction rate constant is given by the *Arrhenius* law

$$k = A \exp\left(-\frac{E_{act}}{R^0 T}\right) \quad (2.3)$$

where A is the *pre-exponential factor* and E_{act} is the *activation energy*. These quantities come from experiment or statistical mechanics calculations. The presence of the exponential can be understood by the following argument. We have already mentioned that not all molecular collisions will result in reaction, but only those with kinetic energy higher than the energy needed to break bonds inside the reactants' molecules. This energy barrier is described by the activation energy. The proportion of collisions occurring between molecules that have kinetic energy higher than E_{act} is given by $\exp(-E_{act}/R^0 T)$; this results from Kinetic Theory of Gases. The important point to notice is that the reaction rate constant *increases very fast with temperature*. This is the fundamental reason why combustion reactions occur at high temperatures and not at room temperature and explains a host of phenomena, as we will see later.

Examples

Using Eqs. (2.1) and (2.2), we can write that for the elementary reaction R-2,

$$\frac{d[CH_4]}{dt} = -k_1[CH_4][O]; \quad \frac{d[O]}{dt} = -k_1[CH_4][O]; \quad \frac{d[CH_3]}{dt} = k_1[CH_4][O]; \quad \frac{d[OH]}{dt} = k_1[CH_4][O]$$

while for the elementary reaction



we have

$$\frac{d[H]}{dt} = -2k_5[H]^2[M], \quad \frac{d[H_2]}{dt} = k_5[H]^2[M], \quad \frac{d[M]}{dt} = 0$$

Reaction mechanisms

If many elementary reactions take place, the net amount of reactant or product consumed or produced will come from adding the contribution from each elementary reaction. So, for the mechanism composed of elementary reactions R-2 to R-4, it should be evident that

$$\frac{d[CH_4]}{dt} = -k_1[CH_4][O] - k_2[CH_4][H] - k_3[CH_4][OH]$$

$$\frac{d[CH_3]}{dt} = k_1[CH_4][O] + k_2[CH_4][H] + k_3[CH_4][OH]$$

In general, species will participate in some reactions as reactants and in others as products. The overall consumption or generation rate will be the net outcome of all the elementary reactions. The possibility emerges that $d[R]/dt$ becomes exactly (or approximately) zero. This concept is called the *steady-state approximation* and is explored later.

Forward and backward reactions

Many elementary reactions can proceed in both directions, i.e. to the right and to the left. Hence the “products” can become “reactants” and vice versa. The specific reaction rates will, in general, be very different. Elementary reactions that are both forward and backward are written with an equal sign instead of an arrow. For example, we write



and we mean that this is equivalent to the mechanism



that gives

$$\frac{d[R_1]}{dt} = -a_1 k_{7f} [R_1]^{a_1} [R_2]^{a_2} + a_1 k_{7b} [P_1]^{b_1} [P_2]^{b_2}.$$

Both reaction rate constants must be prescribed, but we will see in Chapter 3 that they are related through the equilibrium constant of the reaction. So, in general, knowing the rate constant of the forward reaction suffices.

The reaction rate in the species conservation equation

We are now in a position to write down the mass generation (or consumption) rate for each species in the species conservation equation and hence close our system of equations that describe a reacting flow. As an example and in order to introduce a very important chemical mechanism, let us consider the following reactions for the formation of nitric oxide, which is a major pollutant from combustion:



This is the **Zel'dovich mechanism** or *thermal* mechanism for *nitric oxide* and is extremely important. The net rate of formation of NO will be given by

$$\hat{w}_{NO} \equiv \frac{d[NO]}{dt} = k_{Z1f} [N_2][O] - k_{Z1b} [NO][N] + k_{Z2f} [O_2][N] - k_{Z2b} [NO][O] \quad (\text{2.4})$$

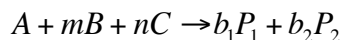
where the symbol $\hat{}$ denotes molar rate of formation ($\text{kmol m}^{-3} \text{s}^{-1}$). Then, in terms of ($\text{kg m}^{-3} \text{s}^{-1}$), the units needed in the species conservation equation (Eq. 1.30),

$$\dot{w}_{NO} = \hat{w}_{NO} MW_{NO} \quad (\text{2.5})$$

and of course this can be generalized for all species. **The net rate of generation \dot{w}_i for species i should not be confused with the reaction rate ω in the Law of Mass Action (Eq. 2.2).** Note that ω has units ($\text{kmol m}^{-3} \text{s}^{-1}$). The pre-exponential factor A for each elementary reaction has units such that the r.h.s. of Eq. (2.2) will also have units ($\text{kmol m}^{-3} \text{s}^{-1}$).

