## Module 2: Chemical Kinetics

### 1.0 Objectives, Scope, Required Reading \& Assignment Schedule

## Objectives

By the end of this module, students should be able to:

- Identify variables that influence the rate at which chemical reactions proceed
- Compose a rate expression for a given reaction
- Define simple and complex reactions
- Understand the Arrhenius Rate Expression
- Explain the difference between $1^{\text {st }}, 2^{\text {nd }}$, and $3^{\text {rd }}$ order reactions
- Define chain reactions
- Understand chain branching explosions
- Understand the theory of homogeneous ignition of gases
- Understand the Frank-Kamenetski analysis and how it can be utilized for understanding a materials propensity to self-heat and spontaneously ignite


## Scope

- Analysis of chemical kinetics and reaction rates
- Analysis of ignition pertaining to gases
- Analysis of self-heating and spontaneous ignition


## Reading Assignments

- Turns: Chapter 4
- Drysdale: Chapter 6.1, Chapter 8.1


## Assignment Schedule

Three problems worth 10 points total are to be completed and submitted online. There is also an extra credit problem available ( 4 points). See the last page of this module for more details.

There are exercises within the module that should be attempted by the student, these will not count toward your grade. The discussion question in 6.1 (Self-heating) of the module will count towards your class participation grade.

### 2.0 Background

In Module 1, we learned about the chemical thermodynamics that govern combustion. Thermodynamics determines equilibrium in a system and, therefore, establishes the direction
that the system wants to go. For example, as we saw, thermodynamics determines adiabatic flame temperature, a limiting temperature that is virtually never achieved in practice.
Thermodynamics is like a signpost that points the way to the destination. However, thermodynamics does not tell us how quickly we will get to the destination, for that we need chemical kinetics. A good example of this is the occurrence of a natural gas leak inside a building. We all know that equilibrium dictates that the methane (or higher hydrocarbons for that matter) will combine with the oxygen in the air in a highly exothermic reaction to form carbon dioxide and water. However, we also know that this does not occur at room temperature unless we introduce an ignition source such as a spark. In this case, the spark serves to accelerate the chemical reactions that are necessary to convert $\mathrm{CH}_{4}$ to $\mathrm{CO}_{2}$ and $\mathrm{H}_{2} \mathrm{O}$ so that the equilibrium state can be achieved. Thus, chemical kinetics is like the speed limit sign along our thermodynamic route. Thermodynamics points the direction to equilibrium but chemical kinetics determines how quickly we get there. As we will see later in the course, most often it is the chemical kinetics that determine the nature of a fire including its heat release rate and the products of combustion it produces, including smoke and toxic gases. So, before we can discuss in detail the nature of premixed and diffusion flames we must first understand the role of chemical kinetics in combustion.

Figure M2-1

## Flame Kinetics

## Thermodynamics points the way to equilibrium

BUT<br>Kintetics<br>determines the rate

55
Speed Limit

### 3.0 Chemical Reactions and their Rates

Chemical Thermodynamics tells us what reaction will occur and what the equilibrium products of the reaction(s) will be but, since it deals in state functions, it cannot tell us how
quickly equilibrium is approached. The rate of approach to equilibrium is governed by chemical kinetics.

## Chemical Kinetics

All chemical reactions take place at a finite well defined rate which can depend on

- species concentrations
- temperature
- pressure
- presence of catalyst or inhibitor
- radiative effects

One step chemical reaction is represented by

$$
\sum_{i} \gamma_{i}^{\prime} \mathrm{M}_{\mathrm{i}} \rightarrow \sum_{\mathrm{i}} \gamma_{\mathrm{i}}^{\prime \prime} \mathrm{M}_{\mathrm{i}}
$$

Where $\gamma_{i}^{\prime}$ and $\gamma_{i}^{\prime \prime}$ are stoichiometric coefficients (which may be zero)
e.g.

$$
\begin{gathered}
2 \mathrm{H}_{2}+\mathrm{O}_{2} \rightarrow 2 \mathrm{H}_{2} \mathrm{O} \\
\mathrm{M}_{1}=\mathrm{H}_{2}, \quad \mathrm{M}_{2}=\mathrm{O}_{2}, \quad \mathrm{M}_{3}=\mathrm{H}_{2} \mathrm{O} \\
\gamma_{1}^{\prime}=2, \quad \gamma_{2}^{\prime}=1, \quad \gamma_{3}^{\prime}=0 \\
\gamma_{1}^{\prime \prime}=0, \\
\gamma_{2}^{\prime \prime}=0, \quad \gamma_{3}^{\prime \prime}=0
\end{gathered}
$$

Or

$$
\begin{array}{ll}
\quad \mathrm{H}+\mathrm{H}+\mathrm{H} \rightarrow \mathrm{H}_{2}+\mathrm{H} & \\
\mathrm{M}_{1}=\mathrm{H} & \mathrm{M}_{2}=\mathrm{H}_{2} \\
\prime \prime \\
\gamma_{1}^{\prime}=3 & \gamma_{2}^{\prime}=0 \\
\gamma_{1}^{\prime \prime}=1 & \gamma_{2}^{\prime \prime}=1
\end{array}
$$

In general the rate of a reaction can be written from the "law of mass action" as

$$
R R_{i}=k \prod_{j}\left[M_{j}\right]^{\gamma_{i}^{\prime}}
$$

where []$=\frac{\mathrm{n}}{\mathrm{V}}=$ concentration of a species, and $k$ is called the "rate constant" for the reaction.

That is, the rate of disappearance of a species in a reaction is proportional to the concentration of the reactants raised to their stoichiometric coefficients so
$\checkmark$ note the 2 because 2 moles of $\mathrm{H}_{2}$ disappear for every 1 mole of $\mathrm{O}_{2}$
$\mathrm{RR}_{\mathrm{H}_{2}}=\frac{-\mathrm{d}\left[\mathrm{H}_{2}\right]}{\mathrm{dt}}=2 \mathrm{k}\left[\mathrm{H}_{2}\right]^{2}\left[\mathrm{O}_{2}\right]$
or

$$
\mathrm{RR}_{\mathrm{O}_{2}}=\frac{-\mathrm{d}\left[\mathrm{O}_{2}\right]}{\mathrm{dt}}=\mathrm{k}\left[\mathrm{H}_{2}\right]^{2}\left[\mathrm{O}_{2}\right] .
$$

Clearly $\mathrm{H}_{2}$ must disappear at twice the rate of $\mathrm{O}_{2}$.
Similarly

$$
\mathrm{RR}_{\mathrm{H}}=\frac{-\mathrm{d}[\mathrm{H}]}{\mathrm{dt}}=2 \mathrm{k}[\mathrm{H}]^{3}
$$

Note: the reaction can be simple or complex.
For a "simple" (or "elementary") reaction: reaction occurs on a molecular level as written. e.g.

$$
\mathrm{H}+\mathrm{H}+\mathrm{H} \rightarrow \mathrm{H}_{2}+\mathrm{H} .
$$

In this case, the simple reaction implies that three atoms of hydrogen collide simultaneously and react to form one molecule of $\mathrm{H}_{2}$ and one hydrogen atom.

For "complex" reaction:
The reaction equation only defines overall process which may consist of a series of "simple" or "elementary" reactions
e.g.

$$
\mathrm{N}_{2}+\mathrm{O}_{2} \rightarrow 2 \mathrm{NO}
$$

This reaction does NOT occur by a molecule of oxygen colliding with a molecule of nitrogen, rather it occurs by a series of elementary reactions:

$$
\begin{aligned}
& \mathrm{O}_{2}+\mathrm{h} \gamma \rightarrow 2 \mathrm{O} \\
& \mathrm{O}+\mathrm{N}_{2} \rightarrow \mathrm{NO}+\mathrm{N} \\
& \mathrm{~N}+\mathrm{O}_{2} \rightarrow \mathrm{NO}+\mathrm{O} \\
& \mathrm{O}+\mathrm{O}+\mathrm{N}_{2} \rightarrow \mathrm{~N}_{2}+\mathrm{O}_{2} \\
& \mathrm{O}+\mathrm{O}+\mathrm{O}_{2} \rightarrow 2 \mathrm{O}_{2}
\end{aligned}
$$

But, we can write an overall reaction rate for the process of oxygen and nitrogen combining to form NO, i.e.

$$
-\frac{\mathrm{d}\left[\mathrm{O}_{2}\right]}{\mathrm{dt}}=\mathrm{k}\left[\mathrm{O}_{2}\right]\left[\mathrm{N}_{2}\right]
$$

sometimes called a "global" rate.

