

# Chemical Equilibrium

- \* It is NOT that the reaction stops occurring
  - Forward and reverse occur at the same rate
  - Chemical equilibrium = the state where concentration of all reactants and products remain constant
- \* On a molecular level, equilibrium is a highly dynamic situation (not static)
- \* Equilibrium does NOT imply that the concentration of reactants and products are equal.
  - Some rxns reach eq only after most reactants have formed products
  - Others reach eq when only a small fraction of reactants have formed products

It depends on the reaction

A reaction that can proceed in both the forward and reverse direction is  
= reversible.

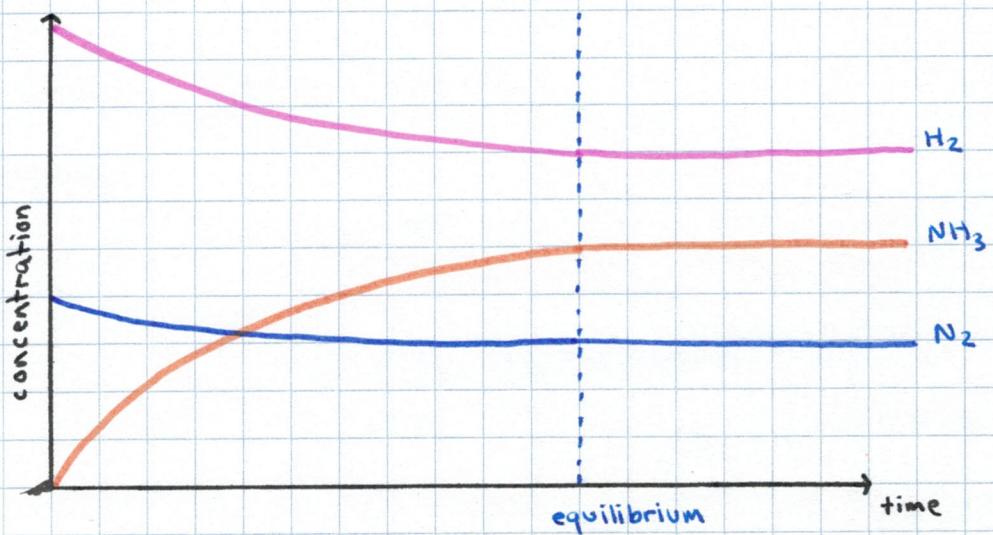
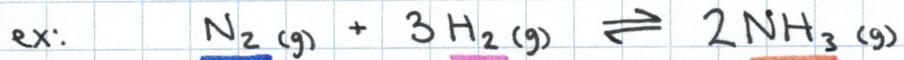
# The concept of Dynamic Equilibrium

When equilibrium is reached:

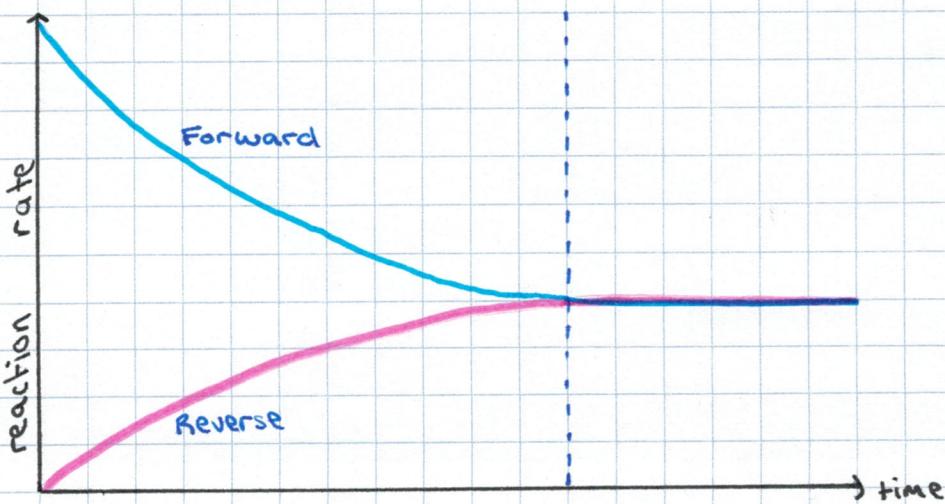
→ No further change at macroscopic levels

- Concentrations stop changing
- rate (forward) = rate (reverse)

→ Dynamic at molecular level



\* Note: Once some product is formed, the reverse reaction can start occurring.



