

# Combustion Chemistry

Michael J Pilling, University of Leeds, UK

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Leeds

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Michael J Pilling, University of Leeds, UK  
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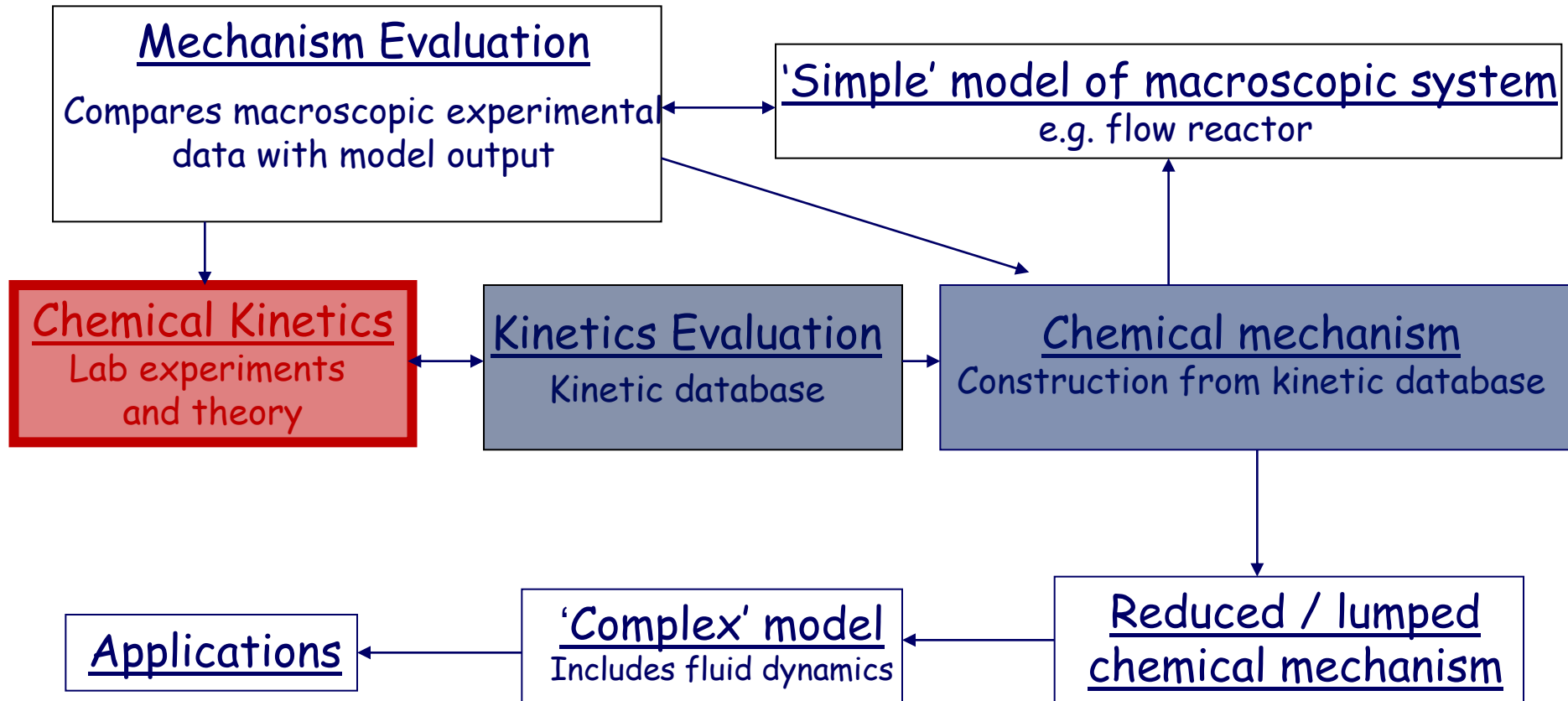
# Background 1

- Combustion involves the oxidation of a fuel, ideally leading, for an organic fuel such as octane or ethanol, to the formation of carbon dioxide and water, with the release of heat.
- The overall chemical equation, e.g.  
$$\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$$
does not describe the detailed way in which the reaction occurs.
- Instead the reaction involves a sequence of elementary, or single step reactions, many of which involve atoms or radicals, which are short-lived species with high reaction rates.

## Background 2

This series of lectures examines how the rates of these elementary reactions can be determined experimentally and understood and calculated theoretically; how chemical mechanisms describing the overall sequence of reactions can be constructed and then used to model the chemistry of combustion systems.

# Reaction kinetics contributions to combustion models



Understanding

Similar approaches in atmospheric chemistry, interstellar chemistry.

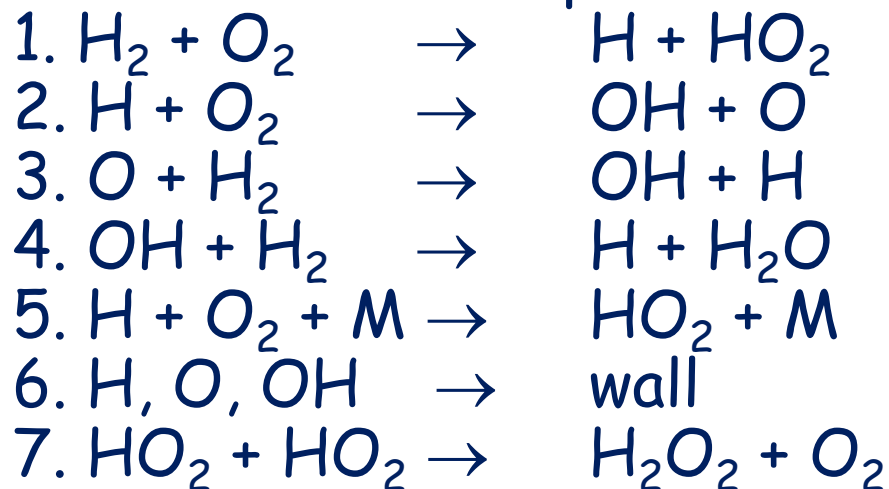
# Lecture Synopsis

- Background material
  - Chemical mechanisms. Chemical Kinetics. Thermodynamics, Statistical Mechanics, Quantum Theory and Electronic Structure Calculations.
- Experimental methods
  - Pulsed photolysis, shock tubes, flow and static methods. Detection techniques
- Theoretical methods
  - Transition state theory. Microcanonical and canonical systems. Bimolecular and Unimolecular Reactions. Master equation methods
- Kinetic and Thermodynamic databases
- Constructing chemical mechanisms
- A couple of examples
  - Autoignition
  - Soot formation

## An example - $\text{H}_2 + \text{O}_2$ and some definitions

The overall reaction is:  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$

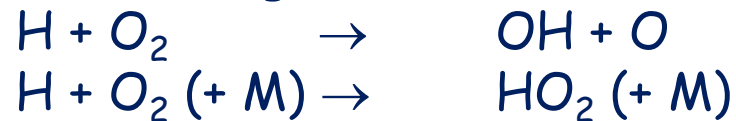
A minimal set of the component **elementary** reactions is:



- An **elementary** reaction is a single step reaction (although we will discuss some issues related to this definition later).
- A **complex** reaction, such as the  $2\text{H}_2 + \text{O}_2$  reaction, is made of several elementary reactions.
- The set of elementary reactions is called the **mechanism** of the overall reaction

# What do we need to know about these reactions?

- What are the reactants and what are the products? There may be more than one set of products and we need to know the yields of each set. E.g.



- How quickly do the reactions occur? This is described in the rate equation and depends on the concentrations of the species involved and the **rate constant**. What is M? Pressure dependent reactions.
- What is the **enthalpy** change of reaction? How much heat is released, or consumed, when the reaction occurs. Heat release is central to combustion.
- The ratio of the rate constants for the forward and reverse reaction (e.g.  $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$  and  $\text{OH} + \text{O} \rightarrow \text{H} + \text{O}_2$ ) is determined by the **equilibrium constant** which is related to the **Gibbs energy** of reaction



# Rates of elementary reactions

- The rate of each elementary reaction is determined by the reactant concentrations and the rate coefficient,  $k$ .  $k$  depends on  $T$  and, in some cases,  $p$ .

We also need to know the products of the reaction, which in some cases aren't clear.



- Rate of this reaction =

$$-\text{d}[\text{OH}]/\text{d}t = k[\text{OH}][\text{CH}_4] = \text{d}[\text{H}_2\text{O}]/\text{d}t = \text{d}[\text{CH}_3]/\text{d}t = -\text{d}[\text{CH}_4]/\text{d}t$$

- $k$  depends on temperature and this is usually expressed in Arrhenius form:

$$k = A \exp(-E_a / R T)$$

or modified Arrhenius form:

$$k = A T^n \exp(-E_a / R T)$$

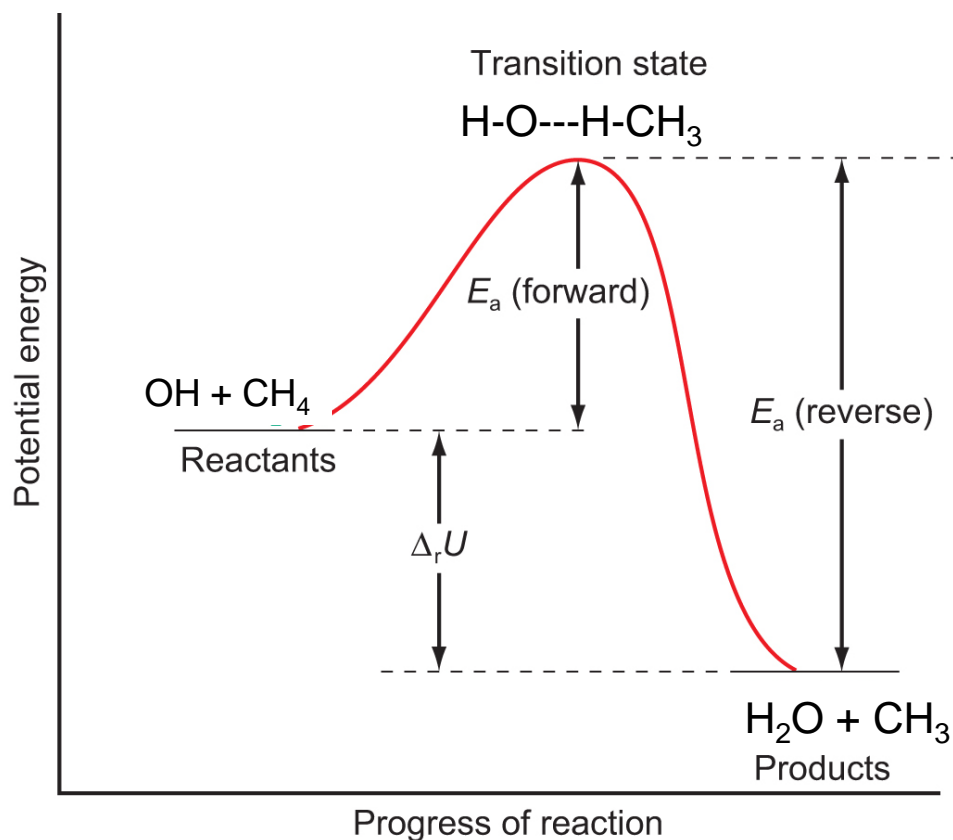
$A$  is the  $A$  factor,  $E_a$  the activation energy,  $n$  the temperature exponent and  $R$  the gas constant.

