

화학 General Chemistry

034.020-005

2018 Spring Semester

Tue/Thr 9:30~10:45
Building 028-302

송윤주 woonjusong@snu.ac.kr

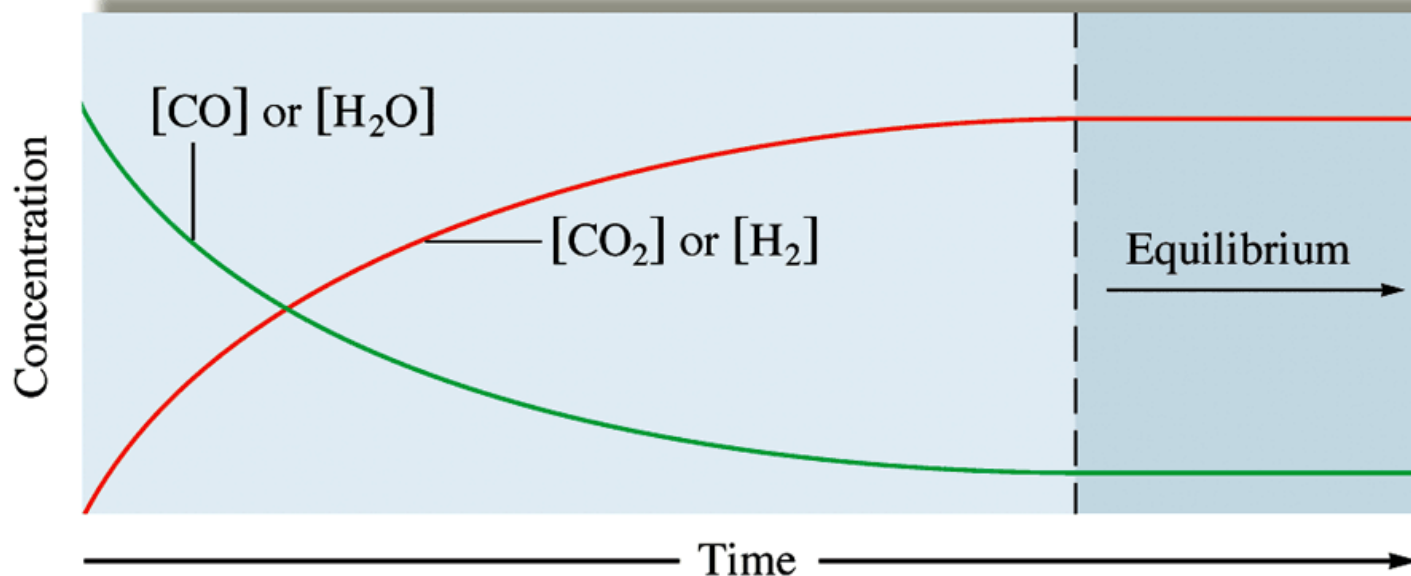
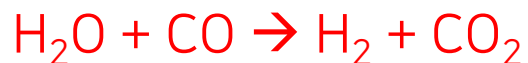
Reactions at Equilibrium

10.1. The Reversibility of Reactions

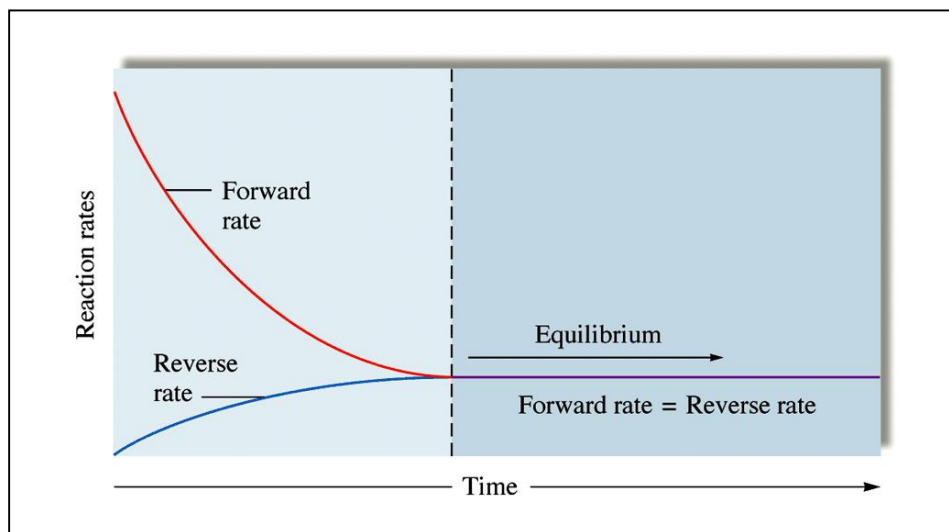
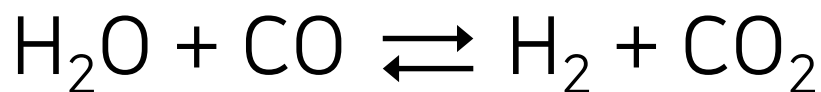
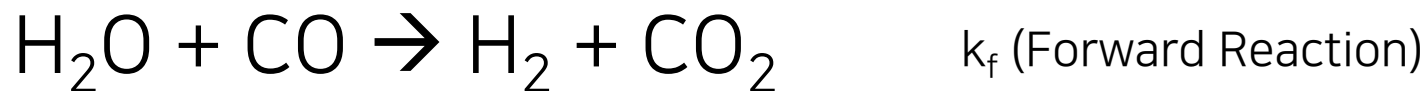
Chemical Equilibrium

