Le Châtelier's Principle

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- If a stress is applied to a system at equilibrium, the system shifts in the direction that relieves the stress
  - A stress is any kind of change in a system at equilibrium that upsets the equilibrium

- You can use Le Châtelier’s Principle to predict how changes in concentration, volume (pressure), and temperature affect equilibrium
  - Changes in volume and pressure are interrelated because decreasing the volume of a reaction vessel at constant temperature increases the pressure inside
  - Conversely, increasing the volume decreases the pressure

Increase in Temperature

- The system shifts to use up the added heat, favoring the endothermic reaction.
  - It changes because the equilibrium position shifts without any substances being added or removed. There is no heat related term in the mass action expression to maintain the ratio.

Decrease in Temperature

- The system shifts to produce more heat, favoring the exothermic reaction.
  - It changes because the equilibrium position shifts without any substances being added or removed. There is no heat related term in the mass action expression to maintain the ratio.

Increase in Volume (Decrease in Pressure)

- The system shifts to the side with the most gas particles, because solids and liquids are incompressible.
  - It does not change, because all reactant and product concentrations change, resulting in the same ratio.

Decrease in Volume (Increase in Pressure)

- The system shifts to the side with the fewest gas particles, because solids and liquids are incompressible.
  - It does not change, because all reactant and product concentrations change, resulting in the same ratio.

Increase in concentration

- The system shifts to decrease the reactant or product that was added.
  - It does not change, because all reactant and product concentrations change, resulting in the same ratio.

Decrease in Concentration

- The system shifts to increase the reactant or product that was removed.
  - It does not change, because all reactant and product concentrations change, resulting in the same ratio.

Addition of a Catalyst

- No change. Catalysts increase the forward and reverse reactions to the same extent, so that they only serve to help bring systems to equilibrium faster.
  - It does not change.

Addition of an Inert Gas

- No change, because it doesn't take part in the reaction.
  - It does not change.

Example

- Change in concentration

PCl_3	+	Cl_2	↔	PCl_5
Increase		Increase		decrease

- Any of these changes causes a shift to the right

PCl_3	+	Cl_2	↔	PCl_5
Increase		Increase		decrease

- Any of these changes causes a shift to the left

Example Question

- Much of the brown haze hanging over large cities is nitrogen dioxide, NO_2(g). Nitrogen dioxide reacts to form dinitrogen tetraoxide, N_2O_4(g), according to the equation:

$$2\ NO_2(g) \leftrightarrow N_2O_4(g) + 57.2\ kJ$$

- Use this equilibrium to explain why the brownish haze over a large city disappears in the winter, only to reappear again in the spring.

Answer

- The stress is a decrease in temperature in the winter.
- The exothermic reaction (a release of heat) would be favored to oppose the decrease of temperature.
- This would favor the production of the colorless dinitrogen tetraoxide gas.

- In the summer, the stress would be an increase in temperature.
- The endothermic reaction (absorption of heat) would be favored to oppose this stress.
- Nitrogen dioxide would therefore be produced and we would see a brown haze over the city.

Concentration vs Time Graphs

Concentration vs Time