- One aim of experimental and theoretical studies of elementary reactions is to determine  $A$ ,  $E_a$ ,  $n$

# Why does the rate constant depend on temperature?

## The idea of the transition state

- As OH approaches CH<sub>4</sub>, one of the C-H bonds extends and electron density moves from that C-H bond into the newly forming O-H bond. This involves an increase in potential energy.



- We need the rate constant and its dependence on  $T$ :

*Kinetics: Experiment, Theory*

- We need to be able to incorporate these data in combustion models

*Mechanism development\*:*

- We need some basic understanding of physics and chemistry:

*thermodynamics, kinetics, quantum mechanics, statistical mechanics*

For a discussion of many of these topics, see Atkins and de Paula, *Physical Chemistry*

\*Note that we use the word mechanism in two different ways:

- to describe the way in which an elementary reaction occurs
- to describe the chemical mechanism of a complex reaction - the list of component chemical reactions

# Basics of chemical kinetics

## Definitions

- **Order of reaction** is equal to the exponent of the reactant concentration in the rate equation. For an **elementary** reaction, this is equal to the stoichiometric number ( $\nu_i$ ) for the reactants in the rate equation e.g.:
  - $O + H_2 \rightarrow H + O_2$ , rate =  $k[O][H_2]$ . Order with respect to O is one, order with respect to  $H_2$  is one, overall order is two.
  - $2CH_3 \rightarrow C_2H_6$ , rate =  $k[CH_3]^2$ . Order with respect to  $CH_3$  is two. Overall order is two.
- **Molecularity** is the number of species involved in forming the transition state e.g.
  - $OH + CH_4 \rightarrow H_2O + CH_3$ . Two species involved in forming transition state: **bimolecular reaction**.
  - $C_2H_6 \rightarrow 2CH_3$ . One species involved in forming the transition state: **unimolecular reaction**.

## Relationship between forward and reverse rate coefficients

$$K = \frac{\prod_{\text{products}} (a_i^{v_i})}{\prod_{\text{reactants}} (a_i^{v_i})}$$

$a$  is the *activity*. For ideal systems,  $a = p/p^\circ = c/c^\circ$  so that  $K$  is dimensionless. Other definitions of equilibrium constants are:

$$K_c = \frac{\prod_{\text{products}} (c_i^{v_i})}{\prod_{\text{reactants}} (c_i^{v_i})} \quad K_p = \frac{\prod_{\text{products}} (p_i^{v_i})}{\prod_{\text{reactants}} (p_i^{v_i})}$$

These have dimensions if  $(\sum v_i)_{\text{reactants}} \neq (\sum v_i)_{\text{products}}$

At equilibrium, forward rate = reverse rate:

$$k_f \prod_{\text{reactants}} (c_i^{v_i}) = k_r \prod_{\text{products}} (c_i^{v_i}) \quad \frac{k_f}{k_r} = K_c$$

Detailed balance  
Use of thermodynamic databases

# Thermodynamic relations: a reminder

## 1. The Laws of Thermodynamics

- First Law of Thermodynamics:

The energy,  $U$ , of an isolated system is constant

$$dU = dq + dw$$

where  $q$  is heat absorbed by system and  $w$  is work done on system

$$H = U + pV$$

$H$  is enthalpy,  $p$  pressure and  $V$  volume

- Second Law of Thermodynamics:

No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work

$$dS \geq \frac{dq}{T}$$

$S$  is the entropy

- Third Law of Thermodynamics:

The entropy of all perfectly crystalline substances at zero Kelvin is zero.

$$S = 0 \text{ at } T = 0$$

## Thermodynamic relations

### 2. Gibbs Energy

Gibbs energy,  $G$ :

$$G = H - TS$$

At constant  $T$ , the change in Gibbs energy,  $\Delta G$  is given by:

$$\Delta G = \Delta H - T\Delta S$$

Equilibrium occurs at minimum  $G$  (at constant  $T, P$ )



and the equilibrium constant,  $K$ , is related to  $\Delta G$  by:

$$\Delta G^\ominus = -RT \ln K$$

Note the standard sign

The equilibrium constant,  $K$ , can be calculated from tabulated or calculated values of the standard enthalpy  $H$  and entropy  $S$ , and hence the reverse rate coefficient (say) determined from the forward rate coefficient and  $K$ . (The  $^\ominus$  sign refers to the standard state)

Later in this lecture we will discuss how thermodynamic quantities can be calculated using statistical mechanics. In a later lecture we will discuss tabulations of thermodynamic data that are widely used in combustion.

# Thermodynamic relations 3

## Heat capacity

- As we shall see, enthalpies of formation are tabulated at 298 K. For combustion applications, we need to be able to determine values at higher  $T$ .
- Heat capacities

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V ; C_p = \left( \frac{\partial H}{\partial T} \right)_p$$

$$C_p = C_V + R \text{ (ideal gas)}$$

- Kirchhoff's Law

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p dT$$
$$\Delta_r H(T_2) = \Delta_r H(T_1) + \int_{T_1}^{T_2} \Delta_r C_p dT$$

# Quantisation of energy

- Using statistical mechanics we can calculate energies and entropies of molecules - a key process in a quantitative understanding of the incorporation of both kinetics and thermodynamics in combustion models - requires us to understand the quantisation of their different forms of energy - electronic, vibrational, rotational and translational.
- The occurrence of energy levels, and their spacing, is a consequence of the wave properties of matter - atomic and molecular particles behave as both particles and waves.
- The next few slides outline the basis of quantisation and of the use of statistical mechanics.



# Quantum Mechanics - in 6 slides.

## de Broglie relation

$$p = h/\lambda$$

$p$  = momentum,  $h$  = Planck's constant;  
 $\lambda$  = wavelength ( $h=6.626 \times 10^{-34}$  J s)

## Schrödinger Equation (1 dimension, time independent)

kinetic energy operator       $V$  = potential energy,  $E$  = total energy

$$\{-(\hbar^2/2m)(d^2/dx^2) + V(x)\}\psi = E\psi,$$

Hamiltonian      (classically,  $H = T + V$ )

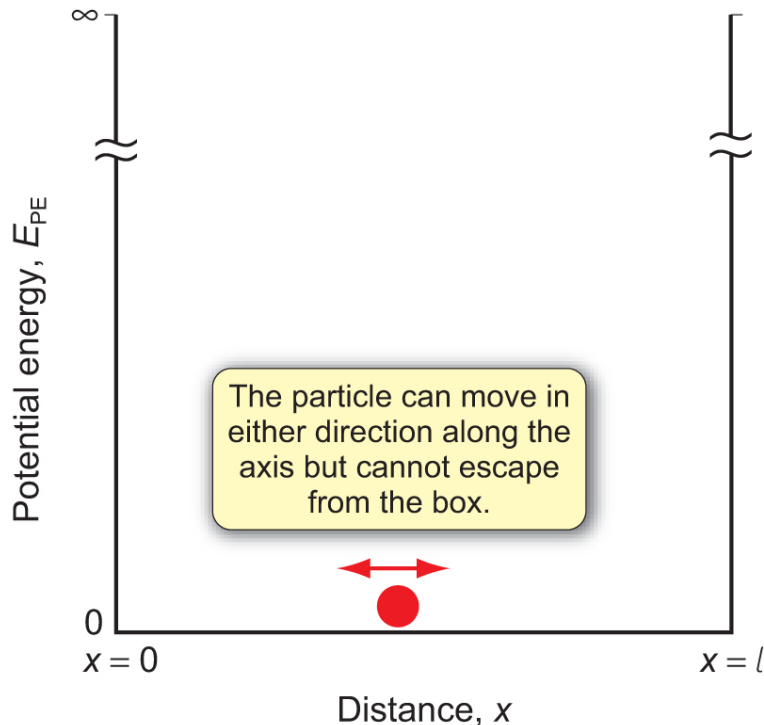
## Wavefunction, $\psi$

$\psi$  is continuous with continuous slope, single valued, finite everywhere;

$$\psi \rightarrow 0 \text{ as } x \rightarrow \infty.$$

$\psi^2$  is the particle probability density;  $\int_{-\infty}^{\infty} \psi^2 dx = 1$

# Particle in a one dimensional box



- $\psi$  is zero outside the box and must be zero at  $x=0, l$
- de Broglie - wavelength of  $\psi$  depends on  $p$  and therefore on kinetic and total energy ( $V$  is zero):  $\lambda = 2l/n$ ,  $n=1, 2, \dots$
- Alternatively, solve the Schrödinger equation:

