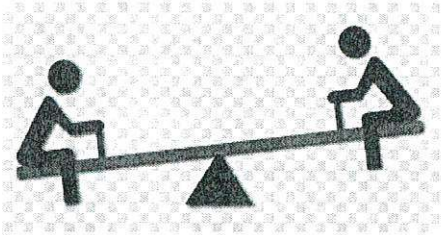
Le Châtelier's Principle

If a "stress" (change) is applied to a system at equilibrium,
equilibrium will shift in the direction that will partially relieve that stress.

Nothing can ever completely reverse the effects of stress! (Tell me about it, am I right? ;P)



Changes in Concentration

- Increasing the concentration of a reactant causes system to shift right to make more products.
- Increasing the concentration of a product causes system to shift left to form more reactants.
- Decreasing the concentration of a product causes system to shift right to form more products.
- Decreasing the concentration of a reactant causes system to shift left to make more reactants.

Important note: adding or subtracting the amount of a **pure solid or **liquid** will NOT cause a shift.**

A change in concentration of reactants or products will NOT affect the value of *K*.

$$A(aq) + B(aq) \rightleftarrows C(aq) + D(aq)$$

Stress	Effect	Stress	Effect
Add A or B	reaction will shift right to make more products	Add C or D	reaction will shift left to make more reactants
Remove A or B	reaction will shift left to make more reactants	Remove C or D	reaction will shift right to make more products

Example: $N_2(g) + 3\,H_2(g) \rightleftarrows 2\,NH_3(g)$

What will happen to the equilibrium system above when the following stresses are applied?

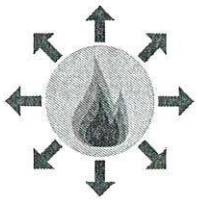
Stress	Effect	Stress	Effect
Add N_2	reaction will shift right to make more products	Add H_2	reaction will shift right to make more products
Add NH_3	reaction will shift left to make more reactants	Remove NH_3	reaction will shift left to make more reactants

Changes in Temperature

Changes in temperature may easily be treated as changes in concentration if you think of heat as a reactant (endothermic reaction) or product (exothermic reaction).

Exothermic Reactions: Heat is a product

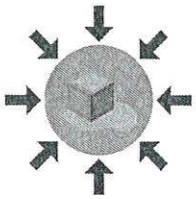
$$A + B \rightleftharpoons C + 56\ kJ$$



- Increasing temperature causes system to shift left. *K* will decrease.
- Decreasing temperature causes system to shift right. *K* will increase.

Endothermic Reactions: Heat is a reactant

$$D + E + 43\ kJ \rightleftharpoons F + G$$



- Increasing temperature causes system to shift right. *K* will increase.
- Decreasing temperature causes system to shift left. *K* will decrease.

****Only a change in temperature will change the value of *K*.****

Let's Practice!

1. Given the reaction: $2\ SO_3(g) \rightleftharpoons O_2(g) + 2\ SO_2(g) + 32.5\ kJ$

   What will happen to the equilibrium system above when the following stresses are applied?

Stress	Effect on Reaction System	Effect on K
Decrease the temperature	reaction will shift right to make more products	The value of K will: increase
Add SO_3	reaction will shift right to make more products	The value of K will: Stay the same
Increase the temperature	reaction will shift left to make more reactants	The value of K will: decrease

2. When a certain amount of nitrogen gas and hydrogen gas are placed in a 1.5 L evacuated container and heated to 773 K, ammonia gas, NH_3, is formed according to the following equation: $N_2(g) + H_2(g) \rightleftharpoons 2\ NH_3(g)$. When equilibrium is established, 0.565 mol of $NH_3(g)$ is present in the flask. When the same reaction is carried out at 298 K, the number of moles of $NH_3(g)$ is much larger than 0.565 mol. Is the forward reaction endothermic or exothermic? Justify your answer.

