Lecture 2

- Introduced quantities to characterise multi-component mixture and defined equivalence ratio, AFR

- Introduced stoichiometry relation

- Discussed methods to estimate adiabatic flame temperature

- Simple derivation of conservation equations for species

- Advective flux, $\rho Y_i U$, diffusive flux (Fick's Law)

- Discussed significance of energy equation

$$\frac{\partial \rho\, Y_i}{\partial t} + \frac{\partial \rho U\, Y_i}{\partial x} = \frac{\partial}{\partial x}\left(\rho\, \mathcal{D}\frac{\partial Y_i}{\partial x}\right) + \underline{w_i}$$
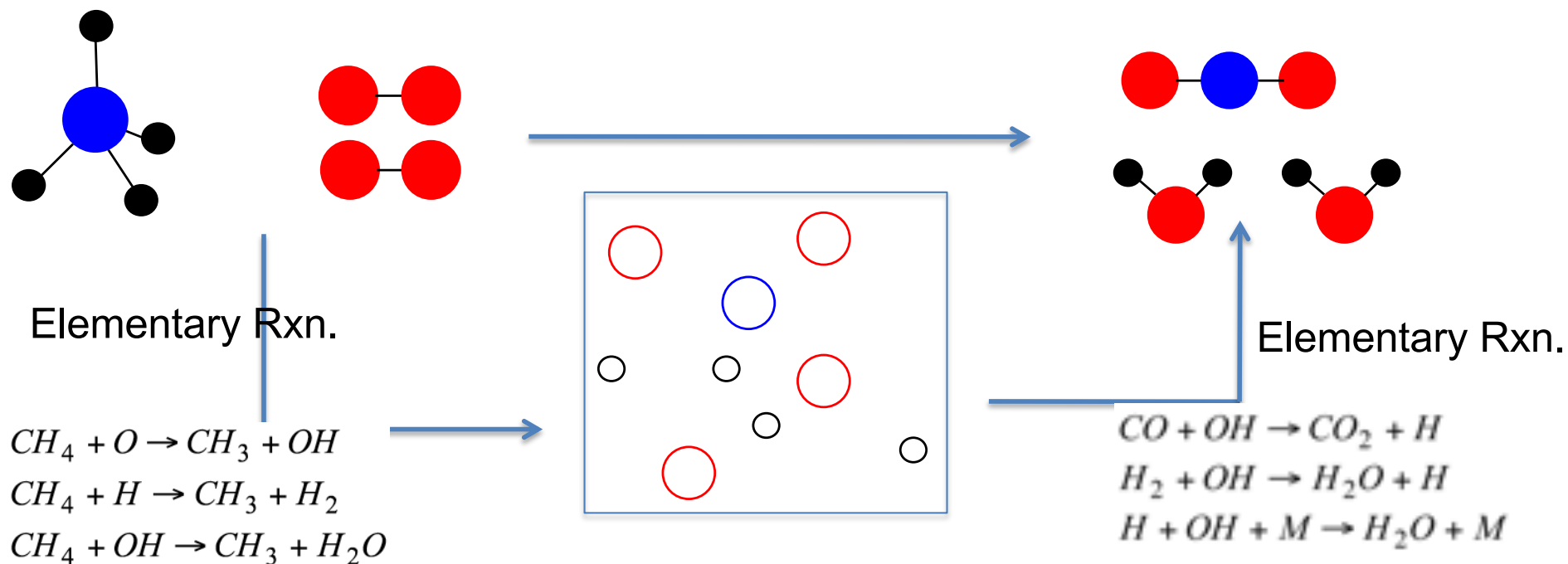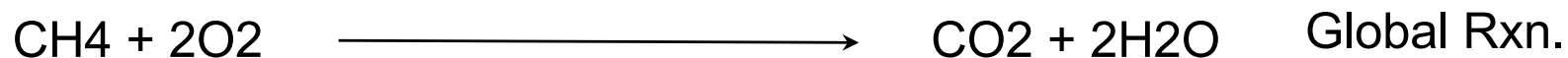
Today: Chemical Kinetics & Equilibrium

Objectives – Chemical kinetics

- Introduce chemical kinetics concept

- Simple model for fuel consumption rate

  - Use NO formation as an example

- Qualitative description for hydrocarbon combustion

- How do we go from reactants to products?

$$CH4 + 2O2 \longrightarrow CO2 + 2H2O \qquad \text{Global Rxn.}$$

Elementary Rxn.