$$-\frac{h^2}{8\pi^2m} \frac{d^2\psi}{dx^2} = E\psi$$

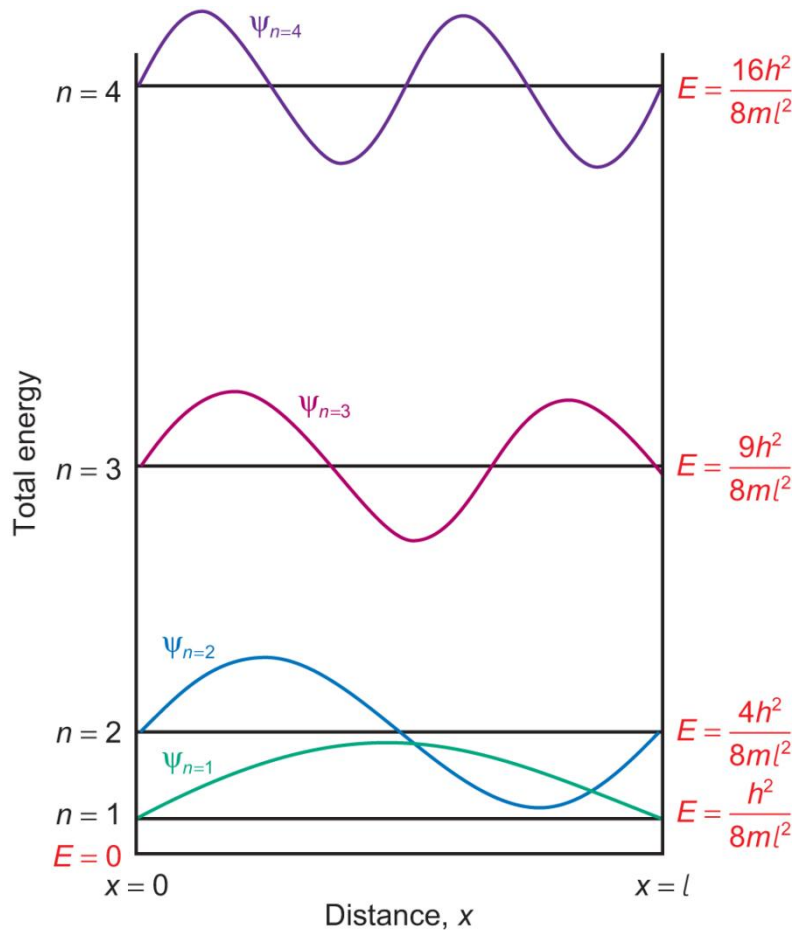
$$\psi = Ae^{ikx} = A\sin kx$$

$$\psi = A\sin\left(\frac{n\pi x}{l}\right)$$

$$E = \frac{k^2h^2}{8\pi^2m} = \frac{n^2h^2}{8ml^2}$$

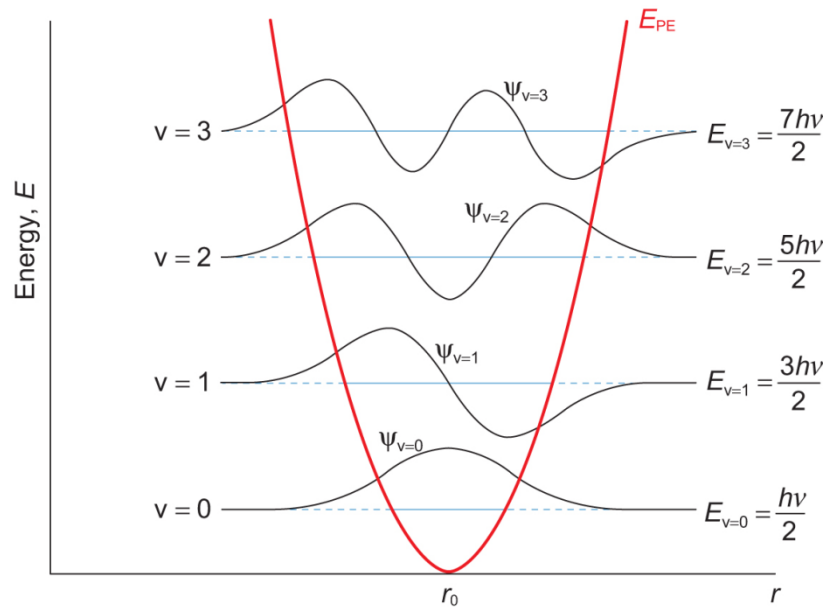
- $A$  is determined from the normalisation property:  $\int_0^l \psi^2 dx = 1$

# Wavefunctions and energy levels for a particle in a box



- Note form and properties of wavefunctions:
  - Zero at edges of box
  - Wavelength decreases as  $E$  increases (cf de Broglie)
  - Zero kinetic energy is not allowed - there is a so-called *zero point energy*
- Note the form, of the energy levels:
  - Energy is quantised and described by a *quantum number, n*:
$$E = \frac{n^2 h^2}{8ml^2}$$
- Note the operation of the *Correspondence Principle*: high mass,  $l$ , give large quantum numbers at significant energies - quantisation and wave properties are unimportant for classical systems

# Vibrational energy levels and wavefunctions

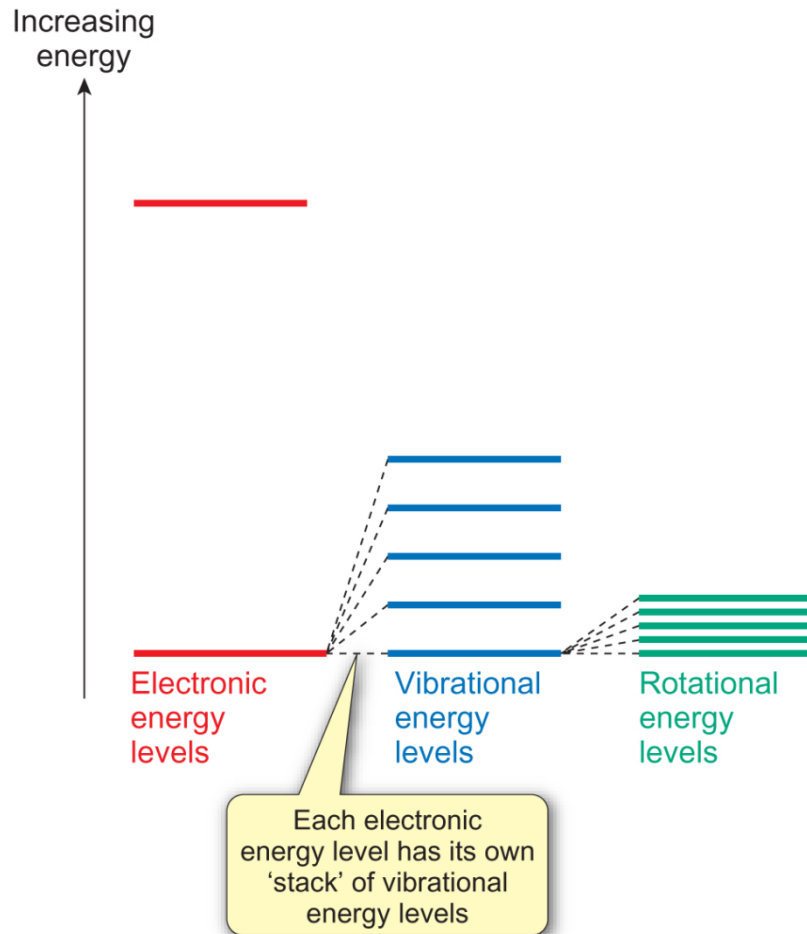


- Model for vibrational motion in a molecule - harmonic oscillator

$$V = \frac{1}{2}k(r - r_0)^2$$

- Wavefunctions are Gaussian functions - they are not simple sine functions because  $(E - V)$  depends on  $r$ .
- Note the penetration of the wavefunction into the *non-classical* region where  $V > E$ : the kinetic energy is negative - *quantum mechanical tunnelling*
- In this region, the wavefunction is no longer oscillatory but decreases to zero at  $(r - r_0) = \infty$

# Quantisation of different types of energy



- The spacing of the energy levels is in the order: electronic > vibrational > rotational > translational.
- Most combustion processes involve the ground electronic state, but excited states can be important (e.g. electronically excited oxygen atoms.)

# Quantum mechanical tunnelling - an indication of the issues

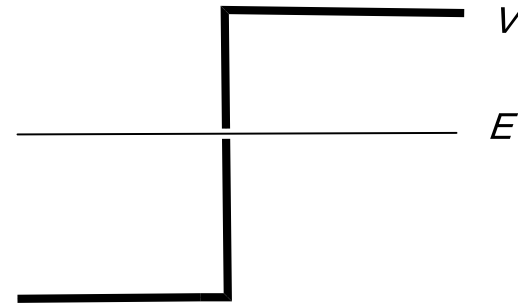
$$-\frac{d^2\psi}{dx^2} = \frac{8\pi^2m}{h^2}(E - V)\psi$$

For  $E - V = \text{constant}$  a solution of the Schroedinger equation is

$$\psi = A \exp(ikx)$$

$$k = \sqrt{\frac{8\pi^2m(E - V)}{h^2}}$$

For  $E > V$  the solution is oscillatory, as discussed for the particle in a box



For  $V > E$ ,  $k = i\kappa$ , where

$$\kappa = \sqrt{\frac{8\pi^2m(V - E)}{h^2}}$$
$$\psi = B \exp(-\kappa x)$$

i.e. the wavefunction penetrates into the non-classical region where  $V > E$  (and the kinetic energy is negative) and decays exponentially in this region

**NB the dependence on mass**

# Statistical mechanics

- Statistical mechanics is the determination of macroscopic properties (thermodynamic, but also kinetic) from the microscopic properties of the component molecules.
- It relies heavily on a description of the energy levels of molecules and of the distribution of molecules throughout those energy levels.
- We shall examine the thermodynamic properties of **canonical** ensembles, with fixed numbers of molecules,  $N$ , fixed volume,  $V$ , and fixed temperature,  $T$ .
- We shall base our discussion on the most probable distribution of molecules throughout the energy levels, which is dependent on maximising the entropy (spreading the molecules as widely as possible throughout the energy levels), consistent with a fixed overall energy, defined by the temperature,  $T$ . This distribution is the **Boltzmann distribution**.

# Boltzmann distribution 1



- Molecules are arranged through the energy levels subject to a constant total number,  $N$

$$N = \sum N_i$$

and constant total energy,  $E$

$$E = \sum N_i \varepsilon_i$$

- $N$  is very large ( $\sim 10^{23}$ ) and the most probable distribution, subject to the above restrictions, dominates.
- If  $W$  is the weight of this configuration, its entropy  $S$  is

$$S = k \ln W$$

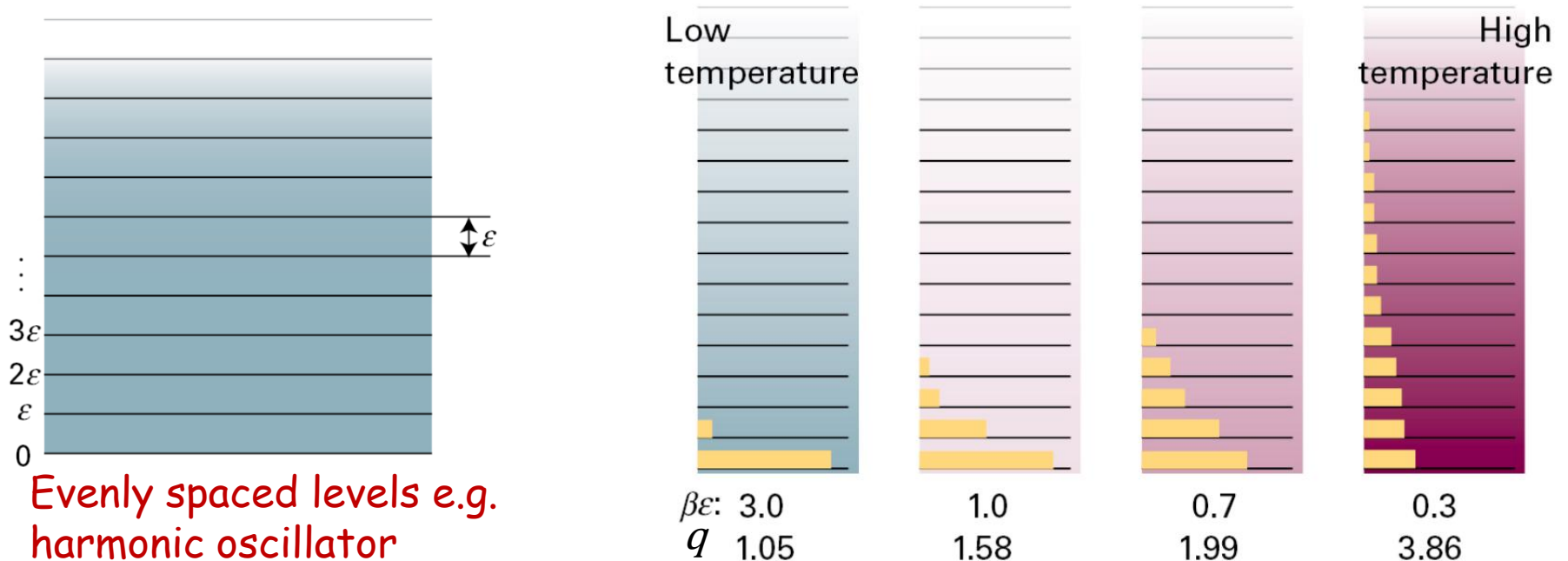
where  $k$  is the Boltzmann constant. This distribution is found by maximising  $W$ .



