LE CHATELIER'S PRINCIPLE

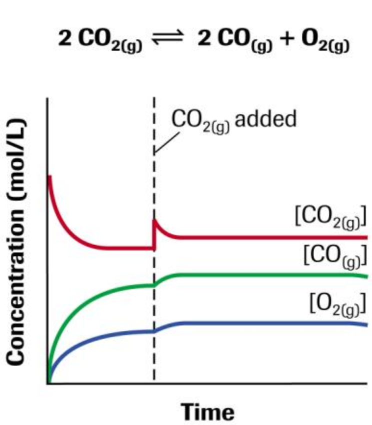
- When a chemical system at equilibrium is subjected to an external stress (disturbed by a change in a property), the system establishes a new equilibrium to minimize the effects of that stress
- Le Chatelier's principle provides a method of predicting the response of a chemical system to a change in conditions

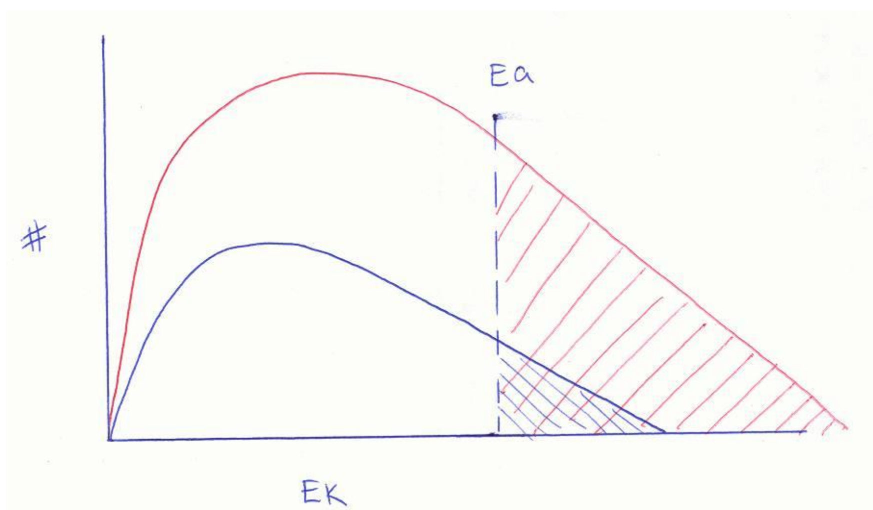
Le Chatelier and a Change in Concentration

- Le Chatelier's principle predicts that, if the concentration of a substance is increased, the reaction will shift in a direction that will use up the substance added
- If the concentration of a substance is decreased, the reaction will shift in a direction that will produce more of the substance

Eg) $2CO_2(g) \leftrightarrow 2CO(g) + O_2(g)$

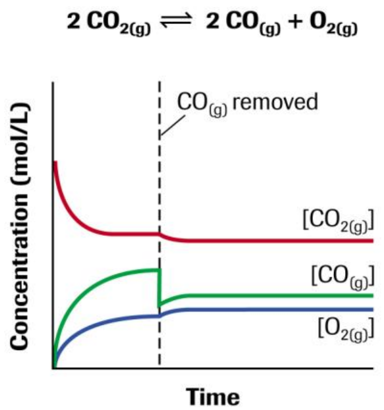
- If the $[CO_2]$ is increased:
    - there will be more particles of CO_2 to collide thereby increasing the probability of collision
    - there will be more particles with their energy $\geq$ Ea
- these factors cause the rate of the forward reaction to increase while the rate of the reverse reaction stays the same
- therefore the reaction shifts to the right (using up CO_2 and producing more CO and O_2