Elementary Rxn.

$$CH_4 + O \rightarrow CH_3 + OH$$
$$CH_4 + H \rightarrow CH_3 + H_2$$
$$CH_4 + OH \rightarrow CH_3 + H_2O$$

$$CO + OH \rightarrow CO_2 + H$$
$$H_2 + OH \rightarrow H_2O + H$$
$$H + OH + M \rightarrow H_2O + M$$

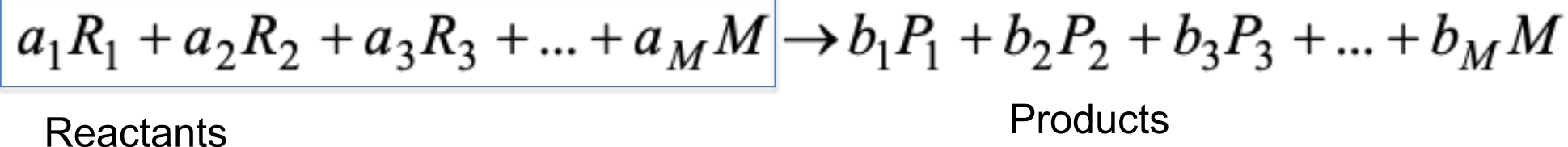|	Reaction	A	n	Ea
1	$H + O_2 = O + OH$	2.650E+16	−0.6707	17041.0
2	$O + H_2 = H + OH$	3.870E+04	2.7	6260.0
3	$OH + H_2 = H + H_2O$	2.160E+08	1.51	3430.0
4	$2OH = O + H_2O$	3.570E+04	2.4	−2110.0
5[a]	$H + O_2 + M = HO_2 + M$	2.800E+18	−0.86	0.0
6	$H + O_2 + H_2O = HO_2 + H_2O$	1.126E+19	−0.76	0.0
7	$H + O_2 + N_2 = HO_2 + N_2$	2.535E+19	−1.3392	0.0
8	$H + O_2 + He \Rightarrow HO_2 + He$	7.000E+17	−0.8	0.0
9	$H + O_2 + Ar \Rightarrow HO_2 + Ar$	7.000E+17	−0.8	0.0
10	$H + 2O_2 = HO_2 + O_2$	2.080E+19	−1.24	0.0
11	$H + HO_2 = 2OH$	8.316E+13	0	635.0
12	$H + HO_2 = O_2 + H_2$	4.480E+13	0	1068.0
13(D)	$OH + HO_2 = O_2 + H_2O$	1.450E+13	0	−500.0
14(D)	$OH + HO_2 = O_2 + H_2O$	5.000E+15	0	17330.0
15	$H + HO_2 = O + H_2O$	3.970E+12	0	671.0
16	$O + HO_2 = OH + O_2$	2.000E+13	0	0.0
17(D)	$2HO_2 = O_2 + H_2O_2$	1.300E+11	0	−1630.0
18(D)	$2HO_2 = O_2 + H_2O_2$	4.200E+14	0	12000.0
19[b]	$2OH(+M) = H_2O_2(+M)$	7.400E+13	−0.37	0.0
20	$H + H_2O_2 = OH + H_2O$	1.000E+13	0	3600.0
21(D)	$OH + H_2O_2 = HO_2 + H_2O$	1.700E+18	0	29410.0
22(D)	$OH + H_2O_2 = HO_2 + H_2O$	2.000E+12	0	427.0
23	$H + H_2O_2 = HO_2 + H_2$	1.210E+07	2	5200.0
24	$O + H_2O_2 = OH + HO_2$	9.630E+06	2	4000.0
25[c]	$2H + M = H_2 + M$	1.000E+18	−1	0.0
26	$2H + H_2 = 2H_2$	9.000E+16	−0.6	0.0
27	$2H + CO_2 = H_2 + CO_2$	5.500E+20	−2	0.0
28	$2H + H_2O = H_2 + H_2O$	6.000E+19	−1.25	0.0
29[d]	$H + OH + M = H_2O + M$	2.200E+22	−2	0.0
30[e]	$2O + M = O_2 + M$	1.200E+17	−1	0.0
31[f]	$O + H + M = OH + M$	5.000E+17	−1	0.0
32	$OH + CO = H + CO_2$	4.689E+07	1.228	70.0
33	$HO_2 + CO = OH + CO_2$	1.500E+14	0	24544.0
34[g]	$O + CO(+M) = CO_2(+M)$	1.800E+10	0	2385.0
35	$H + HCO = H_2 + CO$	7.340E+13	0	0.0
36	$OH + HCO = H_2O + CO$	5.000E+13	0	0.0
37	$HCO + O_2 = HO_2 + CO$	1.345E+13	0	400.0
38[h]	$HCO + M = H + CO + M$	1.870E+17	−1	17000.0
39	$HCO + H_2O = H + CO + H_2O$	1.500E+18	−1	17000.0
40	$O + HCO = H + CO_2$	3.000E+13	0	0.0
41	$O + CH_4 = OH + CH_3$	1.020E+09	1.5	8600.0
42	$OH + CH_4 = CH_3 + H_2O$	1.000E+08	1.6	3120.0
43	$O + CH_3 = H + CH_2O$	5.060E+13	0	0.0
44	$O + CH_3 \Rightarrow H + H_2 + CO$	3.370E+13	0	0.0
45	$O + CH_2O = OH + HCO$	3.900E+13	0	3540.0
46[i]	$H + CH_3(+M) = CH_4(+M)$	1.390E+16	−0.534	536.0