## Law of mass action: Equilibrium Constant ( $K$ )

= describes the relationship between the concentrations of the reactants and products found in the rxn at equilibrium.

→ For gaseous rxns, we can express the equilibrium constant in terms of partial pressures ( $\because$  partial  $P \propto$  concentration)

Equilibrium constant ( $K_c$  and  $K_p$ )



$$K_c = \frac{[C]^r \cdot [D]^s}{[A]^p \cdot [B]^q}$$

No unit

$M = \frac{\text{mol}}{\text{L}}$

$$K_p = \frac{(P_C)^r \cdot (P_D)^s}{(P_A)^p \cdot (P_B)^q}$$

atm

- All concentrations / partial pressures are eq. values
- $K$  depends on particular rxn and temp.
- ↳ At a given temp.  $K$  is the same for a rxn regardless of the initial amount of reactants / products

$$K = \frac{(\text{products})^{\text{coefficient}}}{(\text{reactants})^{\text{coefficient}}}$$

## Converting $K_c$ to $K_p$

$$K_p = K_c (RT)^{\Delta n}$$

- $\Delta n = (\text{mol product - gaseous}) - (\text{mol of reactant - gaseous})$
- $T = \text{temp. in Kelvin}$
- $R = 0.08206 \text{ L.atm/k.mol}$

$$K_p = \frac{(P_c)^r \cdot (P_d)^s}{(P_A)^p \cdot (P_B)^q}$$

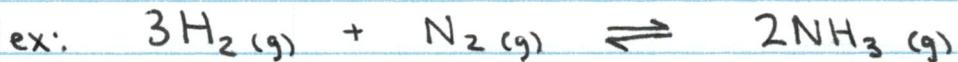
$$PV = nRT$$

$$P = \frac{n}{V} \cdot RT$$

$$P_A = [A]RT$$

$$= \frac{[C]RT)^r \cdot (D)RT)^s}{([A]RT)^p \cdot ([B]RT)^q}$$

$$= \underbrace{\frac{[C]^r \cdot [D]^s}{[A]^p \cdot [B]^q}}_{K_c} \cdot \underbrace{(RT)^{(r+s)-(p+q)}}_{(RT)^{\Delta n}}$$



$K_p = 5.3 \times 10^5$  at  $25^\circ C$ , find  $K_c$ :

$$K_p = K_c \cdot (RT)^{\Delta n}$$

$$K_c = \frac{K_p}{(RT)^{\Delta n}}$$

$$= \frac{5.3 \times 10^5}{[(0.08206)(298\text{K})]^{-2}}$$

$$K_c = 3.2 \times 10^8$$

## Significance of K

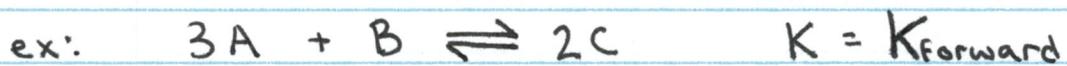
- A large K ( $K \gg 1$ ) = forward reaction is favored and forward rxn proceeds essentially to completion.
- A small K ( $K \ll 1$ ) = forward reaction does not proceed very far
- $K \approx 1$  = reaction proceeds about half way

$$K = \frac{\text{product}}{\text{reactant}}$$

$K \gg 1$  more product than reactants at eq.

$K \ll 1$  more reactants than products at eq.