### 3.2 Arrhenius Rate Expression

For a "simple" reaction such as $A+B \rightarrow C+D$
e.g.

$$
\begin{aligned}
& \mathrm{O}+\mathrm{N}_{2} \rightarrow \mathrm{NO}+\mathrm{N} \\
& \mathrm{RR}=\frac{-\mathrm{d}[\mathrm{~A}]}{\mathrm{dt}}=\mathrm{k}[\mathrm{~A}][\mathrm{B}]=\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{dt}}
\end{aligned}
$$

This suggests that every collision of $A+B$ leads to products $C$ and $D$. Experimentally this is found not to be true.

Arrhenius postulated that only collisions with sufficiently high energy would produce a reaction, so Arrhenius said

$$
R R=Z_{A B} e^{-E / R T}
$$

where

$$
Z_{A B}=\text { collision frequency }
$$

and

$$
\mathrm{e}^{-\mathrm{E} / \mathrm{RT}}=\text { Boltzman factor }
$$

i.e. $R R=$ fraction of collision with energy greater the $E$.

So $E$ is some potential energy barrier that must be overcome before the reaction can proceed to products. This is illustrated in the graph below. The reactants $A$ and $B$ begin at some initial energy level. As they collide, if they have sufficient energy to overcome the energy barrier, $\mathrm{E}_{\mathrm{A}, \mathrm{f}}$, then they will react to products C and D and produce energy equal to $\Delta H_{R X N}$, i.e.


The collision frequency, $Z_{A B}$, comes from the kinetic theory of gases (i.e. the theory of molecular collision dynamics) and is given by:

$$
\mathrm{Z}_{\mathrm{AB}}=[\mathrm{A}][\mathrm{B}] \sigma_{\mathrm{AB}}{ }^{2}\left[\frac{8 \pi \mathrm{kT}}{\mu}\right]^{1 / 2}
$$

where $k=$ Boltzman constant,

$$
\begin{aligned}
& \sigma_{A B}=\text { collision cross section, and } \\
& \mu=\text { reduced mass }=\frac{m_{A} m_{B}}{m_{A}+m_{B}}
\end{aligned}
$$

so

$$
\mathrm{Z}_{\mathrm{AB}}=\mathrm{Z}_{\mathrm{AB}}^{\prime}[\mathrm{A}][\mathrm{B}]
$$

then

$$
R R=Z_{A B}{ }^{\prime} \mathrm{e}^{-\mathrm{E} / R T}[\mathrm{~A}][\mathrm{B}]=\mathrm{k}[\mathrm{~A}][\mathrm{B}]
$$

by comparison with law of mass action, the rate constant k is given by

$$
k=Z_{A B}^{\prime} e^{-E / R T}=Z_{A B}^{\prime \prime} T^{1 / 2} e^{-E / R T}
$$

Thus, $k=k(T)$ normally has a weak $T$ dependence and so $T^{1 / 2}$ is frequently absorbed into $Z_{A B}^{\prime \prime}$ especially for narrow $T$ ranges.

However, this result for $k$ still does not quite agree with experiment, since not every collision is of correct orientation so we introduce a steric factor, $P$, then

$$
k=Z_{A B}^{\prime \prime} T^{1 / 2} e^{-E / R T} P
$$

or the rate constant is given by
$k=A e^{-E / R T}$ where the $A$ factor is given by $A=Z_{A B}^{\prime \prime} T^{1 / 2} P$
From this equation for the rate constant then a plot of $\ln k$ vs. $1 / T$ should give a straight line with slope $=-E / R$


This is called an "Arrhenius Plot".
For example, for the reaction:

$$
\mathrm{D}_{2}+\mathrm{O} \rightarrow \mathrm{D}+\mathrm{OD}
$$

an Arrhenius plot of experimental data leads to the result

$$
\frac{E}{R}=4480^{\circ} R
$$

In some cases, i.e. low activation energy radical reactions, $A$ has stronger $T$ dependence then predicted by the theory, so we allow for an explicit dependence on temperature in the "pre-exponential" factor such that:


Using this form of the rate constant, Dryer et al predicted

$$
\mathrm{CO}+\mathrm{OH} \rightarrow \mathrm{CO}_{2}+\text { H reactions }
$$

strong temperature dependence

$$
\mathrm{k}=1.51 \times 10^{7} \mathrm{~T}^{1.3} \mathrm{e}^{+390 / \mathrm{T}}
$$

so most researchers adopt

$$
\mathrm{k}=A T^{\mathrm{n}} \mathrm{e}^{-\mathrm{E} / R T}
$$

so called "modified Arrhenius" form of the rate constant with

$$
2 \geq n \geq-2
$$

## Exercise 2.1:

Given the following data for the reaction $\mathrm{CO}+\mathrm{O}->\mathrm{CO}_{2}+\mathrm{O}$, make an Arrhenius plot and determine the activation energy of the reaction.

| $\frac{\mathrm{T}(\mathrm{K})}{1605}$ | $\mathrm{k}\left(\mathrm{cm}^{3} / \mathrm{mole}-\mathrm{sec}\right)$ |
| :---: | :---: |
| 1680 | 1.81 ee 6 |
| 1755 | 2.82 ee 7 |
| 1830 | 4.85 ee 7 |

### 3.3 Radical Recombination

A radical is a highly reactive species, usually a molecular fragment that is important to the propagation of combustion reactions. Some important radicals in combustion include $\mathrm{H}, \mathrm{O}$, $\mathrm{OH}, \mathrm{CH}, \mathrm{CH}_{2}$, etc. Since these radicals are often very energetic, when they recombine to form a stable molecule, they frequently need another atom or molecule to collide with them to remove sufficient excess energy to form a stable product. This additional atom or molecule is called a "third body" and is usually designated by M. An example of a radical recombination reaction is:

$$
\mathrm{H}+\mathrm{H}+\mathrm{M} \rightarrow \mathrm{H}_{2}+\mathrm{M}
$$

where M can be any other atom or molecule. These reactions normally have a weak negative temperature dependence i.e.

$$
\begin{aligned}
& \mathrm{O}+\mathrm{O}+\mathrm{M} \rightarrow \mathrm{O}_{2}+\mathrm{M} \\
& \mathrm{k}=1.9 \times 10^{13} \mathrm{e}^{9000} / \mathrm{T}
\end{aligned}
$$

Note the very weak T dependence as indicated by the very small activation energy.

### 3.4 Chemical Reactions of Various Orders

Chemical reactions can have different reaction "orders" depending upon the number of reactants. The reaction order is taken as the sum of the exponents of the reactant concentrations in the reaction rate expression. For example, the reaction

$$
\mathrm{CO}+\mathrm{O}_{2}->\mathrm{CO}_{2}+\mathrm{O}
$$

has a reaction rate given by

$$
\mathrm{RR}=\mathrm{k}[\mathrm{CO}]^{1}\left[\mathrm{O}_{2}\right]^{1}
$$

The sum of the exponents of the concentrations is $1+1=2$, so this is a second order reaction. In this section we will examine $1^{\text {st }}, 2^{\text {nd }}$ and $3^{\text {rd }}$ order reactions is some detail.

## First order reaction

$$
\begin{aligned}
& \mathrm{A}_{2} \xrightarrow{\mathrm{k}_{\mathrm{t}}} 2 \mathrm{~A} \\
& \frac{\mathrm{~d}[\mathrm{~A}]}{\mathrm{dt}}=2 \mathrm{k}_{\mathrm{f}}\left[\mathrm{~A}_{2}\right]=-2 \frac{\mathrm{~d}\left[\mathrm{~A}_{2}\right]}{\mathrm{dt}}
\end{aligned}
$$

we can solve this differential equation using separation of variables to get:

$$
\int_{\left[\mathrm{A}_{2}\right]_{0}}^{\left[\mathrm{A}_{2}\right]} \frac{\mathrm{d}\left[\mathrm{~A}_{2}\right]}{\left[\mathrm{A}_{2}\right]}=\mathrm{k}_{\mathrm{f}} \int_{0}^{\mathrm{t}} \mathrm{dt}
$$

which upon integration gives

$$
\ln \frac{\left[A_{2}\right]}{\left[A_{2}\right]_{0}}=-k_{f} t
$$

or

$$
\left[A_{2}\right]=\left[A_{2}\right]_{0} e^{-k_{t} t}
$$

so for a $1^{\text {st }}$ order reaction, the concentration of the reactant decreases exponentially with time.