Detailed chemical mechanism:
    involves 100s of elementary reactions,
        10s of species

even for a simplest hydrocarbon, CH4

(Combust. Flame,160, p.56-75, 2013,
    Nikolaou, Chen, Swaminathan)

Elementary reaction:

$$a_1 R_1 + a_2 R_2 + a_3 R_3 + \ldots + a_M M \rightarrow b_1 P_1 + b_2 P_2 + b_3 P_3 + \ldots + b_M M$$

Reactants

Products

$$\frac{d[R_1]}{dt} = -a_1 \omega, \quad \frac{d[R_2]}{dt} = -a_2 \omega, \quad \frac{d[R_3]}{dt} = -a_3 \omega, \ldots$$

$$\frac{d[P_1]}{dt} = b_1 \omega, \quad \frac{d[P_2]}{dt} = b_2 \omega, \quad \frac{d[P_3]}{dt} = b_3 \omega, \ldots$$

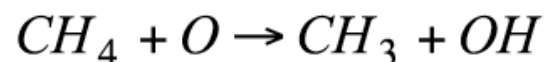$$\frac{d[M]}{dt} = b_M \omega - a_M \omega$$

$$\omega = k[R_1]^{a_1}[R_2]^{a_2}[R_3]^{a_3}\ldots$$

Arrhenius Rate & Rate Constant

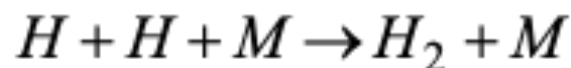$$\omega = k[R_1]^{a_1}[R_2]^{a_2}[R_3]^{a_3}\,...$$

(kmol/m³-s)