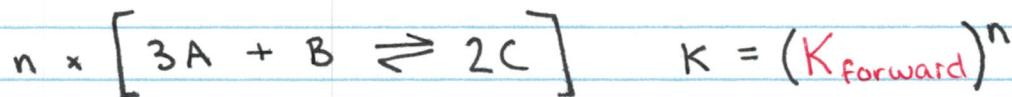
## Relationship between Equilibrium Constant and Chemical Reaction Equation



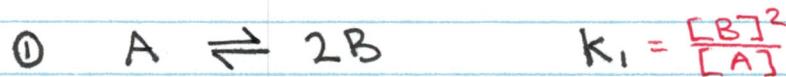
(i) if you reverse equation, invert  $K$ :



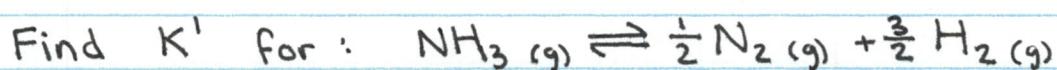
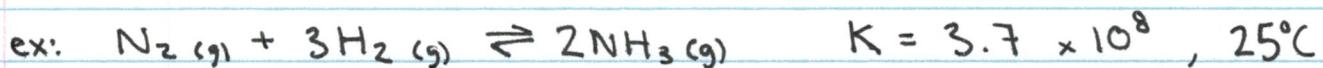
(ii) if you multiply by coefficient, raise  $K$  to the same factor:



(iii) if you add 2 individual chemical reactions, multiply corresponding  $K$ 's by each other:



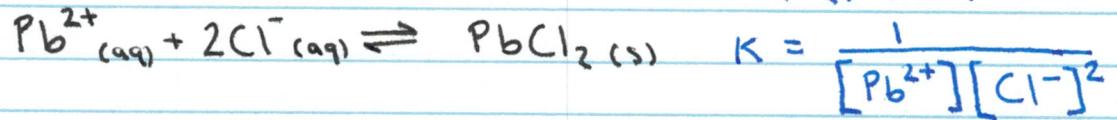
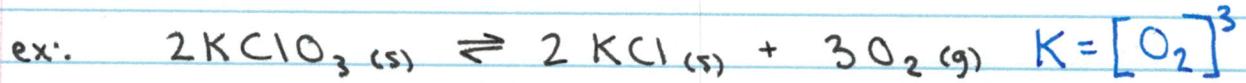
$$= \frac{[B]^2}{[A]} \cdot \frac{[C]^3}{[B]^2} = \frac{[C]^3}{[A]}$$



reverse and  $\times \frac{1}{2} \therefore K' = \left( \frac{1}{3.7 \times 10^8} \right)^{1/2} = 5.2 \times 10^{-5}$

