

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:



- Predict the direction of reaction when chlorine gas is added to the reaction mixture.
- Predict the direction of reaction when carbon monoxide gas is removed from the mixture.

Solution:

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

Note: reverse = left = \leftarrow .

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

EQUILIBRIUM OF GASES AND PRESSURE

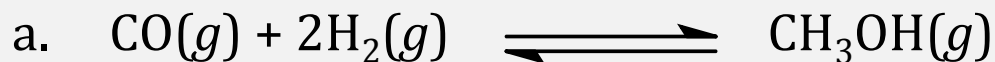
In case of gases, a change in the total pressure occurs because of a change in the *volume* of the reaction container.

Three Possibilities:

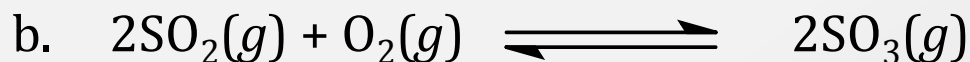
1. When the size of the container **decreases**, the overall pressure **increases**. The reaction will shift to reduce the pressure—that is, it will shift toward the side of the reaction with fewer gas molecules.
(lower $V \rightarrow$ higher $P \Rightarrow$ low mols)
2. When the size of the container **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 $V \rightarrow$ lower $P \Rightarrow$ 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?



Shift to left because more mols on the left.



Shift to the left because more mols are on left.



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 ΔH° .
- Two Possibilities:

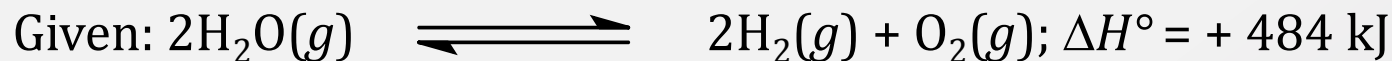
For an **endothermic reaction**, $\Delta H^\circ > 0$ (positive), **heat is a reactant** so:

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

For an **exothermic reaction**, $\Delta H^\circ < 0$ (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.

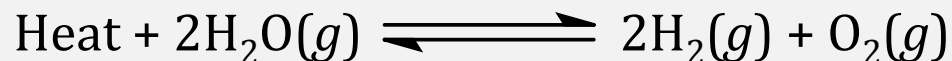
EXAMPLE



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

Solution:

Rewrite the reaction to include heat:



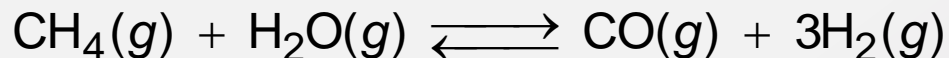
When heat is added, the reaction shifts forward = right = \rightarrow

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 Exothermic: shift eq left	Endothermic: shift eq left 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,



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

(a) $\text{H}_2\text{O}(g)$ 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) $\text{H}_2(g)$ 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.