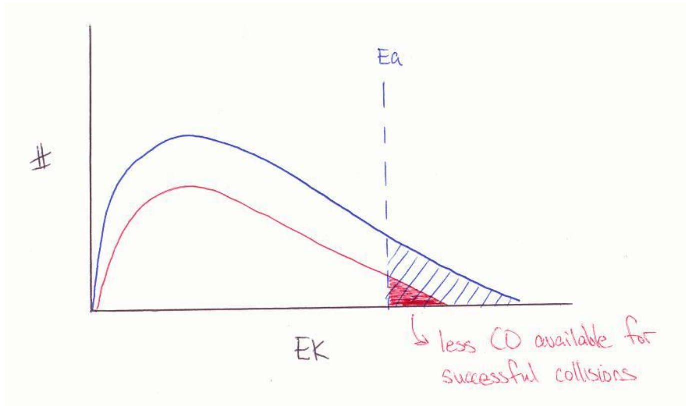


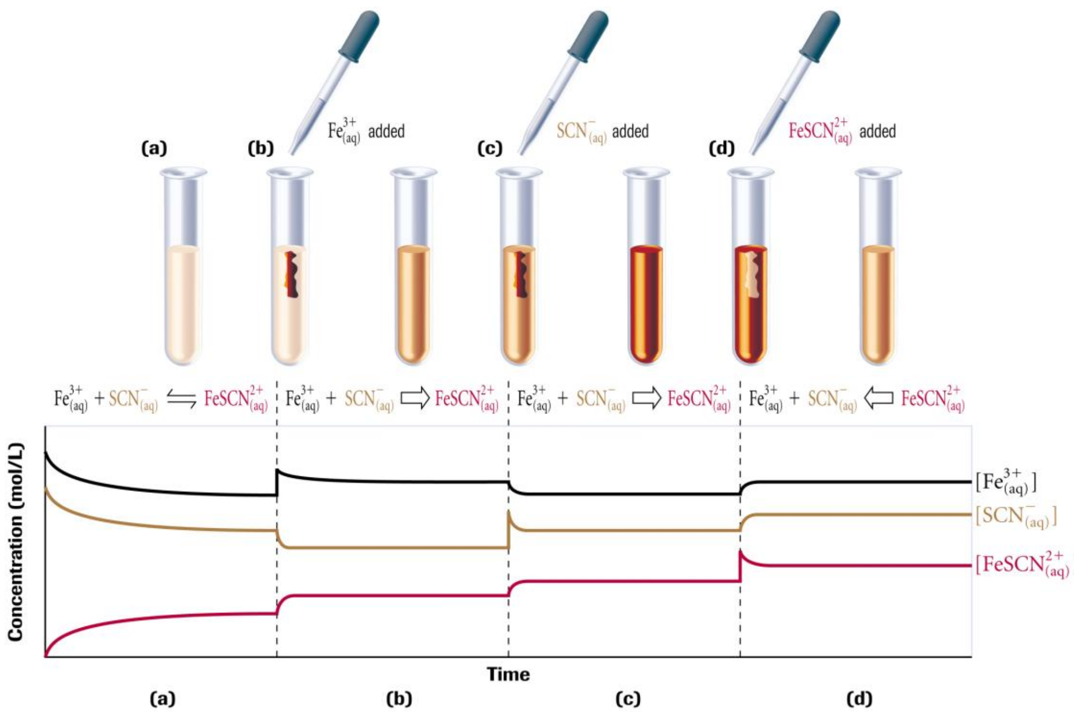


- if the [CO] is decreased:
    - there will be less CO molecules to collide with oxygen molecules thereby decreasing the probability of collision
    - there will be less CO molecules with their energy $\geq$ Ea

- these factors cause the rate of the reverse reaction to decrease while the rate of the forward reaction stays the same
- therefore the reaction shifts to the right (to produce more CO)







When solutions containing $Fe^{3+}_{(aq)}$ (colourless) and $SCN^{-}_{(aq)}$ (brown) are mixed, an equilibrium is reached with the product, $FeSCN^{+}_{(aq)}$ (deep red), as shown by the constant, uniform light brown colour of the equilibrium solution. On the graph, notice that the concentrations of $Fe^{3+}_{(aq)}$ and $SCN^{-}_{(aq)}$ drop after mixing as they react to form $FeSCN^{2+}_{(aq)}$. All three concentrations become constant when equilibrium is reached (flat lines).

$Fe^{3+}_{(aq)}$ is added. In response the system shifts to the right, producing more red $FeSCN^{2+}_{(aq)}$. Notice the spike in the graph of $Fe^{3+}_{(aq)}$ when more is added, and that the concentration of $Fe^{3+}_{(aq)}$ subsequently drops. The concentration of $FeSCN^{2+}_{(aq)}$ rises as more is produced. As $SCN^{-}_{(aq)}$ ions are used up, the concentration drops. Equilibrium is reestablished at a new level (flat lines).

The addition of more solution containing $SCN^{-}_{(aq)}$ shifts the equilibrium to the right, producing more of the dark red $FeSCN^{2+}_{(aq)}$ ions. Note the corresponding changes in the graph.