Types of elementary reactions

Elementary reactions can be classified according to the number of molecules participating in the reactants side. For the generic elementary reaction



we say that the reaction is of **overall order** $(1+m+n)$, while it is of order 1 with respect to reactant A , etc. The overall order is also called **molecularity**. Depending on the molecularity, we have the following types of elementary reactions:

1. First order (unimolecular): $A \rightarrow b_1P_1 + b_2P_2 + \dots$

This reaction is an idealisation, since molecules normally do not disintegrate spontaneously. For that to happen, a collision with another molecule is necessary (which, by the way, makes the reaction effectively second-order). The rate is given by $\omega = -k[A]$ and k has units $(1/s)$.

2. **Second order (bimolecular)**: $R_1 + R_2 \rightarrow b_1P_1 + b_2P_2 + \dots$

This is the most common reaction in combustion since the collision probability is highest for two molecules. The rate is given by $\omega = -k[R_1][R_2]$ and k has units $(\text{kmol}/\text{m}^3)^{-1} \text{s}^{-1}$.

3. Third order (trimolecular): $R_1 + R_2 + R_3 \rightarrow b_1P_1 + b_2P_2 + \dots$

The probability that three molecules collide is small, but nevertheless third-order reactions are very important. *Radical recombination reactions*, for example between OH and H to produce water, take place only if a third body M participates in the collision and hence these are third-order reactions. The reason a third body is needed is that recombination reactions are exothermic and the third body must carry away some of the energy. The rate is $\omega = -k[R_1][R_2][R_3]$ and k has units $(\text{kmol}/\text{m}^3)^{-2} \text{s}^{-1}$.

Chain reactions

Another classification is according to the net number of radicals that are produced. Consider the following elementary reactions, which are present in both hydrogen and hydrocarbon combustion:



These reactions are examples of *chain reactions*. Chain reactions involve the production of a radical species, which in turn reacts to produce another radical. Reaction I is a **chain-initiating** reaction. Reaction II is a **chain-branching** reaction; more radicals exist in the products than in the reactants. Reaction III is a **chain-propagating** reaction: the radicals may change identity, but the number of radicals does not change. Finally, Reaction IV is a **chain-terminating** reaction, which is so-called because the chain terminates by the consumption of the radicals.

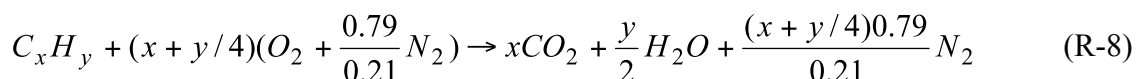
Chain reactions are crucial for combustion. Flames would not be self-sustaining if the chemistry did not have this property. With chain reactions, the reaction rate may grow exponentially and this leads to explosions. In a normal flame, this does not happen because heat is removed from reaction zone by diffusion or convection (cf. Eq. 1.31). As we shall see throughout the course, the

fine balance between heat transfer and heat release is what makes combustion so rich in physical phenomena.

Simplified chemical mechanisms

Empirical one-step combustion mechanisms

We discussed that global reactions do not represent an actual reaction that occurs during a collision and that the combustion processes follows many elementary reactions. However, global reactions can represent very well what an engineer may want from combustion: to examine the overall fate of the fuel and the overall stoichiometry. Such engineering approximations to the overall rate of combustion exist and are called *reduced reaction mechanisms*. Reduced mechanisms are a sequence of artificial steps that range in number from, say ten to one. The global reaction R-1 is a *one-step* mechanism. Based on experiments, such one-step mechanisms have been developed for most hydrocarbon fuels and provide useful approximations for many flame problems. In the context of a one-step reaction, the combustion of a hydrocarbon is written as (Eq. 1.3, repeated here as R-8:



The rate of the global reaction is written empirically as

$$\frac{d[C_xH_y]}{dt} = -A_G \exp\left(-E_{act}/R^0T\right) [C_xH_y]^p [O_2]^q \quad (2.6)$$

with p , q , A_G , and E_{act} obtained from experiments and numerical optimisation so that Eq. (2.6) gives an overall rate of fuel and oxygen consumption close to that of the data or to that of a detailed reaction mechanism. Note that p and q have nothing to do with the stoichiometric coefficients in R-2. Equation (2.6) will be used very often in this course with $p=q=1$, so that the overall reaction is second-order. Such a simplification of the chemistry allows analytic solutions to be obtained and significant physical insight can then be developed.

