Chemical Kinetics

Thursday, September 21, 2017 2:45 PM

Types of reactions

$$CH_4 + 2O_2 \rightarrow 1CO_2 + 2H_2O$$

global reaction

$$F + a\,Ox \rightarrow b\,Pr$$

$$CH_4 + O_2 \rightarrow CH_3 + HO_2$$
$$CH_3 + O_2 \rightarrow CH_3O + O$$
$$CH_3O \rightarrow H + CH_2O$$
$$CH_4 + HO_2 \rightarrow H_2O_2 + CH_3$$
$$H_2O_2 \rightarrow OH + OH$$
$$CH_2O + OH \rightarrow HCO + \boxed{H_2O}$$
$$HCO \rightarrow H + CO$$
$$CO + O \rightarrow 1CO_2$$

elementary rxns

global: overall chemistry of a system lumping several reactions into 1

elementary: the simplest reaction possible which describes the actual breaking and/or forming of bonds

reaction mechanism → complete listing of elementary reactions in a system

Species:

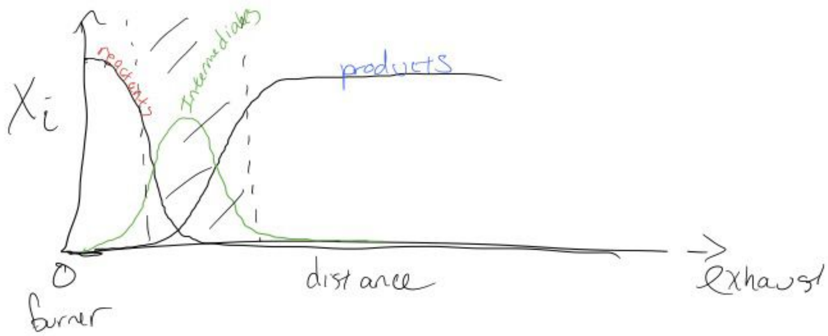
reactants: CH_4, O_2 initiate rxn

products: CO_2, H_2O, CO, H_2,

CH_4, HO_2, OH, CH_3...

CH_3, HO_2, OH, CH_3O ....

intermediate species



radicals: 1 free electron (unpaired)

- H, OH, HCO, HO_2

Types of reactions

reaction order

unimolecular rxn (1st order)

$$A \rightarrow B + C + \ldots$$

bimolecular rxn (2nd order)

$$A + B \rightarrow \text{Products}$$

termolecular rxn (3rd order))

$$A + B + C \rightarrow \text{products}$$

$$\boxed{A + B + M \rightarrow \text{products}}$$

M - 3rd body non-reactive collider

H_2 combustion

$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O$$

- 1.5th order overall

- 1st order wrt H_2
- $\frac{1}{2}$th order wrt O_2

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$$

$$\left.\begin{array}{l} H_2 \rightarrow H + H \\ O_2 \rightarrow O + O \end{array}\right\} \text{Initiation steps, Chain initiation}$$

$$\left.\begin{array}{l} H + O_2 \rightarrow OH + O \\ \rightarrow O + H_2 \rightarrow OH + H \end{array}\right\} \text{chain branching}$$

$$\rightarrow OH + H_2 \rightarrow H_2O + H \quad \} \text{ chain propagation}$$

$$\left.\begin{array}{l} H + H \rightarrow H_2 \\ H + O_2 + m \rightarrow HO_2 + m \end{array}\right\} \text{Chain termination}$$

order of reactivity of major radicals

$$OH > H > CH_3 > O > HO_2$$

Reaction rates

$$aA + bB \rightarrow cC + dD$$

$$\text{rate} = \left[\frac{\text{conc}}{\text{time}}\right]$$

conc $\frac{\text{moles}}{V}$

$$\text{rate} = \frac{1}{a}\frac{d[A]}{dt} = -k\,[A]^a[B]^b$$

rate const.
rate coefficient

$k(T)$ generally $\Leftarrow$

$k(T,P)$ sometimes

$$\frac{1}{c}\frac{d[C]}{dt} = +k[A]^a[B]^b$$

in general:

