UNIT 7: CHEMICAL KINETICS AND EQUILIBRIUM

Chapter 19: Reaction Rates and Equilibrium

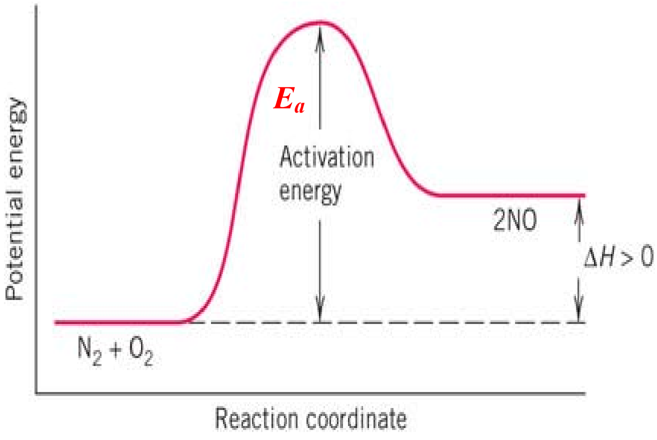
19.1: Rates of Reaction

Reaction Rates: - the speed of which the concentration of a reactant or product changes over time.

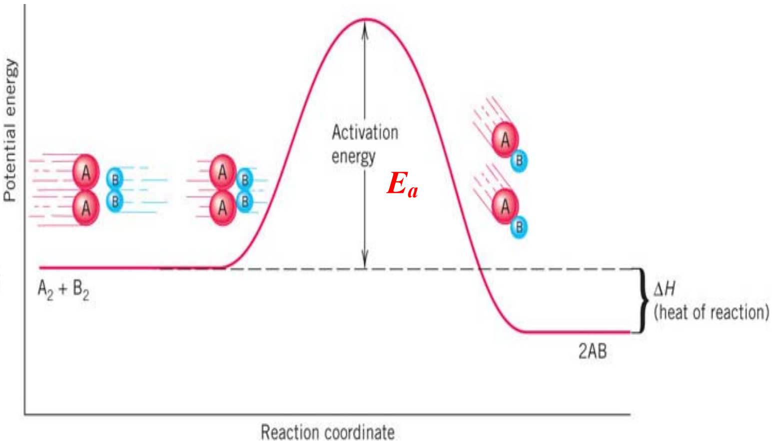
Collision Model: - a model that state for a reaction to occur, molecules must collide with each other.

Factors Affecting the Collision Model:

1. **Activation Energy** (E_a): - the threshold energy molecules needed to overcome to cause a chemical reaction that was first proposed by Svante Arrhenius.
   - **E_a is the highest energy (top of the hill - E_{max}) minus the sum of energy of the reactants ($\Sigma H_{reactants}$) on the potential energy diagram.**
   - in general, the **Lower the Activation Energy, the Faster is the Rate of Reaction**.

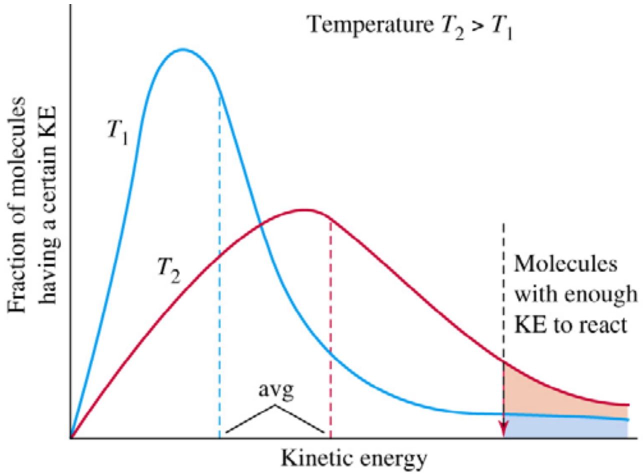


Activation Energy of an Endothermic Reaction



Activation Energy of an Exothermic Reaction

2. **Temperature** (T): - the effective number of collisions increases exponentially with temperature.



Because $T_2 > T_1$, there are more molecules colliding with enough Kinetic Energy causing a reaction to occur.

In general, the Higher the Temperature, the Faster the Rate of Reaction.

