

Chemical Equilibrium

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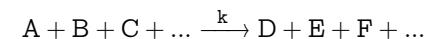
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Rate Laws & Reaction Order

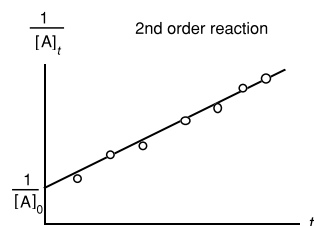
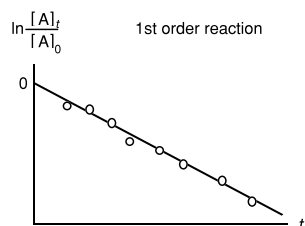


- Reaction Rate (RR) = $\frac{d[A]}{dt} = -k[A]^a[B]^b[C]^c \dots$
 a, b, c, \dots are **reaction orders** wrt. A, B, C, \dots ,
 k is the **rate coefficient** of the reaction,
the sum of all the exponents is the **overall reaction rate**.
- If some species are in excess, $[B], [C], \dots$ remains constant,

$$RR = \frac{d[A]}{dt} = -k[A]^a$$
- If the time behaviour is measured, the reaction order can be determined.



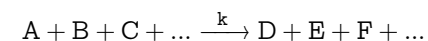
- For **first-order systems** ($a = 1$): $\ln \frac{[A]_t}{[A]_0} = -k(t - t_0)$
 $[A]_0$ & $[A]_t$ denote the concentration of species A at time t_0 and t , respectively.
- For **second-order systems** ($a = 2$): $\frac{1}{[A]_t} - \frac{1}{[A]_0} = k(t - t_0)$
- For **third-order systems** ($a = 3$): $\frac{1}{[A]_t^2} - \frac{1}{[A]_0^2} = 2k(t - t_0)$



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Relation of Forward & Reverse Reactions



- Forward reaction rate for production of A , $\frac{d[A]}{dt} = -k_f[A]^a[B]^b[C]^c \dots$
 - Reverse reaction rate for production of A , $\frac{d[A]}{dt} = k_b[D]^d[E]^e[F]^f \dots$
 - At chemical equilibrium, forward and backward reaction rates are same and no net reaction can be observed.
- $\Rightarrow -k_f[A]^a[B]^b[C]^c \dots = k_b[D]^d[E]^e[F]^f \dots$
- \Rightarrow Equilibrium constant (based on concentration), K_c
- $$K_c \equiv \frac{k_f}{k_b} = \frac{[D]^d[E]^e[F]^f}{[A]^a[B]^b[C]^c}$$



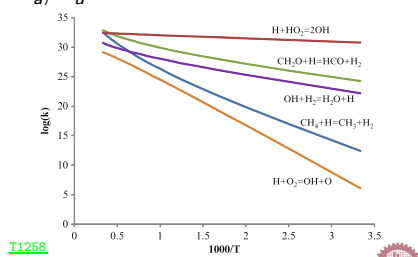
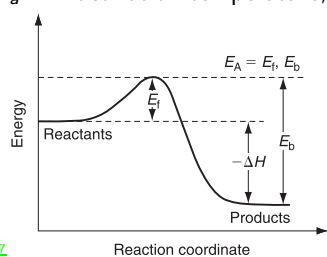
Temperature Dependence of Rate Coefficients

Arrhenius law:

$$k = A_o \exp\left(-\frac{E_a/R_u}{T}\right) = A_o \exp\left(-\frac{T_a}{T}\right)$$

 A_o \equiv pre-exponential factor

 E_a \equiv activation energy, corresponds to an energy barrier which has to be overcome during reaction.

 T_a \equiv activation temperature, $T_a \equiv E_a/R_u$


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Global One-step Reaction

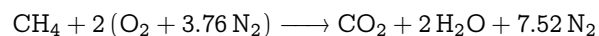
$$RR = A_o \exp\left(-\frac{E_a/R_u}{T}\right) [Fuel]^a [O_2]^b$$

Fuel	A_o	E_a (kcal/mol)	a	b
CH_4^*	$1.3 \cdot 10^9$	48.4	-0.3	1.3
CH_4	$8.3 \cdot 10^5$	30	-0.3	1.3
C_2H_6	$1.1 \cdot 10^{12}$	30	0.1	1.65
C_3H_8	$8.6 \cdot 10^{11}$	30	0.1	1.65
C_4H_{10}	$7.4 \cdot 10^{11}$	30	0.15	1.6
C_5H_{12}	$6.4 \cdot 10^{11}$	30	0.25	1.5
C_6H_{14}	$5.7 \cdot 10^{11}$	30	0.25	1.5
C_7H_{16}	$5.1 \cdot 10^{11}$	30	0.25	1.5
C_8H_{18}	$4.6 \cdot 10^{11}$	30	0.25	1.5
C_9H_{20}	$4.2 \cdot 10^{11}$	30	0.25	1.5
$C_{10}H_{22}$	$3.8 \cdot 10^{11}$	30	0.25	1.5
CH_3OH	$3.2 \cdot 10^{11}$	30	0.25	1.5
C_2H_5OH	$1.5 \cdot 10^{12}$	30	0.15	1.6
C_6H_6	$2.0 \cdot 10^{11}$	30	-0.1	1.85
C_7H_8	$1.6 \cdot 10^{11}$	30	-0.1	1.85

^a Units of A_o : $(\text{mol}/\text{cm}^3)^{1-a-b}/\text{s}$.