Systematically-reduced combustion mechanisms

A more scientific way to reduce a detailed chemical mechanism is to use the *steady-state approximation* and the *partial equilibrium assumption*. These are included here partly because they lead to a closed-form model for nitric oxide formation, presented below.

The *steady-state approximation* refers to a species: species A is said to be in steady-state if $d[A]/dt \approx 0$, i.e. if its net production rate from the mechanism is approximately zero. Let us show the power of this method by way of an example, the Zel'dovich mechanism composed of elementary reactions Z-1 and Z-2. Assume that all the backward reactions have zero rate, as for example could occur at the initial stages of the flame. If we needed to evaluate Eq. (2.4), we would need to know the concentrations of O_2 , N_2 , O , and N . Assume now that the N atom is in steady state. This happens when all the reactions that consume N are very fast, so that as soon as some N is formed, it is immediately consumed. For the Zel'dovich mechanism, this would occur if Z-2 was very much faster than Z-1, and this is indeed the case. The steady-state approximation for N then gives

$$\begin{aligned} \frac{d[N]}{dt} &= 0 \\ \Leftrightarrow k_{Z1f}[N_2][O] - k_{Z2f}[O_2][N] &= 0 \end{aligned}$$

$$\Leftrightarrow [N] = \frac{k_{Z1f}[N_2][O]}{k_{Z2f}[O_2]} \quad (2.7)$$

Substituting Eq. (2.7) into (2.4) and neglecting the backward reactions, we obtain

$$\frac{d[NO]}{dt} = k_{Z1f}[N_2][O] + k_{Z2f}[O_2] \frac{k_{Z1f}[N_2][O]}{k_{Z2f}[O_2]} = 2k_{Z1f}[N_2][O] \quad (2.8)$$

Hence, we have eliminated the species N from our mechanism and the rate of the second reaction does not appear. However, the *presence* of Z-2 is felt from the factor 2 that has emerged. Physically, what we have done is to say that if N disappears as soon as it is formed, then by reaction Z-2, a second molecule of NO appears as soon as one is formed by reaction Z-1. By employing the steady-state approximation, many species may be eliminated from the reaction rate expressions by relating their concentrations to those of other species.

The partial equilibrium assumption refers to a reaction. Let us assume that our mechanism is now supplemented by the partially-equilibrated reaction



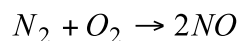
a dissociation reaction (more on this in Chapter 3). The partial equilibrium assumption states that the forward and backward rates of an elementary reaction are equal, i.e.

$$k_{Z3f}[O_2] = k_{Z3b}[O]^2 \Leftrightarrow \frac{[O]^2}{[O_2]} = \frac{k_{Z3f}}{k_{Z3b}} \Leftrightarrow [O] = \left(\frac{k_{Z3f}}{k_{Z3b}} \right)^{1/2} [O_2]^{1/2} \quad (2.9)$$

This equation essentially poses a constraint on the relative amounts of O_2 and O: their concentrations have to satisfy Eq. (2.9) at all times. An elementary reaction will be in partial equilibrium if both its forward and backward rates are very much faster than those of the other reactions in the mechanism. Using Eq. (2.9) in (2.8) gives

$$\frac{d[NO]}{dt} = 2k_{Z1f} \left(\frac{k_{Z3f}}{k_{Z3b}} \right)^{1/2} [O_2]^{1/2} [N_2] \quad (2.10)$$

This is our reduced model for NO generation. Essentially, we have reduced the detailed scheme Z-1, Z-2, and Z-3 to the one-step global chemical mechanism



with a rate given by Eq. (2.10). This procedure was done here analytically because the Zel'dovich mechanism was small. For realistic combustion mechanisms the same concepts are used in complicated computer programs. The identification of steady-state species and partial-equilibrium reactions is the subject of intensive research in the combustion community.

We presented this development here in order to introduce the concepts of steady-state and partial equilibrium and in order to derive the one-step mechanism for NO production (Eq 2.10). By reference to Eq. (2.10), we will understand certain very important pollution-reduction technologies (Chapter 8), which currently form a billion-pound worldwide market.