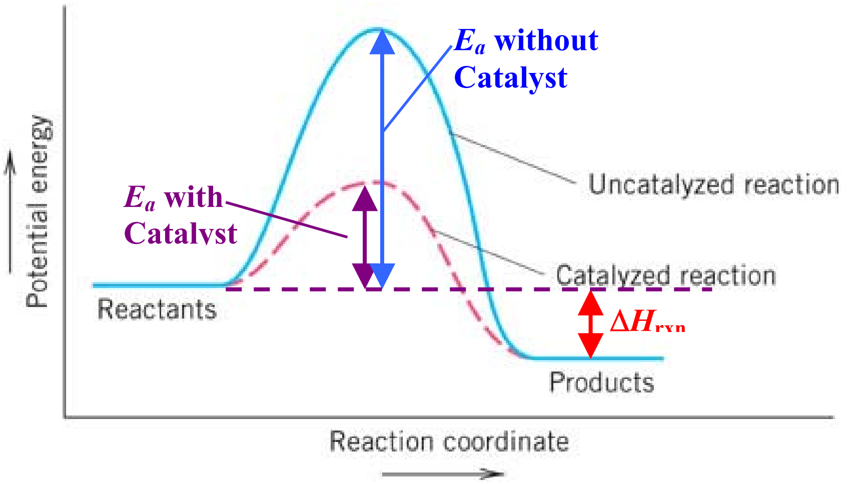
3. **Particle Size**: - the **Smaller the Particle Size (the Larger the Surface Area exposed), the Faster the Reaction Rate.**

Example 1: Grain sugar dissolves faster than equal mass of sugar cubes because of smaller particle size and therefore increased surface area of the grain sugar.

4. **Concentration**: - the **higher the Concentration (the more molecules in an available space, the higher the chance of collision), the Faster the Reaction Rate.**

5. **Catalyst**: - a substance that speeds up the reaction **without** being consumed in the reaction.
   - unlike intermediates, catalyst is used and recycled in the reaction.
   - lowers activation energy by providing an alternate reaction pathway.
   (ΔE_a is lowered but ΔH_{rxn} remains the same.)
   - in general, **the Addition of a Catalyst INCREASES the Rate of Reaction**.

Example 2: Enzyme is a catalyst in the body that speeds up certain bodily reaction.



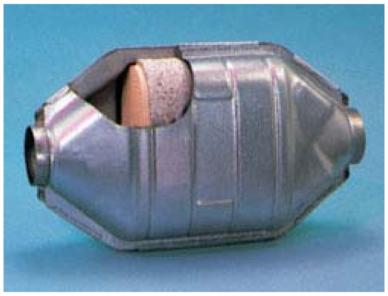
6. **Inhibitor**: - a substance that "inhibit" the function of a catalyst to speed up the reaction.
   - in general, the **Addition of an Inhibitor DECREASES the Reaction Rate**.

Example 3: Ammonia is formed from its elements using heterogeneous catalyst such as $Pt_{(s)}$:

$$N_{2\,(g)} + 3\,H_{2\,(g)} \xrightarrow{Pt} 2\,NH_{3\,(g)}$$

(Check out Video at http://www.dac.neu.edu/physics/b.maheswaran/phy1121/data/ch11/anim/anim11-5b.mov)

Example 4: The catalytic converter converts $NO_{(g)}$ (result of burning nitrogen at high temperature) to $N_{2\,(g)}$ and $O_{2\,(g)}$. The $O_{2\,(g)}$ along with the catalytic converter is used to produce $CO_{2\,(g)}$ from $CO_{(g)}$.