# Boltzmann distribution 2

- Boltzmann distribution:  $\frac{N_i}{N} = \frac{g_i e^{-\beta \epsilon_i}}{q}$  where  $\beta = 1/kT$
- $N_i$  is the number of molecules in energy level  $i$ ,  $N$  is the total number of molecules,  $g_i$  is the degeneracy and  $k$  is the Boltzmann constant.
- Partition function: 
$$q = \sum_{\text{levels}, i} g_i e^{-\beta \epsilon_i}$$

The partition function is a sum over the energy levels, weighted according to their probability of occupation



# Energy levels

- $h$  = Planck's constant =  $6.626 \times 10^{-34}$  Js;  $\hbar = h/2\pi$ ,  $c$  = speed of light.  $kT/hc = 207.2 \text{ cm}^{-1}$  at 298 K.
- Translation. Particle, mass  $m$ , in cubic box, side  $a$ , quantum numbers  $n_x, n_y, n_z$ . Spacing  $\ll kT$

$$\varepsilon_{n_x, n_y, n_z} = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)$$

- Rotation, linear molecule, moment of inertia,  $I$ , quantum number  $J$ . Spacing  $< kT$ , except at very low  $T$ .

$$\varepsilon_J = \frac{J(J+1)h^2}{8\pi^2 I} \quad B = h/(8\pi^2 Ic)$$

$B$  and  $\omega$  have units  $\text{cm}^{-1}$   
 They can be determined spectroscopically and using quantum mechanics  
 Degeneracy =  $2J+1$

- Vibration, diatomic molecule, vibrational frequency  $\nu$ , quantum number  $v$ ,  $k$  is the force constant,  $\mu$  reduced mass.

$$\varepsilon_v = \left(v + \frac{1}{2}\right) h\nu \quad v = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad v = \omega c$$

$$V = \frac{1}{2} k(r - r_0)^2$$

Similar expressions for rotational and vibrational energy levels for non-linear and for polyatomic molecules

# Electronic states and energy levels 1. Atoms

- Most of the atoms and molecules we encounter in combustion are in their ground electronic states. There are some exceptions.
- The electronic states of **atoms** are described by their **term symbols**. The oxygen atom has three low lying states,  $^3P_2$ ,  $^3P_1$ ,  $^3P_0$ .

————	$^3P_0$	$E = 227.0 \text{ cm}^{-1} = 2.72 \text{ kJ mol}^{-1}$
————	$^3P_1$	$E = 158.3 \text{ cm}^{-1} = 1.89 \text{ kJ mol}^{-1}$
————	$^3P_2$	$E = 0$

- Superscript 3 is the multiplicity  $= 2S + 1$ , where  $S$  is the total spin. In the case of O,  $S = 1$ .
- P describes the electronic orbital angular momentum,  $L$ . S states have  $L = 0$ ; P states  $L = 1$ ; D,  $L = 2$  etc.
- The subscript refers to the total angular momentum,  $J$ , formed from the quantized vector sum of  $L$  and  $S$
- Other atoms: H  $^2S_{1/2}$ , C  $^3P_{0,1,2}$ , N  $^4S_{3/2}$ , S  $^3P_{2,1,0}$

## Electronic states and energy levels 2. Diatomic Molecules

- Diatomic molecules are described by similar term symbols. Most are in  $^1\Sigma$  ground states. The superscript is  $2S+1$  and the Greek symbol refers to the orbital angular momentum along the internuclear axis,  $\Lambda$ .  $\Sigma$  corresponds to  $\Lambda = 0$ . So such states have both  $S$  and  $\Lambda = 0$ .
- Both OH and NO have  $^2\Pi$  ground states with  $S = \frac{1}{2}$  and  $\Lambda = 1$ . We now need to consider the total angular momentum,  $\Omega$ , along the internuclear axis. For both OH and NO, we have  $\Omega = 3/2$  and  $1/2$  states; the former is the ground state and the latter lies higher by  $139.2 \text{ cm}^{-1}$  for OH and  $121.1 \text{ cm}^{-1}$  for NO

## Electronic states and energy levels 2. Polyatomic Molecules

- Most molecules have singlet ground states, i.e.  $2S+1=1$  and  $S=0$  - there is no net spin.
- Radicals such as  $\text{CH}_3$  have a single unpaired electron and are in doublet states, with  $2S+1 = 2$  and  $S = \frac{1}{2}$ .
- Methylene,  $\text{CH}_2$ , is a **biradical** - we need to consider two electrons. In the ground state, the spin angular momenta of these electrons are parallel, so that the total spin,  $S = 1$  and  $2S+1 = 3$ . This state is termed **triplet methylene**. The first excited state has paired (ie opposed) spins and  $S = 0$ ,  $2S+1 = 1$  - it is a singlet state.
- The singlet lies  $37.6 \text{ kJ mol}^{-1}$  above the ground state and is much more reactive than it.

# Partition functions

- Translational partition function.  $V$  = volume,  $m$  = molecular mass
- Rotational partition functions  
(i) linear molecule (ii) non-linear.  
 $\sigma$  = symmetry number  
 $A, B, C$  = rotational constants
- Vibrational partition functions  
(i) diatomic, (ii) polyatomic with  
 $\alpha = 3n - 5$  (linear molecule);  $3n - 6$  (non-linear)  $\omega_i$  is vibrational constant.
- **NB. These vibrational partition functions refer to the zero point energy as the energy zero. Harmonic oscillators**

$$q = \sum_{\text{levels}, i} g_i e^{-\beta \epsilon_i}$$

$$q_{\text{trans}} = \left[ \frac{2\pi m k T}{h^2} \right]^{3/2} V$$

NB - the term in  $V$ :

- Origin
- $Q = q/V$

$$q_{\text{rot}} = \frac{kT}{\sigma h B c}$$

$$q_{\text{rot}} = \frac{\sqrt{\pi}}{\sigma} \left\{ \frac{\left( \frac{kT}{hc} \right)^3}{ABC} \right\}^{1/2}$$

$$q_{\text{vib}} = \left( 1 - e^{-\frac{hc\omega}{kT}} \right)^{-1}$$

$$q_{\text{vib}} = \prod_{i=1}^{\alpha} \left( 1 - e^{-\frac{hc\omega_i}{kT}} \right)^{-1}$$

# Degeneracy

$$\frac{N_i}{N} = \frac{g_i e^{-\beta \epsilon_i}}{q}$$

$$q = \sum_{\text{levels}, i} g_i e^{-\beta \epsilon_i}$$

- where  $g_i$  is the degeneracy - the number of states at energy  $\epsilon_i$ .
- For a rotational level,  $J$ , the degeneracy is  $2J+1$ .
- For an atom, the degeneracy is also  $2J+1$ , so that the degeneracies of the low three lowest states in  $O^3P_{2,1,0}$  are 5, 3 and 1, while the lowest state of  $H^2P_{1/2}$  is 2.
- For diatomic molecules, the degeneracy depends on  $\Omega$ , which is constrained to lie along the internuclear axis. For  $\Omega > 0$ , the degeneracy is 2.
- Note that, as we shall see later, we need to include these electronic degeneracies in calculations of entropies, equilibrium constants and in transition state calculations of rate constants

# Partition functions and thermodynamic quantities

- Total molecular energy:  $\varepsilon = \varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{elec}}$
- Total molecular partition function:  $q = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}}$
- The molar thermodynamic energy,  $U$ , is obtained from the energy  $E$  which is referred to the zero point energy:  $U = U(0) + E$ ; where  $U(0)$  is the internal energy at 0 K.

$$U = U(0) - N \left( \frac{\partial \ln q}{\partial \beta} \right)_V = U(0) + NkT^2 \left( \frac{\partial \ln q}{\partial T} \right)_V \quad E = \sum N_i \varepsilon_i$$

- The entropy is determined from  $S = k \ln W$

Gas phase molecules of the same type are indistinguishable and this must be recognised in calculating the molar entropy:

$$S = \frac{U - U(0)}{T} + R \ln q - R \ln N_A + R$$

The  $-R \ln N + R$  term derives from the indistinguishability of similar molecules in the gas phase, and is associated with the translational contribution to the entropy. It is omitted if you want to calculate, say, the rotational entropy.



## Other thermodynamic functions and equilibrium constants

- The Helmholtz Energy,  $A$ , is readily calculated from  $A = U - TS$ . Note that the total partition function has been defined at constant volume, to define the translational partition function.
- To calculate the Gibbs energy, the system needs to be referred to standard conditions, which define the volume term in the partition function.
- For our purposes, the most useful equilibrium constant is  $K_c$

For the reaction  $\sum v_i X_i = 0$

$$K_c = \prod (q_{X_i}/V)^{v_i} \exp\left(-\frac{\Delta \varepsilon_0}{kT}\right)$$

where  $\Delta \varepsilon_0$  is the change in zero point energy in the reaction. Don't forget the electronic contributions to  $q$  (*Exercise*)

## Exercise: Electronic partition functions

- As we discussed earlier, molecules such as OH and NO have an unpaired electron and also one unit of orbital angular momentum. This results in two states, each with a degeneracy of 2, separated by an energy difference  $\Delta\varepsilon$ .
- Consider the general case of a two level system, separation  $\Delta\varepsilon$  and degeneracies  $g_1$  and  $g_2$ :
  - Write down the electronic partition function for this system.
  - Derive an expression for the molar electronic energy,  $U$ , as a function of temperature.
  - Derive an expression for the contribution of electronic energy to the heat capacity.
  - Sketch the electronic energy and heat capacity vs  $T$ .

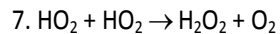
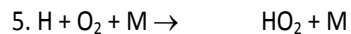
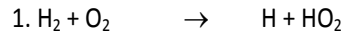
## Electronic energy

- $q = g_1 + g_2 \exp\left(-\frac{\Delta\varepsilon}{kT}\right)$
- $U = N_A kT^2 \frac{d \ln q}{dT} = \frac{N_A \Delta\varepsilon g_2}{g_1 \exp\left(\frac{\Delta\varepsilon}{kT}\right) + g_2}$
- $C_V = \frac{dU}{dT} = R g_1 g_2 \left(\frac{\Delta\varepsilon}{kT}\right)^2 \frac{\exp\left(\frac{\Delta\varepsilon}{kT}\right)}{\left(g_1 \exp\left(\frac{\Delta\varepsilon}{kT}\right) + g_2\right)^2}$

# Chemical kinetics

Constructing chemical mechanisms  
Interactions between coupled chemical  
reactions

## Constructing coupled differential (rate) equations from chemical mechanisms



The chemical mechanism is set up together with the associated rate coefficients

The coupled rate equations are then written down for each species  
 $d[\text{X}]/dt = \text{Total rate of forming X} - \text{Total rate of removing X}:$

$$\frac{d[\text{H}]}{dt} = k_1[\text{H}_2][\text{O}_2] - k_2[\text{H}][\text{O}_2] + k_3[\text{O}][\text{H}_2] + k_4[\text{OH}][\text{H}_2] \\ - k_5[\text{H}][\text{O}_2][\text{M}] - k_6[\text{H}]$$

$$\frac{d[\text{O}]}{dt} = k_2[\text{H}][\text{O}_2] - k_3[\text{O}][\text{H}_2] - k_6[\text{O}]$$

etc .....

