# Dynamic Equilibrium

*…going back and forth…*

*…at the same time…*

*…at the same rate…*

# LeChatelier's Principle

- If a system at equilibrium is disturbed it will respond in the direction that counteracts the disturbance and re-establishes equilibrium
- The value of K is unchanged
  - Unless T is changed
- Disturbed(?)
  1. add/remove a chemical
  2. change pressure (gases)
  3. change temperature
  4. add/remove catalyst

# Dynamic Equilibrium

**Remember:** <u>"what's in your dish" at that moment</u>

For the reaction: aW + bX ⇌ cY + dZ

$$Q = \frac{[Y]^c[Z]^d}{[W]^a[X]^b}$$

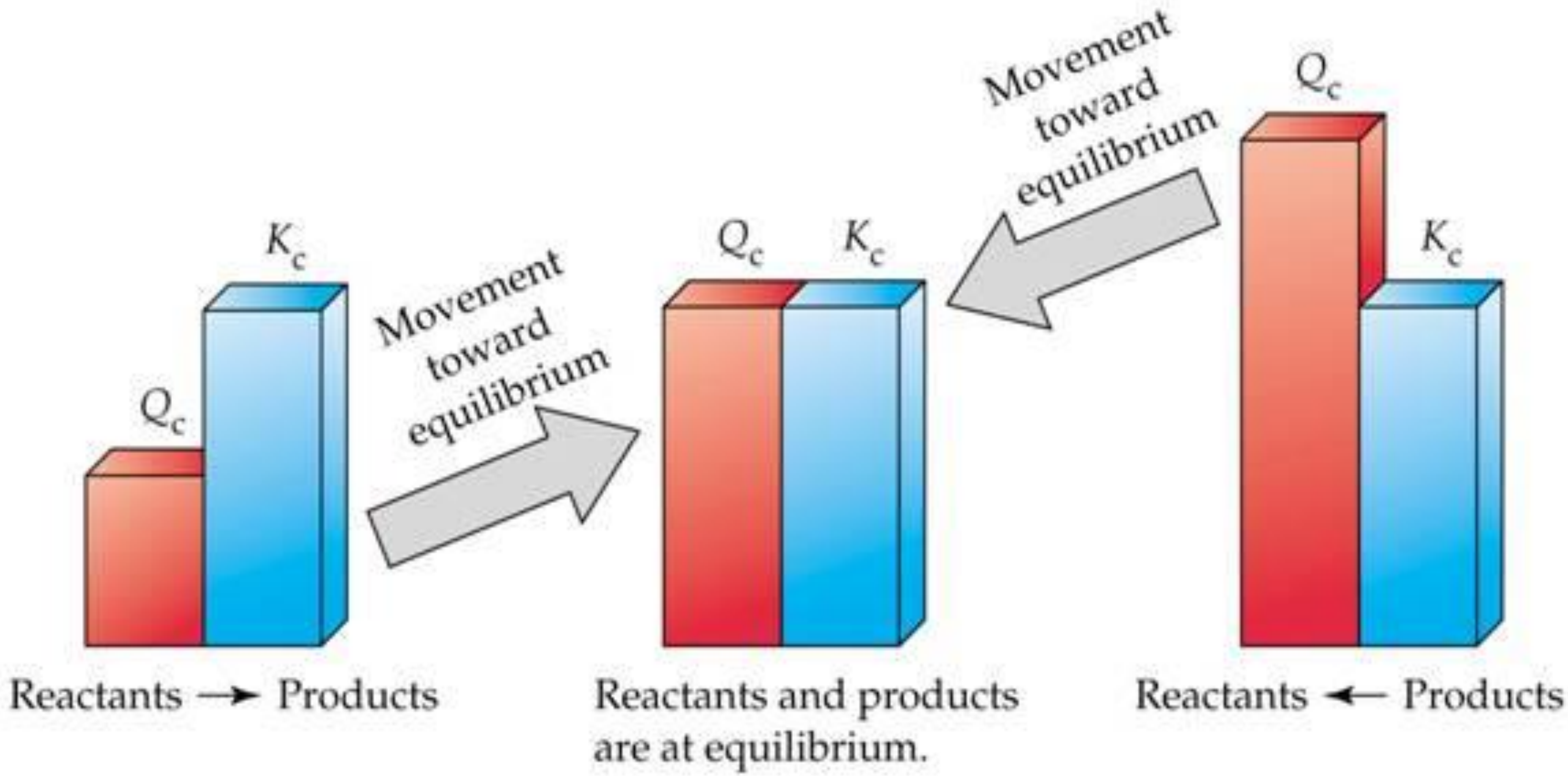
**At equilibrium**, the *concentrations stop changing*, so Q becomes a constant we call "K"