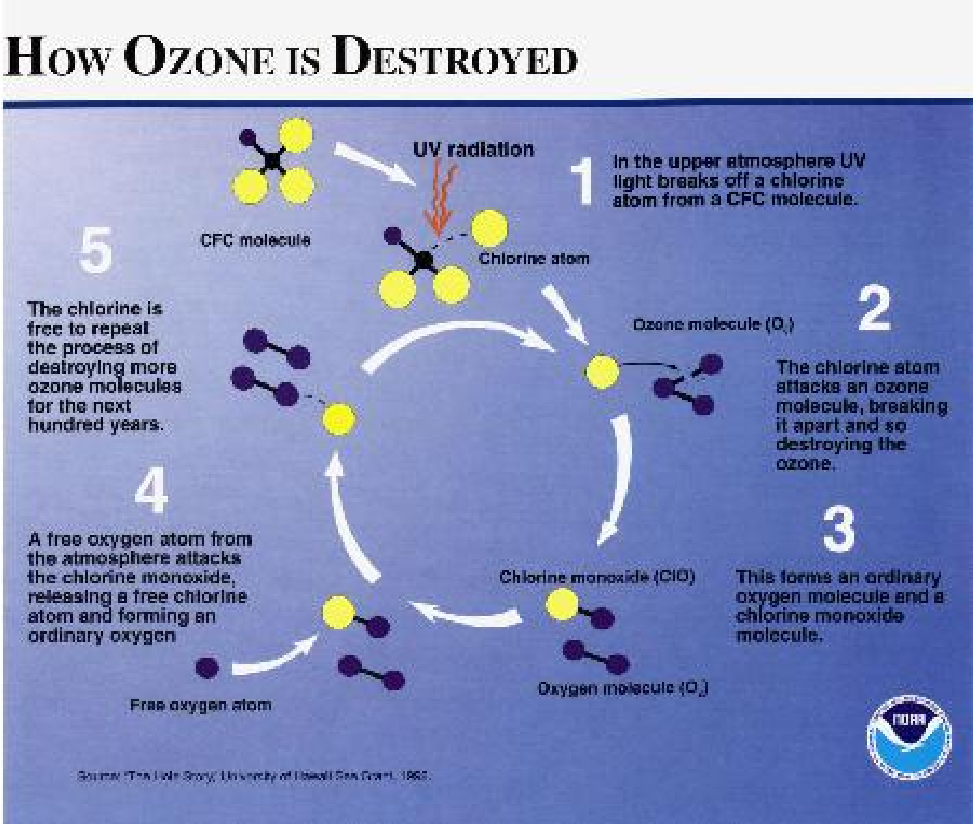
$$2\,NO_{(g)} \xrightarrow{\text{catalytic converter}} N_{2\,(g)} + O_{2\,(g)}$$
$$2\,CO_{(g)} + O_{2\,(g)} \xrightarrow{\text{catalytic converter}} 2\,CO_{2\,(g)}$$

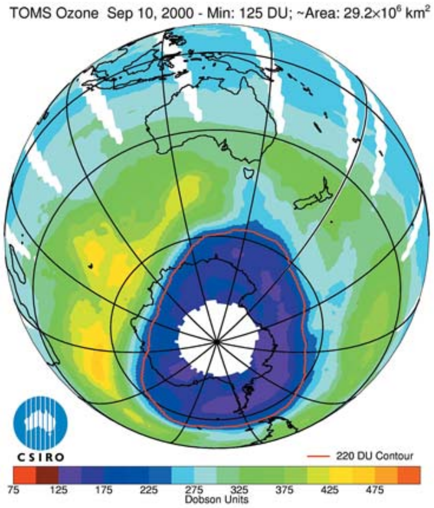
(Left): A catalytic converter for most modern vehicle. Leaded gasoline, an inhibitor, deactivates catalytic converter. Hence, it is not legally used in vehicles

Example 5: The destruction of ozone in upper atmosphere can be attributed to $NO_{(g)}$ and CFCs acting as catalysts. $NO_{(g)}$ is produced from the combustion of $N_{2\,(g)}$ at high temperature commonly found in internal combustion engine (high-altitude aircraft produces lots of NO gas). CFCs (Chloro-Fluoro-Carbon compounds) are found in aerosol can propellants, refrigerators, and air conditioners. They break down to form $Cl_{(g)}$ with the presence of light.

$$\begin{array}{c} NO_{(g)} + O_{3\,(g)} \rightarrow NO_{2\,(g)} + O_{2\,(g)} \\ \underline{O_{(g)} + NO_{2\,(g)} \rightarrow NO_{(g)} + O_{2\,(g)}} \\ O_{(g)} + O_{3\,(g)} \rightarrow 2\,O_{2\,(g)} \end{array}$$

$$\begin{array}{c} Cl_{(g)} + O_{3\,(g)} \rightarrow ClO_{(g)} + O_{2\,(g)} \\ \underline{O_{(g)} + ClO_{(g)} \rightarrow Cl_{(g)} + O_{2\,(g)}} \\ O_{(g)} + O_{3\,(g)} \rightarrow 2\,O_{2\,(g)} \end{array}$$





(Above) The Ozone Hole over the South Pole (Sept 2000). A similar hole is present over the Arctic. (Left) Process of Ozone Depletion. Ozone blocks harmful UV rays that can otherwise cause skin cancer.