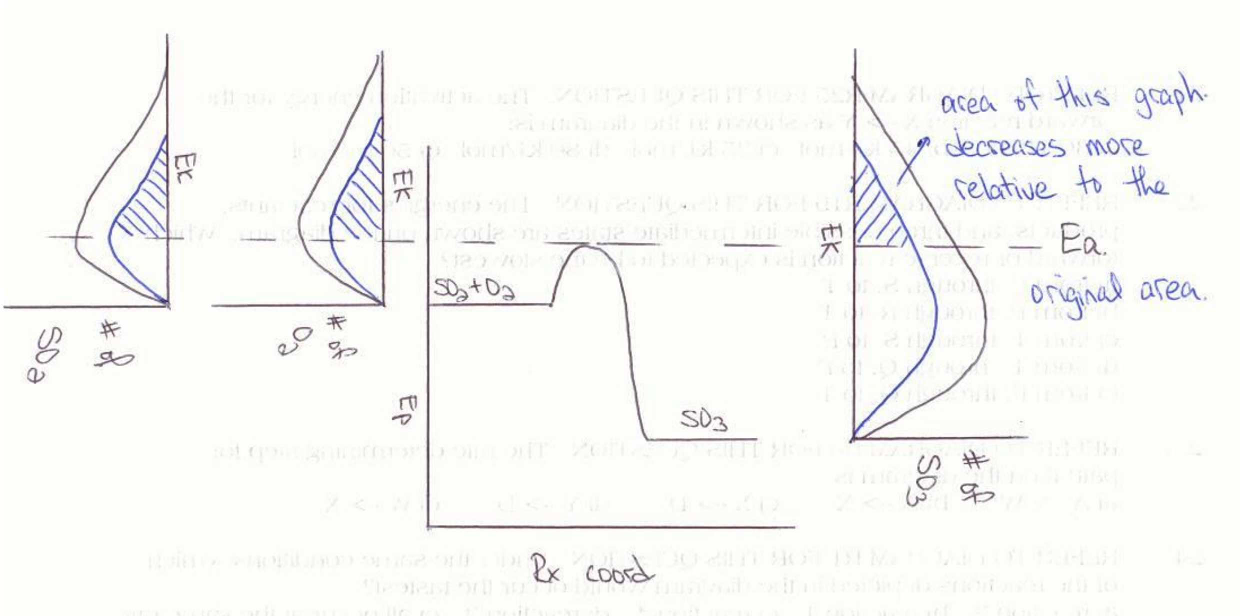
Adding $FeSCN^{2-}_{(aq)}$ ions to the mixture forces the equilibrium to shift toward the reactants, giving the solution a paler colour. Note the corresponding changes in the graph

Le Chatelier and a Change in Temperature

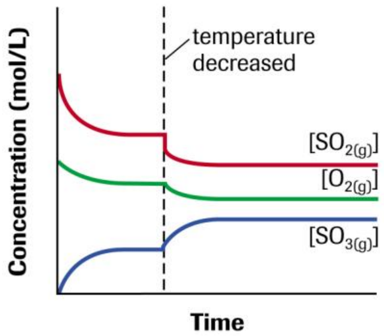
- Le Chatelier's principle predicts that if we increase the temperature of a system, the reaction will shift in a direction away from the energy term (to use up the energy)
- If we decrease the temperature of a system, the reaction will shift in a direction towards the energy term (to make more energy/heat)

Eg) $2SO_2(g) + O_2(g) \leftrightarrow SO_3(g)$ + energy

- For this exothermic reaction, if the temperature in decreased:
  - The reactant and product particles will slow down which will decrease the number of collisions
  - Looking at the shift in a Maxwell-Boltzman graph, the number of particles with their energy ≥ Ea will decrease for both the reactants and products BUT it will decrease the number of product particles above Ea more significantly
- These factors cause the rate forward to decrease but causes the rate reverse to decrease even more
- Therefore the reaction "shifts" to the right (producing more energy/heat)