$$K = \frac{[Y]^c[Z]^d}{[W]^a[X]^b}$$

# If **Q ≠ K**, the system is NOT at equilibrium

- The reaction will proceed in the direction that heads toward being at equilibrium
- Is **Q < K**?
  - **reactants → products makes Q get larger**
    - “proceed forward” or “toward the product side”
- Is **Q > K**?
  - **products → reactants makes Q get smaller**
    - “proceed in reverse” or “toward the reactant side”

# LeChatelier’s Principle



# LeChatelier's Principle

Consider: A + B $\rightleftharpoons$ C + D

$$K = \frac{[C][D]}{[A][B]}$$

How many different sets of values for A, B, C, and D will give the same value for K?

**Infinite!**

# 1. adding/removing a chemical

- If you add a chemical, the system tries to "remove" it
- This is done by reacting it away
- This uses up the chemicals on its "side" of the equation and makes more of the chemicals on the other "side"
- ***Equilibrium is re-established (Q =K), but the individual concentrations are different***

# 1. adding/removing a chemical

- Consider: A + B ⇌ C + D at EQ
- If you add more A…
- The system tries to remove it by reacting it away, which makes more products

*Once equilibrium is re-established…*

- [C] ↑
- [D] ↑
- [B] ↓
- It is said the equilibrium has "shifted to the right" or "shifted towards the products"

# 1. adding/removing a chemical

- Consider: A + B ⇌ C + D at EQ
- If you add more C…
- The system tries to remove it by reacting it away, which makes more reactants

*Once equilibrium is re-established…*

- [A] ↑
- [B] ↑
- [D] ↓
- It is said the equilibrium has "shifted to the left" or "shifted towards the reactants"

# 1. adding/removing a chemical

- Consider: A + B ⇌ C + D at EQ
- If you *remove* some B…
- The system tries to replace it by reacting to make more of it (and whatever else is on its side of the equation)

*Once equilibrium is re-established…*

- [A] ↑
- [C] ↓
- [D] ↓
- It is said the equilibrium has "shifted to the left" or "shifted towards the reactants"

# 1. adding/removing a chemical

- Consider: A + B ⇌ C + D at EQ
- If you *remove* some D…
- The system tries to replace it by reacting to make more of it (and whatever else is on its side of the equation)

*Once equilibrium is re-established…*

- [C] ↑
- [A], [B] ↓
- The reaction is driven forward in this case, or towards the products

# 1. adding/removing a chemical

- Consider: A + B $\rightleftharpoons$ C + D

One of the best ways to force a reversible reaction to go all the way towards the product side and <u>not</u> reach equilibrium is to some how “remove” one of the products from “the dish”.