Factors Affecting Reaction Rate

1.	**Activation Energy (E_a) ↓**	**Reaction Rate ↑**
2.	**Temperature (T) ↑**	**Reaction Rate ↑**
3.	**Particle Size ↓ (Surface Area ↑)**	**Reaction Rate ↑**
4.	**Concentration ↑**	**Reaction Rate ↑**
5.	**Catalyst ↑**	**Reaction Rate ↑**
6.	**Inhibitor ↑**	**Reaction Rate ↓**

Assignment

19.1: pg. 538 #1 to 5; pg. 572 #39 to 43; pg. 573 #74

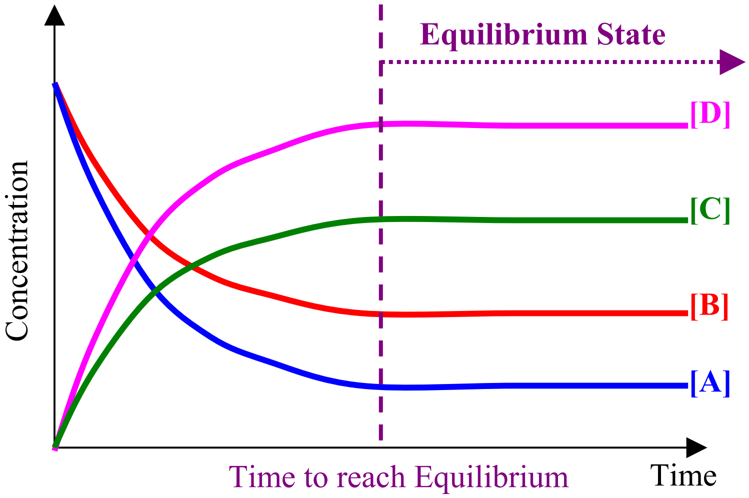
19.2A: Reversible Reactions

Reversible Reactions: - reactions that can go from the right hand side of the equation (products) to the left hand side of the equation (reactants).

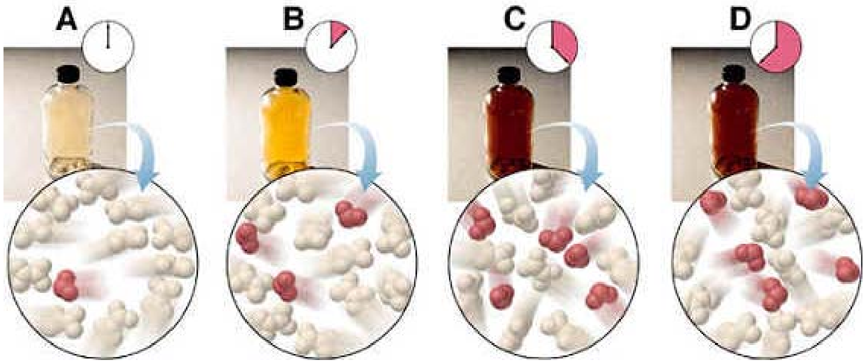
Chemical Equilibrium: - the state at which the concentrations of all reactants and products remain constant with time (**the Forward Reaction Rate = Reverse Reaction Rate**).
- **the equilibrium state is dynamic (not static).** Chemical species are continuously converting from reactants to products and vice versa. It appears that the reaction has stopped only because the rate of consumption = rate of production.
- **if an equilibrium state is disturbed** (changing concentrations of species, pressure, volume and temperature change), **the reaction will shift towards one side in order to re-establish the new equilibrium state.**
- like reaction rate, **Equilibrium is affected by Temperature**.

$$aA + bB \rightleftharpoons cC + dD$$

***a* and *b*: Coefficients of reactant species A and B**
***c* and *d*: Coefficients of product species C and D**
$\rightleftharpoons$ equilibrium symbol (indicating forward and reverse reactions)



(Check out Video at http://www.carlton.paschools.pa.sk.ca/chemical/mtom/contents/chapter2/images/h2osimulation.mpg)



The $N_2O_{4\,(g)} \rightleftharpoons 2\ NO_{2\,(g)}$ equilibrium.

Initially (Picture A), there were very little $NO_{2\,(g)}$. As time proceeded forward, more $NO_{2\,(g)}$ (brown color) is produced (Pictures B & C). However, there are still $N_2O_{4\,(g)}$ present at the equilibrium state (Picture D).