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

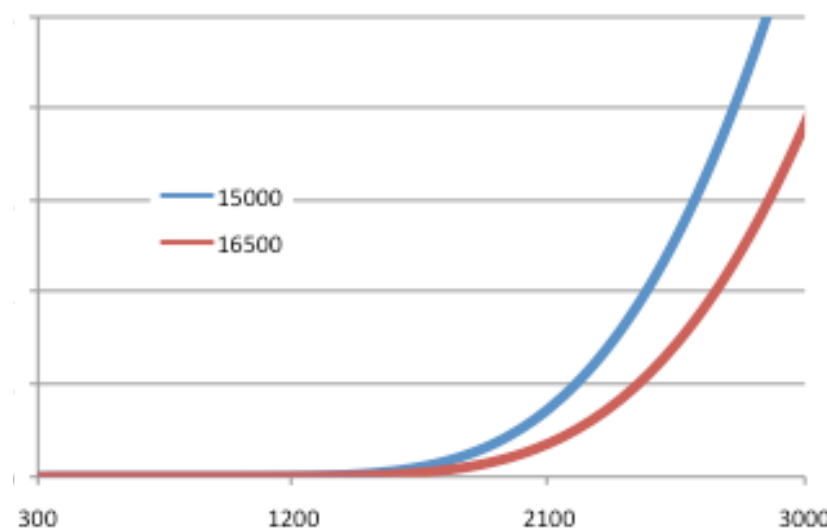Proportions of successful collisions with enough energy to break bonds

Number of collisions per unit time

$$CH_4 + O \rightarrow CH_3 + OH$$

$$\frac{d[CH_4]}{dt} = -k_1[CH_4][O]$$

$$H + H + M \rightarrow H_2 + M$$

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

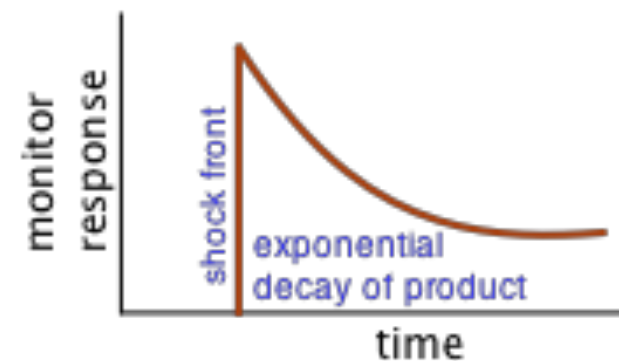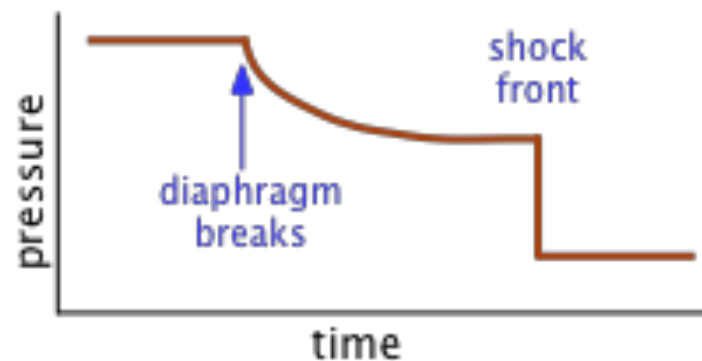15000
16500

300   1200   2100   3000

Statistical mechanics calculations
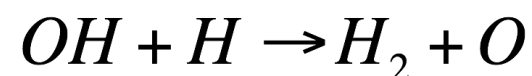shock tube experiments are used to measure the followings

$$H_2 + O \rightarrow OH + H$$

$$\frac{d[H2]}{dt} = -k[O][H2]$$

In k

Slope $\Rightarrow E_{act}/R^0$
Intercept $\Rightarrow$ In A

T

[O]

[H2]