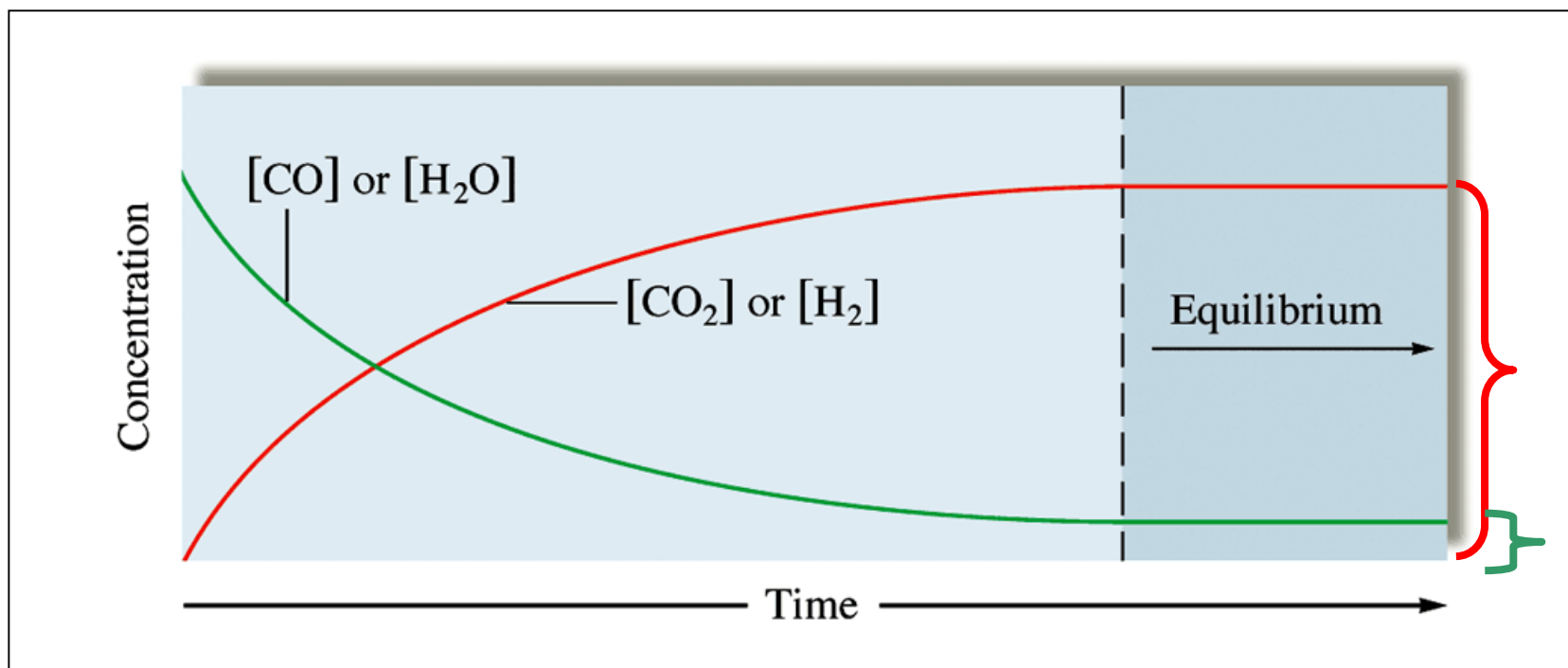
- The state where the concentrations of all reactants and products remain **constant** with time.

For the rxn:



At equilibrium, two reactions are occurring at the same rate

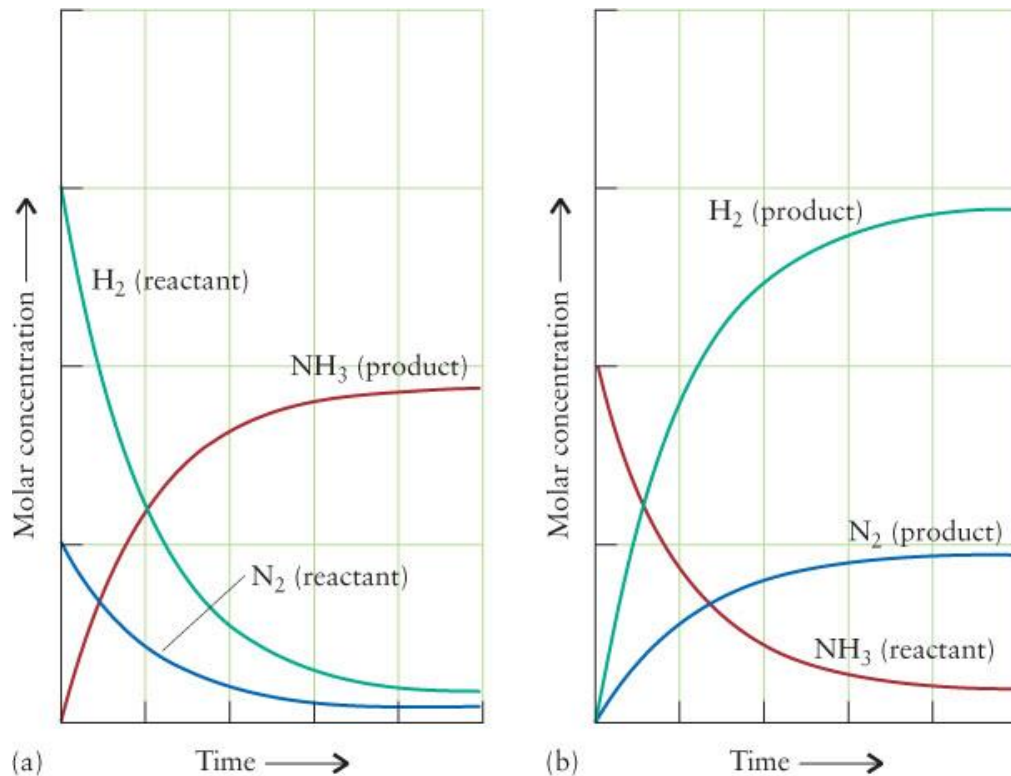




How much CO_2 and CO do we have at equilibrium?

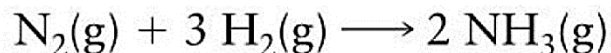
What determines the equilibrium concentration?

Chemical equilibrium:



- K_{eq} = concentration of reactant and product remain constant.
- Forward and backward reactions are occurring at the same time

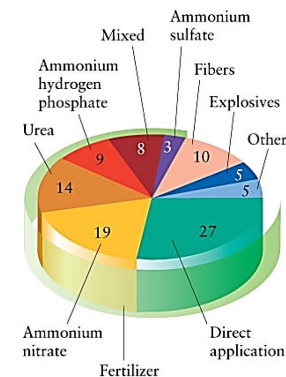
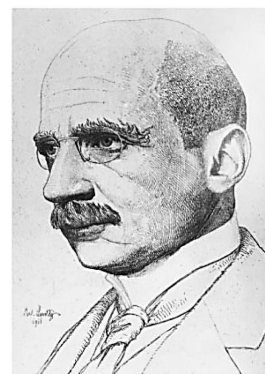
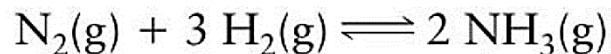
Forward:



Backward:

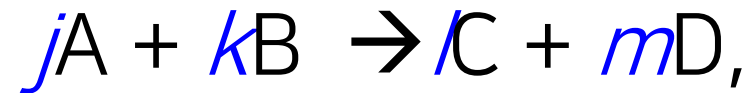


Dynamic Equilibrium:



Haber-Bosch process

10.2. Equilibrium and the Law of Mass Action



K : equilibrium constant

** K is usually written without any unit*

Note:

- The K is a constant for a given **temperature** (T)
- However, the **equilibrium concentrations** will not always be the same.