Solve the set of coupled differential equations numerically, subject to initial conditions. E.g. using CHEMKIN - see later

## Some kinetics formalities - set of coupled first order reactions

$$\frac{d\mathbf{c}}{dt} = \mathbf{f}(\mathbf{c}, \mathbf{k}); \quad \mathbf{c}(t = 0) = \mathbf{c}_0$$

$\mathbf{c}$  is an  $n$ -dimensional concentration vector

For a set of first order reactions, we may solve using an eigenvalue approach:  $\frac{d\mathbf{c}}{dt} = \mathbf{M}\mathbf{c}$

$\mathbf{M}$  is an  $n \times n$  matrix of rate constants. The  $n$  eigenvalues,  $\lambda$ , of  $\mathbf{M}$  are obtained from  $\det(\mathbf{M} - \lambda\mathbf{I}) = 0$

We also need the eigenvectors,  $\mathbf{x}$ :  $\mathbf{M}\mathbf{x} = \lambda\mathbf{x}$

The time dependent concentrations  $\mathbf{c}(t)$  are then given by:

$$\mathbf{c}(t) = \mathbf{x}e^{\lambda t}\mathbf{x}^{-1}\mathbf{c}(0)$$

Two simple examples: 1.  $A \rightarrow B \rightarrow C$ , with rate coefficients  $k_1$  and  $k_2$

Set up the rate equations, with  $a = [A]$ , etc

$$\frac{da}{dt} = -k_1 a; \quad \frac{db}{dt} = k_1 a - k_2 b$$

$$c = a_0 - a - b$$

$$\mathbf{M} = \begin{pmatrix} -k_1 & k_1 \\ 0 & -k_2 \end{pmatrix}$$

$$\mathbf{c} = \begin{pmatrix} a \\ b \end{pmatrix}$$

$$\det(\mathbf{M} - \lambda \mathbf{I}) = 0$$

$$\begin{bmatrix} -k_1 - \lambda & k_1 \\ 0 & -k_2 - \lambda \end{bmatrix} = 0$$

$$(-k_1 - \lambda)(-k_2 - \lambda) = 0$$

$$\lambda_1 = -k_1; \quad \lambda_2 = -k_2$$

$$a = A e^{-k_1 t} + B e^{-k_2 t}$$

$$b = C e^{-k_1 t} + D e^{-k_2 t}$$

$$a = a_0 \exp(-k_1 t)$$

$$b = \frac{a_0 k_1}{(k_2 - k_1)} \{ \exp(-k_1 t) - \exp(-k_2 t) \}$$

$$c = a_0 - a - b$$

# Quasi steady state approximation (QSSA)

Figure (a):  $k_1 > k_2$   $b = \frac{a_0 k_1}{(k_1 - k_2)} \{ \exp(-k_2 t) - \exp(-k_1 t) \}$

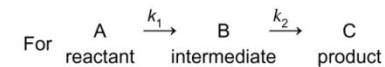
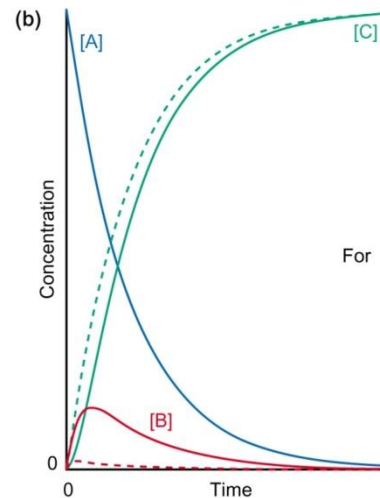
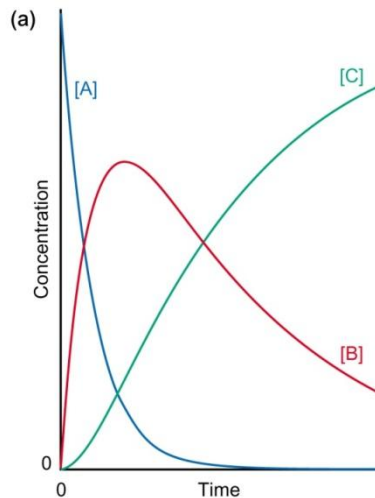


Figure (b): full,  $k_2 = 5k_1$   
 dashed,  $k_2 = 50k_1$

Figure (b):  $k_1 < k_2$   $b = \frac{a_0 k_1}{(k_2 - k_1)} \{ \exp(-k_1 t) - \exp(-k_2 t) \}$

For  $k_1 \ll k_2$  and for times long compared with  $(k_2)^{-1}$

$$b = \frac{a_0 k_1}{(k_2 - k_1)} \{ \exp(-k_1 t) \} \approx \frac{a_0 k_1}{k_2} \{ \exp(-k_1 t) \} = \frac{a k_1}{k_2}$$

$$\therefore b \ll a \text{ and } \frac{db}{dt} \ll \frac{da}{dt}$$

- QSSA:  $db/dt \approx 0$ : rate of forming of B  $\approx$  rate of removing B



# On the error in the QSSA

Turanyi et al J. Phys. Chem. 1993,97, 163-172

- Applying the QSSA to a species in a numerical integration introduces an error in the species concentration that propagates as the numerical integration proceeds.
- For a system of rate equations  $\frac{dc}{dt} = f(c, k); \quad c(t = 0) = c_0$  the instantaneous error in concentration in a single species  $i$  is:

$$\Delta c_i^s = \frac{1}{J_{ii}} \frac{dc_i}{dt}$$

- Here  $J_{ii}$  is a diagonal Jacobian element:

$$J_{ik} = \frac{\partial f_i(c, k)}{\partial c_k}$$

- The lifetime,  $\tau$ , of species  $i$  is given by  $\tau = -\frac{1}{J_{ii}}$
- So the error in applying the QSSA is least for species with short lifetimes (or slow rates of change).
- Turanyi et al also discussed errors for groups of QSSA species

# Pressure dependent association reactions:

## an example of the application of QSSA

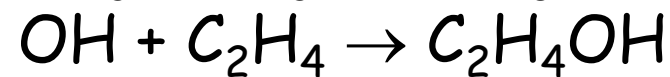
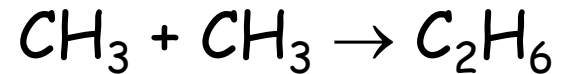
An association reaction involves collisional stabilisation of the adduct:



Apply QSSA:

$$k = \frac{k_a k_s [M]}{k_{-a} + k_s [M]}$$

Examples include



$$\text{As } [M] \rightarrow \infty, k \rightarrow k_a = k^\infty$$

$$\text{As } [M] \rightarrow 0, k \rightarrow \frac{k_a k_s [M]}{k_{-a}} = k_0 [M]$$

Substituting in first equation

$$k = \frac{k_0 [M] k^\infty}{k^\infty + k_0 [M]}$$

Similar treatment  
for dissociation  
reactions



$$\frac{da}{dt} = -k_1 a + k_{-1} b$$

$$\frac{db}{dt} = k_1 a - (k_{-1} + k_2) b$$

$$\mathbf{M} = \begin{pmatrix} -k_1 & k_1 \\ k_{-1} & -k_{-1} - k_2 \end{pmatrix}$$

$$\mathbf{c} = \begin{pmatrix} a \\ b \end{pmatrix}$$

$$\begin{bmatrix} -k_1 - \lambda & k_1 \\ k_{-1} & -k_{-1} - k_2 - \lambda \end{bmatrix} = 0$$

$$(-k_1 - \lambda)(-k_{-1} - k_2 - \lambda) - k_1 k_{-1} = 0$$

$$2\lambda_{\pm} = -(k_1 + k_{-1} + k_2) \pm \sqrt{(k_1 + k_{-1} + k_2)^2 - 4k_1 k_2}$$

If  $k_1 \approx k_{-1} \gg k_2$  binomial expansion gives:

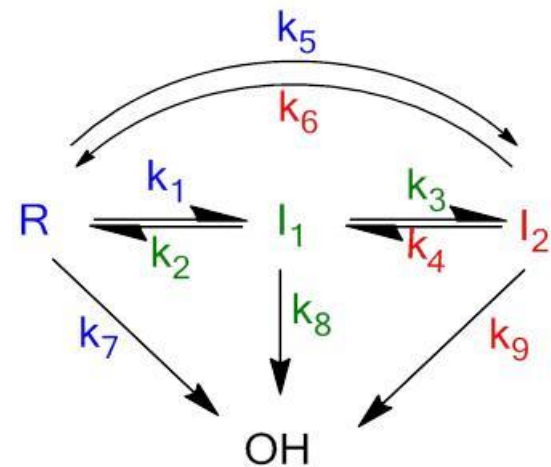
$$\lambda_- \approx -(k_1 + k_{-1} + k_2) \approx -(k_1 + k_{-1})$$

$$\lambda_+ \approx \frac{-k_1 k_2}{(k_1 + k_{-1} + k_2)} \approx \frac{-k_1 k_2}{(k_1 + k_{-1})}$$

The larger magnitude eigenvalue describes the relaxation of A, B to equilibrium.  $1/(k_1 + k_{-1})$  is termed the relaxation time. The smaller magnitude eigenvalue describes the loss of the equilibrated A, B system to form C. If  $k_2 = 0$ , the A, B system is conservative. There are still two eigenvalues,  $-(k_1 + k_{-1})$  and 0. The zero eigenvalue relates to the equilibrium distribution.

## Exercise: eigenvalue determination

- Consider the following reaction system:



- Set up the rate equations for R, I<sub>1</sub> and I<sub>2</sub> and express in matrix form.
- This results in a 3 eigenvalue system and a cubic equation in  $\lambda$ . However, I<sub>2</sub> is short-lived and the quasi steady state approximation can be applied to it. This allows the matrix **M** to be expressed as a 2x2, for the two variable system, [R] and [I<sub>1</sub>], with the rate constants determined from the elimination of [I<sub>2</sub>] using the QSSA. Obtain expressions for the two eigenvalues of the system.
- We shall re-examine this reaction system on Friday when we discuss peroxy radical reactions

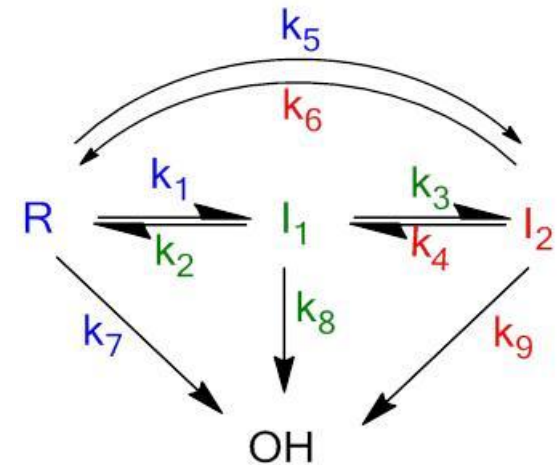
## Analytic expressions for the two smallest eigenvalues 1.