$\downarrow T \Rightarrow \uparrow [NH_3] = \uparrow [products]$

Exothermic, b/c a decrease in temp. caused the rxn to shift towards products, so heat must be produced by the rxn.

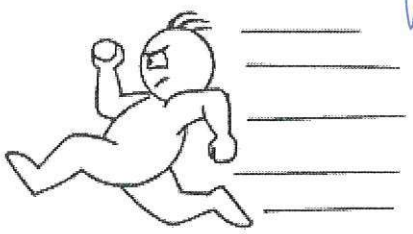
Oh Shift: Le Châtelier and Rate of Reaction

A shift to the left or right does **NOT** say anything about the rate of the reaction!

For example, consider the reaction: $A + B \rightleftharpoons C + \text{heat}$

If the temperature of this system was increased, equilibrium would shift to the left. This does NOT mean that the rate will be slower! It simply means that a new equilibrium will be reached which has more A and B and less C.

Increasing temperature causes equilibrium to be reached more quickly (regardless of shift!)



Changes in Pressure

Changes in pressure only affect equilibrium systems that have gaseous reactants and/or products.

- Increasing the pressure of a gaseous system causes system to shift to the side with fewer gas particles.
- Decreasing the pressure of a gaseous system causes system to shift to the side with more gas particles.
- If system has the same number of moles of gas on both sides, changes in pressure have no effect.
- Adding an inert gas does NOT affect the location of equilibrium, since the partial pressures of the gases in the reaction are not affected.

Changes in Volume: The opposite of changes in pressure.

- Increasing the volume of a gaseous system causes system to shift to the side with more gas particles.
- Decreasing the volume of a gaseous system causes system to shift to the side with fewer gas particles.

A change in pressure or volume will NOT affect the value of *K*.

Addition of a Catalyst: No effect on equilibrium position!

- Adding a catalyst increases the rate of both the forward and reverse reactions equally.
- Equilibrium will be reached more quickly. ;D

Example: $\underbrace{N_2(g) + 3\,H_2(g)}_{4 \text{ particles}} \rightleftarrows \underbrace{2\,NH_3(g)}_{2 \text{ particles}}$

What will happen to the equilibrium system above when the following stresses are applied?

Stress	Effect	Stress	Effect
Increase pressure	reaction will shift right to make more products	Ar(g) added	reaction will shift n/a to make more n/a
Increase volume	reaction will shift left to make more reactants	Decrease pressure	reaction will shift left to make more reactants

Let's Practice!

Consider the following equilibrium equation:

no gas — 1 gas — endo

heat + $Ca(HCO_3)_2(aq) \rightleftharpoons CaCO_3(s) + H_2O(l) + CO_2(g)$ $\Delta H_{rxn} = +2.1$ kJ/mol

A vessel contains $Ca(HCO_3)_2$, $CaCO_3(s)$, $NO_2(g)$, $H_2O(l)$, and $CO_2(g)$ at equilibrium. Predict how each of the following stresses will affect the variables specified.

Stress	Shift?	Effect on K?	Other Effect
CO_2 is added.	left	none	The concentration of $Ca(HCO_3)_2$ will: increase
$CaCO_3$ is removed.	none	none	The concentration of CO_2 will: stay the same
The volume is halved.	left	none	The amount of $CaCO_3$ will: decrease
He(g) is added. ↖ inert!	none	none	The amount of $Ca(HCO_3)_2$ will: stay the same
The temperature is decreased.	left	decrease	The concentration of $CaCO_3$ will: stay the same ↖ b/c it's a solid!
The pressure is decreased.	right	none	The concentration of $CaCO_3$ will: stay the same
$CaCO_3$ is added.	none (s) = no effect	none	The concentration of $Ca(HCO_3)_2$ will: stay the same
A catalyst is added.	none	none	The amount of CO_2 will: stay the same
The volume is increased.	right	none	The concentration of $Ca(HCO_3)_2$ will: decrease
The temperature is increased.	right	increase	The amount of CO_2 will: increase