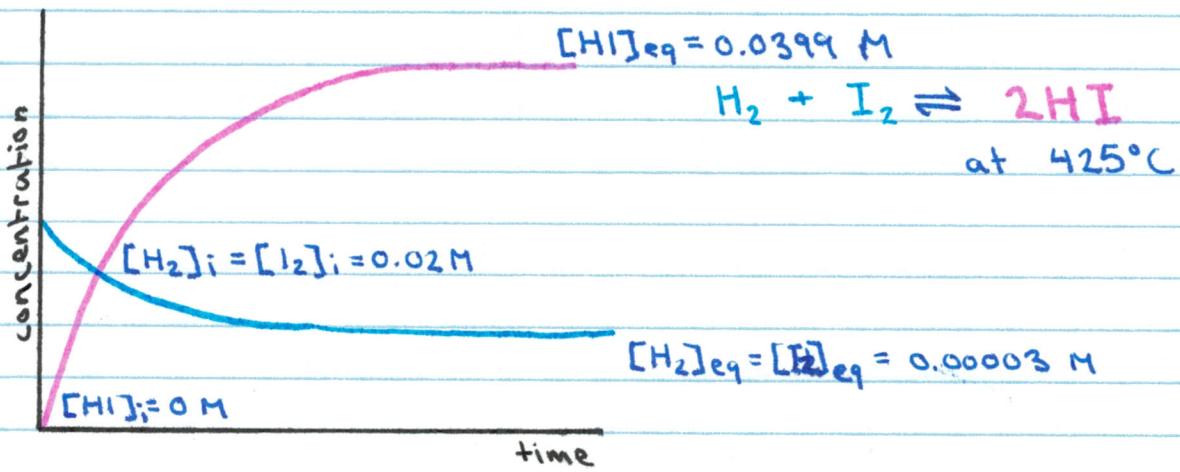
## Heterogeneous Equilibria

- Homogeneous equilibrium = equilibrium where all the reactants and products are in the same phase.
  - Heterogeneous equilibrium = equilibrium involving reactants and products in more than one phase.
- \* Chemical reactions with pure solids and liquids : their concentrations are not included in equilibrium constant expression  
(Think : concentration = 1)  
→ b/c concentration of pure solid / liquid remains constant ∴ position of equil. does not depend on them.



Determining  $K$  having concentration of ALL species at equilibrium

- Ensure rxn is balanced
- Write  $K$  expression
- Use  $[ ]_{eq}$  values to calculate  $K_c$



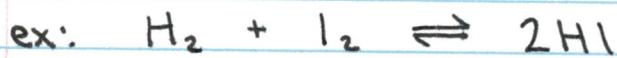
$$K_c = \frac{[HI]^2}{[I_2] \cdot [H_2]}$$

$$= \frac{(0.0399)^2}{(0.00003)^2}$$

$$= 1.77 \times 10^6 \text{ at } 425^\circ\text{C}$$

# Calculate K from initial and equilibrium concentrations

1. Tabulate all known (initial and eq) concentrations that appear in K expression (only gas and aq) in ICE table.
2. For species for which both  $[ ]_i$  and  $[ ]_{eq}$  are known, calculate change in concentration
3. Use stoichiometry to calculate change for other rxns.
4. Use equilibrium concentrations to calculate K



initial :  $1.00 \times 10^{-3} M H_2$  and  $2.00 \times 10^{-3} M I_2$  at  $448^\circ C$

at equil :  $1.87 \times 10^{-3} M HI$

$H_2 + I_2 \rightleftharpoons 2HI$			
Initial	$1 \times 10^{-3} M$	$2 \times 10^{-3} M$	0
Change	$-(1.87 \times 10^{-3}) \cdot \frac{1}{2}$	$-(1.87 \times 10^{-3}) \cdot \frac{1}{2}$	$+1.87 \times 10^{-3} M$
Equilibrium	$0.065 \times 10^{-3} M$	$1.065 \times 10^{-3} M$	$1.87 \times 10^{-3} M$

$$K_c = \frac{[HI]_{eq}^2}{[H_2]_{eq} \cdot [I_2]_{eq}}$$

\* Use equilibrium values.

## Predicting the Direction of Rxn

- If a reaction mixture contains only reactants, they generally react to form products
- If a reaction mixture not at equilibrium contains both reactants and products

Reaction Quotient ( $Q$ ) = ratio, at any point in the rxn.



$$K_c = \frac{[C]_{eq}^2}{[A]_{eq} \cdot [B]_{eq}}$$

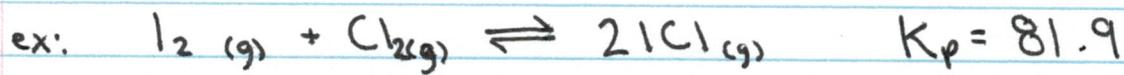
$$Q_c = \frac{[C]^2}{[A] \cdot [B]}$$

[ ] at  
any given time

- \*  $Q$  relative to  $K$  is a measure of progress of the rxn towards equilibrium

$$Q = \frac{\text{product}}{\text{reactant}}$$

- $Q < K$  : rxn shifts right  
not enough product  
 $\therefore$  consume reactant, form product
- $Q = K$  : no shift  $\therefore$  at equilibrium
- $Q > K$  : rxn shifts left  
too much product  
 $\therefore$  consume product, form reactant