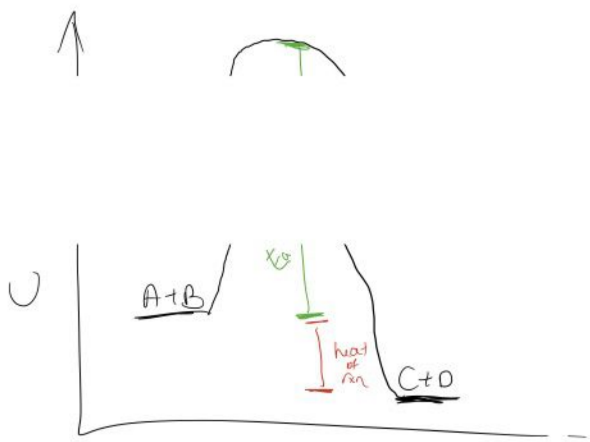
$$\text{rate} = \frac{1}{x}\frac{d[X]}{dt} = \overset{\text{form}}{+}/\underset{\text{consume}}{-}\; k(T)[A]^a[B]^b$$

Arrhenius expression:

$$k(T) = A\exp\left(-E_a/R_uT\right)$$

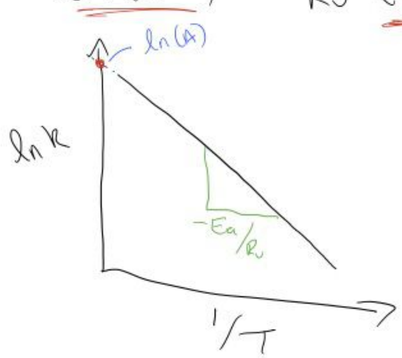
A = Arrhenius factor or pre-exponential factor

E_a = Activation energy



$$k(T) = A\exp\left(-E_A/R_uT\right)$$

$$\ln(k(T)) = \frac{-E_a}{R_u}\left(\frac{1}{T}\right) + \ln(A)$$



$$k(T) = A\, T^{\cdot} \exp\left(-\omega / i\, R_u T\right)$$

$$= A\, T^{b} \exp\left(-E_a / R_u' T\right)$$

Table 1. Rate coefficients in the Arrhenius form $k = AT^n \exp[-E/(R^{\circ}T)]$ for the skeletal me chanism. Units are mol, s, cm^3, cal, and K.

No.	Reaction		A^a	n	E^a
1	$H + O_2 \rightleftharpoons OH + O$		3.52×10^{16}	-0.70	17,069.79
2	$H_2 + O \rightleftharpoons OH + H$		5.06×10^{4}	2.67	6,290.63
3	$H_2 + OH \rightleftharpoons H_2O + H$		1.17×10^{9}	1.30	3,635.28
4	$H_2O + O \rightleftharpoons 2OH$		7.00×10^{5}	2.33	14,548.28
5	$H + O_2 + M^{(1)} \rightleftharpoons HO_2 + M^{(1)}$	k_0	5.75×10^{19}	-1.40	0.00
		k_∞	4.65×10^{12}	0.44	0.00
6	$H + OH + M^{(2)} \rightleftharpoons H_2O + M^{(2)}$		4.00×10^{22}	-2.00	0.00
7	$HO_2 + H \rightleftharpoons 2OH$		7.08×10^{13}	0.00	294.93
8	$HO_2 + H \rightarrow H_2 + O_2$		1.66×10^{13}	0.00	822.90
9	$HO_2 + H \rightleftharpoons H_2O + O$		3.10×10^{13}	0.00	1720.84
10	$HO_2 + O \rightarrow OH + O_2$		2.00×10^{13}	0.00	0.00
11	$HO_2 + OH \rightleftharpoons H_2O + O_2$		7.00×10^{12}	0.00	-1,094.65
			4.50×10^{14}	0.00	10,929.73
12	$H_2O_2 + M^{(3)} \rightarrow 2OH + M^{(3)}$	k_0	7.60×10^{30}	-4.20	51,071.86
		k_∞	2.63×10^{19}	-1.27	51,071.86
13	$2HO_2 \rightarrow H_2O_2 + O_2$		1.030×10^{14}	0.00	11042.07
			1.940×10^{11}	0.00	-1408.94
14	$CO + OH \rightleftharpoons CO_2 + H$		4.40×10^{6}	1.50	-740.92
15	$HCO + M^{(4)} \rightarrow CO + H + M^{(4)}$		1.86×10^{17}	-1.00	17,000.48
16	$HCO + H \rightarrow CO + H_2$		5.00×10^{13}	0.00	0.00
17	$HCO + OH \rightarrow CO + H_2O$		3.00×10^{13}	0.00	0.00