## Pseudo first order reaction

A pseudo first order reaction is a reaction where one of the reactants is present in large excess compared to the other reactant such that its concentration does not change significantly with time. In this case, the concentration of the excess reactant can be assumed to be constant and is absorbed into the rate constant $k$ to give a pseudo first order rate constant $k^{\prime}=k[\mathrm{C}]$. For example:

$$
A+C \xrightarrow{k_{f}} D \quad \text { where }[C] \gg[A]
$$

then $\Delta[\mathrm{C}] \approx \mathrm{O}$, and so

$$
\frac{\mathrm{d}[\mathrm{~A}]}{\mathrm{dt}}=-\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{dt}}=-\mathrm{k}_{\mathrm{f}}[\mathrm{~A}][\mathrm{C}]=-\mathrm{k}^{\prime}[\mathrm{A}] \text { where } \mathrm{k}^{\prime}=\mathrm{k}[\mathrm{C}]
$$

then

$$
[\mathrm{A}]=[\mathrm{A}]_{0} \mathrm{e}^{-\mathrm{k}^{\prime} t}
$$

## Second order reactions

$$
\begin{aligned}
& \mathrm{A}+\mathrm{B} \rightarrow \mathrm{C}+\mathrm{D} \\
& \frac{-\mathrm{d}[\mathrm{~A}]}{\mathrm{dt}}=\frac{-\mathrm{d}[\mathrm{~B}]}{\mathrm{dt}}=\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{dt}}=\mathrm{k}[\mathrm{~A}][\mathrm{B}]
\end{aligned}
$$

if we take

$$
\begin{aligned}
& {[\mathrm{A}]=[\mathrm{A}]_{0}-[\mathrm{x}]} \\
& {[\mathrm{B}]=[\mathrm{B}]_{0}-[\mathrm{x}]}
\end{aligned}
$$

where $[\mathrm{x}]$ is concentration of $A$ or $B$ consumed and products produced, then

$$
\frac{\mathrm{d}[\mathrm{x}]}{\mathrm{dt}}=\mathrm{k}_{\mathrm{f}}\left([\mathrm{~A}]_{0}-[\mathrm{x}]\right)\left([\mathrm{B}]_{0}-[\mathrm{a}]\right)
$$

gives

$$
[\mathrm{x}]=\ln \left(\frac{[\mathrm{x}]-[\mathrm{B}]_{0}}{[\mathrm{x}]-[\mathrm{A}]_{0}}\right)+\mathrm{k}_{\mathrm{f}}\left([\mathrm{~B}]_{0}-[\mathrm{A}]_{0}\right) \mathrm{t}+\ln \left([\mathrm{B}]_{0} /[\mathrm{A}]_{0}\right)
$$

## Third order reactions

Virtually all third order reactions that we will be concerned about involve a third body M. Since $M$ can be any atom or molecule in the vicinity of the reaction, its concentration is approximately constant if the pressure is constant. So, for a third order reaction such as:

$$
A+A+M \rightarrow A_{2}+M
$$

The rate is given by

$$
\frac{\mathrm{d}\left[\mathrm{~A}_{2}\right]}{\mathrm{dt}}=\mathrm{k}[\mathrm{~A}]^{2}[\mathrm{M}]=\frac{-1}{2} \frac{\mathrm{~d}[\mathrm{~A}]}{\mathrm{dt}}
$$

But, if $[\mathrm{M}]$ is constant then this reaction becomes $2^{\text {nd }}$ order with a rate constant $k^{\prime}=k[\mathrm{M}]$.

### 3.5 Consecutive Reactions

Using different combinations of $1^{\text {st }}, 2^{\text {nd }}$, and/or $3^{\text {rd }}$ order reactions, we can construct more complex reaction schemes from a series of simple reactions. These reaction schemes generally involve either consecutive reactions or competitive reactions or combinations of both. We can use our knowledge of the individual reactions to obtain rate laws for the overall reaction scheme.

For consecutive reactions take the example of:

$$
\mathrm{A}+\mathrm{B} \xrightarrow{\mathrm{~K}_{1}} \mathrm{AB} \xrightarrow{\mathrm{~K}_{2}} \mathrm{C}+\mathrm{D}
$$

from first reaction

$$
\frac{\mathrm{d}[\mathrm{AB}]}{\mathrm{dt}}=\mathrm{k}_{1}[\mathrm{~A}][\mathrm{B}]
$$

from second reaction

$$
\frac{\mathrm{d}[\mathrm{AB}]}{\mathrm{dt}}=-\mathrm{k}_{2}[\mathrm{AB}]
$$

so

$$
\left(\frac{\mathrm{d}[\mathrm{AB}]}{\mathrm{dt}}\right)_{\mathrm{net}}=\mathrm{k}_{1}[\mathrm{~A}][\mathrm{B}]-\mathrm{k}_{2}[\mathrm{AB}]
$$



These figures show qualitatively the concentrations of the various species in the consecutive reaction scheme given above. Of particular note is the behavior of the intermediate, $A B$, which initially rises rapidly until a significant amount of reactants $A$ and $B$ are consumed and then decreases as the reaction of $A B$ to form $C+D$ overtakes the formation of $A B$.

## Example:

Determine expression for $[B]$ in the consecutive reaction

$$
\mathrm{A} \xrightarrow{\mathrm{k}_{1}} \mathrm{~B} \xrightarrow{\mathrm{k}_{2}} \mathrm{C}+\mathrm{D}
$$

## Solution:

$$
\frac{\mathrm{d}[\mathrm{~A}]}{\mathrm{dt}}=-\mathrm{k}_{1}[\mathrm{~A}]
$$

which upon integration gives

$$
[\mathrm{A}]=[\mathrm{A}]_{0} \mathrm{e}^{-k_{1} t}
$$

next

$$
\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{dt}}=\mathrm{k}_{2}[\mathrm{~B}]=\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{dt}}
$$

and

$$
\frac{\mathrm{d}[\mathrm{~B}]}{\mathrm{dt}}=\mathrm{k}_{1}[\mathrm{~A}]-\mathrm{k}_{2}[\mathrm{~B}]
$$

or

$$
\frac{\mathrm{d}[\mathrm{~B}]}{\mathrm{dt}}=\mathrm{k}_{1}[\mathrm{~A}]_{0} \mathrm{e}^{-\mathrm{k}_{1} \mathrm{t}}-\mathrm{k}_{2}[\mathrm{~B}]
$$

which integrates to

$$
[\mathrm{B}]=[\mathrm{A}]_{0} \frac{\mathrm{k}_{1}}{\mathrm{k}_{2}-\mathrm{k}_{1}}\left(\mathrm{e}^{-\mathrm{k}_{1} t}-\mathrm{e}^{-\mathrm{k}_{2} t}\right)
$$

since $[C]=[D],[C]$ is obtained from
$[\mathrm{A}]+[\mathrm{B}]+2[\mathrm{C}]=[\mathrm{A}]_{0}$

### 3.6 Competitive Reactions

In a competitive reaction scheme, the same reaction can lead to two different products or a given reactant can react with two different reactants to produce two different products. We can determine the rate law for the following competitive reaction scheme by analyzing the contribution from each of the competing reactions.

For

$$
\begin{aligned}
& A+B \xrightarrow{k_{1}} A B \\
& A+B \xrightarrow[k_{2}]{ } E+F
\end{aligned}
$$

From the first reaction we get

$$
\frac{\mathrm{d}[\mathrm{~A}]}{\mathrm{dt}}=-\mathrm{k}_{1}[\mathrm{~A}][\mathrm{B}]
$$

Second reaction gives us

$$
\frac{\mathrm{d}[\mathrm{~A}]}{\mathrm{dt}}=-\mathrm{k}_{2}[\mathrm{~A}][\mathrm{B}]
$$

By combining these two we get a net rate for the loss of reactant $A$ :

$$
\left(\frac{\mathrm{d}[\mathrm{~A}]}{\mathrm{dt}}\right)_{\mathrm{net}}=-\left(\mathrm{k}_{1}+\mathrm{k}_{2}\right)[\mathrm{A}][\mathrm{B}]
$$

Note: this gives an apparent rate constant for the disappearance of $A+B$ by $k_{f=}\left(\mathrm{k}_{1}+\mathrm{k}_{2}\right)$; however, since the rates may have very different $E_{A}$ and $T$ dependence this result can not readily be extrapolated to other temperatures.