Ex)



$$K = [C] / ([A][B]) = 10$$

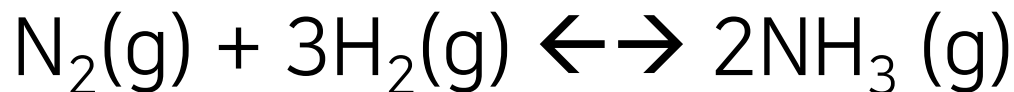
Equilibrium concentrations can be any of the following:

$$[C] = 10, [A] = 1, [B] = 1 ; K = 10 / (1 \times 1) = 10$$

$$[C] = 20, [A] = 2, [B] = 1 ; K = 20 / (2 \times 1) = 10$$

Equilibrium Expressions Involving Pressures

- Two different ways to define equilibrium constants:



- a. Use concentration:

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

Note:

$$PV = nRT,$$

$$P = (n/V)RT = [A]RT$$

$$[A] = P/(RT)$$

- b. Use Partial Pressure:

$$K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3} = \frac{([\text{NH}_3]RT)^2}{([\text{N}_2]RT)([\text{H}_2]RT)^3} = K_c (RT)^{-2}$$

Thermodynamic description of the equilibrium state:

- For ideal gas: $aA + bB \rightarrow cC + dD$

$$\begin{aligned}\Delta G_{rxn} &= cG_f(C) + dG_f(D) - aG_f(A) - bG_f(B) \\ &= \left(cG_f^o(C) + dG_f^o(D) - aG_f^o(A) - bG_f^o(B) \right) \\ &\quad + RT \left(c \ln(P_C / P^0) + d \ln(P_D / P^0) - a \ln(P_A / P^0) - b \ln(P_B / P^0) \right) \\ &= \Delta G_{rxn}^o + RT \ln \left(\frac{(P_C / P^0)^c (P_D / P^0)^d}{(P_A / P^0)^a (P_B / P^0)^b} \right) = \Delta G_{rxn}^o + RT \ln(Q)\end{aligned}$$

G^o : Free energy at standard condition

$$G = G^o + RT \ln(P / P^0)$$

G^o : Free energy at standard condition (1 bar)

$$Q = K \text{ and } \Delta G_{rxn} = 0$$

Therefore,

$$\Delta G_{rxn}^o + RT \ln(K) = 0, \quad \Delta G_{rxn}^o = -RT \ln(K),$$

$$K = \exp \left(-\frac{\Delta G_{rxn}^o}{RT} \right) \quad K = \left(\frac{(P_{C,eq} / P^0)^c (P_{D,eq} / P^0)^d}{(P_{A,eq} / P^0)^a (P_{B,eq} / P^0)^b} \right) = \left(\frac{(P_{C,eq})^c (P_{D,eq})^d}{(P_{A,eq})^a (P_{B,eq})^b} \right)$$

Law of Mass Action

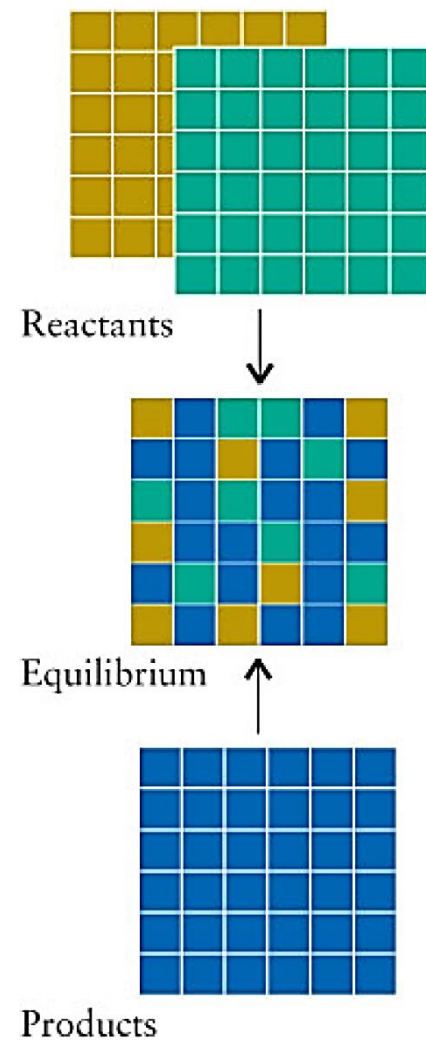


P_{SO_2} (bar)	P_{O_2} (bar)	P_{SO_3} (bar)	K^*
0.660	0.390	0.0840	0.0415
0.0380	0.220	0.00360	0.0409
0.110	0.110	0.00750	0.0423
0.950	0.880	0.180	0.0408
1.44	1.98	0.410	0.0409

$$K = \frac{(P_{\text{SO}_3})^2}{(P_{\text{SO}_2})^2 P_{\text{O}_2}} \approx 0.0413 \text{ (const)}$$

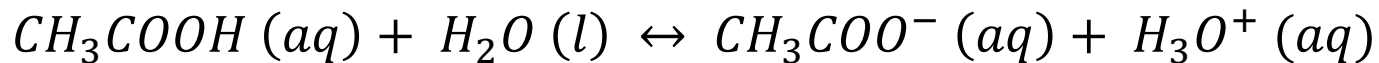
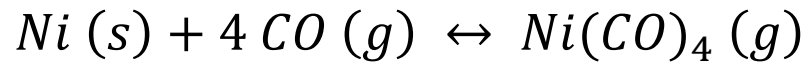
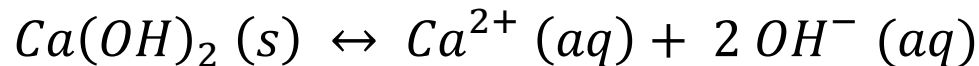
*Law of mass
action*

Reaction	T (K)*	K	K_c^\dagger
$\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{HCl}(\text{g})$	300	4.0×10^{31}	4.0×10^{31}
	500	4.0×10^{18}	4.0×10^{18}
	1000	5.1×10^8	5.1×10^8
$\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2 \text{HBr}(\text{g})$	300	1.9×10^{17}	1.9×10^{17}
	500	1.3×10^{10}	1.3×10^{10}
	1000	3.8×10^4	3.8×10^4
$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$	298	794	794
	500	160	160
	700	54	54
$2 \text{BrCl}(\text{g}) \rightleftharpoons \text{Br}_2(\text{g}) + \text{Cl}_2(\text{g})$	300	377	377
	500	32	32
	1000	5	5
$2 \text{HD}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{D}_2(\text{g})$	100	0.52	0.52
	500	0.28	0.28
	1000	0.26	0.26
$\text{F}_2(\text{g}) \rightleftharpoons 2 \text{F}(\text{g})$	500	3.0×10^{-11}	7.3×10^{-13}
	1000	1.0×10^{-2}	1.2×10^{-4}
	1200	0.27	2.7×10^{-3}
$\text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{Cl}(\text{g})$	1000	1.0×10^{-5}	1.2×10^{-7}
	1200	1.7×10^{-3}	1.7×10^{-5}
$\text{Br}_2(\text{g}) \rightleftharpoons 2 \text{Br}(\text{g})$	1000	3.4×10^{-5}	4.1×10^{-7}
	1200	1.7×10^{-3}	1.7×10^{-5}
$\text{I}_2(\text{g}) \rightleftharpoons 2 \text{I}(\text{g})$	800	2.1×10^{-3}	3.1×10^{-5}
	1000	0.26	3.1×10^{-3}
	1200	6.8	6.8×10^{-2}
$\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$	298	6.8×10^5	4.2×10^8
	400	41	4.5×10^4
	500	3.6×10^{-2}	62
$2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$	298	4.0×10^{24}	9.9×10^{25}
	500	2.5×10^{10}	1.0×10^{12}
	700	3.0×10^4	1.7×10^6
$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$	298	0.15	6.1×10^{-3}
	400	47.9	1.44
	500	1.7×10^3	41



- Homogeneous equil. : reactants and products all in the same phase
- Heterogeneous equil. : reactants and products with different phase

