

Lecture 3

Chemical Kinetics and Chemical Equilibrium

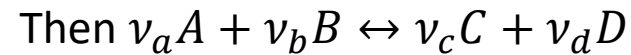
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Rate of Chemical Reaction

ν_a, ν_b, ν_c , etc. are stoichiometric coefficients in a chemical balance equation where A, B, C, D are chemical formulae.



There are forward and reverse (backward) reaction rates here: Ω_{ab} and Ω_{cd}

C_a, C_b, C_c, C_d are concentrations in (moles/volume)

$$\begin{aligned}\Omega_{ab} &= -\frac{1}{\nu_a} \frac{dC_a}{dt} \Big|_{\text{forward}} = k_{ab} C_a^{\nu_a} C_b^{\nu_b} \\ &= -\frac{1}{\nu_b} \frac{dC_b}{dt} \Big|_{\text{forward}}\end{aligned}$$

k_{ab} is a specific rate constant

$$\begin{aligned}\Omega_{cd} &= -\frac{1}{\nu_c} \frac{dC_c}{dt} \Big|_{\text{reverse}} = k_{cd} C_c^{\nu_c} C_d^{\nu_d} \\ &= -\frac{1}{\nu_d} \frac{dC_d}{dt} \Big|_{\text{reverse}} = +\frac{1}{\nu_a} \frac{dC_a}{dt} \Big|_{\text{reverse}} = +\frac{1}{\nu_b} \frac{dC_b}{dt} \Big|_{\text{reverse}}\end{aligned}$$

k_{cd} is a specific rate constant

Equilibrium Constant $K_p(T)$

At chemical equilibrium there is no net change
so that: $\Omega_{ab} = \Omega_{cd}$ and $k_{ab}C_a^{\nu_a}C_b^{\nu_b} = k_{cd}C_c^{\nu_c}C_d^{\nu_d}$

Note that:

$$\frac{dC_a}{dt} = 0 = \left. \frac{dC_a}{dt} \right|_{fwd} + \left. \frac{dC_a}{dt} \right|_{rev}$$

$$\frac{k_{ab}}{k_{cd}} = \frac{C_c^{\nu_c}C_d^{\nu_d}}{C_a^{\nu_a}C_b^{\nu_b}}$$

Partial pressure: $P_i = \frac{n_i}{V}RT$

For a perfect gas

So: $C_i = \frac{P_i}{RT}$ $P_i = C_iRT = C_iW_i \frac{R}{W_i}T = \rho_i R_i T$

$$\frac{k_{ab}}{k_{cd}} = \frac{P_c^{\nu_c}P_d^{\nu_d}}{P_a^{\nu_a}P_b^{\nu_b}} (RT)^{\nu_a+\nu_b-\nu_c-\nu_d}$$

$$K_p(T) = \frac{P_c^{\nu_c}P_d^{\nu_d}}{P_a^{\nu_a}P_b^{\nu_b}} = \frac{k_{ab}}{k_{cd}} (RT)^{\nu_c+\nu_d-\nu_a-\nu_b}$$

Where $K_p(T) = \exp\left[-\frac{\Delta G^\circ(T)}{RT}\right] = \exp\left[\frac{G^\circ_{ab}-G^\circ_{cd}}{RT}\right]$

G is Gibbs Free Energy
 G° is the value at one
atmosphere

$$G = H - TS$$

Rate of Chemical Reaction

Since K_p is a function of T , we expect k to be a function of T also.