Let  $x=R$ ,  $y=I_1$ ,  $z = I_2$ .

$$\frac{dx}{dt} = -(k_1 + k_5 + k_7)x + k_2y + k_6z$$

$$\frac{dy}{dt} = -(k_2 + k_3 + k_8)x + k_1x + k_4z$$

$$\frac{dz}{dt} = -(k_4 + k_6 + k_9)z + k_5x + k_3y$$



Apply QSSA to  $z$

$$z = \frac{k_5x + k_3y}{k_4 + k_6 + k_9} \quad \text{Substitute in 1 and 2, } k = k_4 + k_6 + k_9$$

$$\frac{dx}{dt} = -(k_1 + k_5 + k_7)x + k_2y + \frac{k_6k_5x}{k} + \frac{k_6k_3y}{k}$$

$$\frac{dy}{dt} = -(k_2 + k_3 + k_8)x + k_1x + \frac{k_4k_5x}{k} + \frac{k_4k_3y}{k}$$

# Analytic expressions for the two smallest eigenvalues 2

- $\frac{dx}{dt} = -(k_1 + k_5 + k_7)x + k_2y + \frac{k_6k_5x}{k} + \frac{k_6k_3y}{k}$
- $\frac{dy}{dt} = -(k_2 + k_3 + k_8)x + k_1x + \frac{k_4k_5x}{k} + \frac{k_4k_3y}{k}$

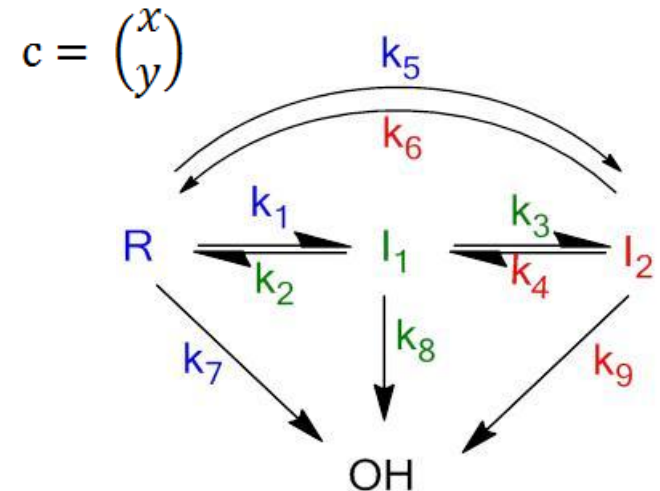
$$\frac{dc}{dt} = \begin{pmatrix} -(k_1 + k_5 \left(1 - \frac{k_6}{k}\right) + k_7) & k_1 + \frac{k_5k_4}{k} \\ k_2 + \frac{k_3k_6}{k} & -(k_2 + k_3 \left(1 - \frac{k_4}{k}\right) + k_8) \end{pmatrix} c = \begin{pmatrix} -A & B \\ C & -D \end{pmatrix} c$$

$$\lambda_{\pm} = \frac{-(A + D) \pm \sqrt{(A + D)^2 - 4(AD - BC)}}{2}$$

If  $(A + D)^2 \gg 4(AD - BC)$ , binomial expansion gives

$$\lambda_- = -(A + D)$$

$$\lambda_+ = \frac{-(AD - BC)}{A + D}$$



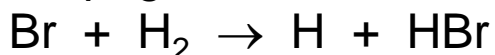
# Chain reactions. 1. straight chain reactions - e.g. $\text{H}_2 + \text{Br}_2$

- Chain carriers (also called chain centres, i.e. reactive intermediates) are generated in the initiation steps.
- In the propagation steps the chain carriers react with the reactants, produce products and regenerate the chain carriers.
- In the termination steps the chain carriers are consumed

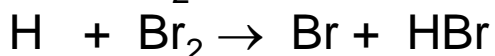
## Initiation



## Propagation

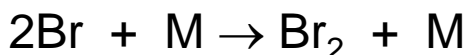


$$r_2 = k_2[\text{Br}][\text{H}_2]$$

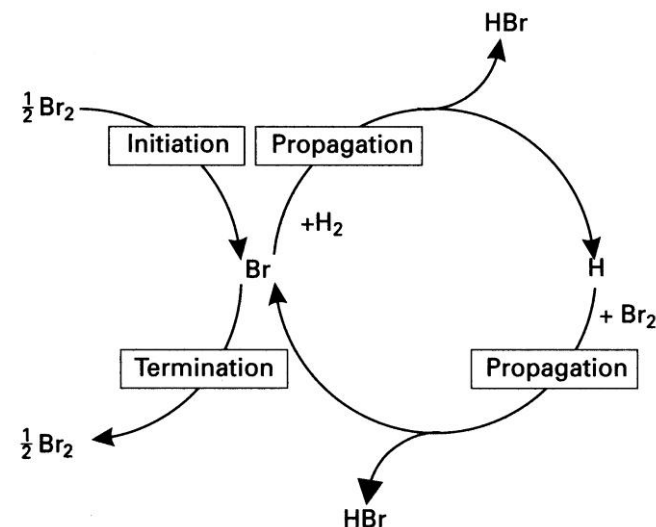
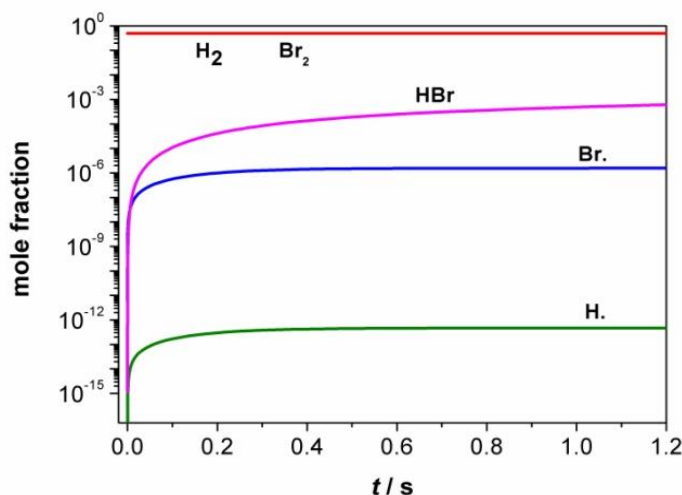


$$r_3 = k_3[\text{H}][\text{Br}_2]$$

## Termination

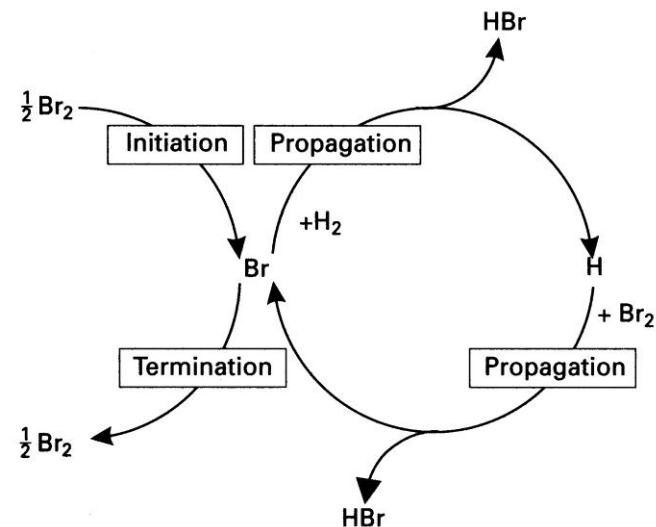


$$r_4 = 2k_4[\text{Br}]^2[\text{M}]$$



stoichiometric mixture,  
 $T = 600 \text{ K}$ ,  $p = 1 \text{ atm}$

Relative rates of reaction after 1s,  
 stoichiometric mixture,  $T = 600\text{ K}$ ,  $p = 1\text{ atm}$   
 $r_1 = r_4 = 1\text{ unit}$   
 $r_2 = r_3 = 100\text{ units}$   
Chain length = 100 (number of propagation  
 cycles per initiation (or termination) event).



$$\begin{aligned} \frac{d[\text{Br}]}{dt} &= 2k_1[\text{Br}_2][\text{M}] - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - 2k_4[\text{Br}]^2[\text{M}] = 0 & (\text{QSSA}) \\ \frac{d[\text{H}]}{dt} &= +k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] = 0 \end{aligned}$$

Adding:

$$2k_1[\text{Br}_2][\text{M}] = 2k_4[\text{Br}]^2[\text{M}]$$

$$[\text{Br}] = \sqrt{\{k_1[\text{Br}_2]/k_4\}}$$

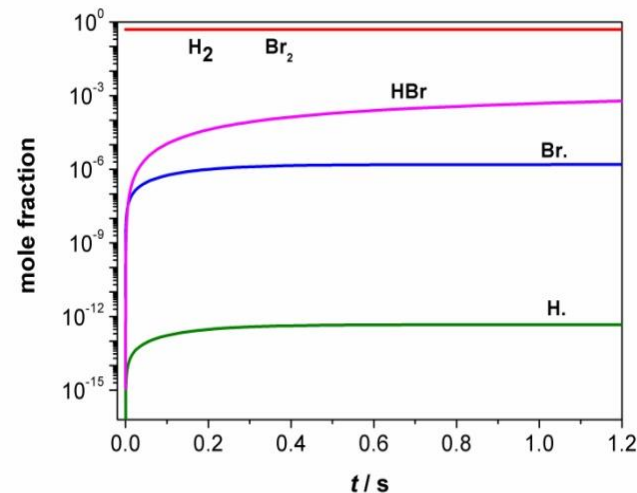
From  $d[\text{H}]/dt = 0$   $[\text{H}]/[\text{Br}] = k_2[\text{H}_2]/k_3[\text{Br}_2]$

$$= k_2/k_3$$

(for stoichiometric mixtures)

The activation energy of reaction 2 is  $82\text{ kJ mol}^{-1}$   
 and that for reaction 3 is  $4\text{ kJ mol}^{-1}$ . The  $A$   
 factors are similar.

At  $600\text{ K}$ , the ratio of concentrations is  $\sim 1.5 \times 10^{-7}$





## Chain reactions. 2. branched chain reactions - e.g. $\text{H}_2 + \text{O}_2$

- In addition to initiation, propagation and termination steps, these reactions have **branching** steps in which one radical generates 2 radicals, e.g.