Examples



Heterogeneous Equilibria

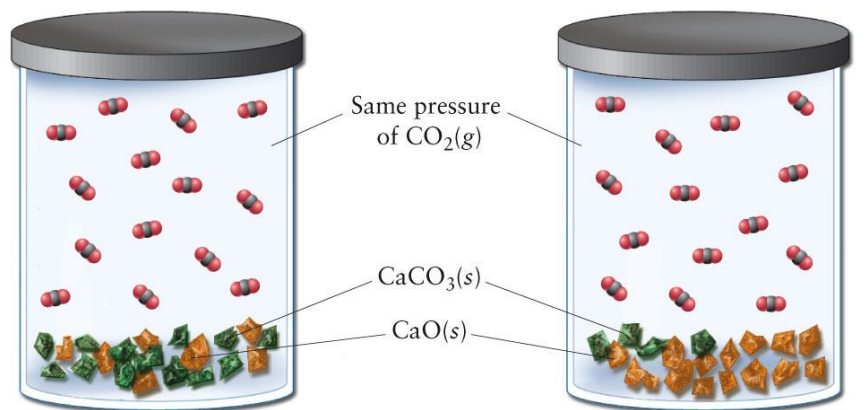
- Homogeneous equil. : reactants and products all in the same phase
- Heterogeneous equil. : reactants and products with different phase



The position of a heterogeneous equilibrium does not depend on the amounts of pure solids or liquids present, as long as there exist some amount of the solid and liquid in the equilibrium mixture.

→ Pure solid and pure liquid concentration do not appear in the equilibrium equation !

$$K = [\text{CO}_2(g)] \times 1/(1) = \text{constant.}$$



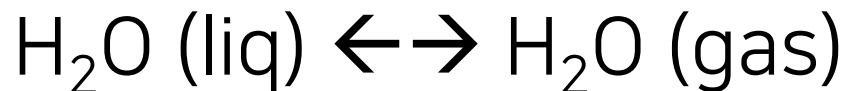
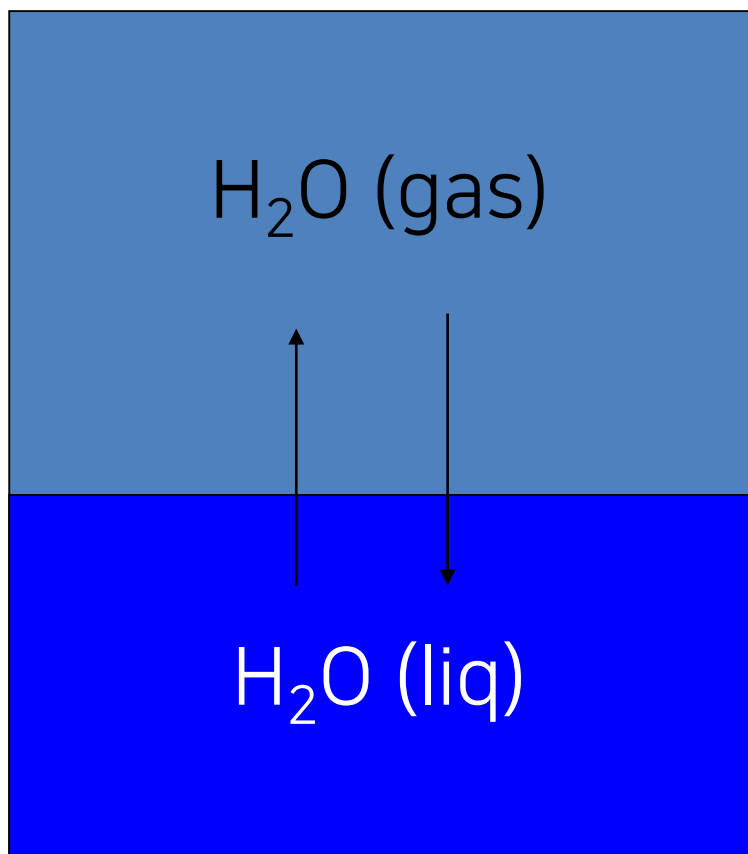
Much $\text{CaCO}_3(s)$, little $\text{CaO}(s)$

Little $\text{CaCO}_3(s)$, much $\text{CaO}(s)$

Why do we omit pure liquids and solids in equilibrium expression?

- **Densities** of pure liquids and solids are **constant** for a given temperature.
- Therefore, "**concentration**" of pure liq. and solids are **constant**.

An example of heterogeneous equilibrium



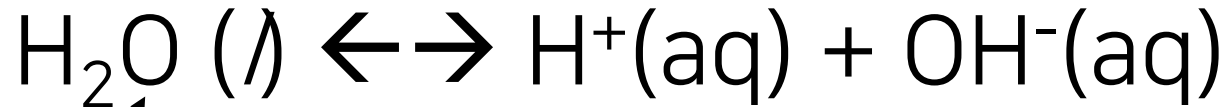
$$K' = [\text{H}_2\text{O(gas)}] / [\text{H}_2\text{O(liq)}]$$

Constant!!
55 M for pure water.

Therefore, we write:

$$K = [\text{H}_2\text{O(gas)}]$$

Heterogeneous Equilibria: other examples



Pure liquid

$$K = [\text{H}^+][\text{OH}^-] = 10^{-14}$$

For neutral water , $[\text{H}^+] = [\text{OH}^-] = x$

$$K = [\text{H}^+][\text{OH}^-] = x^2 = 10^{-14}$$

Therefore, $[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ M}$

10.3. The Thermodynamic Origin of K

$$G = G(T, P, x_i)$$

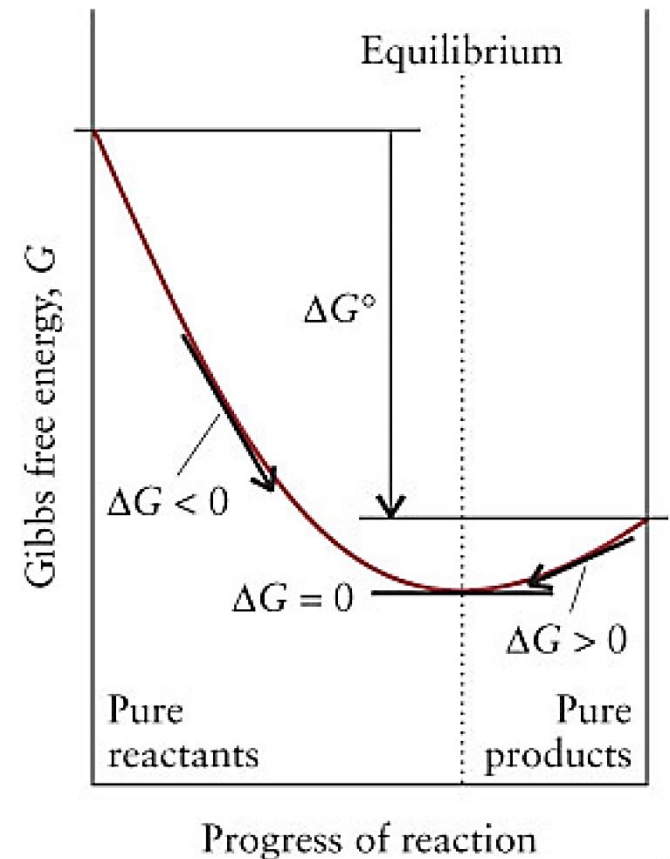
x_i = mole fraction of component i

→ At constant T and P , it depends only on the extent of reaction, ξ

$$\left(\frac{\partial G}{\partial \xi} \right)_{T,P} = 0 \quad \text{at equilibrium}$$