$\Rightarrow \dfrac{d[H2]}{dt}$

t

t

t

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

1/T

Shock Tube

inert driver gas at high pressure

shock front

reaction mixture

frangible diaphragm

monitoring device

Stephen Lower

pressure

diaphragm breaks

shock front

time

monitor response

shock front

exponential decay of product

time

UNIVERSITY OF CAMBRIDGE

$$H_2 + O \rightleftharpoons OH + H$$

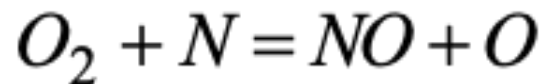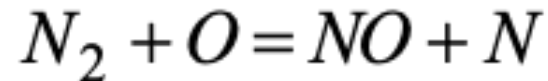$$H_2 + O \rightarrow OH + H$$
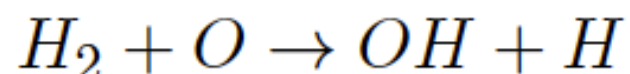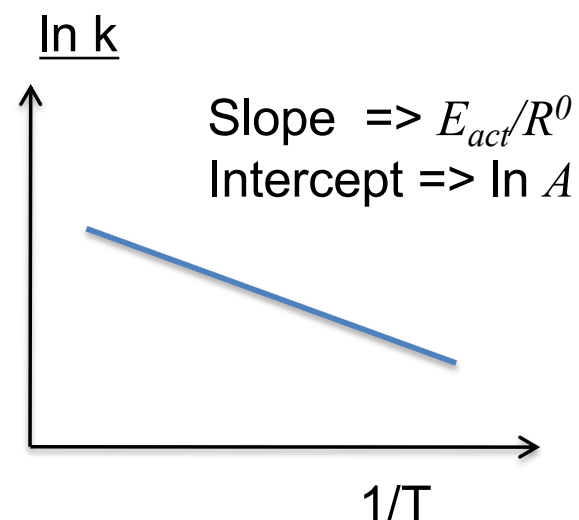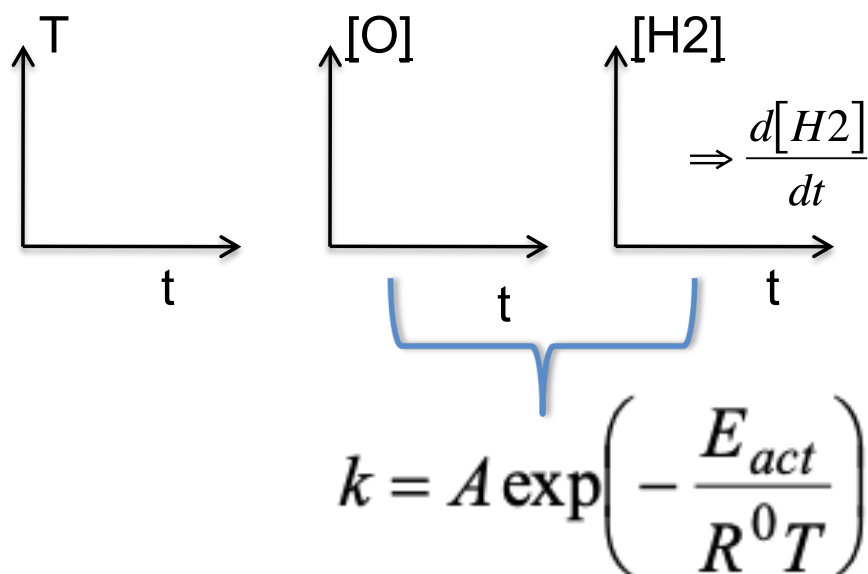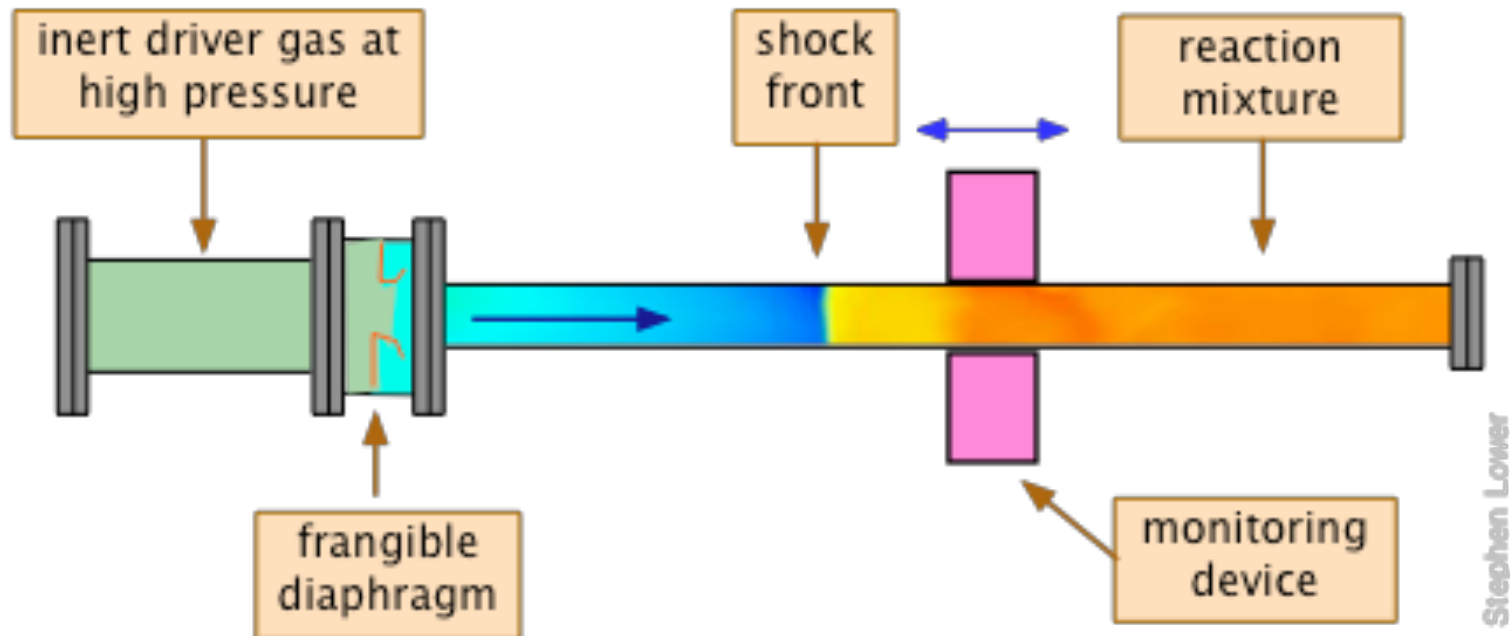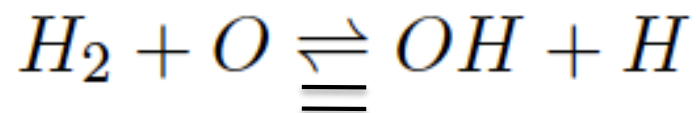
$$OH + H \rightarrow H_2 + O$$