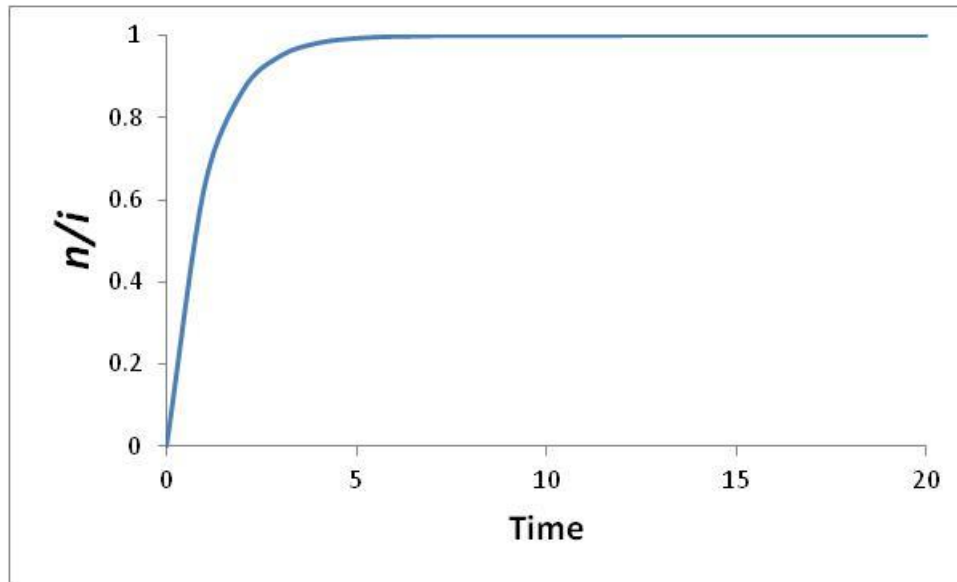
- Propagation steps don't change the radical concentration and in determining the time dependence of the radical concentration,  $n$ , we only need consider the other three reaction types.  
Considering only linear termination

$$\frac{dn}{dt} = i + gn - fn = i + \phi n; \quad \phi = g - f$$

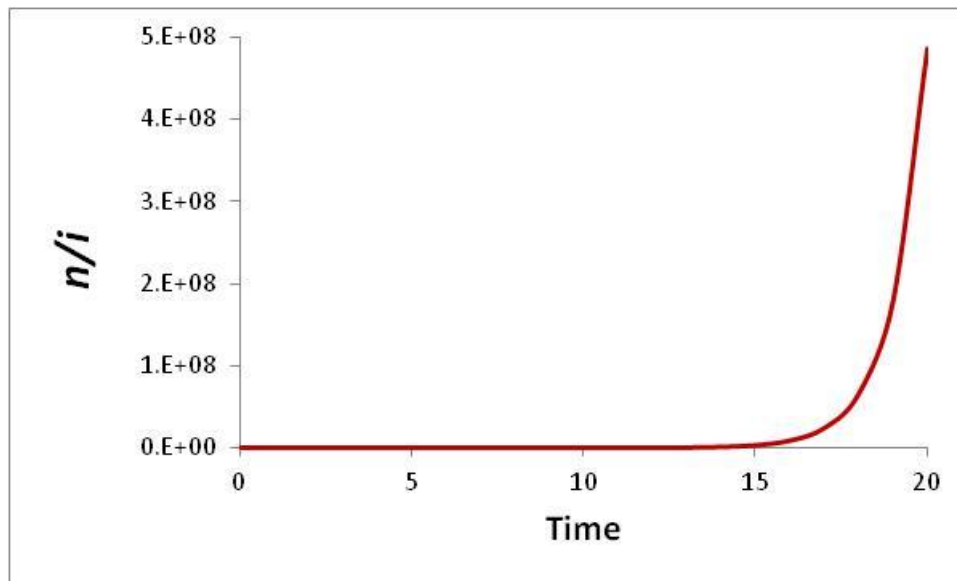
where  $i$  is the rate of initiation and  $g$  and  $f$  are the first order rate constants for branching and termination respectively.  
Integrating:

$$n = i\{\exp(\phi t) - 1\}/\phi$$

## Plots of $n/i$ vs $t$ for negative and positive $\phi$

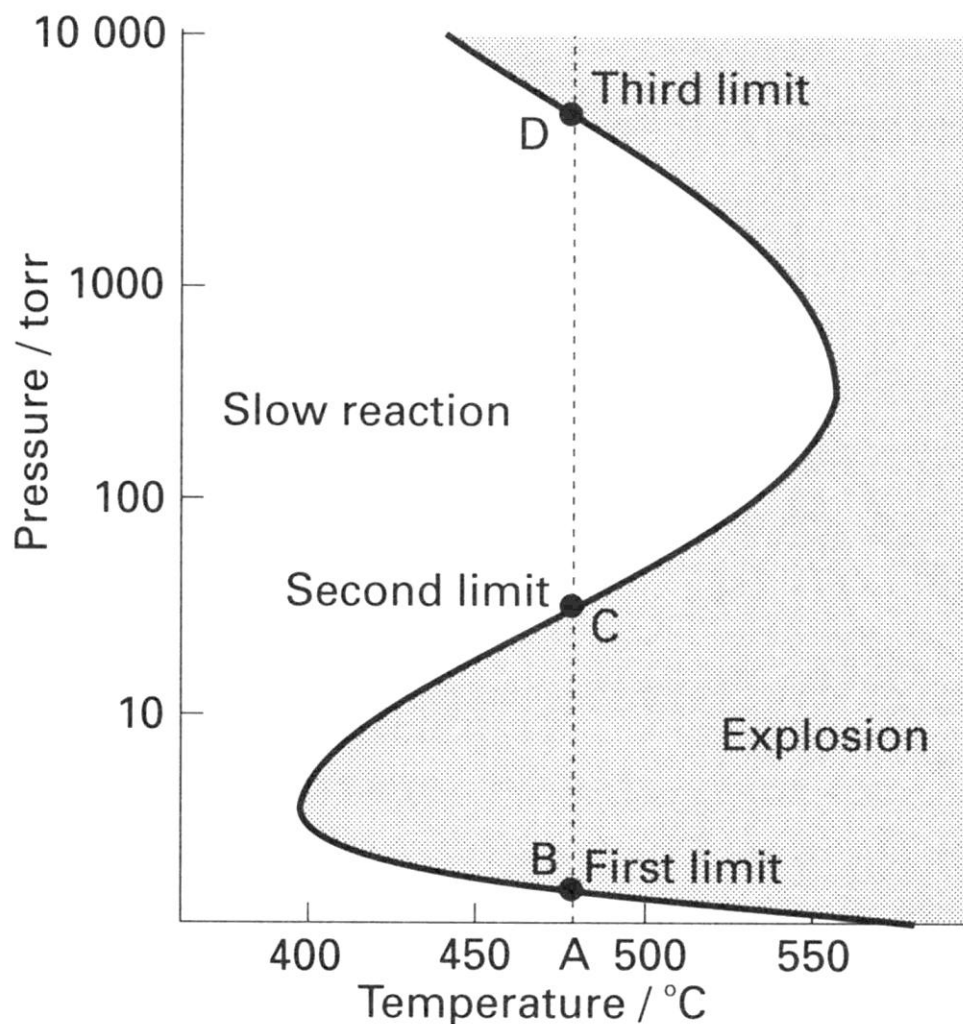
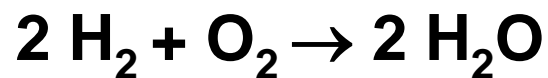


For plot 1,  $g-f = -1$ .  
Termination is faster than branching and  $n$  approaches a steady state,  $n = i/\phi$ , as  $\exp(\phi t)$  tends to zero.



For plot 2,  $g-f = +1$ .  
Branching is faster than termination and the number of radicals increases exponentially:  
 $n = (i/\phi)\exp(\phi t)$

# Explosion of hydrogen–oxygen mixtures



## Observations:

The 1<sup>st</sup> explosion limit depends on the size of the vessel and the quality of the wall.

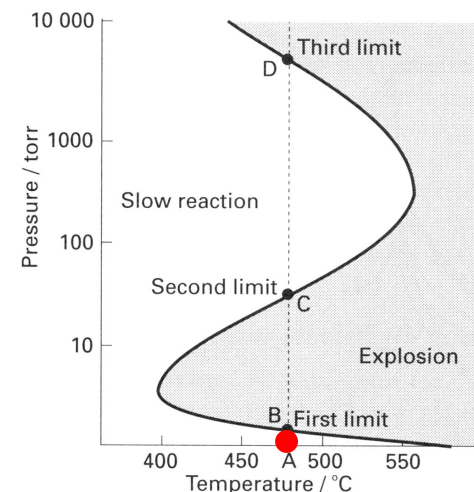
The 2<sup>nd</sup> and 3<sup>rd</sup> limits do not depend on these

## Slightly extended mechanism

1	$\text{H}_2 + \text{O}_2 \rightarrow \cdot\text{H} + \cdot\text{HO}_2$	initiation
2	$\cdot\text{OH} + \text{H}_2 \rightarrow \cdot\text{H} + \text{H}_2\text{O}$	propagation
3	$\cdot\text{H} + \text{O}_2 \rightarrow \cdot\text{OH} + \cdot\text{O}$	branching
4	$\cdot\text{O} + \text{H}_2 \rightarrow \cdot\text{OH} + \cdot\text{H}$	branching
5	$\cdot\text{H} + \text{O}_2 + \text{M} \rightarrow \cdot\text{HO}_2 + \text{M}$	termination*
6	$\cdot\text{H} \rightarrow \text{wall}$	termination
7	$\cdot\text{O} \rightarrow \text{wall}$	termination
8	$\cdot\text{OH} \rightarrow \text{wall}$	termination
9	$\cdot\text{HO}_2 + \text{H}_2 \rightarrow \cdot\text{H} + \text{H}_2\text{O}_2$	initiation *
10	$2 \cdot\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	termination
11	$\text{H}_2\text{O}_2 \rightarrow 2 \cdot\text{OH}$	initiation

1	$\text{H}_2 + \text{O}_2 \rightarrow \cdot\text{H} + \cdot\text{HO}_2$	initiation
2	$\cdot\text{OH} + \text{H}_2 \rightarrow \cdot\text{H} + \text{H}_2\text{O}$	propagation
3	$\cdot\text{H} + \text{O}_2 \rightarrow \cdot\text{OH} + \cdot\text{O}$	branching
4	$\cdot\text{O} + \text{H}_2 \rightarrow \cdot\text{OH} + \cdot\text{H}$	branching
5	$\cdot\text{H} + \text{O}_2 + \text{M} \rightarrow \cdot\text{HO}_2 + \text{M}$	termination*
6	$\cdot\text{H} \rightarrow \text{wall}$	termination
7	$\cdot\text{O} \rightarrow \text{wall}$	termination
8	$\cdot\text{OH} \rightarrow \text{wall}$	termination
9	$\cdot\text{HO}_2 + \text{H}_2 \rightarrow \cdot\text{H} + \text{H}_2\text{O}_2$	initiation *
10	$2 \cdot\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	termination
11	$\text{H}_2\text{O}_2 \rightarrow 2 \cdot\text{OH}$	initiation

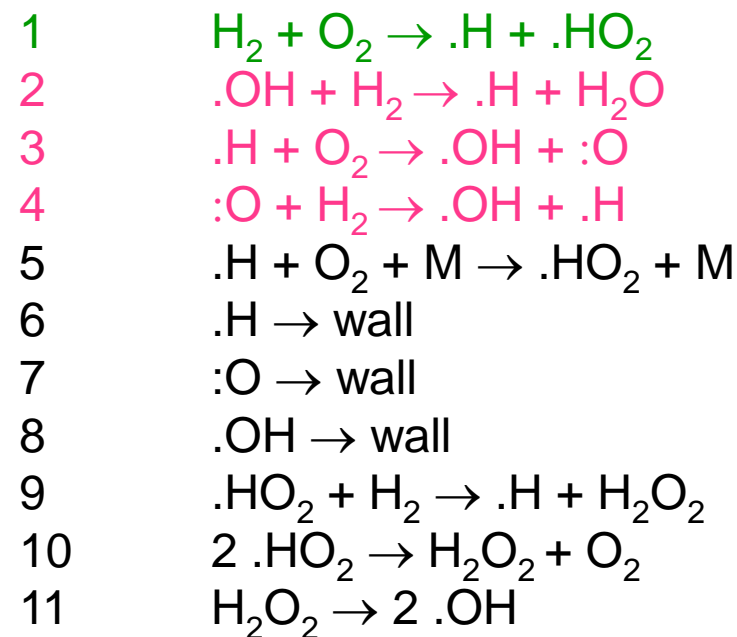
This is a slightly extended version of the mechanism we saw before