Hydrocarbon combustion chemistry

The elementary reactions forming a detailed reaction mechanism for hydrocarbon combustion could number many hundreds of reactions in which 40-200 stable species and radicals may participate. The overall features, which also explain some experimental observations, are approximately the same for all hydrocarbons. The reaction sequence is very complex, but we can describe the basic ideas as a series of three steps.

Typical combustion sequence

Step 1: Breakdown of the fuel into smaller hydrocarbons from radical attack, for example $C_2H_6 + O \rightarrow C_2H_5 + OH$. These smaller hydrocarbons could also be stable species, not necessarily radicals. For example, significant amounts of C_2H_2 are found in the initial stages of the combustion of almost all fuels.

Step 2: All the carbon from the fuel eventually results in CO and the hydrogen results in H_2 .

Step 3: Final oxidation of CO and H_2 into CO_2 and H_2O . The main elementary reactions here are



A large part of the heat release associated by combustion occurs here. Reactions R-10 and R-11 are also active in the earlier stages of combustion and hence H_2O is the first combustion product to appear, with CO_2 the last.

Other features

1. Rich combustion

If combustion is rich, then fuel fragments may collide to form larger hydrocarbons. This process leads to *soot*, which are agglomerated solid particles. Soot radiates intensely in the hot flame products and gives rich flames their characteristic yellow colour.

2. Radical formation

None of the steps above (fuel breakdown, partial oxidation into CO and H_2 , and final oxidation) can occur if radicals such as O, H, and OH are absent. One of the most important elementary reactions in combustion is



which is a chain-branching reaction and proceeds at appreciable rates only at high temperatures ($>1500K$), as it has a high activation energy. This reaction is one of the few that produces the O atom. Hence, if its rate drops below that of the chain-terminating reactions, the flame will not stay alight. The removal of H (and other) radicals from the reaction zone is what some fire extinguishers aim to achieve by introducing agents that absorb H strongly (e.g. halon). On the other hand, injection of radicals (e.g. by plasma) allows ignition under very unfavourable conditions and the combustion of very lean mixtures. Plasma igniters in aircraft gas turbines have a wider operational range compared to conventional sparks because of this.

Summary of main points

- The rate of elementary reactions is described by the Law of Mass Action (Eq. 2.2).
- The rate of global reactions may be estimated by empirical relations (Eq. 2.6).
- The reaction rate constant of elementary reactions is given by the Arrhenius Law (Eq. 2.3).
- Using the steady-state approximation and the partial equilibrium assumption, we derived a one-step mechanism for thermal NO formation (Eq. 2.10).
- The combustion of all hydrocarbons follows approximately the same sequence of steps, first into CO and H₂ and then to CO₂ and H₂O. For successful combustion, the presence of radicals is necessary and these are produced only at high temperatures.

Suggested reading

Turns:

Ch. 4 (elementary and global reactions; chain reactions, steady state approximation, Zel'dovich mechanism); Quick look through Ch. 5 (hydrocarbon combustion steps).

Glassman:

Ch. 2 (sections A, B1, C, D, F)

Worked examples

Example 2-1. A closed vessel with propane and air mixture at $\phi=0.1$ is kept at $T=1200\text{K}$ and $P=1\text{bar}$. Assume that combustion is described by a one-step global reaction with $A_G=8.6 \times 10^8 \text{ (kmol m}^{-3}\text{)}^{-1} \text{ s}^{-1}$, $T_{act}=15000 \text{ K}$ and $p=q=1$ in Eq. (2.6). Neglecting any oxygen consumption (the mixture is very lean), calculate the time taken for complete consumption of the fuel. Repeat the calculation for $T=1500 \text{ K}$.

The fuel consumption rate is given by the one-step expression

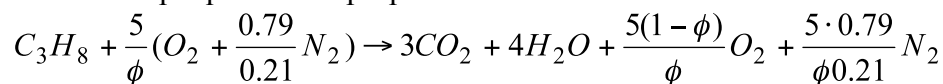
$d[C_3H_8]/dt = -A_G \exp(-T_{act}/T)[C_3H_8][O_2]$. Assuming constant T and $[O_2]$ and denoting the initial propane concentration by $[C_3H_8]_{in}$, we can integrate to get

$$\frac{d[C_3H_8]}{[C_3H_8]} = -A_G \exp(-T_{act}/T)[O_2]dt \Leftrightarrow \ln\left(\frac{[C_3H_8]}{[C_3H_8]_{in}}\right) = -A_G \exp(-T_{act}/T)[O_2]t$$

$$\Leftrightarrow [C_3H_8] = [C_3H_8]_{in} \exp(-t/\tau), \text{ with } \tau^{-1} = A_G \exp(-T_{act}/T)[O_2].$$