$$\frac{d[H]}{dt} = \underbrace{k_f[H_2][O]}_{\text{forward}} - \underbrace{k_b[OH][H]}_{\text{backward}}$$

$$\frac{d[H]}{dt} = 0 \implies \frac{k_f}{k_b} = \frac{[OH][H]}{[H_2][O]}$$

k_b from k_f and thermodynamic data

Multiple reactions & w_i

$$N_2 + O = NO + N$$
$$O_2 + N = NO + O$$

Zeldovich Mechanism for thermal nitric oxide

$$\hat{w}_{NO} \equiv \frac{d[NO]}{dt} = k_{Z1f}[N_2][O] - k_{Z1b}[NO][N] + k_{Z2f}[O_2][N] - k_{Z2b}[NO][O]$$
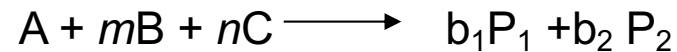
(kmol m^{-3} s^{-1})

$$\dot{w}_{NO} = \hat{w}_{NO} MW_{NO}$$

(This is for the species conservation equation)

(kg m^{-3} s^{-1})

$$A + mB + nC \longrightarrow b_1P_1 + b_2 P_2$$

$$d[A]/dt = -k[A][B]^m[C]^n$$

- m^{th} order w.r.t. species B; n^{th} order w.r.t. species C
- overall order $(m+n+1)$
- molecularity - # of molecules taking part in the reaction – overall order
- dissociation - first order & unimolecular

  $A + M <=> A^* + M; A^* \rightarrow$ products
- bimolecular and second order - most probable and common in combustion
- trimolecular - less probable but plays very important role in flames

  $H + O2 + M \longrightarrow HO2 + M$ (usually process terminator)

  $H + H + M \longrightarrow H2 + M$
- reactions may be classified

Classification of (chain) Reactions

- Initiation - forms an unstable/excited molecule or atom

    $H_2 + O_2 \rightarrow 2OH$; $CH_4 + H \longrightarrow CH_3 + H_2$ $H_2 + M \longrightarrow H + H + M$
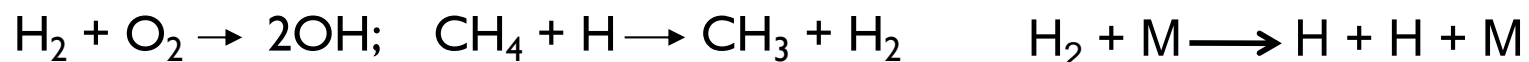
- propagation - # of unstable species remain constant

    $OH + H_2 \longrightarrow H_2O + H$; $CO + OH \longrightarrow CO_2 + H$ $HO_2 + H \longrightarrow OH + OH$
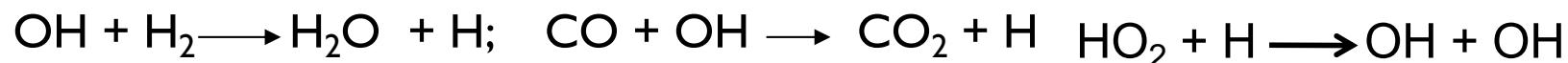
- branching - # of unstable species grow - responsible for a type explosion

    $H + O_2 \longrightarrow OH + O$; $CH + O_2 \longrightarrow CHO + O$

- termination - # of unstable species produced is zero

    - wall/gas termination

    $H + H \rightarrow H_2$; $H + H + M \longrightarrow H_2 + M$

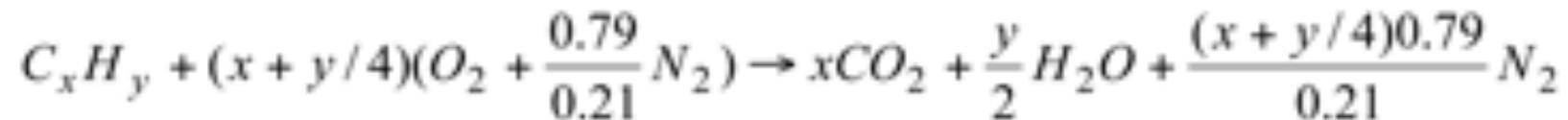 $H + OH + M \longrightarrow H_2O + M$
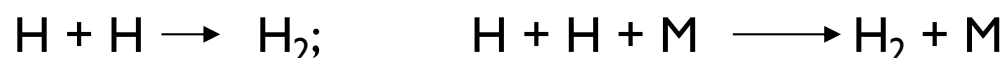
Simplification: one step model

$$\frac{dc_i}{dt} = \sum_{r=1}^{R} \hat{w}_r(c_i, p, T)$$

- Coupled non-linear ODEs

- Many time scales ('stiff')

- Specialized solvers
  - ChemKin, Cosilab, Cantera

For this module:

$$C_x H_y + (x + y/4)(O_2 + \frac{0.79}{0.21} N_2) \rightarrow xCO_2 + \frac{y}{2} H_2O + \frac{(x + y/4)0.79}{0.21} N_2$$