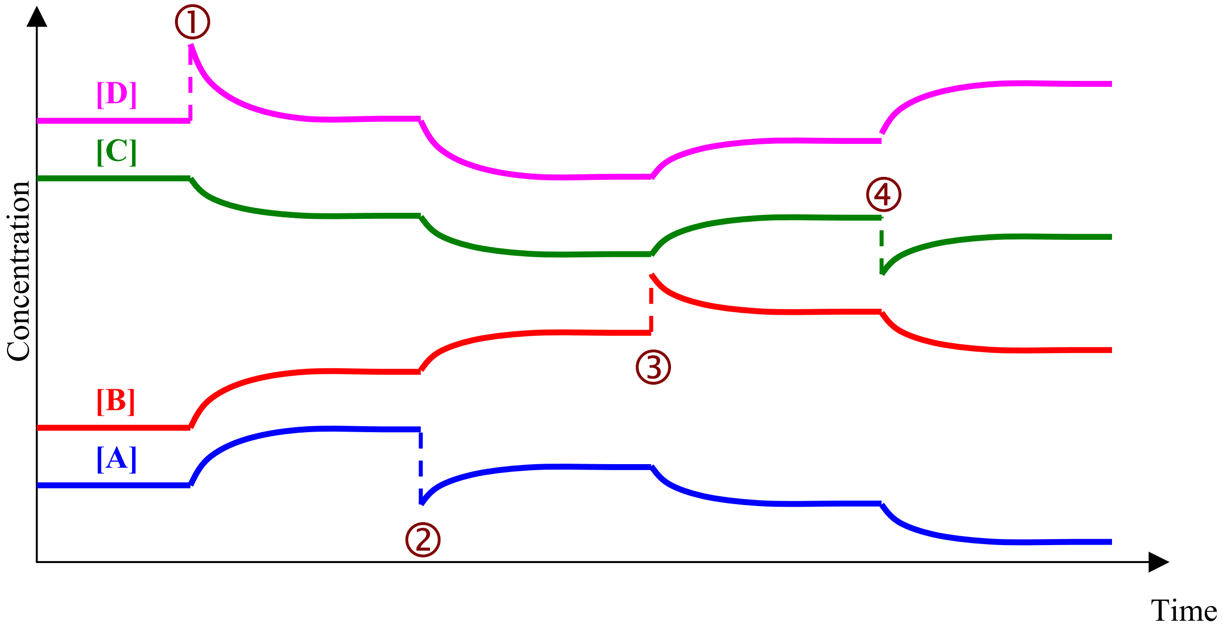
Le Châtelier's Principle: - a qualitative method to **predict the shift on an equilibrium system** if it is disturbed by means of **changing concentration, pressure and temperature**.
- ***the equilibrium will shift in the direction that minimizes the change imposed on the system.***

1. Effects of a Change in Concentration:

a. ***An ADDITION of a species on one side of the equilibrium will Drive the System TOWARDS the Opposite Side.*** (There is more concentration of the species being added. Hence, the system will shift towards the opposite side to reduce the increased amount of that particular species.)

b. ***A REMOVAL of a species on one side of the equilibrium will Drive the system TOWARDS the Same Side.*** (There is less concentration of the species being removed. Hence, the system will shift towards the removal side to compensate.)

Changes in Concentrations on Equilibrium System $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$



① **indicates an Increase in [D]. As [D]↑, equilibrium shifts to the left ($a\text{A} + b\text{B} \overset{\longleftarrow}{\rightleftharpoons} c\text{C} + d\text{D}$).** Hence, **[A]**↑, **[B]**↑, and **[C]**↓.

② **indicates a Decrease in [A]. As [A]↓, equilibrium shifts to the left ($a\text{A} + b\text{B} \overset{\longleftarrow}{\rightleftharpoons} c\text{C} + d\text{D}$).** Hence, **[B]**↑, **[C]**↓, and **[D]**↓.

③ **indicates an Increase in [B]. As [B]↑, equilibrium shifts to the right ($a\text{A} + b\text{B} \overset{\longrightarrow}{\rightleftharpoons} c\text{C} + d\text{D}$).** Hence, **[A]**↓, **[C]**↑, and **[D]**↑.

④ **indicates a Decrease in [C]. As [C]↓, equilibrium shifts to the right ($a\text{A} + b\text{B} \overset{\longrightarrow}{\rightleftharpoons} c\text{C} + d\text{D}$).** Hence, **[A]**↓, **[B]**↓, and **[D]**↑.