### 3.7 Opposing Reactions

All reactions can proceed in both the forward and reverse directions, although one direction may have a much faster rate than the reverse reaction. The reverse reaction is sometimes called the opposing reaction. Again we can apply our knowledge of elementary reactions to this opposing reaction scheme. For the reactions:

$$
\mathrm{A}+\mathrm{B} \underset{\mathrm{k}_{\mathrm{b}}}{\stackrel{k_{\mathrm{f}}}{\leftrightarrows}} \mathrm{C}+\mathrm{D}
$$

In this reaction scheme, $A$ is removed by the reaction of $A+B$, but $A$ is formed by the reverse reaction of C+D, so from the forward reaction

$$
\frac{-\mathrm{d}[\mathrm{~A}]}{\mathrm{dt}}=\mathrm{k}_{\mathrm{f}}[\mathrm{~A}][\mathrm{B}]
$$

and from the reverse (or opposing reaction)

$$
\frac{-\mathrm{d}[\mathrm{~A}]}{\mathrm{dt}}=-\mathrm{k}_{\mathrm{b}}[\mathrm{C}][\mathrm{D}]
$$

So the net removal of $A$ is given by:

$$
-\left(\frac{\mathrm{d}[\mathrm{~A}]}{\mathrm{dt}}\right)_{\mathrm{net}}=\mathrm{k}_{\mathrm{f}}[\mathrm{~A}][\mathrm{B}]-\mathrm{k}_{\mathrm{b}}[\mathrm{C}][\mathrm{D}]
$$

note at equilibrium the forward and reverse reaction must be equal and the net rate of disappearance of A must be zero. That is,

$$
\mathrm{RR}_{\mathrm{f}}=\mathrm{RR}_{\mathrm{b}} \circ \mathrm{or}\left(\frac{\mathrm{~d}[\mathrm{~A}]}{\mathrm{dt}}\right)_{\mathrm{net}}=0
$$

so

$$
\frac{\mathrm{k}_{\mathrm{f}}}{\mathrm{k}_{\mathrm{b}}}=\frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]}=\mathrm{K}_{\mathrm{eq}}
$$

In other words, the equilibrium constant (which is a thermodynamic property of the system) is equal to the ratio of the forward and reverse rate constants for a given reaction. Note that in general $K_{e q}$ is much better known than $k_{f}$ or $k_{b}$. Thus, one usually obtains the reverse reaction rate constant from the best measured rate constant and $\mathrm{K}_{\text {eq }}$ using
e.g.

$$
\mathrm{k}_{\mathrm{b}}=\frac{\mathrm{k}_{\mathrm{f}}}{\mathrm{~K}_{\mathrm{eq}}}
$$

if $\mathrm{k}_{\mathrm{f}}$ is known at a series of $T$ 's, $\mathrm{k}_{\mathrm{b}}$ can be calculated and an apparent $E_{A}$ can be determined from an Arrhenius plot.

### 3.8 Steady State Approximation

When there is a consecutive reaction scheme such as $A+B \xrightarrow{k_{1}} C+D \xrightarrow{k_{2}} E+F$, the intermediates are frequently radicals which exist only at very low concentrations. The rate of formation and destruction of these radical intermediates is frequently much greater than the absolute rate of change of their concentrations. In such a case one can use the "steady-state approximation" in order to obtain a rate law that only includes stable species that can be more readily measured.
This approximation says that for a radical intermediate, $\mathrm{C}, \frac{\mathrm{d}[\mathrm{C}]}{\mathrm{dt}} \approx 0$. In this case one can write an expression for [C]ss by

$$
\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{dt}}=\mathrm{k}_{1}[\mathrm{~A}][\mathrm{B}]-\mathrm{k}_{2}[\mathrm{C}][\mathrm{D}]
$$

but since at steady-state

$$
\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{dt}} \approx 0
$$

then

$$
[\mathrm{C}] \mathrm{ss}=\frac{\mathrm{k}_{1}}{\mathrm{k}_{2}} \frac{[\mathrm{~A}][\mathrm{B}]}{[\mathrm{D}]}
$$

In this way radicals that are hard to measure can be eliminated from the rate law.
For a steady-state species, a qualitative graph of the species as a function of time looks like:


### 3.9 Chain Reactions

An overall reaction statement can be very misleading since many reactions are actually chain mechanisms. Chain mechanisms have three main parts:

Initiation: usually to form one or more radicals

$$
\text { i.e. } A_{2} \rightarrow 2 \mathrm{~A}
$$

Chain propagation: radicals \& stable molecules $\rightarrow$ other radicals \& stable molecules

$$
\left.\begin{array}{r}
\text { i.e. } A \cdot+B_{2} \rightarrow A B+B \cdot \\
B \cdot+A_{2} \rightarrow A B+A \cdot \\
\left\{\begin{array}{r}
A \cdot+A B \\
B \cdot+A B
\end{array}\right\} A_{2}+B \cdot A \cdot
\end{array}\right\} \text { Usuallv fast }
$$

(could also have radical and stable combining to form two radicals such as $A \cdot+C_{2} \rightarrow A C \cdot+C \cdot$, as we will see shortly such reactions are explosive)

Chain termination : radical + radical to form stable molecule
$\left.\begin{array}{l}M+2 A \cdot \rightarrow A_{2}+M \\ M+2 B \cdot \rightarrow B_{2}+M\end{array}\right\}$ pressure dependant
Many apparently simple reactions are actually comprised of chain reactions. Such chain reaction mechanisms are important in initiation of combustion as well as in extinguishment. An example of a chain mechanism is given below.

### 3.10 Hydrogen-Bromine Reaction

An example of a reaction that appears simple but is a complex chain reaction is the reaction to form HBr from hydrogen and bromine as shown below.

$$
\mathrm{H}_{2}+\mathrm{Br}_{2} \rightarrow 2 \mathrm{HBr}
$$

Despite the simple appearance of this reaction, the experimental rate law has been determined to be:

$$
\frac{\mathrm{d}[\mathrm{HBr}]}{\mathrm{dt}}=\frac{\mathrm{a}_{1}\left[\mathrm{H}_{2}\right]\left[\mathrm{Br}_{2}\right]^{1 / 2}}{1+\frac{[\mathrm{HBr}]}{\mathrm{a}_{2}\left[\mathrm{Br}_{2}\right]}}
$$

Clearly, this is not a simple reaction since the simple reaction would give $\mathrm{d}[\mathrm{HBr}] / \mathrm{dt}=2\left[\mathrm{H}_{2}\right]\left[\mathrm{Br}_{2}\right]$. A more complex reaction scheme has been proposed for this reaction to explain this complex rate law as we will see in the next section.

### 3.11 Proposed Reaction Scheme

The proposed reaction scheme for formation of HBr from hydrogen and bromine is:
(or $h v$ )
$\mathrm{M}+\mathrm{Br}_{2} \xrightarrow{\mathrm{k}_{1}} 2 \mathrm{Br} \cdot+\mathrm{M}$ chain-initiation


Reverse is Very slow

$$
\mathrm{M}+2 \mathrm{Br} \cdot \xrightarrow{\mathrm{k}_{5}} \mathrm{Br}_{2}+\mathrm{M}
$$

chain termination.

$$
\left(\mathrm{M}+2 \mathrm{H} \cdot \rightarrow \mathrm{H}_{2}+\mathrm{M}\right) \quad \text { not important at low } T
$$

Note: since $\mathrm{Br}_{2}$ bond energy $46 \mathrm{kcal} /$ mole and $\mathrm{H}_{2}$ bond energy $104 \mathrm{kcal} / \mathrm{mole}$ the initiation reaction is always:

$$
\mathrm{Br}_{2} \rightarrow 2 \mathrm{Br}
$$

We can write an expression for formation of HBr by the propped mechanisms as follows:

$$
\frac{\mathrm{d}[\mathrm{HBr}]}{\mathrm{dt}}=\mathrm{k}_{2}[\mathrm{Br}]\left[\mathrm{H}_{2}\right]+\mathrm{k}_{3}[\mathrm{H}]\left[\mathrm{Br}_{2}\right]-\mathrm{k}_{4}[\mathrm{H}][\mathrm{HBr}]
$$

In order to compare the proposed reaction scheme to the experimental rate law given above, we can eliminate $[\mathrm{H}]$ and $[\mathrm{Br}]$ by using the Steady State assumption and then develop a rate law for HBr that depends only on stable species. Applying the steady state assumption we get:

$$
\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{dt}}=\mathrm{k}_{2}[\mathrm{Br}]\left[\mathrm{H}_{2}\right]-\mathrm{k}_{3}[\mathrm{H}]\left[\mathrm{Br}_{2}\right]-\mathrm{k}_{4}[\mathrm{H}][\mathrm{HBR}] \approx 0
$$

and

$$
\frac{\mathrm{d}[\mathrm{Br}]}{\mathrm{dt}}=2 \mathrm{k}_{1}[\mathrm{M}]\left[\mathrm{Br}_{2}\right]-\mathrm{k}_{2}[\mathrm{Br}]\left[\mathrm{H}_{2}\right]+\mathrm{k}_{3}[\mathrm{H}]\left[\mathrm{Br}_{2}\right]+\mathrm{k}_{4}[\mathrm{H}][\mathrm{HBr}]-2 \mathrm{k}_{5}[\mathrm{M}][\mathrm{Br}]^{2} \approx 0
$$

so

$$
\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{dt}} \approx 0 \approx \frac{\mathrm{~d}[\mathrm{Br}]}{\mathrm{dt}} \text { when }[\mathrm{H}]=[\mathrm{H}]_{\mathrm{ss}} \text { and }[\mathrm{Br}]=[\mathrm{Br}]_{\mathrm{ss}}
$$