Extent of reaction, /sa1/

- Regardless of the initial composition of a reaction mixture, the composition tends to adjust until the activities give rise to the characteristic value of K for the reaction and temperature.



$$\Delta G_r^o = -RT \ln K$$

$$\Delta G_r = \sum_{products} n G - \sum_{reactants} n G$$

$$\Delta G_r^o = \sum_{products} n G^o - \sum_{reactants} n G^o$$

$$G(A) = G^o(A) + RT \ln \left(\frac{P_A}{P^o} \right) \text{ for ideal gas}$$

P^o : 1 bar standard pressure
 c^o : 1 M standard molar conc,

$$G(A) = G^o(A) + RT \ln \left(\frac{[A]}{c^o} \right) \text{ for solute in a dilute (ideal) solution}$$

$$G(A) = G^o(A) + RT \ln(1) = G^o(A) \text{ for pure solids and liquids}$$

$$G(A) = G^o(A) + RT \ln a_A \text{ for any substance in any state}$$

For a reaction, $\alpha A + \beta B \leftrightarrow \gamma C + \delta D$,

$$\therefore \Delta G_r = \Delta G_r^o + RT \ln \frac{(a_C)^\gamma (a_D)^\delta}{(a_A)^\alpha (a_B)^\beta}$$

$$\rightarrow 0 = \Delta G_r^o + RT \ln \frac{(a_C)^\gamma (a_D)^\delta}{(a_A)^\alpha (a_B)^\beta} = \Delta G_r^o + RT \ln K \text{ at equilibrium}$$

$$\therefore \Delta G_r^o = -RT \ln K$$

- The reaction Quotient Q defined as

$$\Delta G_r = \Delta G_r^o + RT \ln \frac{(a_C)^\gamma (a_D)^\delta}{(a_A)^\alpha (a_B)^\beta} = \Delta G_r^o + RT \ln Q$$

Q : reaction
quotient

Example

For the reaction $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{SO}_3(\text{g})$, $\Delta G_r^o = -141.74 \text{ kJ} \cdot \text{mol}^{-1}$ at 298 K. (a) what is the Gibbs free energy of reaction when the partial pressure of each gas is 100 bar, (b) what is the direction of spontaneous reaction ? $G(A) > 0$ or < 0 ??

$$G(A) = G^o(A) + RT \ln(K)$$

- Additionally,

$$\Delta G_r^o = \Delta H_r^o - T \Delta S_r^o$$

$$\Delta G_r^o = -RT \ln K$$

$$K = \exp(-\Delta G_r^o / RT) = \exp\left(\frac{-\Delta H_r^o}{RT} + \frac{\Delta S_r^o}{R}\right)$$

An highly **endothermic** reaction ($\Delta H_r^o \gg 0$) is likely to have $K < 1$.

An highly **exothermic** reaction ($\Delta H_r^o \ll 0$) is likely to have $K > 1$.

Example

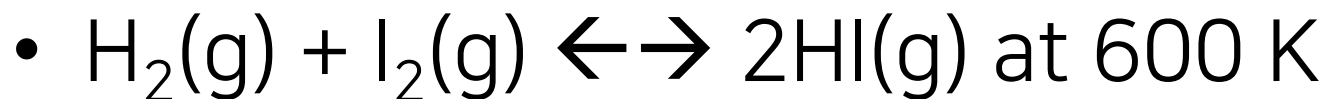
For the reaction $\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{I}_2(\text{g}) \rightarrow \text{HI}(\text{g})$, $\Delta G_r^o = +1.7 \text{ kJ} \cdot \text{mol}^{-1}$ at 298 K. Calculate K.

$$\Delta G_r^o = -RT \ln K$$

Applications of the Equilibrium Constant

- Equilibrium constant
 - What are the equilibrium concentrations?
 - Which direction does the reaction want to go?

Determination of Equilibrium Concentrations



Initial concentrations $\rightarrow P_{\text{H}_2} = 1.98 \text{ atm}, P_{\text{I}_2} = 1.710 \text{ atm}$

Equilibrium constant $\rightarrow K_p = P(\text{HI})^2 / \{ P(\text{H}_2) \times P(\text{I}_2) \} = 92.6$

What are the equilibrium concentrations (or pressures) of the products and reactants?

	H_2	I_2	HI
Before the reaction	1.98	1.71	0
After the reaction	$1.98 - x$	$1.71 - x$	$2x$

Calculating Equilibrium Pressures II



1 Liter,
Initially

0.298 mol, $\text{PCl}_3(\text{g})$
 8.70×10^{-3} mol $\text{PCl}_5(\text{g})$

1 Liter,
Finally

2.00×10^{-3} mol $\text{Cl}_2(\text{g})$

$[\text{PCl}_5]$, $[\text{PCl}_3]$, and $K = ?$

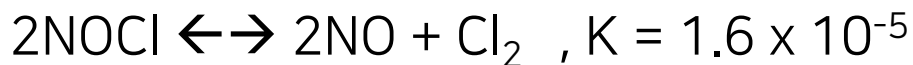
Exer Calculating Equilibrium Concentrations

Carbon monoxide reacts with steam to produce carbon dioxide and hydrogen. At 700 K, the equilibrium constant is 5.10.

Calculate the equilibrium concentrations of all species if 1.000 mol of each component is mixed in a 1.000 liter flask.

Some Trick for complicated situations

Consider:



	[NOCl]	[NO]	[Cl ₂]
Initially	0.5	0	0

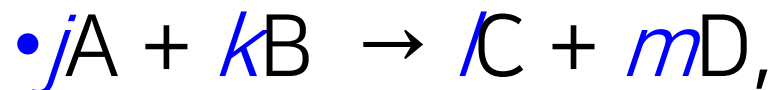
- (a) equilibrium constant is a very small number.
- (b) In this case, x is also a very small number.

Applications of the Equilibrium Constant

- Equilibrium constant
 - What are the equilibrium concentration?
 - Which direction does the reaction want to go?

Reaction Quotient, Q

• For



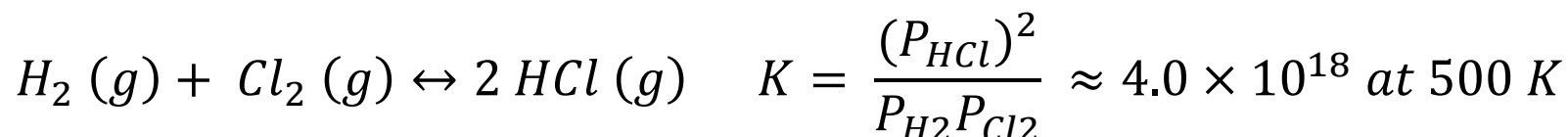
$$Q = \frac{[C]_0^l [D]_0^m}{[A]_0^j [B]_0^k}$$

$[X]_0$ = *Initial concentrations* of reagents and products.