A rxn mixture contains:

$$P(I_2) = 0.114 \text{ atm}, P(Cl_2) = 0.102 \text{ atm}$$

$$P(ICl) = 0.355 \text{ atm}$$

In which direction will the rxn proceed?

$$Q_p = \frac{(P_{ICl})^2}{(P_{I_2}) \cdot (P_{Cl_2})}$$
$$= \frac{(0.355)^2}{(0.114)(0.102)}$$

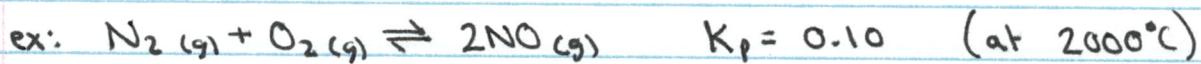
$$Q_p = 10.8 < K_p$$

$\therefore$  not enough product

$\therefore$  rxn shifts to the right.

# Calculating Equilibrium Concentrations

1. Set up ICE table with  $[ ]_i$
2. Find  $Q$  to determine direction of shift toward equilibrium
3. Use variable  $x$  to determine shift and  $[ ]_{eq}$
4. Sub  $[ ]_{eq}$  with  $x$  into  $K$  expression and solve for  $x$
5. Verify answer by calculating  $K$  from  $[ ]_{eq}$  values found



Rxn mixture contains: 0.200 atm of  $N_2$  and 0.200 atm of  $O_2$

Find equilibrium pressures.

$$Q_p = \frac{(0)^2}{(0.2) \cdot (0.2)} = 0 \quad Q_p < K_p$$

$\therefore$  rxn shifts right to equil  
 $\therefore$  reactant:  $\ominus$ , product:  $\oplus$

		$N_2$	+	$I_2$	$\rightleftharpoons$	$2NO$
I		0.2 atm		0.2 atm		0 atm
C		-x		-x		+2x
E		0.2 - x		0.2 - x		2x

$$K_p = 0.10 = \frac{(2x)^2}{(0.2-x)^2} \quad \therefore \text{ if } x = 0.027$$

$$\sqrt{0.1} = \frac{2x}{0.2-x}$$

$$P_{N_2} = P_{I_2} = 0.173 \text{ atm}$$

$$0.2\sqrt{0.1} - x\sqrt{0.1} = 2x$$

$$P_{NO} = 0.054 \text{ atm}$$

$$0.2\sqrt{0.1} = x(2 + \sqrt{0.1})$$

$$x = 0.027$$

## 5% rule

- Approximation when  $K$  is small (equilibrium achieved early)
  - ↳ reaction does not proceed far to right
- If initial reactant concentration / PP is large ( $400 \times K_c$  or  $K_p$ ) we can make the assumption that  $x$  (the change in concentration) is small
- Ratio  $x$  to the number it is added to should be less than 5% (0.05) for approximation to be valid

$$100 \times \frac{\text{change } (x \text{ or } 2x)}{\text{initial } (0.2)} < 5\%$$

- $x$  is approximated to be 0
  - if it is added or subtracted from number (if there is initial concentration)
- if initial concentration is 0, don't approximate

\* When looking for equilibrium concentration, put  $x$  back in.

ex:  $K_c = 1.67 \times 10^{-7}$  for decomposition  $H_2S \rightleftharpoons H_2 + S_2$   
 A 0.5 L vessel contains 0.0125 mol  $H_2S$   
 Find  $[H_2]_{eq}$  and  $[S_2]_{eq}$

	$2H_2S \rightleftharpoons 2H_2 + S_2$	$\frac{0.0125 \text{ mol}}{0.5 \text{ L}} = 0.025 \text{ M}$
I	0.025 M	0 0
C	- 2x	+ 2x + x
E	0.025 - 2x	2x x