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

$$p = q = 1$$

Simplification: systematic reduction

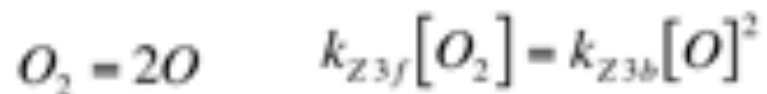$$N_2 + O \rightarrow NO + N \qquad O_2 + N \rightarrow NO + O$$

$$\frac{d[NO]}{dt} = k_{Z1f}[N_2][O] + k_{Z2f}[O_2][N]$$

Steady state for N:

$$\frac{d[N]}{dt} = k_{Z1f}[N_2][O] - k_{Z2f}[O_2][N] = 0$$

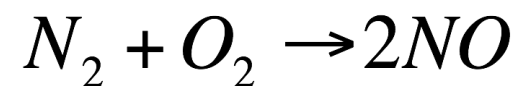$$[N] = \frac{k_{Z1f}[N_2][O]}{k_{Z2f}[O_2]}$$

Partial equilibrium:

$$O_2 = 2O \qquad k_{Z3f}[O_2] = k_{Z3b}[O]^2$$

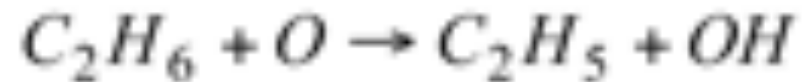$$[O] = \left(\frac{k_{Z3b}}{k_{Z3f}}\right)^{1/2} [O_2]^{1/2}$$

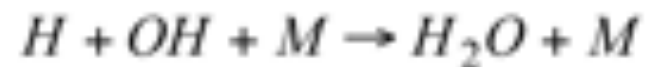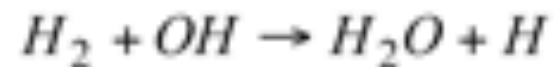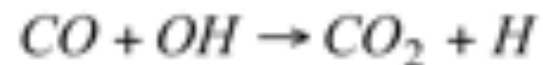$$\frac{d[NO]}{dt} = 2k_{Z1f}\left(\frac{k_{Z3f}}{k_{Z3b}}\right)^{1/2}[O_2]^{1/2}[N_2] \qquad N_2 + O_2 \rightarrow 2NO$$

Typical combustion sequence

1. Fuel Attack by radicals – Break down of fuel

$$C_2H_6 + O \rightarrow C_2H_5 + OH$$

2. Formation of CO and H2

3. Oxidation of H2 to H2O and CO to CO2 – large part of heat is released here

$$CO + OH \rightarrow CO_2 + H$$
$$H_2 + OH \rightarrow H_2O + H$$
$$H + OH + M \rightarrow H_2O + M$$

Summary: chemical kinetics

- Global reaction rate is typically empirical

- Elementary reaction rate is given by Law of Mass action $\quad k\prod_{i=1}^{N}\left[R_i\right]^{a_i}$

- Rate constant - Arrhenius rate – energetic collisions are required

- Types of reactions

- Full mechanism is very large and complex

- Simplification possible: steady state and equilibrium approximations
  - NO formation as an example

Example 2-1

To introduce species lifetime and how to calculate it?

$$d[C_3H_8]/dt = -A_G \exp(-T_{act}/T)[C_3H_8][O_2]$$

$$\frac{d[C_3H_8]}{[C_3H_8]} = -A_G \exp(-T_{act}/T)[O_2]dt$$

$$[C_3H_8] = [C_3H_8]_{in} \exp(-t/\tau)$$

$$\tau^{-1} = A_G \exp(-T_{act}/T)[O_2]$$

$$\tau(1200\ K) = 149 \times 10^{-3}\ s\ , \text{ and}$$
$$\tau(1500\ K) = 15 \times 10^{-3}\ s\ .$$

Why this change?

High *Tact* => high sensitivity of Rxn rate to *T*

How about *P* effects?

As $P \uparrow [O_2] \uparrow\ => \tau\downarrow$