We can set the equations for formation of H and Br equal (since they are both equal to zero) and eliminate $[\mathrm{H}]_{\mathrm{ss}}$ to get

$$
[\mathrm{Br}]_{\mathrm{ss}}^{2}=\frac{\mathrm{k}_{1}}{\mathrm{k}_{5}}\left[\mathrm{Br}_{2}\right]
$$

or

$$
[\mathrm{Br}]_{\mathrm{ss}}=\sqrt{\frac{\mathrm{k}_{1}}{\mathrm{k}_{5}}}\left[\mathrm{Br}_{2}\right]^{1 / 2}
$$

and then

$$
[\mathrm{H}]_{\mathrm{ss}}=\frac{\mathrm{k}_{2}[\mathrm{Br}]_{\mathrm{ss}}\left[\mathrm{H}_{2}\right]}{\mathrm{k}_{3}\left[\mathrm{Br}_{2}\right]+\mathrm{k}_{4}[\mathrm{HBr}]}
$$

Thus, we get the following rate law based on the proposed chain mechanism:

$$
\frac{\mathrm{d}[\mathrm{HBr}]}{\mathrm{dt}}=\frac{2 \mathrm{k}_{2}\left(\mathrm{k}_{1} / \mathrm{k}_{5}\right)^{1 / 2}\left[\mathrm{H}_{2}\right]\left[\mathrm{Br}_{2}\right]^{1 / 2}}{1+\frac{\mathrm{k}_{4}[\mathrm{HBr}]}{\mathrm{k}_{3}\left[\mathrm{Br}_{2}\right]}}
$$

Note, this matches the experimental result with

$$
\begin{aligned}
& a_{1}=2 k_{2}\left(\frac{k_{1}}{k_{5}}\right)^{1 / 2} \\
& a_{2}=\frac{k_{3}}{k_{4}}
\end{aligned}
$$

Thus, the mechanism is "consistent with" the experimental data and shows the truly complex nature of the apparently "simple" reaction for formation of HBr .

Note: at early times $[\mathrm{HBr}] \approx 0$ so this rate law gives

$$
\frac{\mathrm{d}[\mathrm{HBr}]}{\mathrm{dt}}=\mathrm{k}\left[\mathrm{H}_{2}\right][\mathrm{Br}]^{1 / 2} \quad 11 / 2 \text { order }
$$

and at late times

$$
\frac{[\mathrm{HBr}]}{\mathrm{Br}_{2}} \gg 1
$$

so, again the rate is one and a half order:

$$
\frac{\mathrm{d}[\mathrm{HBr}]}{\mathrm{dt}}=\mathrm{k} \cdot \frac{\left[\mathrm{H}_{2}\right]\left[\mathrm{Br}_{2}\right]^{3 / 2}}{[\mathrm{HBr}]} \text { order } 11 / 2
$$

Thus, for complex reactions the order changes with time and is not necessarily integer.

### 3.12 Partial Equilibrium Assumption

Some rates to interchange species are much faster than the rates that deplete these species. In this case a partial equilibrium is observed for the fast reaction.
E.g. $\mathrm{CO}+\mathrm{OH} \rightarrow \mathrm{CO}_{2}+\mathrm{H}$

$$
\frac{\mathrm{d}\left[\mathrm{CO}_{2}\right]}{\mathrm{dt}}=-\frac{\mathrm{d}[\mathrm{CO}]}{\mathrm{dt}}=\mathrm{k}[\mathrm{CO}][\mathrm{OH}]
$$

$[\mathrm{OH}]$ is hard to measure, can we eliminate it by using stable species? Assume $\mathrm{H}, \mathrm{OH}, \mathrm{H}_{2}, \mathrm{O}_{2}, \mathrm{H}_{2} \mathrm{O}$ system in partial equilibrium. The reaction

$$
\frac{1}{2} \mathrm{H}_{2}+\frac{1}{2} \mathrm{O}_{2} \Leftrightarrow \mathrm{OH}
$$

and

$$
\mathrm{H}_{2}+\frac{1}{2} \mathrm{O}_{2} \Leftrightarrow \mathrm{H}_{2} \mathrm{O}
$$

are equilibrated. We can write an equilibrium expression as

$$
\mathrm{K}_{\mathrm{OH}}^{2}=\frac{[\mathrm{OH}]_{\mathrm{eq}}^{2}}{\left[\mathrm{H}_{2}\right]_{\mathrm{eq}}\left[\mathrm{O}_{2}\right]_{\mathrm{eq}}}
$$

and

$$
\mathrm{K}_{\mathrm{H}_{2} \mathrm{O}}=\frac{\left[\mathrm{H}_{2} \mathrm{O}\right]_{\mathrm{eq}}}{\left[\mathrm{H}_{2}\right]_{\mathrm{eq}}\left[\mathrm{O}_{2}\right]_{\mathrm{eq}}^{1 / 2}}
$$

Solving for $[\mathrm{OH}]_{\text {eq }}$ gives

$$
[\mathrm{OH}]_{\mathrm{eq}}=\left[\mathrm{H}_{2} \mathrm{O}\right]^{1 / 2}\left[\mathrm{O}_{2}\right]^{1 / 4}\left(\frac{\mathrm{~K}_{\mathrm{OH}}^{2}}{\mathrm{~K}_{\mathrm{H}_{2} \mathrm{O}}}\right)^{1 / 2}
$$

then

$$
\frac{\mathrm{d}\left[\mathrm{CO}_{2}\right]}{\mathrm{dt}}=\mathrm{k}\left[\frac{\mathrm{~K}_{\mathrm{OH}}^{2}}{\mathrm{~K}_{\mathrm{H}_{2} \mathrm{O}}}\right]^{1 / 2}[\mathrm{CO}]\left[\mathrm{H}_{2} \mathrm{O}\right]^{1 / 2}\left[\mathrm{O}_{2}\right]^{1 / 4}
$$

This agrees with experimental results.

## Exercise 2.2:

In over ventilated flaming combustion, temperatures in the region where CO is converted to $\mathrm{CO}_{2}$ are around 1500 C . In smoldering combustion, the temperatures in the CO to $\mathrm{CO}_{2}$ conversion region can be as low as 500C. Assuming that both the flaming and smoldering combustion takes place in room air (i.e. $21 \% \mathrm{O}_{2}$ ) and that the $[\mathrm{CO}]=\left[\mathrm{H}_{2} \mathrm{O}\right]$. Using the rate expression given above for conversion of CO to $\mathrm{CO}_{2}$, what can you say about the relative rates of removal of CO from a smoldering fire as compared with a flaming fire? Now assume the flaming fire is under ventilated such that $\left[\mathrm{O}_{2}\right]=1$ ee- -4 . How does this flaming rate of CO consumption compared to the other two cases. What does this tell us about net CO production in fires?

### 4.0 Explosion Reactions

Now that we have reviewed chemical kinetics, we can use this information to look at two different types of explosions:

Thermal explosions: exponential increase in rates due to exothermic reactions
Chain Branching explosions: rates increase rapidly due to chain branching

## Thermal Explosions

Thermal explosions occur because of the exponential dependence on temperature of the rates of combustion reactions. In an adiabatic system (i.e. no heat loss) any exothermic reaction will cause the environment to increase in temperature. This increase in temperature will cause an increase in reaction rate through the exponential term in the Arrhenius expression for the rate constant. This increase in rate will lead to a still greater increase in temperature which will in turn further increase the reaction rate. Thus, in an adiabatic system, initiation of any exothermic reaction will lead to a thermal explosion. In practice, thermal explosions involve a trade-off between heat gain from the reaction and heat loss to the surroundings. As we will see below, this model of the thermal explosions will be useful in examining ignition of flames and in understanding the process of self-heating.

## Chain Branching Explosions

A chain branching explosion is one that occurs isothermally as a result of the generation of radicals (it is similar to a nuclear chain reaction). As an example, let us consider a 1 cc container at room temperature and pressure that supports a chain reaction.

Example: $1 \mathrm{~cm}^{3}$ container with 1 chain particle i.e. radical
At normal conditions, $\mathrm{N} / \mathrm{V}=10^{19} \mathrm{molecules} / \mathrm{cc}$ and $Z=10^{8}$ collisions $/ \mathrm{sec}$.
We can define a chain branching ratio, $\alpha$, such that $\alpha$ is the number of radicals that are generated for each radical that reacts in a chain branching reaction.
i.e. $R+S->\alpha R+S '$

For the case of a chain carrying reaction, $\quad \alpha=1.0$ (i.e. 1 radical creates 1 radical).
We can then calculate how long it will take for all of the molecules in our 1cc of gas to react:

$$
\mathrm{t}=\frac{10^{19} \mathrm{coll}}{10^{8} \mathrm{coll} / \mathrm{sec}}=10^{11} \mathrm{sec} \approx 30,000 \text { years }
$$

Now if $\alpha=2.0$ we have a condition where we are multiplying the number of radicals with each collision such that the number of generation of collisions necessary for all molecules to react is given by the expression

$$
\frac{2^{N+1}-1}{2-1}=10^{19} \text { molecules }
$$

solving gives $\mathrm{N}=64$ generations of collisions for all molecules to react, therefore in this case Z $=64$ collisions $\times 10^{-8} \mathrm{sec} /$ collision $\approx 10^{-6} \mathrm{sec}=1 \mu \mathrm{sec}$

Thus, if the reaction is exothermic or creates more molecules of products than reactants, the system is explosive. However, even a small branching ratio, $\alpha$, can cause an explosive result. Consider the case where $\alpha=1.01$.