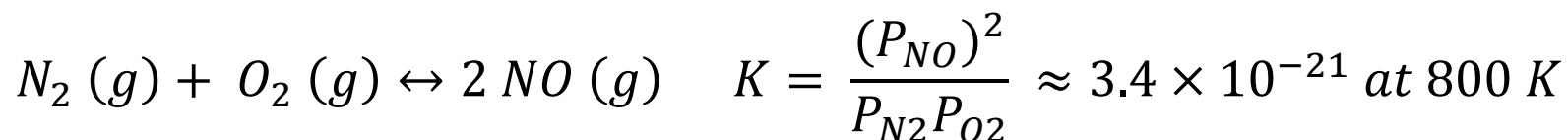
$$K = \frac{[C]_{eq}^l [D]_{eq}^m}{[A]_{eq}^j [B]_{eq}^k} \quad \text{Equilibrium constant = Concentrations at equilibrium}$$

10.4. The Extent of Reaction

- Large K



- Small K



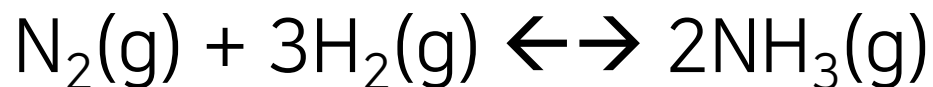
- Guidelines (not a rule)

If $K > 10^3$, products are favored.

If $10^{-3} < K < 10^3$, neither reactants nor products are strongly favored.

If $K < 10^{-3}$, reactants are favored.

Exer Using the Reaction Quotient



$$Q = \frac{[\text{NH}_3]_0^2}{[\text{N}_2]_0[\text{H}_2]_0^3} \quad [\text{X}]_0 = \text{Initial Concentrations}$$

$[\text{NH}_3]_0$	$[\text{N}_2]_0$	$[\text{H}_2]_0$	Q	$Q \text{ vs } K (6.0 \times 10^{-2})$
1.0×10^{-3}	1.0×10^{-5}	2.0×10^{-3}	1.3×10^7	
2.0×10^{-4}	1.5×10^{-5}	3.54×10^{-1}	6×10^{-2}	
1.0×10^{-4}	5.0	1.00×10^{-2}	2×10^{-3}	

10.5. The Direction of Reaction

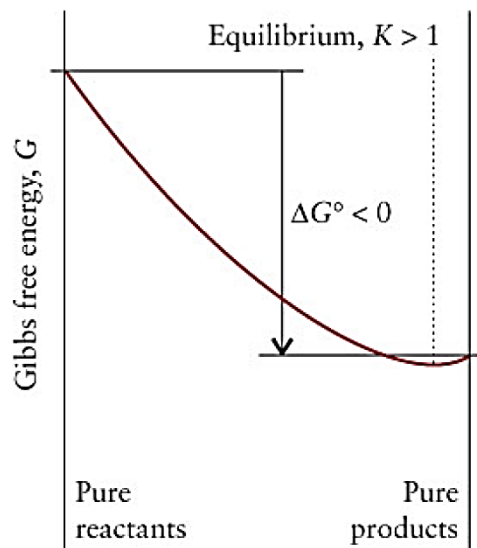
- For a reaction, $\alpha A + \beta B \leftrightarrow \gamma C + \delta D$,

$$K = \left(\frac{(a_C)^\gamma (a_D)^\delta}{(a_A)^\alpha (a_B)^\beta} \right)_{\text{equilibrium}} \quad \text{and} \quad Q = \left(\frac{(a_C)^\gamma (a_D)^\delta}{(a_A)^\alpha (a_B)^\beta} \right)_{\text{not at equilibrium}}$$

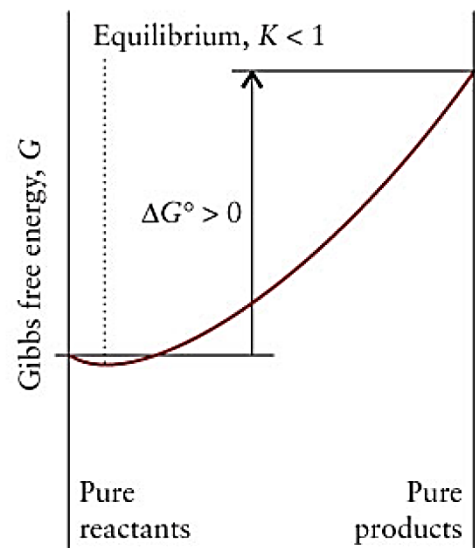
If $Q < K$, the reaction proceeds in the forward direction (\rightarrow).

If $Q > K$, the reaction proceeds in the reverse direction (\leftarrow).

If $Q = K$, dynamic equilibrium (\leftrightarrow).



(a) Progress of reaction



(b) Progress of reaction

Equilibrium Calculation

10.6. The Alternative Form of K

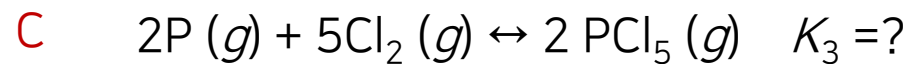
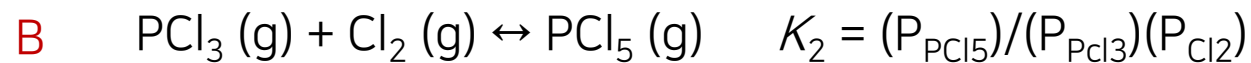
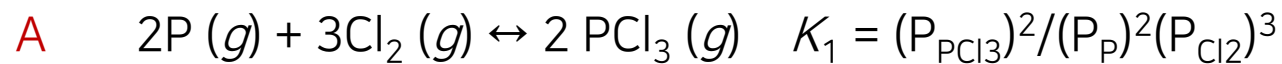
$$\alpha A + \beta B \leftrightarrow \gamma C + \delta D \quad K_1 = \left(\frac{(a_C)^\gamma (a_D)^\delta}{(a_A)^\alpha (a_B)^\beta} \right)_{equil}$$

$$\gamma C + \delta D \leftrightarrow \alpha A + \beta B \quad K_2 = \left(\frac{(a_A)^\alpha (a_B)^\beta}{(a_C)^\gamma (a_D)^\delta} \right)_{equil} = K_1^{-1}$$

$$n\alpha A + n\beta B \leftrightarrow n\gamma C + n\delta D \quad K_3 = \left(\frac{(a_C)^{n\gamma} (a_D)^{n\delta}}{(a_A)^{n\alpha} (a_B)^{n\beta}} \right)_{equil} = K_1^n$$

$$\Delta G_r^o = \sum_{products} n G^o - \sum_{reactants} n G^o$$

$$\Delta G_r^o = -RT \ln K$$



10.6. Le Chatelier's Principle

If **a change** is imposed on a system at equilibrium, *the position of the equilibrium will shift in a direction that tends to reduce that change.*