In fact, we find that:

$$k = aT^\lambda \exp \left[-\frac{(G^* - G)}{RT} \right] \quad \boxed{\text{Note: } \ln K_p = \frac{\Delta G}{RT}}$$

$$\ln K_p = \ln k_{ab} - \ln k_{cd} + [(\nu_c + \nu_d) - (\nu_a + \nu_b)] \ln RT$$

$$\ln K_p \approx \ln k_{ab} - \ln k_{cd} \quad \text{The remaining dependence on temperature is not that strong!}$$

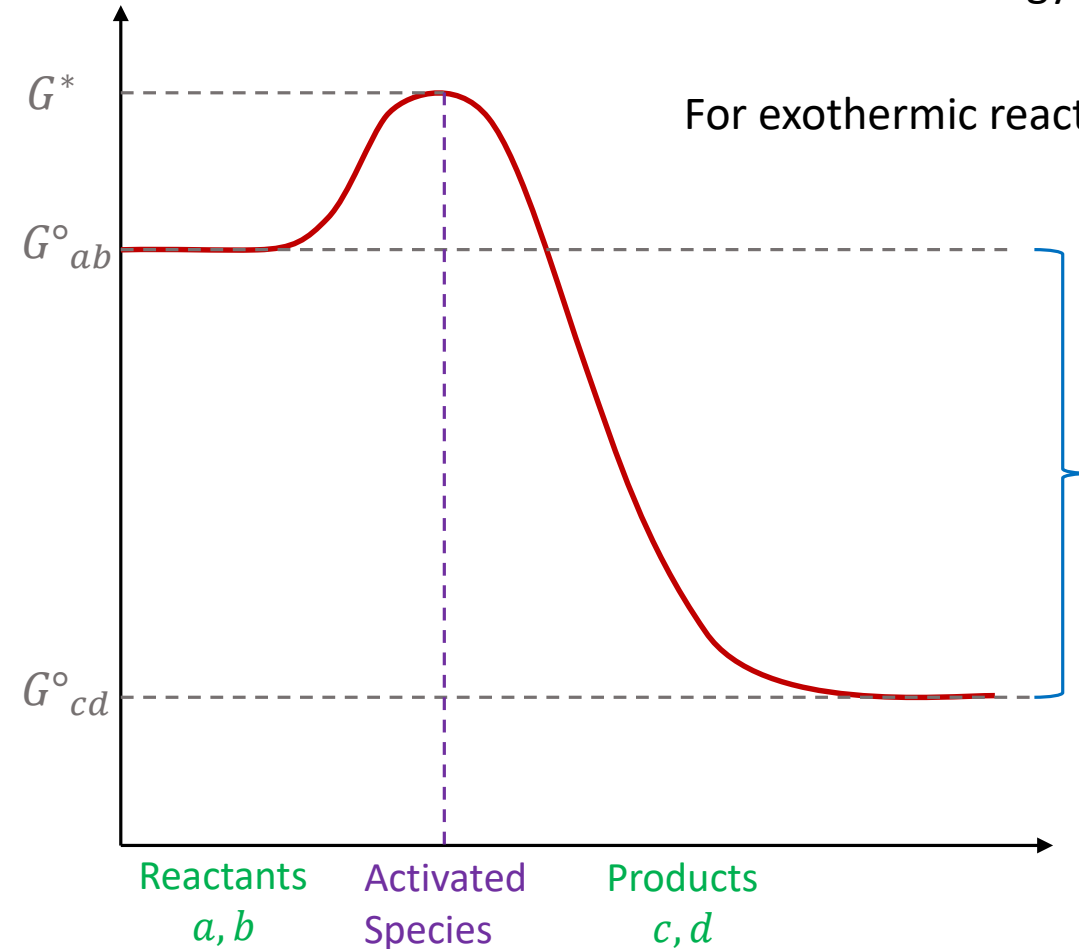
$$\text{So: } \ln K_p \approx \ln k_{ab} - \ln k_{cd} = \frac{G^\circ_{ab} - G^\circ_{cd}}{RT}$$

$$\ln K_p = -\frac{G^* - G^\circ_{ab}}{RT} + \frac{G^* - G^\circ_{cd}}{RT}$$

$$\text{Then we can consider: } k_{ab} = A \exp \left[-\frac{G^* - G^\circ_{ab}}{RT} \right] \quad ; \quad k_{cd} = A \exp \left[-\frac{G^* - G^\circ_{cd}}{RT} \right]$$

Rate of Chemical Reaction

G^* is the free energy of an activated species



For exothermic reaction: $\exp\left[-\frac{\Delta G}{RT}\right] = \exp\left[-\frac{\Delta H}{RT}\right] \exp\left[-\frac{\Delta S}{R}\right]$

$$\exp\left[-\frac{\Delta G}{RT}\right] = \exp\left[-\frac{E}{RT}\right] \exp\left[-\frac{\Delta S}{R}\right]$$

E is the activation energy

$$E \equiv \Delta H$$

Consider as an example:



A barrier exists for the reaction to occur; only a fraction of those colliding will react!