For $\alpha=1.01$ the number of generations of collisions is given by:

$$
\frac{\alpha^{\mathrm{N}+1}-1}{\alpha-1}=\frac{1.01^{\mathrm{N}+1}}{0.01}=10^{19}
$$

Solving for N gives $\mathrm{N}=3934$ which leads to a time for the complete reaction in 1 cc of

$$
t \approx 40 \mu \mathrm{sec}
$$

So even for very low branching ratio, $\alpha$, reaction is very fast.

## Chain Explosion Mechanism

Let us now examine more closely a chain explosion mechanism using our understanding of kinetic mechanisms and reactions. Consider the following chain explosion mechanism where $P$ is a stable product, $R$ is a radical and $\alpha$ is the chain branching ratio (i.e. the number of radicals generated for each radical consumed in the chain branching reaction):

$$
\begin{aligned}
& \left.\begin{array}{l}
\mathrm{M} \xrightarrow{k_{1}} \mathrm{R} \\
\mathrm{R}+\mathrm{M} \rightarrow \alpha \mathrm{R}+\mathrm{M}^{*} \quad \begin{array}{l}
\text { initiation reaction } \\
\text { chain-branching }
\end{array} \\
\mathrm{R}+\mathrm{M} \xrightarrow{k_{3}} \mathrm{P}+\mathrm{R} \\
\mathrm{R} \xrightarrow[k_{4}]{\mathrm{k}_{4}} \mathrm{M} \quad \text { wall } \\
\mathrm{R} \xrightarrow{k_{5}} \text { non reactive }
\end{array}\right\} \text { chain termination }
\end{aligned}
$$

In this mechanism, some of the reactions of radicals lead to chain termination, so the determining factor for whether this system will be explosive or not is the relative rates of the branching reaction and the chain terminating reactions. We can analyze this mechanism to determine the value of $\alpha$ that is necessary in order to cause an explosion. We can write the following rate expressions:

$$
\begin{aligned}
& \frac{d[P]}{d t}=k_{3}[R][M] \\
& \frac{d[R]}{d t}=k_{1}[M]+k_{2}(\alpha-1)[R][M]-k_{4}[M][R]-k_{5}[R]
\end{aligned}
$$

and apply the steady-state assumption on R

$$
\begin{aligned}
& \frac{d[R]}{d t}=0 \\
& {[R]_{s s}=\frac{k_{1}[M]}{k_{4}[M]+k_{5}-k_{2}(\alpha-1)[M]}}
\end{aligned}
$$

then

$$
\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{dt}}=\frac{\mathrm{k}_{1} \mathrm{k}_{3}[\mathrm{M}]^{2}}{\mathrm{k}_{4}[\mathrm{M}]+\mathrm{k}_{5}-\mathrm{k}_{2}(\alpha-1)[\mathrm{M}]}
$$

Examination of this expression shows that when the denominator $\rightarrow 0 \Rightarrow$ explosive, since the rate of production of product will be infinite. So we can solve for a when the denominator is zero to get the critical $\alpha$ for the system to be explosive.

$$
\alpha_{\text {crit }}=1+\frac{\mathrm{k}_{4}(\mathrm{M})+\mathrm{k}_{5}}{\mathrm{k}_{2}[\mathrm{M}]}
$$

thus

$$
\begin{array}{ll}
\alpha \geq \alpha_{\text {crit }} & \text { chain-branch explosion } \\
\alpha<\alpha_{\text {crit }} & \text { no explosion }
\end{array}
$$

In summary, chain branching explosions occur when the rate of generation of radicals exceeds their rate of removal by chain terminating steps. As can be seen in the expression for $\alpha_{\text {crit }}$ above, the value of $\alpha_{\text {crit }}$ can change as a result of changes in temperature (through the rate constants) or changes in pressure (through the value of [M]). Thus, a system that is not explosive at one temperature or pressure can become explosive at another condition.

### 5.0 I gnition

## Thermal Homogeneous I gnition

The ignition of gaseous mixtures often can be explained in terms of a thermal explosion model based on an energy balance on the fuel/oxidizer mixture as we discussed above. The overall combustion reaction is exothermic, which increases the gas temperature. Since the reaction rate increases with temperature, the overall energy release rate tends to increase, which results in a further increase in temperature and a subsequent acceleration of the reaction. Hence, the thermal model assumes that ignition (explosion) occurs as a result of self-heating. In an adiabatic system, the occurrence of any exothermic reaction always results in thermal ignition. However, in non-adiabatic systems heat losses remove some of the energy released by the chemical reaction. If those losses are sufficiently high, the temperature of the reacting mixture will decrease and the reaction will be quenched and ignition will not occur.

A simple description of the thermal ignition processes involves writing the energy equation for a homogeneous fuel-oxidizer mixture in an enclosed vessel of volume, $V$, immersed in a bath of uniform and constant vessel wall temperature, $T_{o}$.


$$
\begin{equation*}
\underbrace{\dot{\mathrm{q}}_{\mathrm{r}} \mathrm{~V}}_{\text {Generation }}-\underbrace{\rho \mathrm{C}_{\mathrm{v}} \mathrm{~V} \frac{\mathrm{dT}}{\mathrm{dt}}}_{\text {Storage }}-\underbrace{\mathrm{hS}\left(\mathrm{~T}-\mathrm{T}_{0}\right)}_{\text {Loss }}=0 \tag{M2-1}
\end{equation*}
$$

Here, the heat added is given by the fuel consumed times the heat of combustion as:

$$
\dot{\mathrm{q}}_{\mathrm{r}}=-\dot{\mathrm{C}}_{\mathrm{f}} \Delta \mathrm{H}_{\mathrm{C}}^{\circ}=-\frac{\mathrm{d}[\mathrm{~F}]}{\mathrm{dt}} \Delta \mathrm{H}_{\mathrm{C}}^{\circ}
$$

and the rate of consumption of the fuel is given by the global reaction rate of the fuel and oxidizer as:

$$
-\dot{C}_{f}=C_{f}^{m} C_{o}^{n} A T^{b} e^{(-E / R T)}=\frac{-d[F]}{d t}=[F]^{m}[O]^{n} A T^{b} e^{(-E / R T)}
$$

The storage term is given by the increase in the temperature times the heat capacity and the loss term is given by a heat transfer coefficient times the surface area of the vessel and the temperature difference between the gas temperature and the wall temperature.
For an isothermal system, $\mathrm{dT} / \mathrm{dt}=0$, and ignition can occur only by chain initiation. For an
adiabatic system, the heat loss term is zero, and $d T / d t>0$. Since $q_{r}$ is a monotonically increasing function of temperature, the system always exhibits explosive behavior. In practice, systems are between these two extremes, and whether explosions occur or not depend on the relative magnitude of the heat generation and heat loss terms. We can rewrite equation (M2-1) by dividing by the volume, V , as:

$$
\underbrace{\rho \mathrm{C}_{\mathrm{v}} \frac{\mathrm{dT}}{\mathrm{dt}}}_{\text {Storage }}=\underbrace{\dot{q}_{\mathrm{r}}}_{\text {EnergyGeneration }}-\underbrace{\frac{\mathrm{hS}}{\mathrm{~V}}\left(\mathrm{~T}-\mathrm{T}_{\mathrm{o}}\right)}_{\text {EnergyLoss }}
$$

or taking the energy loss term as $\dot{q}_{1}$, as

$$
\rho C_{v} \frac{d T}{d t}=\dot{q}_{r}-\dot{q}_{l}
$$

Hence, for a thermal explosion to occur, $d T / d t>0$, which implies $\dot{q}_{r}>\dot{q}_{1}$
For a fixed reactant concentration and $\frac{h S}{V}$ (i.e. geometry dependant), we can plot $\dot{q}_{\mathrm{r}}$ and $\dot{\mathrm{q}_{1}}$ as functions of $T$, the temperature of the reactant mixture.