Hence the fuel concentration reaches zero in an asymptotic manner. The time constant τ is a measure of the *lifetime* of the species. Hence if we define as “complete consumption” the state where, for example, $[C_3H_8]/[C_3H_8]_{in} < 10^{-4}$, this first occurs at $t/\tau=9.2$.

The one-step equation for propane combustion is



and hence for $\phi=0.1$, the mole fractions in the reactants are

$$X_{C_3H_8}=1/(1+5 \cdot 4.76/0.1)=0.004182, \quad X_{O_2}=0.21 \cdot (1-X_{C_3H_8})=0.209122$$

The initial $[O_2]$ concentrations are

$$[O_2]=X_{O_2}P/R^0T=2.096 \times 10^{-3} \text{ kmol/m}^3 \text{ at } 1200 \text{ K and } 1.677 \times 10^{-3} \text{ kmol/m}^3 \text{ at } 1500 \text{ K.}$$

Therefore the time constant τ is

$$\tau(1200 \text{ K})=149 \times 10^{-3} \text{ s, and}$$


$$\tau(1500 \text{ K})=15 \times 10^{-3} \text{ s.}$$

Notes:

- The high activation temperature makes the reaction rate increase fast with temperature.
- The lifetime decreases linearly with pressure (can you see this?). This is due to the assumed first-order dependence on $[O_2]$.
- Vessels with dilute fuel and air kept under isothermal conditions are often used in experiments. Usually, the reactants flow in a tube and time is equivalent to distance downstream of the fuel injection point. These are called “plug flow reactors”. Measuring the concentration of fuel at various points downstream gives information on the reaction rate through a model such as the one in this example.

Example 2-2. Calculate the initial rate of formation of NO in **atmospheric air** at $T=1500, 2000$ and 2500K and $P=1\text{atm}$. Use the following values in Eq. (2.10): $k_{Z1f}=1.82 \times 10^{11} \exp(-38370/T)$ ($\text{kmol m}^{-3})^{-1} \text{s}^{-1}$; $(k_{Z3f}/k_{Z3b})^{1/2}=3.617 \times 10^{-7}, 5.172 \times 10^{-5},$ and 1.0×10^{-3} at $1500, 2000,$ and 2500K respectively.

Atmospheric air has $X_{O_2}=0.21$ and $X_{N_2}=0.79$. Hence, $[O_2]=0.21P/R^0T$ and $[N_2]=0.79P/R^0T$, with $P=101.3 \text{ kPa}$. Using Eq. (2.10), $d[NO]/dt = 2k_{Z1f} (k_{Z3f}/k_{Z3b})^{1/2} [O_2]^{1/2} [N_2]$, we obtain that

@ 1500 K , $d[NO]/dt = \underline{2.7 \times 10^{-10}} \text{ kmol m}^{-3} \text{ s}^{-1}$, 

@ 2000 K , $d[NO]/dt = \underline{1.5 \times 10^{-5}} \text{ kmol m}^{-3} \text{ s}^{-1}$,

@ 2500 K , $d[NO]/dt = \underline{0.97 \times 10^{-2}} \text{ kmol m}^{-3} \text{ s}^{-1}$.

Notes:

- **The NO formation rate increases extremely fast with temperature.** Two effects are at play: (i) the high activation energy of the $N_2+O \rightarrow NO+N$ reaction (Z-1) and (ii) the presence of more O from the O_2 dissociation at high temperatures. (Strictly speaking, O_2 dissociation is not the route to make O in real flames.) More on dissociation in Chapter 3.
- Keeping the temperature low will virtually eliminate NO. This is one of the key points of low-NOx combustion technologies (more on this in Chapter 8).
- The activation temperature of the reactions producing NO (e.g. 38370 K) is higher than the activation temperature of fuel combustion (e.g. 15000 K , Ex. 2-1). Combustion “picks-up” at lower temperatures than NO formation. By careful burner modifications, engineers use flames at temperatures within this “window of opportunity” to decrease NO without having to sacrifice fuel efficiency.