

## Chemical Equilibrium

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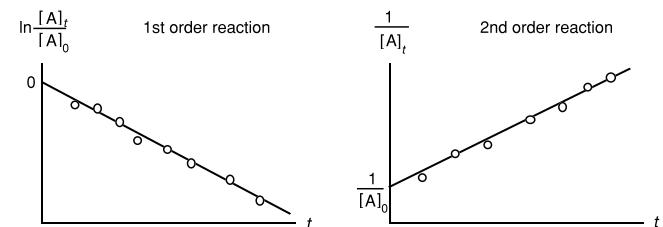
ME 407: Advanced Thermodynamics  
<http://zahurul.buet.ac.bd/ME407/>



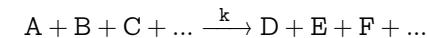
- For **first-order systems ( $a = 1$ )**:  $\ln \frac{[A]_t}{[A]_0} = -k(t - t_0)$   
[ $A$ ]<sub>0</sub> & [ $A$ ]<sub>t</sub> denote the concentration of species  $A$  at time  $t_0$  and  $t$ , respectively.

- For **second-order systems ( $a = 2$ )**:  $\frac{1}{[A]_t} - \frac{1}{[A]_0} = k(t - t_0)$

- For **third-order systems ( $a = 3$ )**:  $\frac{1}{[A]_t^2} - \frac{1}{[A]_0^2} = 2k(t - t_0)$



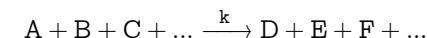
## Rate Laws & Reaction Order



- 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.



## 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.  
 $\Rightarrow -k_f[A]^a[B]^b[C]^c \dots = k_b[D]^d[E]^e[F]^f \dots$
- Equilibrium constant (based on concentration),  $K_c$   
$$K_c \equiv \frac{k_f}{k_b} = \frac{[D]^d[E]^e[F]^f}{[A]^a[B]^b[C]^c}$$



**Reaction Rate Laws**

### 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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**Reaction Rate Laws**

### 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 <sub>4</sub> *	$1.3 \cdot 10^9$	48.4	-0.3	1.3
CH <sub>4</sub>	$8.3 \cdot 10^5$	30	-0.3	1.3
C <sub>2</sub> H <sub>6</sub>	$1.1 \cdot 10^{12}$	30	0.1	1.65
C <sub>3</sub> H <sub>8</sub>	$8.6 \cdot 10^{11}$	30	0.1	1.65
C <sub>4</sub> H <sub>10</sub>	$7.4 \cdot 10^{11}$	30	0.15	1.6
C <sub>5</sub> H <sub>12</sub>	$6.4 \cdot 10^{11}$	30	0.25	1.5
C <sub>6</sub> H <sub>14</sub>	$5.7 \cdot 10^{11}$	30	0.25	1.5
C <sub>7</sub> H <sub>16</sub>	$5.1 \cdot 10^{11}$	30	0.25	1.5
C <sub>8</sub> H <sub>18</sub>	$4.6 \cdot 10^{11}$	30	0.25	1.5
C <sub>9</sub> H <sub>20</sub>	$4.2 \cdot 10^{11}$	30	0.25	1.5
C <sub>10</sub> H <sub>22</sub>	$3.8 \cdot 10^{11}$	30	0.25	1.5
CH <sub>3</sub> OH	$3.2 \cdot 10^{11}$	30	0.25	1.5
C <sub>2</sub> H <sub>5</sub> OH	$1.5 \cdot 10^{12}$	30	0.15	1.6
C <sub>6</sub> H <sub>6</sub>	$2.0 \cdot 10^{11}$	30	-0.1	1.85
C <sub>7</sub> H <sub>8</sub>	$1.6 \cdot 10^{11}$	30	-0.1	1.85

<sup>a</sup> Units of  $A_o$ : (mol/cm<sup>3</sup>)<sup>1-a-b</sup>/s.

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**Reaction Rate Laws**

### Example: Methane Combustion at 1800 K

$$\text{CH}_4 + 2(\text{O}_2 + 3.76 \text{ N}_2) \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 7.52 \text{ N}_2$$

- $RR = A_o \exp\left(-\frac{E_a/R_u}{T}\right) [\text{Fuel}]^a [\text{O}_2]^b$
- $A_o = 1.3 \times 10^9 \text{ mol/cm}^3$
- $E_a = 48.4 \text{ kcal/mol}$ ,  $R_u = 1.987 \text{ cal/mol.K}$
- $a = -0.3$ ,  $b = 1.3$ ,  $[\text{O}_2] = 2[\text{CH}_4]$
- $\frac{d[\text{CH}_4]}{dt} = RR = 1.3 \times 10^9 \exp\left(-\frac{24358}{1800}\right) [\text{CH}_4]^{-0.3} (2[\text{CH}_4])^{1.3}$
- $\Rightarrow \frac{d[\text{CH}_4]}{dt} = -4245.3[\text{CH}_4]$
- $\Rightarrow \frac{[\text{CH}_4]}{[\text{CH}_4]_0} = \exp(-4245.3t)$
- Reduction to 5%,  $\exp(-4245.3t) = 0.05 \rightarrow t = 0.71 \text{ ms}$