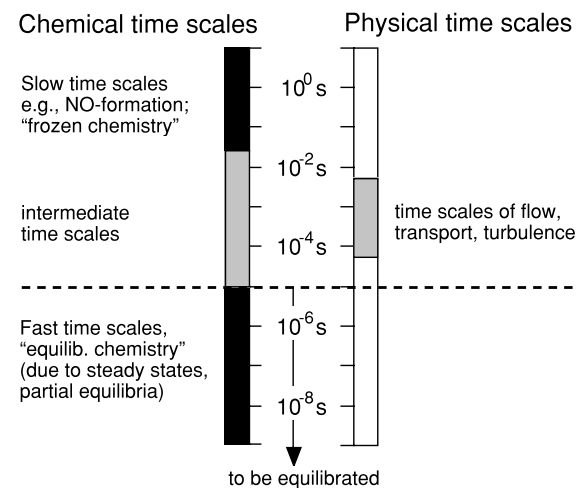
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Example: Methane Combustion at 1800 K



- $RR = A_o \exp\left(-\frac{E_a/R_u}{T}\right) [Fuel]^a [O_2]^b$
- $A_o = 1.3 \times 10^9 \text{ mol}/\text{cm}^3$
- $E_a = 48.4 \text{ kcal}/\text{mol}$, $R_u = 1.987 \text{ cal}/\text{mol}\cdot\text{K}$
- $a = -0.3$, $b = 1.3$, $[O_2] = 2[CH_4]$
- $\frac{d[CH_4]}{dt} = RR = 1.3 \times 10^9 \exp\left(-\frac{24358}{1800}\right) [CH_4]^{-0.3} (2[CH_4])^{1.3}$
- $\Rightarrow \frac{d[CH_4]}{dt} = -4245.3[CH_4]$
- $\Rightarrow \frac{[CH_4]}{[CH_4]_0} = \exp(-4245.3t)$
- Reduction to 5%, $\exp(-4245.3t) = 0.05 \rightarrow t = 0.71 \text{ ms}$

Time Scales in Chemically Reacting Flow



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Pressure Dependence of Rate Coefficients

$$RR = A_o \exp\left(-\frac{E_a/R_u}{T}\right) [Fuel]^a [O_2]^b$$

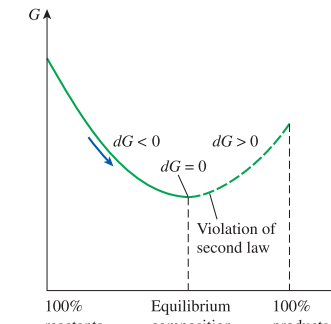
$$= A_o \exp\left(-\frac{E_a/R_u}{T}\right) [X_{fuel}]^a [X_{O_2}]^b \left(\frac{P/R_u}{T}\right)^{(a+b)} \propto P^{(a+b)}$$

- For one-step combustion chemistry model, $(a + b)$ is always positive, ranging from 1.0 to 1.75.
- When the pressure of a combustion system is doubled, the reaction rate can increase threefold for the case $a + b = 1.75$.



Criterion for Chemical Equilibrium

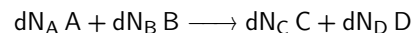
- $dS_{sys} \geq \frac{\delta Q}{T} \rightarrow dS_{sys} \geq 0$ for $\delta Q = 0$
- $\delta Q - PdV = dU \rightarrow dU + PdV - TdS \leq 0$
- $G \equiv H - TS \rightarrow dG = dH - TdS - SdT$
- $(dG)_{P,T} = dU + PdV - TdS \rightarrow (dG)_{P,T} \leq 0$



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Fixed mass reactions at fixed P & T Equilibrium Constant, K_p

Reaction chamber
 T, P

 N_A moles of A N_B moles of B N_C moles of C N_D moles of D

- $dN_A = -\epsilon \nu_A, dN_B = -\epsilon \nu_B$
- $dN_C = +\epsilon \nu_C, dN_D = +\epsilon \nu_D$
- ϵ is a proportionality constant.