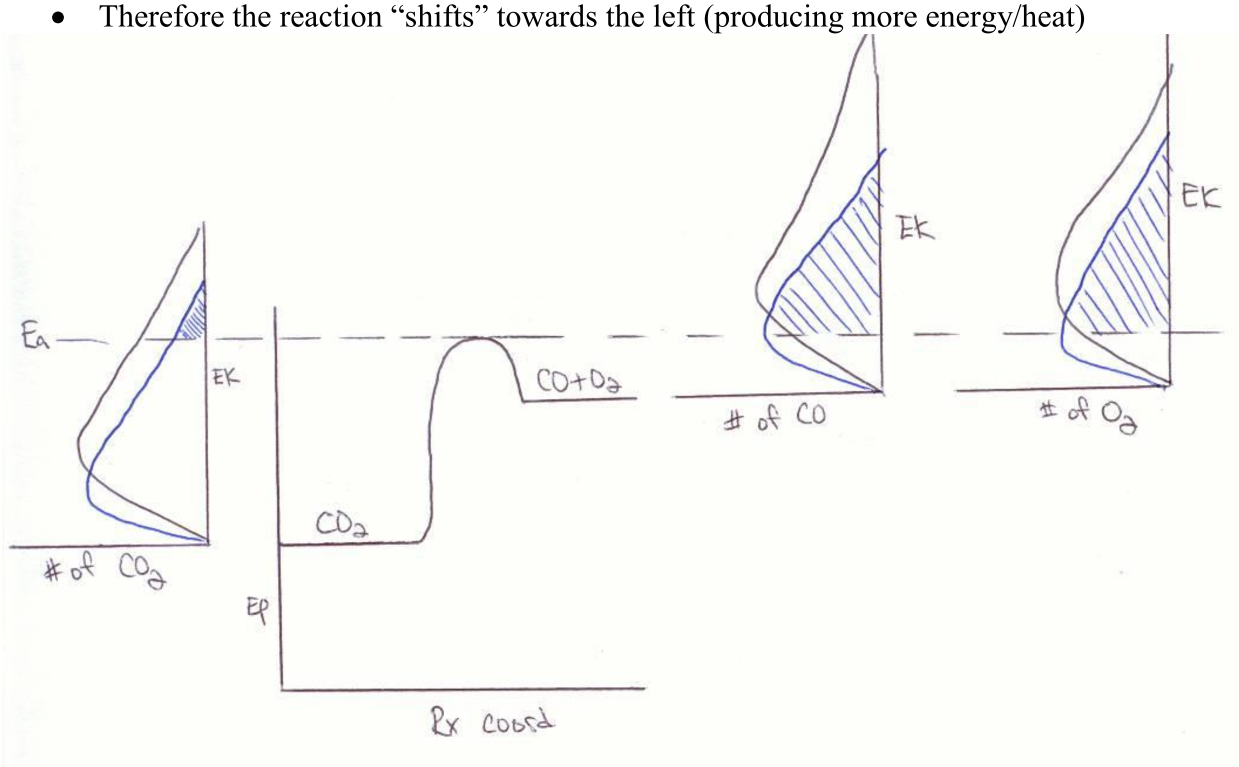


$2\,SO_{2(g)} + O_{2(g)} \rightleftharpoons 2\,SO_{3(g)} + \text{energy}$

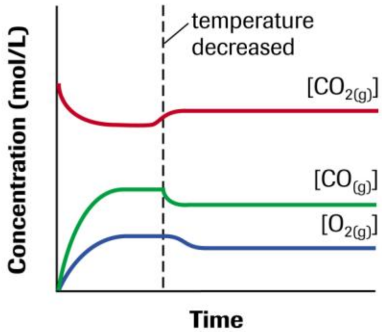


Eg) $2CO_2(g)$ + energy ↔ $2CO(g) + O_2(g)$

- For an endothermic reaction, a decrease in temperature will:
  - Cause the reactant and product particles to slow down which will cause less collisions
  - The number of particles above Ea will also decrease for both sides BUT the number of reactant particles above Ea will decrease much more significantly
- These factors cause the rate of the forward and reverse reactions to decrease but the rate of the forward reaction decreases more
- Therefore the reaction "shifts" towards the left (producing more energy/heat)



$CO_{2(g)}$ + energy $\rightleftharpoons$ 2 $CO_{(g)}$ + $O_{2(g)}$



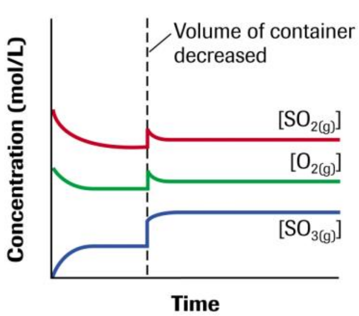
Le Chatelier's Principle and Changes in Gas Volume/Pressure

- Recall Boyle's Law which states the volume is inversely proportional to pressure
  - If you decrease the volume, you increase pressure
  - If you increase the volume, you decrease pressure
- Le Chatelier's principle suggests that if a system's volume is decreased (pressure increased), the reaction will shift in a way to decrease the amount of gas in the system
  - The reaction will shift in a direction to decrease the number of gas particles
- If a system's volume is increased (pressure decreased), the reaction will shift in a way to increase the amount of gas in the system
  - The reaction shifts in a direction to increase the number of gas particles

