# EQUILIBRIUM – 3
# LE CHATLIER'S PRINCIPLE

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# FACTORS AFFECTING EQUILIBRIUM

## Le Châtelier's Principle

When a system in chemical equilibrium is disturbed by a change in

- temperature,
- pressure, or
- concentration,

the system shifts in equilibrium in a way that tends to counteract this change of variable.

# EXAMPLE

The following reaction is at equilibrium:

$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$$

a. Predict the direction of reaction when chlorine gas is added to the reaction mixture.

b. Predict the direction of reaction when carbon monoxide gas is removed from the mixture.

**Solution:**

a. When we add $Cl_2$, the reaction will shift in the reverse direction to use it.

*Note*: reverse = left = ←.

b. When we remove CO, the reaction will shift in the forward direction to produce it. *Note*: forward = right = →.

# EQUILIBRIUM OF GASES AND PRESSURE

In case of gases, a change in the total pressure occurs because of a change in the *volume* of the reaction container.

**Three Possibilities:**

1. When the size of the container **decreases**, the overall pressure **increases.** The reaction will shift to reduce the pressure—that is, it will shift toward the side of the reaction with fewer gas molecules.

   (lower V -> higher P => low mols)

2. When the size of the container **increases**, the overall pressure **decreases.** The reaction will shift to increase the pressure—that is, it will shift toward the side with more gas molecules.

   (larger V -> lower P => more mols)

3. In the event that both sides of the equilibrium reaction have the **same number of moles of gas**, pressure has **no effect on the equilibrium.**

# EXAMPLE

In which direction will each reaction shift when the volume of the reaction container is increased?

a. $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

Shift to left because more mols on the left.

b. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

Shift to the left because more mols are on left.

c. $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

Shift to the right because more mols on the right.

# EQUILIBRIUM AND ENTHALPY

- Changing the temperature changes the value of the equilibrium constant.
- Changing the temperature can also cause a shift in the equilibrium.
- The direction of each of these changes depends on the sign of $\Delta H^o$.
- Two Possibilities:

For an **endothermic reaction**, $\Delta H^o > 0$ (positive), **heat is a reactant** so:

- Increasing temp adds heat to reactant so eq shifts forward.
- Decreasing temp removes heat from reactant to eq shifts to the left

For an **exothermic reaction**, $\Delta H^o < 0$ (negative), **heat is a product** so:

- Increasing temp adds heat to product so eq shifts left.
- Decreasing temp removes heat from product so eq shifts forward.

# EXAMPLE

Given: $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$; $\Delta H° = +484$ kJ

Would you expect this reaction to be favorable at high or low temperatures?

**Solution:**

Rewrite the reaction to include heat:

Heat + $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$

When heat is added, the reaction shifts forward = right = $\rightarrow$

# ALL IN ALL

| Condition | Increasing | Decreasing |
|---|---|---|
| Reactants | shifts eq. forward. | shifts eq. to left. |
| Products | shifts eq. left. | shifts eq. to the right. |
| Pressure/ Volume | Increasing P/decreasing V: shifts eq to less moles | Decreasing P/increasing V: shifts eq to higher moles |
| Heat | Endothermic: shift eq right<br>Exothermic: shift eq left | Endothermic: shift eq left<br>Exothermic: shift eq right |
| Catalyst | No change….Both forward and reverse reaction speed up | |
| Solids | No change….Solids don't affect equilibrium | |
| Adding an inert gas | No change….Volume changes for entire reaction system, not just one side. | |

# EXAMPLE:

Hydrogen is produced by the endothermic reaction,

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

Assuming the reaction is initially at equilibrium, indicate the direction of the shift (left, right, no change) if:

(a) $H_2O(g)$ is removed. **LEFT**

(b) The temperature is increased. **RIGHT**

(c) The quantity of Ni catalyst is increased. **NO CHANGE**

(d) An inert gas (e.g., He) is added. **NO CHANGE**

(e) $H_2(g)$ is removed. **RIGHT**

(f) The volume of the container is tripled. **RIGHT**

# KEY CONCEPTS

- Le Chatlier's Principle
- Predict direction of equilibrium when conditions are changed.