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**Reaction Rate Laws**

### Time Scales in Chemically Reacting Flow

Chemical time scales	Physical time scales
Slow time scales e.g., NO-formation; “frozen chemistry”	$10^0 \text{ s}$
intermediate time scales	$10^2 \text{ s}$
Fast time scales, “equil. chemistry” (due to steady states, partial equilibria)	$10^{-4} \text{ s}$
	$10^{-6} \text{ s}$
	$10^{-8} \text{ s}$
to be equilibrated	

time scales of flow,  
transport, turbulence

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**Reaction Rate Laws**

### 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  $a + b = 1.75$ .

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**Chemical Equilibrium**

### 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	$\nu_A A + \nu_B B \longrightarrow \nu_C C + \nu_D D$ $dN_A A + dN_B B \longrightarrow dN_C C + dN_D D$ <ul style="list-style-type: none"> <li><math>dN_A = -\epsilon \nu_A, dN_B = -\epsilon \nu_B</math></li> <li><math>dN_C = +\epsilon \nu_C, dN_D = +\epsilon \nu_D</math></li> <li><math>\epsilon</math> is a proportionality constant.</li> </ul>
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- $G_{mix} = \sum_{R \rightarrow P} N_i g_{i,T} = \sum_{R \rightarrow P} N_i (g_{i,T}^o + R_u T \ln(\frac{P_i}{P_0}))$
- For fixed  $T & P$ , equilibrium condition:

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

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**Chemical Equilibrium**

### Criterion for Chemical Equilibrium

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

Fixed mass reactions at fixed  $P$  &  $T$

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**Chemical Equilibrium**

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

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

- $K_P = \exp\left[-\frac{\Delta G_T^o}{R_u T}\right]$
- Equilibrium constant,  $K_P \equiv \frac{(P_C/P_0)^{\nu_C} (P_D/P_0)^{\nu_D}}{(P_A/P_0)^{\nu_A} (P_B/P_0)^{\nu_B}}$
- $K_P = e^{(-\Delta G_T^o/R_u T)} = e^{-\Delta H^o/R_u T} e^{\Delta S^o/R_u}$
- For  $K_P > 0$ , which favours products,  $\Delta H^o$  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.

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**Illustrative Example:** Dissociation of CO<sub>2</sub> at 2500 K, 10 atm



$$\begin{array}{lll} T = 298 \text{ K} & 1 & 0 \\ & 0 & 0 \\ T = 2500 \text{ K} & 1 - \alpha & \alpha \\ & & \alpha/2 \end{array}$$

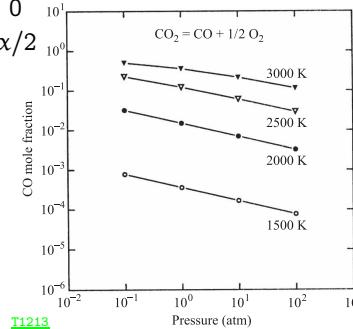
- $\Delta G_{2500}^{\circ} = [g_{\text{CO}} + 0.5g_{\text{O}_2} - g_{\text{CO}_2}]_{2500}$

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

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

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

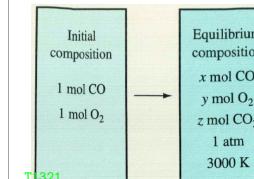
$$\Rightarrow \alpha = 0.06205 \rightarrow X_{\text{CO}} = 0.0602$$



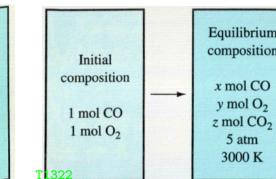
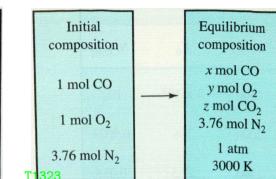
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**Illustrative Example:** Effects of pressure and inert-addition on equilibrium composition

1 atm



5 atm

N<sub>2</sub> addition

- $x = 0.34$
- $y = 0.67$
- $z = 0.66$

- $x = 0.193$
- $y = 0.5965$
- $z = 0.807$

- $x = 0.47$
- $y = 0.736$
- $z = 0.53$