** a change*

= pressure, temperature, and concentration

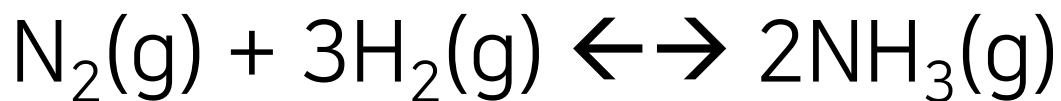
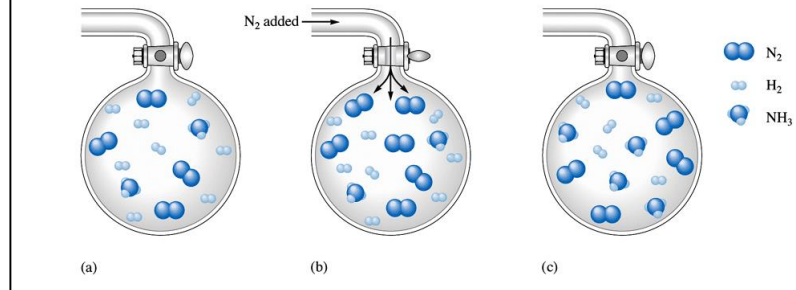


Henry Le Chatelier
1850-1936 (France)

Note: this is not a new principle or discovery.

→ Le Chatelier's principle is already contained in the equilibrium expression. Le Chatelier's principle laid a foundation for Chemical equilibrium theory, actually.

Le Chatelier's Principle-1: Change in Concentration



Initial
Equilibrium

0.399 M

1.197 M

0.202 M

$K = 1.7 \times 10^{-2}$

Add 1.0 M

Le Chatelier's principle:

Concentration of N_2 is too high \rightarrow

FORWARD REACTION (\rightarrow) in
order to DECREASE the N_2
concentration

Final
Equilibrium

1.348 M

1.044 M

0.304 M

$K = 1.7 \times 10^{-2}$

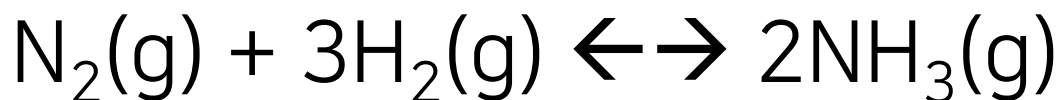
Result :

* Increase in NH_3 concentration * Decrease in H_2 concentration

Le Chatelier's Principle-2:

Change in Pressure

1. Add or remove a gaseous reactant or product (already talked about it).
2. Add an inert gas (one not involved in the reaction).
→ inert gas increase the total pressure, but has **no effect on equilibrium (no change in volume)**.
3. Change the volume of container.
Container volume reduction
→ Try to decrease its own volume by reducing the total number of gas-phase molecules.



4 molecules

2 molecules

Decrease in volume

→ wants to decrease the number of molecules.

→ EQUILIBRIUM SHIFTS TO RIGHT.



Increase in volume

→ wants to INCREASE the number of molecules.

→ EQUILIBRIUM SHIFTS TO LEFT



Using Le Chatelier's principle II

	NO. of gas-phase molecules		Decrease in volume leads to...
	LEFT	RIGHT	
$\text{P}_4(\text{s}) + 6\text{Cl}_2(\text{g}) \rightleftharpoons 4\text{PCl}_3(\text{l})$	6	0	
$\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g})$	2	1	
$\text{PCl}_3(\text{g}) + 3\text{NH}_3(\text{g}) \rightleftharpoons \text{P}(\text{NH}_2)_3(\text{g}) + 3\text{HCl}(\text{g})$	4	4	

Le Chatelier's Principle-3: Change in Temperature

- Note: changes in pressure and volume **change the equilibrium**. However, these **won't change the equilibrium constant**.
- Change in temperature **changes the equilibrium constant**.
- **Equilibrium constant is a function of temperature.**

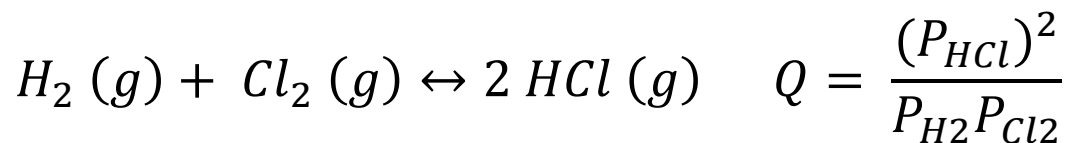
The Response of Equil. to Changes in Conditions

10.7. Adding and Removing Reagents

- Le Chatelier's Principle

When a stress is applied to a system in dynamic equilibrium, the equilibrium tends to adjust to minimize the effect of the stress.

Experimentally discovered, however, thermodynamically expected too.

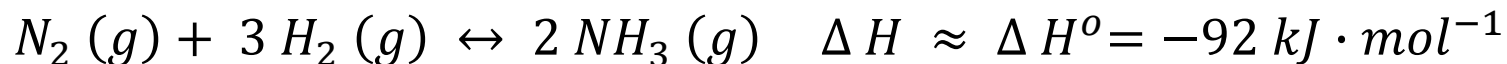


Adding H_2 results in $Q < K$. The system proceeds forward.

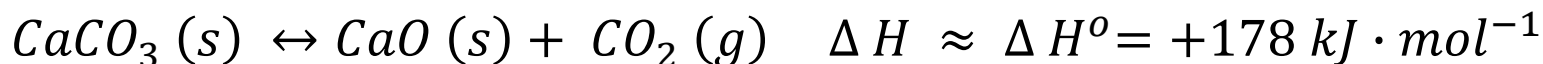
Adding HCl results in $Q > K$. The system proceeds backward.

10.8. Temperature and Equilibrium

- For exothermic reaction, K ?



- For endothermic reaction, K ?



- Thermodynamically,

$$K = \exp(-\Delta G_r^0 / RT) = \exp\left(\frac{-\Delta H_r^0}{RT} + \frac{\Delta S_r^0}{R}\right)$$

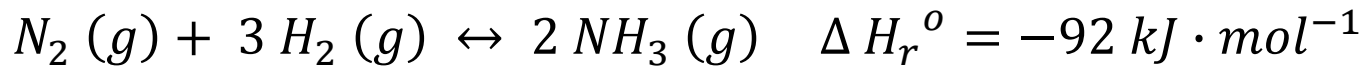
- van't Hoff Equation

$$\ln \frac{K_1}{K_2} \approx - \frac{\Delta H_r^0}{R} \left\{ \frac{1}{T_1} - \frac{1}{T_2} \right\}$$

Example The K for the synthesis of ammonia is 6.8×10^5 at 298 K. Predict its value at 400 K. (compare with the experimental value: 41).