# Just how does one “remove” a chemical?

- Note: [D] is the *concentration* of D
- ***But**:* solids do not have a molarity because they are not dissolved into anything
- *So:* if one product in an aqueous system is a solid, the solid is called a “precipitate”
- Making a solid “removes” the chemical from the system
    - the precipitate is still “in the dish”, but is not a factor in the K calculation!
- This “drives” the reaction forward
- *Double replacements*

# Just how does one "remove" a chemical?

- Same for gases in an open container
- They can bubble out of the mixture (leave the dish)
- Ex: opening a soda bottle
  - $H_2CO_{3(aq)} \rightleftharpoons H_2O_{(l)} + CO_{2(g)}$
- Ex: $Mg_{(s)} + 2\ HCl_{(aq)} \rightleftharpoons H_{2(g)} + MgCl_{2(aq)}$
  - If the container is open, the reaction just keeps going forward

# 2. Changing the volume

- Remember Boyle's Law
- Changing the volume of a container of gases changes their pressure as well
  - Inverse relationship
  - If V↓, P↑
  - If V ↑, P↓
- This, in turn, changes their molarity

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

# 2. Changing the volume

- If V↓, then P↑
- The equilibrium will shift to try to make the P↓
- How is this done?
- <u>Shift to whichever side has less gas</u>
  - Fewer moles of a gas
    - Smaller coefficients in equation = smaller exponents
  - Less gas means lower pressure
- *If there are the same number of moles of gas in the reactants and products, there is no effect*

# 2. Changing the volume

Ex: $N_{2(g)} + 3\ H_{2(g)} \rightleftharpoons 2\ NH_{3(g)}$

- 4 moles of gas in the reactants, 2 in products
- If V↓, P↑…the system will try to make P↓ by shifting to the products (less gas)
- Every time the reaction proceeds forward, 4 moles of gas becomes 2…which means the P↓
- *Vice versa* if V ↑

# 2. Changing the volume

Ex: $N_{2(g)} + 3\ H_{2(g)} \rightleftharpoons 2\ NH_{3(g)}$

- Note: this effect is only when the change in pressure is caused by changing the volume!
- *Changing the pressure by adding another gas not in the reaction has NO EFFECT!*

# 3. Changing the temperature

- Consider : A + B ⇌ C + D + Heat
- For this system…
  - The forward reaction is exothermic
  - The reverse reaction is endothermic
- Treat heat as if it were a substance being added or removed
- Add heat, equilibrium shifts away from the side with heat [A],[B]↑ [C],[D]↓
- Remove heat, equilibrium shifts toward the side with heat [A],[B]↓ [C],[D]↑

# 4. Catalytic effect

- **Adding or removing a catalyst has no effect on the value of K**
- The activation energy is lowered for the forward *<u>and</u>* the reverse reaction, and they *<u>both</u>* speed up by the same amount, so **$Rate_{FWD}$ still = $Rate_{REV}$**
- If not at equilibrium, it will be reached quicker if a catalyst is used.

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# Now…lets try it out…

Ex: $PCl_{3(g)}$ + $Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$ $\Delta H = -88kJ$

**How will $[Cl_2]$ be changed when EQ is re-established by…**

Adding some $PCl_3$?

- System will try to react the $PCl_3$ away
- More products are formed
- To do this, more $Cl_2$ is consumed

$[Cl_2] \downarrow$

# Now…lets try it out…

Ex: $PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$ $\Delta H$= -88kJ

**How will [$Cl_2$] be changed when EQ is re-established by…**

<u>Adding some $PCl_5$?</u>

- The system will try to react it away
- More reactants are formed

[$Cl_2$] ↑

# Now…lets try it out…

Ex: $PCl_{3(g)}$ + $Cl_{2(g)}$ ⇌ $PCl_{5(g)}$ ΔH= -88kJ

**How will [$Cl_2$] be changed when EQ is re-established by…**

Increasing the temperature?

- Heat is added, the system shifts away from the side with heat
- ΔH = negative, so heat is a product
- System shifts towards the reactants

[$Cl_2$] ↑

# Now…lets try it out…

Ex: $PCl_{3(g)}$ + $Cl_{2(g)}$ ⇌ $PCl_{5(g)}$ ΔH= -88kJ

**How will [$Cl_2$] be changed when EQ is re-established by…**

Decreasing the volume?

- If V↓, P↑
- System shifts towards the side with less gas to make P↓
- Product side has fewer moles of gas

[$Cl_2$] ↓