Eg) $2SO_2(g) + O_2(g) \leftrightarrow 2SO_3(g)$

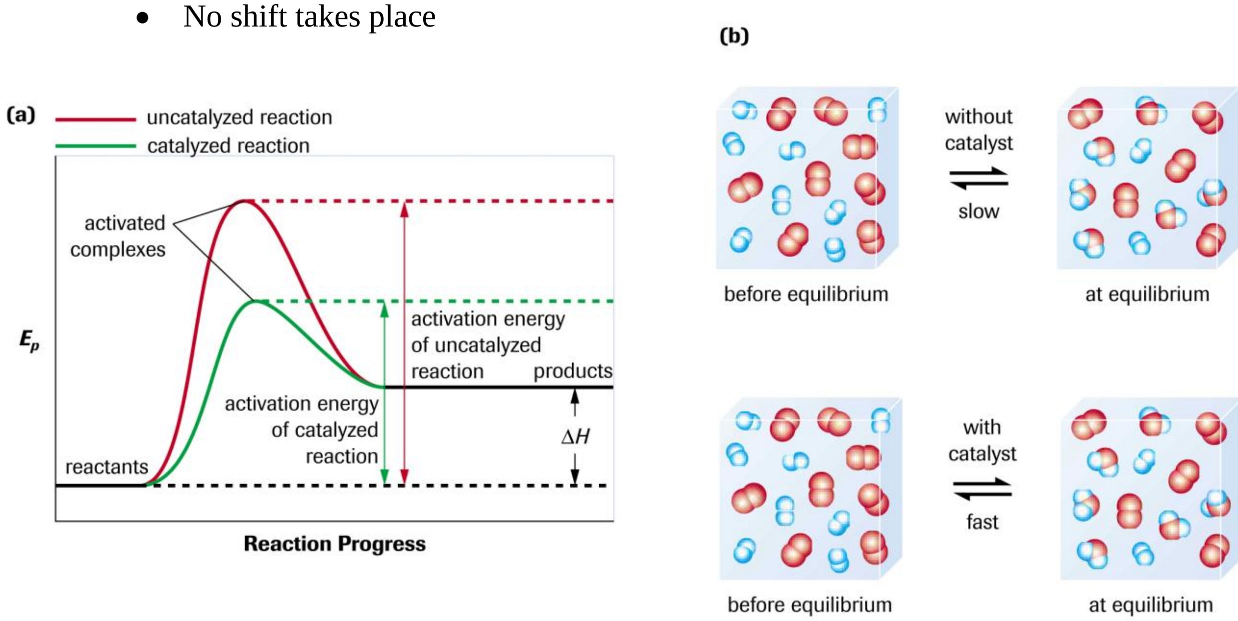
- For this reaction, if the volume was decreased, the pressure would increase
  - The number of particles in a given space would increase thus increasing the probability of collisions for both the forward and reverse reactions
  - The probability of collisions for the forward reaction would be increased more significantly because it is a more difficult reaction (3 particles colliding vs 2 particles colliding in the reverse reaction)
- These factors would increase the rates of both the forward and reverse reactions but the forward reaction rate would increase more
- Therefore, the system shifts to the right (using 3 gas particles to make 2 gas particles = less gas particles)

2 $SO_{2(g)}$ + $O_{2(g)}$ $\rightleftharpoons$ 2 $SO_{3(g)}$ + energy



Changes That Do Not Affect the Equilibrium System

1. Adding a Catalyst/Taking away a Catalyst
   - A catalyst reduces the activation energy by the same amount whether the reaction proceeds to the left or to the right therefore is does not affect the concentrations of the reactants and products
   - No shift takes place



2. Adding Inert Gases
   - The pressure of the system will be increased by adding an inert gas BUT it does not affect the probability of collision for the forward reaction any more than it affects the chance of collision for the reverse reaction
   - No shift takes place

3. Adding a Substance That Is Not Part of the Equilibrium
   - The substance will not influence the number of collisions for any differently for the forward or reverse reactions
   - No shift takes place

Types of Reactions	Changes To The System	Effect of Kc	Direction of Shift
All reactions	Increasing any [reactant] or decreasing [product]	No effect	Towards the products
	Decreasing any [reactant] or increasing [product]	No effect	Towards the reactants
	Using a catalyst	No effect	No shift
Exothermic	Increasing temperature	Decreases	Toward reactants
	Decreasing temperature	Increases	Toward products
Endothermic	Increasing temperature	Increases	Toward products
	Decreasing temperature	Decreases	Toward reactants
Equal # of reactant and product gas molecules	Changing the volume/changing the pressure	No effect	No change
More product gas particles than reactant gas particles	Decreasing the volume/increasing the pressure	No effect	Towards reactants
	Increasing the volume/decreasing the pressure	No effect	Towards products
Fewer product gas particles than reactant gas particles	Decreasing the volume/increasing the pressure	No effect	Towards products
	Increasing the volume/decreasing the pressure	No effect	Towards reactants