As shown in the figure, for a given $T_{0}, \dot{q}_{l}$ is a linear function of $T$ (i.e. the straight lines on the graph), while $\dot{\mathrm{q}}_{\mathrm{r}}$ is exponential in $T$ due its dependence on the reaction rate (i.e. the curve on the graph). For $T_{0}=T_{3}, \dot{q}_{r}$ always exceeds $\dot{q}_{I}$ and an explosion always occurs. For $T_{0}$ = T1, two possible solutions exist fro the point at which the energy lose equals the energy gain, a stable solution corresponding to a slow reaction and a meta-stable solution. At the stable condition any perturbation in T tends to alter the energy balance in a way which will restore the system to the initial condition. At the meta-stable point, any perturbation will cause a departure either to the slow reaction condition or to explosion. Physically, slow reaction (stable solution) is most likely and, hence, for $\mathrm{T}_{1}$ there will be no ignition. The situation for $T=T_{2}$ represents the boundary between the two cases described above, and hence defines the critical ignition condition. For $T o<T_{2}, \dot{\mathrm{q}}_{\mathrm{r}}<\dot{\mathrm{q}}_{1}$ and there will be no ignition. For $T_{o} \geq T_{2}, \quad \dot{q}_{r} \geq \dot{q}_{l}$ and ignition will always occur. Hence, $T_{o}=T_{2}$ represents the minimum To for ignition. The tangency point, where $T_{o}=T_{C}$ is termed the critical point, and TC is termed the critical (spontaneous) ignition temperature. For $T=T_{c}, \dot{\mathrm{q}}_{\mathrm{r}}=\dot{\mathrm{q}}_{\mathrm{l}}$.

Increasing the energy loss can result in an explosive situation becoming non-explosive due to quenching. Since,

$$
\dot{\mathrm{q}}_{1}=\frac{\mathrm{hS}}{\mathrm{~V}}\left(\mathrm{~T}-\mathrm{T}_{\mathrm{o}}\right)
$$

an increase in $S / V$, surface/volume ratio (i.e. a decrease in vessel size) or in the heat transfer coefficient, $h$, can lead to quenching. This can be seen in the figure below where increasing the heat transfer coefficient or the surface to volume ratio changes the slope of the loss line such that a condition that was initially explosive becomes non-explosive.


For a fixed $T_{o}$ and reactant concentration (stoichiometry and pressure), there is a minimum vessel size below which explosion cannot occur. The characteristic dimension of the critical vessel is termed the quenching distance. Note that the flammability characteristics of a fuel/oxidizer mixture depend on vessel geometry.

For a fixed heat loss parameter, $\frac{\mathrm{hS}}{\mathrm{V}}$, fuel/oxidizer ratio and $T_{o}$, increasing pressure will increase $\dot{\mathrm{q}}_{\mathrm{r}}$

$$
\dot{\mathrm{q}}_{\mathrm{r}} \approx \mathrm{C}_{\mathrm{f}}^{m} \mathrm{C}_{\mathrm{o}}^{\mathrm{n}} \approx \mathrm{C}_{\text {total }}^{m+n}\left(\mathrm{x}_{\mathrm{f}}^{m} \mathrm{x}_{\mathrm{o}}^{n}\right) \approx \mathrm{p}^{m+n}
$$

Hence, in general, thermal explosion theory predicts an increasing tendency to ignition (explosion) with increasing pressure.

Since $\dot{q}_{r}$ depends on $\Delta H_{R}^{\circ}$ (which depends on stoichiometry), explosion limits will depend on stoichiometry. A plot of $\Delta H_{R}^{\circ}$ versus stoichiometry is shown below.


Stoichiometric
Hence, the tendency for explosion is greatest near the stoichiometric fuel/air ratio. Lean and rich mixtures have reduced $\Delta H_{R}^{\circ}$. As the mixture becomes very lean or very rich, $q_{r}$ decreases to the point that $\dot{q}_{r}<\dot{q}_{1}$ and explosion is not possible for the given $P, T_{o}$ and $h S / V$, and the mixture lies outside the explosion limits. The explosion limits occur at both the rich and lean limits for $\dot{q}_{r}=\dot{q}_{1}$.

### 6.0 Self-Heating

You have probably heard of the classic problem of oil soak rags self-heating to spontaneous combustion. Now that we have reviewed chemical kinetics and ignition we are ready to apply our knowledge to understanding the process of self-heating. We would like to be able to understand why some system self-heat but others do not. This is particularly confounding when the systems appear to be similar. For example, why is a pile of rags that have been
used to stain wood likely to spontaneously combust and a similar pile of rags covered with motor oil unlikely to combust? To answer this and similar question, we need to understand the process that governs self-heating.

Spontaneous ignition of a fuel results from the self-heating of the material induced by a chemical reaction that produces more heat than the heat losses. This process is very similar to a thermal explosion and we will see that we can use the theory of thermal explosions to understand and analyze the process of self-heating. As with thermal explosions, self-heating to spontaneous ignition is governed by a balance between heat losses to the surroundings and heat gain from the self-heating reaction. The energy balance is given in mathematical terms as (note $\lambda$ is used for thermal conductivity to differentiate it from the rate constant, $k$ ):

$$
\underbrace{\rho C_{p}\left(\frac{\partial T}{\partial t}\right)}_{\text {Storage }}=\underbrace{\Delta H_{c}^{\circ} A C_{f}^{m} C_{o}^{n} T^{b} e^{\left(\frac{-E}{R T_{c}}\right)}}_{\text {Generation }}-\underbrace{\left[\rho C_{p}\left(u \frac{\partial T}{\partial x}+v \frac{\partial T}{\partial y}\right)-\lambda\left(\frac{\partial^{2} T}{\partial \mathbf{x}^{2}}+\frac{\partial^{2} T}{\partial \mathbf{y}^{2}}\right)\right]}_{\text {Losses }}
$$

Just as in the case of homogeneous thermal ignition, ignition by self-heating involves a balance between heat generation by an exothermic reaction and heat loss to the surroundings. As with thermal explosions, if the system has an exothermic reaction (no matter how slow) and the system is adiabatic (i.e. no heat losses), the system will always self-heat to spontaneous combustion. However, in the real world, there are always heat losses so many slow exothermic reactions do not lead to spontaneous combustion. By solving the energy balance given above we can determine if a system is capable of selfheating.

This equation is very complex and cannot be readily solved for real geometries. To simplify the problem, Frank-Kamenetski proposed that self-heating generally occurs in the interior of piles of materials such that convective heat loss is small compared to conductive heat loss. Therefore, Frank-Kamenetski theorized that the critical condition for spontaneous ignition was the temperature where conduction heat losses from the pile are just equal to the energy generated by the combustion reaction. In Frank-Kamenetski's analysis, the critical temperature for self-heating to spontaneous combustion is obtained through the solution to the following equation:

$$
\begin{equation*}
\lambda\left(\frac{\partial^{2} \mathbf{T}}{\partial \mathbf{x}^{2}}+\frac{\partial^{2} \mathbf{T}}{\partial \mathbf{y}^{2}}\right)+\Delta H_{c}^{o} C_{f}^{m} C_{o}^{n} e^{\left(\frac{-E}{R T_{c}}\right)}=0 \tag{M2-2}
\end{equation*}
$$

This form of the energy balance includes a more realistic model of heat transfer within the reacting solid (or pile) by incorporating Fourier's law of heat conduction which allows for variations of temperature within the self-heating body to be calculated. Unfortunately, this approach still requires the solution of a non-linear partial differential equation. Inherent in this form of the energy equation and Frank-Kamenetski's solution are the following assumptions.

- The material is homogeneous and it properties do not change with temperature;
- Sufficiently large heats of reaction and activation energies such that E/RT>>1;
- Self-heating reaction can be characterized by a single global reaction with an Arrhenius rate;
- Neglects fuel consumption (i.e. there is an unlimited supply of fuel during the selfheating process);
- Boundary condition $T=T_{\text {ambient }}$ on walls of boundary (i.e. assumes instantaneous transfer of heat from surface of the body to the surroundings);

Equation (M2-2) is still not readily solved analytically. However, by using an approximation to the Arrhenius function, the modified equation can be solved analytically for a onedimensional infinite slab of material. This same approximation was later shown to hold for an infinite cylinder. Equation (M2-2) can be recast by using parameters that non-dimensionalize the equation. The non-dimensional temperature is given by $\theta$ as:

$$
\begin{equation*}
\theta=\frac{\mathrm{E}\left(\mathrm{~T}-\mathrm{T}_{\mathrm{a}}\right)}{\mathrm{R} \mathrm{~T}_{\mathrm{a}}^{2}} \tag{M2-3}
\end{equation*}
$$

A dimensionless parameter, $\delta$, called the Frank-Kamenetski parameter is defined as:

$$
\begin{equation*}
\delta=\frac{E a \Delta H_{c}^{0} \mathrm{AC}_{f}^{m} \mathrm{C}_{o}^{n} \mathrm{r}^{2} \mathrm{~T}^{\mathrm{b}} \mathrm{e}^{\left(-E \mathrm{E} / R \mathrm{~T}_{\mathrm{a}}\right)}}{\lambda R \mathrm{~T}_{\mathrm{a}}^{2}} \tag{M2-4}
\end{equation*}
$$

where $r$ is defined as one-half of the smallest dimension of the body (e.g. radius of cylinder or sphere, half-width of a slab). Using these non-dimensional parameters, equation (M2-2) becomes:

$$
\begin{equation*}
\left(\frac{\partial^{2} \theta}{\partial \mathbf{x}^{2}}+\frac{\partial^{2} \theta}{\partial \mathbf{y}^{2}}\right)+\delta \mathbf{e}^{(\theta)}=0 \tag{M2-5}
\end{equation*}
$$

with the boundary condition that $\theta=0$ at the boundary of the pile.
Solutions of Equation (M2-5) exist (i.e. an ambient temperature $T_{a}$ that corresponds to a given thickness $\delta$ ) for the boundary condition when $\delta \leq \delta_{\text {critical }}$ where $\delta_{\text {critical }}$ is some number depending on the shape of the body only. Values of $\delta_{\text {critical }}$ for various geometries are listed in the following table.