Rate of Chemical Reaction

$$\Omega_{ab} = k_{ab} C_a^{\nu_a} C_b^{\nu_b}$$

$$\Omega_{ab} = (A C_a^{\nu_a} C_b^{\nu_b}) \exp \left[-\frac{G^* - G^\circ_{ab}}{RT} \right]$$

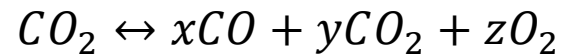
$$\Omega_{ab} = A C_a^{\nu_a} C_b^{\nu_b} \exp \left[-\frac{E}{RT} \right]$$

The definition of A follows from above

The backward reaction above would be an example of an exothermic reaction!

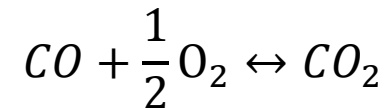
Chemical Reaction Example

Suppose we heat 1 mole of CO_2 from standard temperature to $4880^\circ R$
How much dissociation occurs?



Initially: 1 CO_2

Finally: $(1 - x)CO_2, xCO, \frac{x}{2}O_2$



- Oxygen: $2 = x + 2y + 2z$
 - Carbon: $1 = x + y \rightarrow y = 1 - x$
- $$\left. \vphantom{\begin{matrix} \text{Oxygen: } 2 = x + 2y + 2z \\ \text{Carbon: } 1 = x + y \rightarrow y = 1 - x \end{matrix}} \right\} z = \frac{x}{2}$$

$$n_{CO_2} = 1 - x, n_{CO} = x, n_{O_2} = \frac{x}{2}$$

$$n = n_{CO_2} + n_{CO} + n_{O_2} = 1 + \frac{x}{2}$$

n would be greater if other species were present, i.e. N_2

Chemical Reaction Example

$$P_{CO_2} = \frac{n_{CO_2}}{n} P = \frac{1-x}{1+\frac{x}{2}} P$$

$P = P_{CO_2} + P_{CO} + P_{O_2}$ is measured in atm!

$$P_{CO} = \frac{n_{CO}}{n} P = \frac{x}{1+\frac{x}{2}} P$$

$$P_{O_2} = \frac{n_{O_2}}{n} P = \frac{\frac{x}{2}}{1+\frac{x}{2}} P = \frac{x}{x+2} P$$

Note that partial pressure and K_p remain the same if the number of moles is multiplied. Also, the formula for P_i does not change if n_i and n are replaced by molar density, n/V

$$K_p = \frac{P_{CO_2}}{P_{CO} P_{O_2}^{1/2}} = \frac{n_{CO_2}}{n_{CO} n_{O_2}^{1/2}} \frac{n^{1/2}}{P^{1/2}} = \frac{1-x}{x} \left(\frac{2+x}{x} \right)^{1/2} P^{-1/2} = 10.0 \text{ (at } 4880^\circ R)$$

Chemical Reaction Example

At 1 atmosphere, $P = 1$

$$\frac{1-x}{x} \left(\frac{2+x}{x} \right)^{1/2} P^{-1/2} = 10.0$$

$$(1-x)^2(2+x) = 100x^3 \rightarrow 2 - 3x + 2x^2 + x^3 = 100x^3$$

$$2 - 3x + 2x^2 - 99x^3 = 0$$

Iterations: $x = .272$, $x = .221$, $x = .232$
So: $x = 23\%$

This assumes only CO_2 , CO , and O_2 are present. In a practical case, exhaust would include other species and n would be modified!