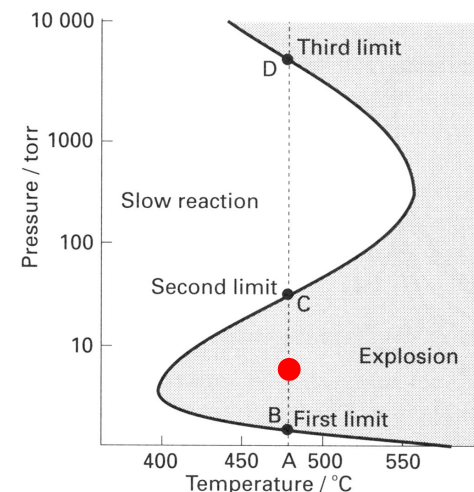
## Below the 1<sup>st</sup> explosion limit:

domination of the termination reactions at the wall

→ no explosion

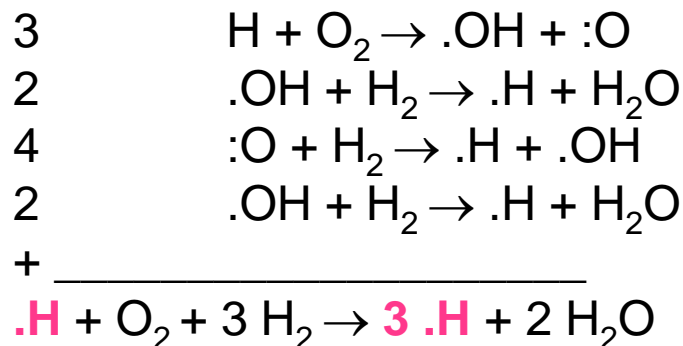


initiation  
 propagation  
 branching  
 branching  
 termination\*  
 termination  
 termination  
 termination  
 initiation \*  
 termination  
 initiation

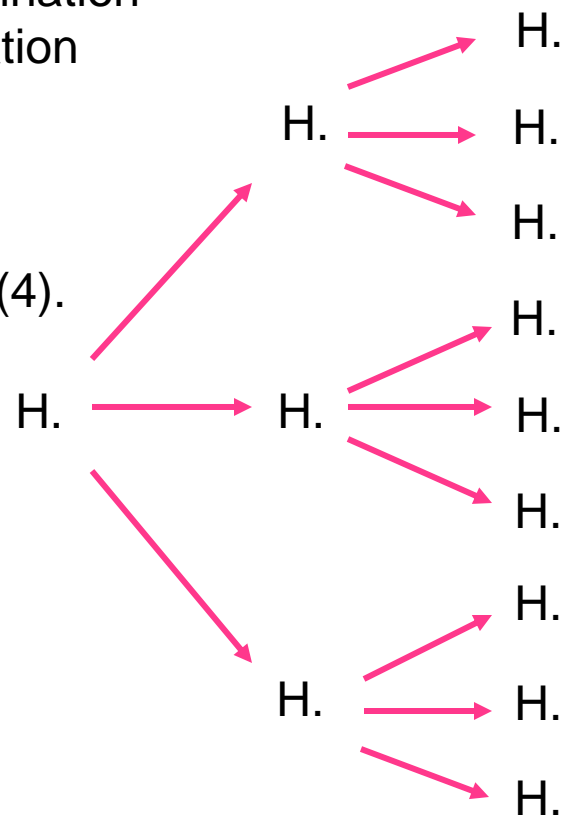


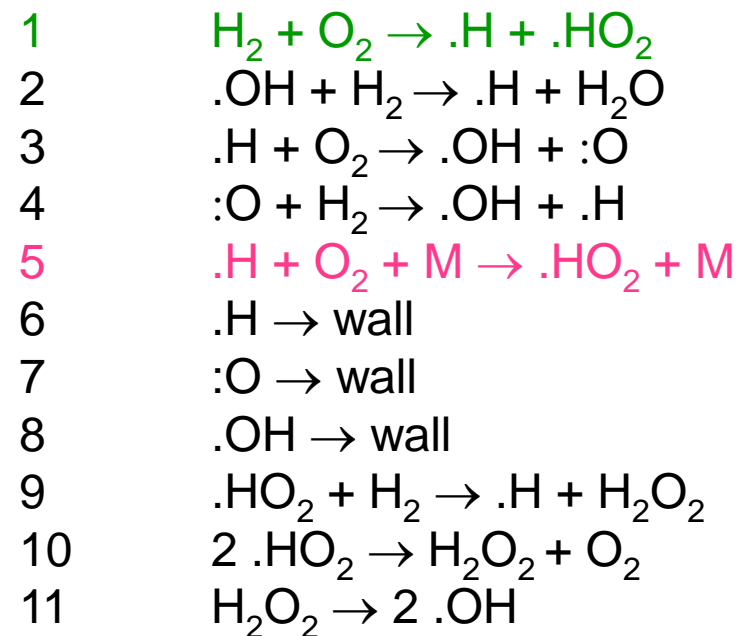
**Between the 1<sup>st</sup> and the 2<sup>nd</sup> explosion limits:**

Propagation step (2). Branching steps (3) and (4).

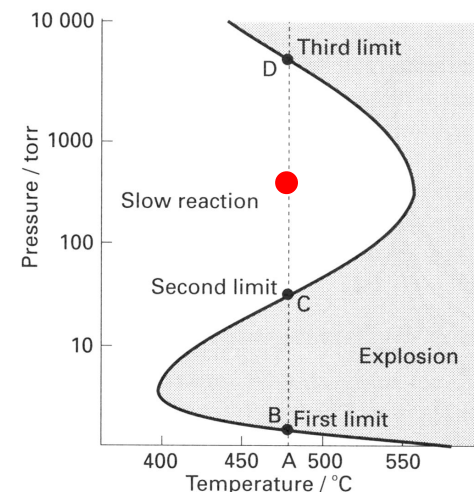


**→ explosion**





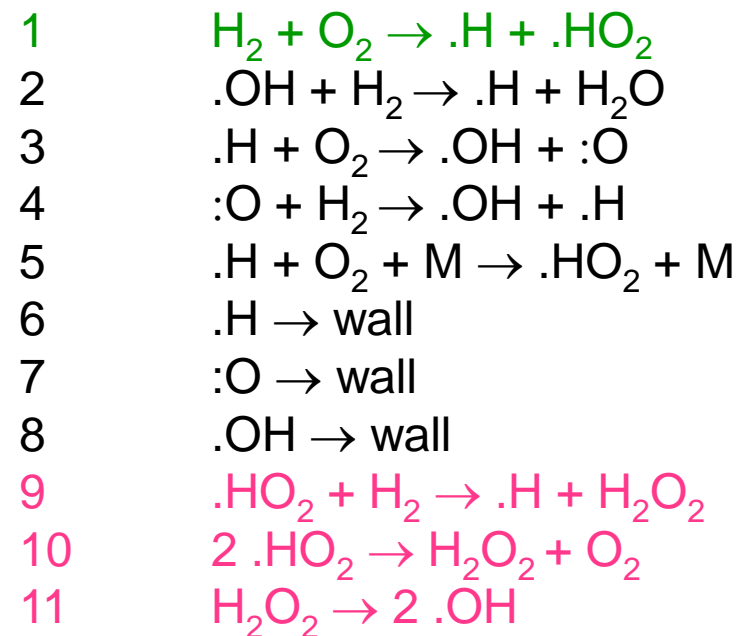
initiation  
 propagation  
 branching  
 branching  
 termination\*  
 termination  
 termination  
 termination  
 initiation \*  
 termination  
 initiation



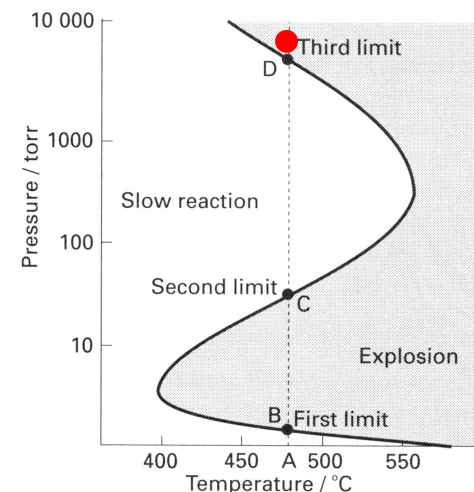
**Between the 2<sup>nd</sup> and the 3<sup>rd</sup> explosion limits:**



**→ no explosion**



initiation  
 propagation  
 branching  
 branching  
 termination\*  
 termination  
 termination  
 termination  
 initiation \*  
 termination  
 initiation



**above the 3<sup>rd</sup> explosion limit**

Reactions (9), (10), and (11) become important

**→ explosion**



# An analysis of the explosion limits of hydrogen-oxygen mixtures

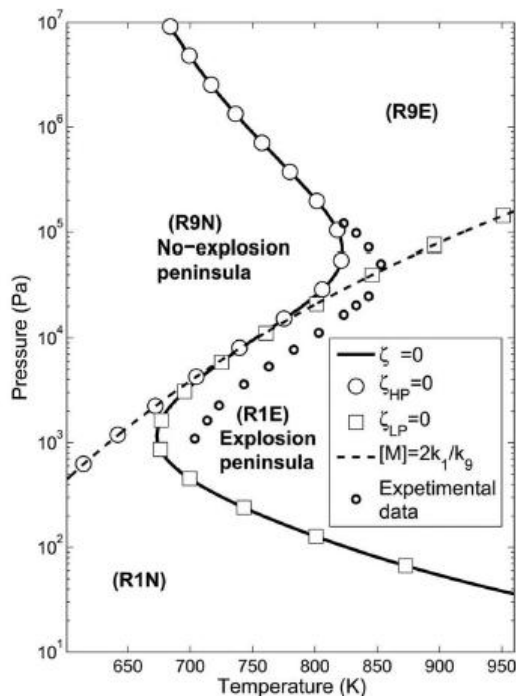
Xianming Wang (王贤明)<sup>1</sup> and Chung K. Law<sup>1,2,a)</sup>

<sup>1</sup>Center for Combustion Energy and Department of Thermal Engineering, Tsinghua University, Beijing 100084, China

<sup>2</sup>Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey 08544-5263, USA

(Received 26 December 2012; accepted 12 March 2013; published online 4 April 2013)

In this study, the essential factors governing the Z-shaped explosion limits of hydrogen-oxygen mixtures are studied using eigenvalue analysis. In particular, it is demonstrated that the wall destruction of H and HO<sub>2</sub> is essential for the occurrence of the first and third limits, while that of O, OH, and H<sub>2</sub>O<sub>2</sub> play secondary, quantitative roles for such limits. By performing quasi-steady-state analysis, an approximate, cubic equation for the explosion limits is obtained, from which explicit expressions governing the various explosion limits including the state of the loss of non-monotonicity are derived and discussed. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4798459>]



Discusses the explosion limits for H<sub>2</sub>/O<sub>2</sub>

Also Liang and Law  
*Phys.Chem.Chem.Phys.*,  
2018, 20, 742

An analysis of the explosion limits of hydrogen/oxygen mixtures with nonlinear chain reactions