$\downarrow$   
 $0.025 - 2x \approx 0$

Set  $x = \Delta [S_2]$   
 $0.025 > 1.67 \times 10^{-7} \times 400$   
 ∴ approximate

$$K_c = 1.67 \times 10^{-7} = \frac{(2x)^2 \cdot (x)}{(0.025)^2}$$

$$\begin{aligned} 1.67 \times 10^{-7} &= x^3 \\ 0.025 &= x^2 \\ 6.68 \times 10^{-5} &= x^3 \\ 2.609 \times 10^{-11} &= x^3 \end{aligned}$$

$$x = 2.97 \times 10^{-4}$$

validation:  $\frac{2x}{0.025} \times 100 = 2.37\% < 5\%$

### equilibrium concentrations

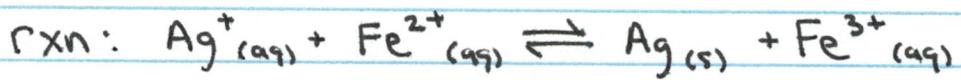
$$[H_2S] = 0.0244 \text{ M}$$

$$[H_2] = 5.94 \times 10^{-4} \text{ M}$$

$$[S_2] = 2.97 \times 10^{-4} \text{ M}$$

ex: Solid silver is added to sol'n with:

$$[\text{Ag}^+]_i = 0.2 \text{ M}, [\text{Fe}^{2+}]_i = 0.1 \text{ M}, [\text{Fe}^{3+}]_i = 0.3 \text{ M}$$



$$K_c = 2.98$$

Note: Do NOT consider solid species

$$Q_c = \frac{(0.3 \text{ M})}{(0.2) \cdot (0.1)} = 15 > K_c = 2.98$$

too much product  
∴ rxn go reverse

$\text{Ag}^{+}_{(\text{aq})} + \text{Fe}^{2+}_{(\text{aq})} \rightleftharpoons \text{Ag}_{(\text{s})} + \text{Fe}^{3+}_{(\text{aq})}$		
I	0.2	0.1
C	+ x	+ x
E	0.2+x	0.1+x

$$K_c = 2.98 = \frac{(0.3-x)}{(0.2+x) \cdot (0.1+x)}$$

$$2.98x^2 + 1.894x - 0.24 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad \left. \begin{array}{l} x_1 = 0.11 \\ x_2 = -0.74 \text{ omit} \end{array} \right\}$$

equilibrium:  $[\text{Ag}^+] = 0.31 \text{ M}$   
 $[\text{Fe}^{2+}] = 0.21 \text{ M}$   
 $[\text{Fe}^{3+}] = 0.19 \text{ M}$

## How a System at Equilibrium responds to Disturbances

Le Châteliers Principle =

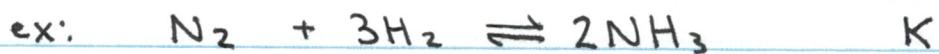
if a change is imposed on the system at eq., the position will shift toward the direction that reduces that change.

3 ways to disturb chemical equilibrium:

1. Change concentration: Add/Remove reactant/product
2. Change pressure or volume
3. Change temperature (change K)

1. Effect of concentration change

- If we increase concentration of a substance, system reacts to consume some of that substance
- If we decrease concentration of a substance, system reacts to produce some of that substance.

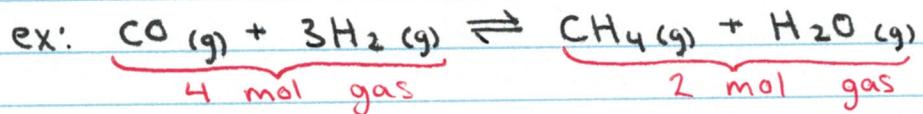


$$Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2] \cdot [\text{H}_2]^3}$$

- Add  $\text{H}_2 \quad Q < K \Rightarrow$  forward  
to consume excess  $\text{H}_2$   
reestablished equil
- Add  $\text{NH}_3 \quad Q > K \Rightarrow$  reverse