Chemical Reaction Example

Consider now: $P = 10.0$ atm

Then:

$$K_p = \frac{1-x}{x} \left(\frac{2+x}{x} \right)^{1/2} (10.0)^{-1/2} = 10.0$$

$$\frac{1-x}{x} \left(\frac{2+x}{x} \right)^{1/2} = 10.0\sqrt{10}$$

$$(1-x)^2(2+x) = 1000x^3$$

$$2 - 3x - 999x^3 = 0$$

Iterations: $x = .1260, x = .1168, x = .1181$

So: $x \approx 11\% - 12\%$

The higher the pressure, the less dissociation since a smaller volume (fewer moles) is preferred!

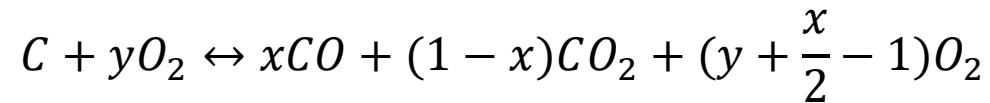
Chemical Reaction Example

Suppose we burn carbon in oxygen (no nitrogen)

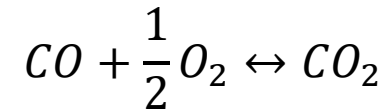
y is given.

$y = 1$ is stoichiometric

$y > 1$ is excess air



The products CO , CO_2 , and O_2
are in equilibrium



$$K_p = \frac{P_{CO_2}}{P_{CO}P_{O_2}^{1/2}} = \frac{n_{CO_2}}{n_{CO}n_{O_2}^{1/2}} \frac{n^{1/2}}{P^{1/2}}$$

Now:

$$n = x + 1 - x + y + \frac{x}{2} - 1 = y + \frac{x}{2}$$

$$K_p = \frac{1 - x}{x \left(y + \frac{x}{2} - 1\right)^{1/2}} \frac{\left(y + \frac{x}{2}\right)^{1/2}}{P^{1/2}}$$

Chemical Reaction Example

Consider: $P = 10.0$ atm and $T = 4880^\circ R$

$$K_p(T) = 10.0$$

$$K_p \sqrt{10} = \frac{1-x}{x \left(y + \frac{x}{2} - 1 \right)^{1/2}} \left(y + \frac{x}{2} \right)^{1/2} = 10.0 \sqrt{10}$$

Consider $y = 1$

Then:

$$K_p \sqrt{10} = \frac{1-x}{x \left(\frac{x}{2} \right)^{1/2}} \left(1 + \frac{x}{2} \right)^{1/2} = 10.0 \sqrt{10}$$

This is same as before: $x = .118$

Chemical Reaction Example

Consider now excess oxygen, $y = 2$

$$\text{Then: } K_p \sqrt{10} = \frac{1-x}{x \left(1 + \frac{x}{2}\right)^{1/2}} \left(2 + \frac{x}{2}\right)^{1/2} = 10.0 \sqrt{10}$$

$$(1-x)^2 \left(2 + \frac{x}{2}\right) = 1000x^2 \left(1 + \frac{x}{2}\right)$$

$$499.5x^3 + 999x^2 + \frac{7}{2}x - 2 = 0$$

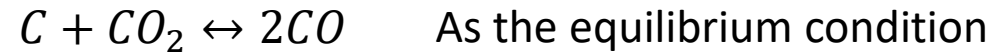
Iterations lead to $x = 0.0426$

So: $x \approx 4\% - 5\%$

Excess oxygen drives reaction toward completion!

Chemical Reaction Example

If $y < 1$ by a slight amount, the same formula holds, but for y too small, no solution may exist! This indicates that carbon may exist in the products and we should consider:



Note that if other species are present, their pressure must be considered in calculating the total number of moles, n .

Example: 1 mole of CO_2 , 3.76 moles of N_2

$$K_p = \frac{P_{CO_2}}{P_{CO}P_{O_2}^{1/2}}$$

- $n_{CO_2} = 1 - x$
- $n_{CO} = x$
- $n_{O_2} = \frac{x}{2}$

$$n = 3.76 + 1 - x + x + \frac{x}{2} = 4.76 + \frac{x}{2}$$