10.9. Catalysts and Haber's Achievement

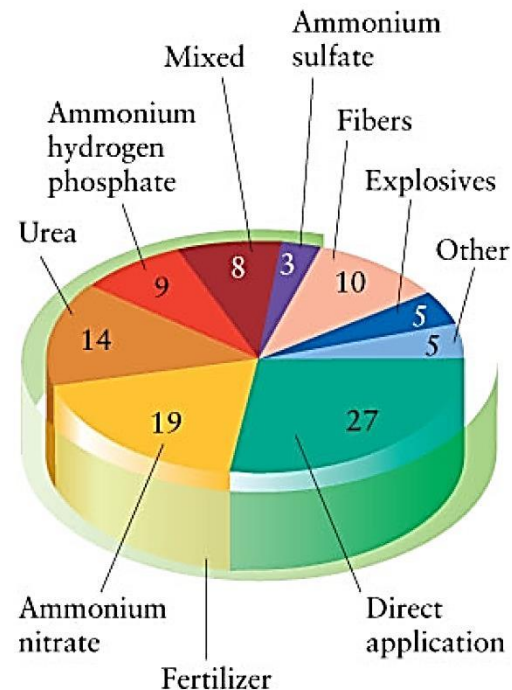
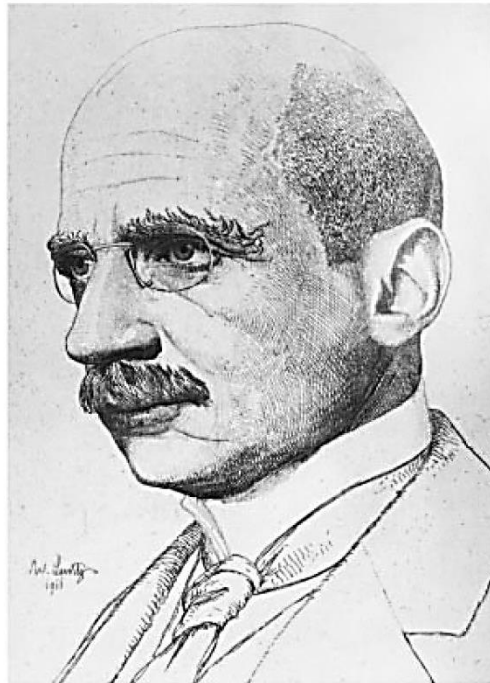
- Catalyst (and activation energy)
 - Rates of **forward and reverse reactions** are increased.
 - Dynamic equilibrium is unaffected.
 - K is not changed.
 - The identity of the catalyst is unchanged.
- Haber's achievement



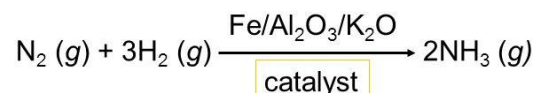
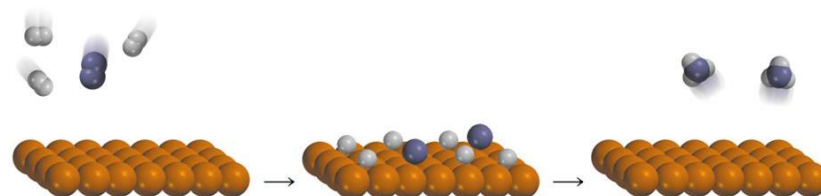
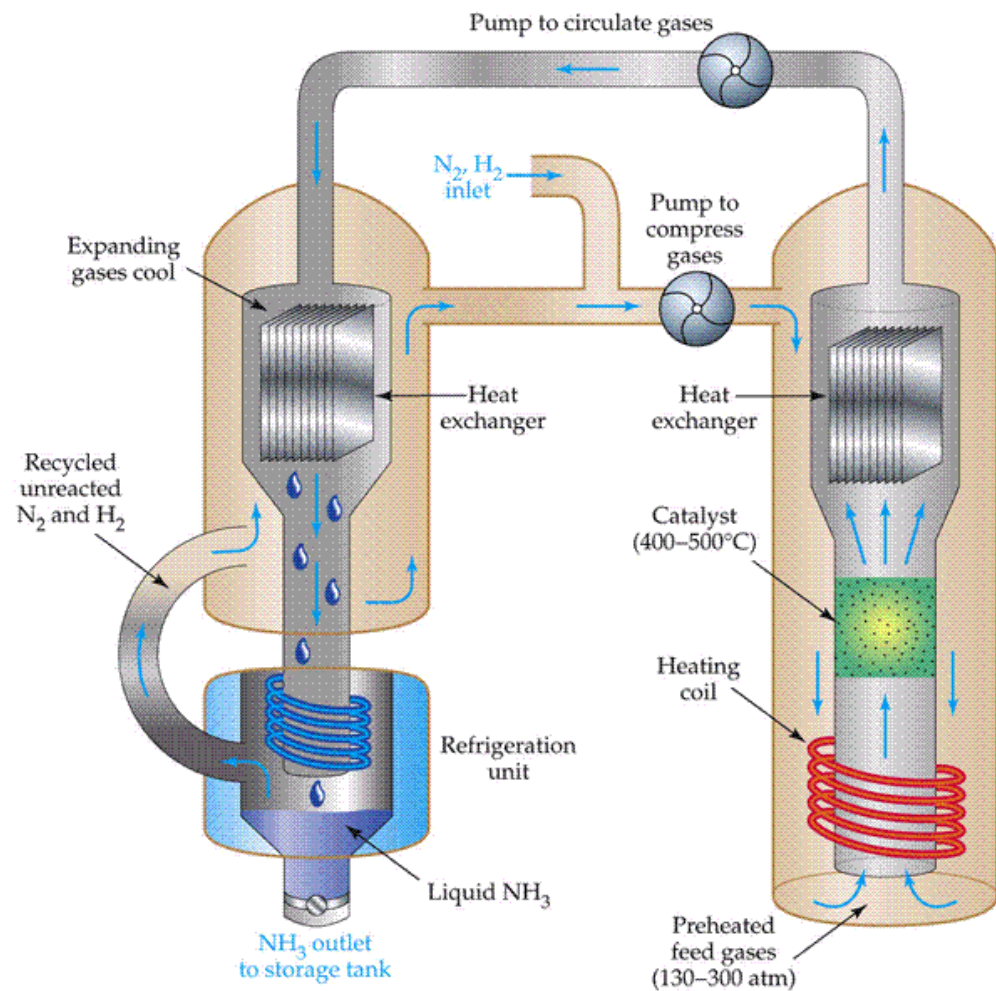
$$\Delta G_r^o = -32.90 \text{ kJ} \cdot \text{mol}^{-1} \quad K = 5.80 \times 10^5$$

- Although thermodynamically favorable, the reaction is very slow at room temperature and pressure.

- Compression of the gas mixture favors product NH_3 .
- Removal of NH_3 as it is formed encourages more to be formed.
- Increasing T is required to increase the reaction rate, but it adversely affects the position of the equilibrium
- Catalyst.



The most popular catalysts are based on iron promoted with K_2O , CaO , SiO_2 , and Al_2O_3 . Initially, Os and U catalysts were used.

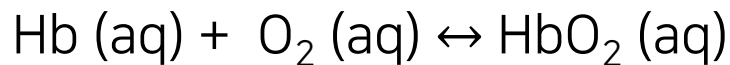


10.10. The Impact on Biology: Homeostasis

- Homeostasis

Mechanism similar to chemical equilibrium, which governed by Le Chatelier's Principle

Hemoglobin: Oxygen carrier



Myoglobin: Oxygen storage protein

CO Poisoning