$$H_2 + \tfrac{1}{2} O_2 \xrightarrow{k} H_2O$$

$$\frac{d[H_2O]}{dt} = +k[H_2][O_2]^{1/2}$$

$$\tfrac{1}{a} \quad \cancel{2}\,\frac{d}{dt}[O_2] = -\frac{k}{2}[H_2][O_2]^{1/2}$$

$$H_2 + O_2 \underset{k_{r1}}{\overset{k_{f1}}{\rightleftharpoons}} HO_2 + H \qquad (R1)$$

$$\boxed{HO_2}$$

$$H + O_2 \underset{k_{r2}}{\overset{k_{f2}}{\rightleftharpoons}} OH + O \qquad (R2)$$

$$OH + H_2 \underset{k_{r3}}{\overset{k_{f3}}{\rightleftharpoons}} H_2O + H \qquad (R3)$$

$$H + O_2 + m \underset{k_{r4}}{\overset{k_{f4}}{\rightleftharpoons}} HO_2 + m \qquad (R4)$$

$k_{f1}(T)$: $H_2 + O_2 \rightarrow HO_2 + H$

$k_{r1}(T)$: $HO_2 + H \rightarrow H_2 + O_2$

$$\frac{d[O_2]}{dt} = k_{r1}[HO_2][H] + k_{r2}[OH][O] + k_{r4}[HO_2][m] + \dots - k_{f1}[H_2][O_2] - k_{f2}[H][O_2] - k_{f4}[H][O_2][m] - \dots$$

$$[m] = \frac{n_m}{V} = \frac{P}{R_u T}$$

$$\frac{d[HO_2]}{dt} = k_{f1}[H_2][O_2] + k_{f4}[H][O_2][m] - k_{r1}[HO_2][H]$$

$$aA + bB \underset{k_r}{\overset{k_f}{\rightleftharpoons}} cC + dD$$

$$\frac{1}{a}\frac{d[A]}{dt} = k_r [C]^c [D]^d - k_f [A]^a [B]^b$$

at Eq: $\dfrac{d[A]}{dt} = 0$

$$0 = k_r [C]^c [D]^d - k_f [A]^a [B]^b$$

$$\frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{k_f}{k_r} = K_c$$

$$K_p = \frac{(P_C/P^\circ)^c \, (P_D/P^\circ)^d}{(P_A/P^\circ)^a \, (P_B/P^\circ)^b}$$

$$[X_i] = \frac{n_i}{V} = \frac{x_i P}{R_u T} = \boxed{\frac{P_i}{R_u T}}$$

$\nu' = a + b + \dots$ (reactants)

$\nu'' = c + d + \dots$ (products)

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{(P_C/R_uT)^c (P_D/R_uT)^d}{(P_A/R_uT)^a (P_B/R_uT)^b}$$

$$= \underbrace{\frac{(P_C/P^\circ)^c (P_D/P^\circ)^d}{(P_A/P^\circ)^a (P_B/P^\circ)^b}}_{K_p} \left(\frac{P^\circ}{R_uT}\right)^{\overbrace{c+d}^{\nu''} \overbrace{-a-b}^{-\nu'}}$$

$$\boxed{\begin{aligned} K_c &= K_p \left(P^\circ/R_uT\right)^{\nu''-\nu'} \\ K_p &= K_c \left(R_uT/P^\circ\right)^{\nu''-\nu'} \end{aligned}}$$

$$\frac{k_f}{k_r} = K_c = K_p \left(\frac{P^\circ}{R_uT}\right)^{\nu''-\nu'} = \exp\left(\frac{-\Delta G}{R_uT}\,\frac{rxn}{\cdot}\right)\left(\frac{P^\circ}{R_uT}\right)^{\nu''-\nu'}$$