T1320

$$G_{mix} = \sum_{R \rightarrow P} N_i g_{i,T} = \sum_{R \rightarrow P} N_i (g_{i,T}^\circ + R_u T \ln\left(\frac{P_i}{P_0}\right))$$

- For fixed T & P , **equilibrium condition**:

$$\Rightarrow dG_{mix} = 0 = \sum_{R \rightarrow P} dN_i (g_{i,T}^\circ + R_u T \ln\left(\frac{P_i}{P_0}\right))$$



$$\nu_C g_{C,T}^\circ + \nu_D g_{D,T}^\circ - \nu_A g_{A,T}^\circ - \nu_B g_{B,T}^\circ = -R_u T \sum_{R \rightarrow P} \nu_i \ln\left(\frac{P_i}{P_0}\right)$$

$$\Rightarrow \Delta G_T^\circ = -R_u T \ln\left[\frac{(P_C/P_0)^{\nu_C} (P_D/P_0)^{\nu_D}}{(P_A/P_0)^{\nu_A} (P_B/P_0)^{\nu_B}}\right] = -R_u T \ln(K_P)$$

$$K_P = \exp\left[-\frac{\Delta G_T^\circ}{R_u T}\right]$$

$$\text{Equilibrium constant, } K_P \equiv \frac{(P_C/P_0)^{\nu_C} (P_D/P_0)^{\nu_D}}{(P_A/P_0)^{\nu_A} (P_B/P_0)^{\nu_B}}$$

$$K_P = e^{(-\Delta G_T^\circ/R_u T)} = e^{-\Delta H^\circ/R_u T} e^{\Delta S^\circ/R_u}$$

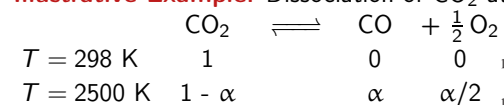
- For $K_P > 0$, which favours products, ΔH° should be negative, exothermic reaction.
- For gaseous mixture, $P_i = X_i P$, and if $\Delta \nu = \nu_C + \nu_D - \nu_A - \nu_B$,

$$\Rightarrow K_P = \frac{X_C^{\nu_C} X_D^{\nu_D}}{X_A^{\nu_A} X_B^{\nu_B}} \left[\frac{P}{P_0}\right]^{\Delta \nu} = \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} \left[\frac{P/P_0}{N_T}\right]^{\Delta \nu}$$

- N_T is the total number of moles present in the reaction vessel.



Illustrative Example: Dissociation of CO₂ at 2500 K, 10 atm



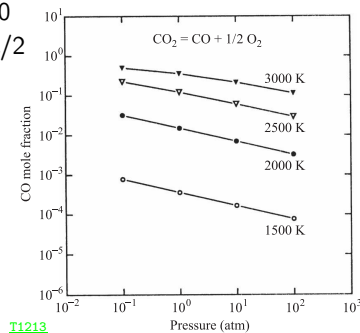
$$\bullet \Delta G_{2500}^{\circ} = [g_{\text{CO}} + 0.5g_{\text{O}_2} - g_{\text{CO}_2}]_{2500}$$

$$\Rightarrow K_P = \exp(-\Delta G_T^{\circ}/R_u T) = 0.0363$$

$$\bullet K_P = \frac{X_{\text{CO}} X_{\text{O}_2}^{0.5}}{X_{\text{CO}_2}} \left(\frac{P}{P_0}\right)^{1+0.5-1}$$

$$\Rightarrow 0.036 = \frac{\left(\frac{\alpha}{1+\alpha/2}\right) \left(\frac{\alpha/2}{1+\alpha/2}\right)^{1/2}}{\left(\frac{1-\alpha}{1+\alpha/2}\right)} 10^{0.5}$$

$$\Rightarrow \alpha = 0.06205 \rightarrow X_{\text{CO}} = 0.0602$$



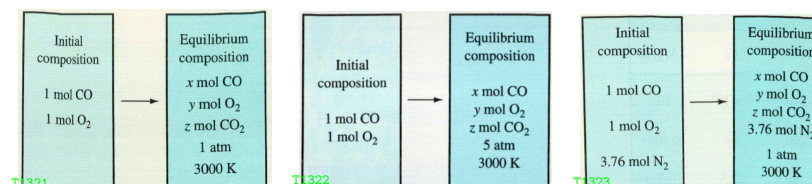
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Illustrative Example: Effects of pressure and inert-addition on equilibrium composition

1 atm

5 atm

N₂ addition

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T1322

T1323

$$\bullet x = 0.34$$

$$\bullet y = 0.67$$

$$\bullet z = 0.66$$

$$\bullet x = 0.193$$

$$\bullet y = 0.5965$$

$$\bullet z = 0.807$$

$$\bullet x = 0.47$$

$$\bullet y = 0.736$$

$$\bullet z = 0.53$$