TABLE M2-1. Values of $\delta_{\text {critical, }}$ for several different geometries.

| GEOMETRY | DIMENSIONS | $\delta_{\text {critical }}$ |
| :--- | :--- | :--- |
| Infinite Plane Slab | Width $2 r$ | 0.878 |
| Rectangular Box | Sides $2 l, 2 r, 2 m$ | 0.873 |
|  | $r<I, m$ | $\left(1+r^{2} / l^{2}+r^{2} / m^{2}\right)$ |
| Cube | Side $2 r$ | 2.52 |
| Infinite Cylinder | Radius $r$ | 2.00 |
| Equi-cylinder | Height $2 r$, radius $r$ | 2.76 |
| Sphere | Radius $r$ | 3.32 |
| Infinite Square Rod | Side $2 r$ | 1.700 |

Thus, when $\delta=\delta_{\text {critical, }}, \mathrm{T}_{\mathrm{a}}=\mathrm{T}_{\mathrm{c}}$. That is, the ambient temperature that leads to a $\delta$ equal to the $\delta_{\text {critical }}$ is the self-heating condition for that system. Any $\delta>\delta_{\text {critical }}$, will lead to a thermal explosion, i.e. to spontaneous combustion.

Examination of equation (M2-4) shows that for a given system (e.g. linseed oil on cotton rags) the only variable in $\delta$ (other than T ) is the pile size r . Thus, self-heating problems depend both on the kinetic properties of the system and the pile size. For a given material that is capable of self-heating, there generally exists a minimum pile size $r$ at a given ambient temperature in order to cause self-heating to spontaneous combustion. For example, while linseed-soaked cotton rags will self-heat to ignition at room temperature in a pile as small as a foot in diameter, the cotton rags themselves wood require a pile size of approximately 100 meters on a side.

So, how do we determine if a given system is prone to self-heating? Once the geometry of the system to be examined is established, $\delta_{\text {critical, }}$, can be determined from Table M2-1 above. Next, using the appropriate kinetic parameters, ambient temperature, $\mathrm{T}_{\mathrm{a}}$, and pile size, $\mathrm{r}, \delta$ can be calculated and compared with $\delta$ critical. If $\delta>\delta_{\text {critical }}$, the system is capable of selfheating to spontaneous combustion. If $\delta<\delta_{\text {critical }}$, the system will not self-heat to spontaneous combustion. It should be noted that systems for which $\delta<\delta_{\text {critical, }}$, can still exhibit self-heating. That is some temperature rise will occur in the pile. However, at some point as the temperature rises in the pile, the rate of heat loss to the ambient increases. In a sub-critical condition, the heat loss will ultimately equal the heat gain by the self-heating reaction and the temperature will cease to rise. Thus, evidence of self-heating alone is not proof that a given system is capable of spontaneous combustion.

Kinetic properties for different materials are usually determined experimentally. The activation energy for the sled-heating reaction can be determined by measuring the critical temperature for a given material in a given geometry and range of pile sizes. Then, the complex dependence of the critical condition on $\mathrm{T}_{\mathrm{a}}$ is dealt with by rearranging Equation (M25) and taking natural logarithms as follows:
$\ln \left[\frac{\delta_{\text {critical }} \mathrm{T}_{\mathrm{a}}^{2}}{\mathrm{r}^{2}}\right]=\ln \left[\frac{E \Delta H_{c}^{\circ} \mathrm{C}_{\mathrm{f}}^{\mathrm{m}} \mathrm{C}_{0}^{\mathrm{n}} \mathrm{AT}^{\mathrm{b}} \mathrm{e}^{\left(-\mathrm{E} / \mathrm{RT} \mathrm{T}_{\text {arritical }}\right)}}{\mathrm{R} \lambda}\right]-\frac{\mathrm{E}}{R T_{\mathrm{a}, \text { critical }}}$
from which it can be seen that a plot of $\ln \left(T_{\mathrm{a},}^{2}, \Delta_{\text {critical }} / \mathrm{r}^{2}\right)$ against $1 / T_{a, \text { critical }}$ will be a straight line with a slope of $-E / R$ and an intercept $\ln \left[\Delta H_{c}^{0} E C_{f}^{m} \mathrm{C}_{0}^{n} A \mathrm{e}^{\left(-E / R \mathrm{~T}_{\text {a,critical }}\right)} / \lambda R \delta_{\text {critical }}\right]$. This plot is analogous to an Arrhenius plot for determination of the activation energy of a reaction.

## Discussion Question:

The Bowes Decorating Company debuted a very successful line of holiday decorations last year. These decorations are constructed from a mixture of sawdust and a polyurethanebased epoxy that is molded into a variety of shapes. The largest of these decorations is a Santa Claus figurine, whose big spherical belly is almost 36 inches in diameter. These figurines where shipped throughout the country last year and were well received by consumers. Due to the success of these decorations, the product line was expanded to include an even larger Frosty the Snowman figurine, whose largest snowball is 44 inches in diameter. However, several instances have been reported back to The Bowes Decorating Company where boxes containing the Frosty the Snowman figurine were opened to find the smoldering remnants of the product. Obviously, distributors of the figurines refused to accept further shipments of these products, fearing that a fire may result in a distribution warehouse. As a Fire Protection engineer, you have been called on to determine why these events were occurring, and why this problem had not surfaced previously.

Self-heating of the sawdust mixture is an obvious consideration. In order to analyze this possibility, it is important to understand the process in which the figurines are made. The Bowes engineers report that in the manufacturing process, the internal temperature of the sawdust and glue mixture reached temperatures of $90^{\circ} \mathrm{C}$ during curing of the epoxy. To further investigate the possibility of self-heating, you ordered standard tests of the sawdust/glue mixture (i.e. test to determine the critical temperature for three different size cubes of the material in a temperature controlled oven). You received the following data back from the Elfin Magic Fire Science laboratory:

| Cube Size, $\mathbf{2 r}(\mathbf{m m})$ | Critical Temperature $\left({ }^{\circ} \mathrm{C}\right)$ |
| :--- | :--- |
| 25.4 | 212 |
| 51 | 185 |
| 76 | 173 |

Table 1.Self-heating Test Data for Bowes Decorating Co material
Using this data, determine whether or not self-heating is a plausible explanation for the smoldering problems with the Snowman figurine. If it is, discuss why it was not a problem with the Santa Claus. If it is not a plausible explanation, discuss alternative theories for the reported problem (feel free to ask for additional information during your discussion). If, in your professional opinion, self-heating is the cause, discuss remedies that you would propose to The Bowes Decorating Co.

Hint: remember that the relationship between Temperature, T, the critical Frank-Kamenetskii parameter, $\delta_{c}$, and the characteristic dimension of a pile of material is of the form:

$$
\ln \frac{\delta_{c} T^{2}}{r^{2}}=A-\frac{B}{T}
$$

## Instructions:

Use the M2-Self-heating discussion space to exchange ideas, data and ask more questions about the situation. Discuss this with your colleagues and present your professional opinion as to what may have caused it and how to remedy it.

### 7.0 Module 2 Assignment

In completing this assignment, you should show all work. The approach that you use is the essential part of developing a solution, where obtaining the correct answer in these assignments is only of modest importance.

## Formats for submitting assignments

Problems that are due on the same date can be completed in one document and submitted as one electronic file. You may complete your assignment in the following formats: word processed (.doc, .rtf, .pdf, etc.) or scanned.

## Due Dates:

See Class Schedule

## Total Points: 10

All problems can be found in the m2_problems.doc in the assignment for module 2.