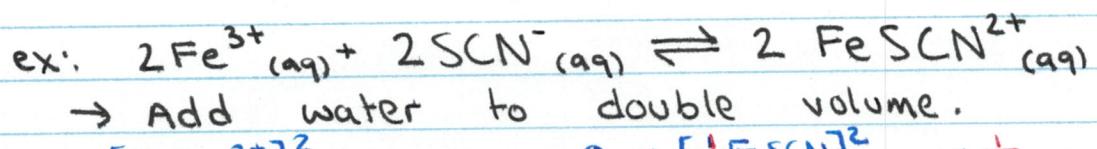
## 2. Effect of Pressure / Volume Change (gaseous)

- Add or remove gaseous reactants or products (same concept as concentration)
- Add inert gas (not involved in rxn)  
→ Does not affect equilibrium  
(same as adding a solid)
- Change volume of container:
  - If volume is decreased (pressure increase), system reacts to reduce pressure
  - If volume is increased (pressure decrease), system reacts to increase pressure  
Reduce number of gas molecules = reduce pressure  
Increase number of gas molecules = increase pressure



• System compressed (reduce volume)  
Pressure ↑ ∵ rxn goes forward direction  
to reduce amount of gas molecules ( $\Delta n$ )

- Volume change in sol'n rxn  
(affects concentration)



$$K_c = \frac{[\text{FeSCN}^{2+}]^2}{[\text{Fe}^{3+}]^2 \cdot [\text{SCN}^-]^2}$$

$$\text{vs. } Q_c = \frac{\left(\frac{1}{2}\text{FeSCN}^{2+}\right)^2}{\left[\frac{1}{2}\text{Fe}^{3+}\right]^2 \cdot \left[\frac{1}{2}\text{SCN}^-\right]^2} = \frac{\frac{1}{4}}{\frac{1}{4} \cdot \frac{1}{4}} \times K_c$$

$$Q_c = 4 \cdot K_c \quad Q_c > K_c \therefore \text{reverse}$$

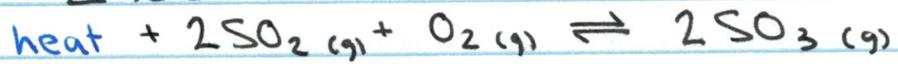
### 3. Effect of temperature change

→ Value of K changes with temperature

Consider heat as a chemical substance

- endothermic rxn : heat = reactant
- exothermic rxn : heat = product

ex: Endo



$$K_c = \frac{[\text{SO}_3]^2 \uparrow 1}{[\text{SO}_2]^2 \cdot [\text{O}_2] \uparrow 2}$$

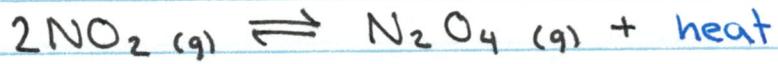
Temp. increase: rxn forward (consume heat)  
toward product

- ①  $K_c$  increase

Temp. decrease: rxn reverse (produce heat)  
toward reactant

- ②  $K_c$  decrease

ex: Exo



$$K_c = \frac{[\text{N}_2\text{O}_4]^2 \uparrow 2}{[\text{NO}_2]^2 \uparrow 1}$$

Temp. increase: rxn toward reactant (consume heat)  
①  $K_c$  decrease

Temp. decrease: rxn toward product (produce heat)  
②  $K_c$  increase

## ex: Le Chatelier's Principle



Predict the shift:

$$K_c = \frac{[CH_4]}{[H_2]^2}$$

Note: No C(s)  
b/c solid

(a) Add more carbon (s) : No change (solid)

(b) Raising temp. : Shift left

(c) Increase volume : P↓ ∴ Shift left

(d) Remove CH<sub>4</sub> : Shift right

(e) Add neon gas : No change (inert gas)

(f) Add H<sub>2</sub> gas : Shift right