2. Effects of a Change in Pressure:

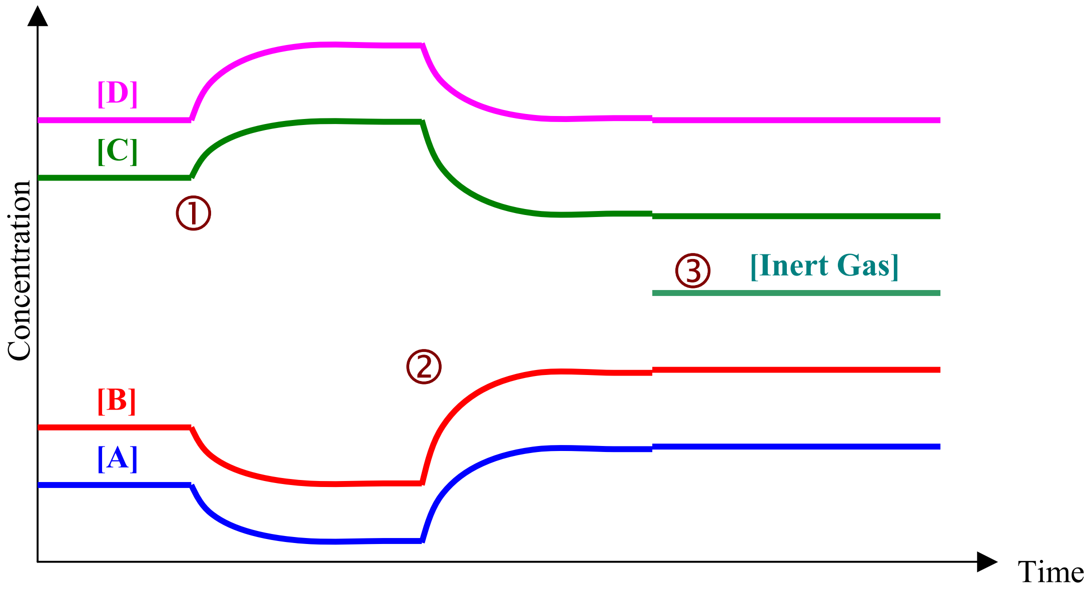
a. ***Adding an Inert Gas has NO CHANGE on the equilibrium system***. This is because an inert gas does not participate in the forward or reverse reaction.

b. ***Reducing the Volume will Drive the System TOWARDS the Side With LESS Gaseous Molecules***. Since there are less space for the number of molecules, the system will have to shift to the side with lesser gaseous molecules to compensate.

c. Conversely, ***Expanding the Volume will Drive the System TOWARDS the Side With MORE Gaseous Molecules***. Now that there is more room for the molecules to move about, the system will shift to the side that has more gaseous molecules to adjust to the new condition.

d. ***When there are Equal Number of Gaseous Molecules on Both Side of the Equilibrium, any Change in Volume will NOT Affect System.***

Changes in Pressures on a Gaseous Equilibrium System $aA + bB \rightleftharpoons cC + dD$ when $(c + d) > (a + b)$



① **indicates an Increase in Volume. As V↑, equilibrium shifts to the right ($aA + bB \overset{\longrightarrow}{\rightleftharpoons} cC + dD$) since there are more gaseous molecules on the product side [$(c + d) > (a + b)$].** Hence, [A]↓, [B]↓, [C]↑, and [D]↑.

② **indicates a Decrease in Volume. As V↓, equilibrium shifts to the left ($aA + bB \overset{\longleftarrow}{\rightleftharpoons} cC + dD$) since there are LESS gaseous molecules on the reactant side [$(c + d) > (a + b)$].** Hence, [A]↑, [B]↑, [C]↓, and [D]↓.

③ **indicates an Addition of an Inert Gas. There is no shifting of the equilibrium. ($aA + bB \rightleftharpoons cC + dD$) as inert gas does not affect the system.** Hence, [A], [B], [C], and [D] **remain unchanged.**

(See the Video at http://www.sasked.gov.sk.ca/docs/chemistry/mission2mars/contents/chapter3/images/pn2o4.mpg)

3. Effects of a Change in Temperature: - ***look at the energy (written in the reactant or product side) as a chemical species***. Then, the predictions will be the same as those found with changing the concentrations.

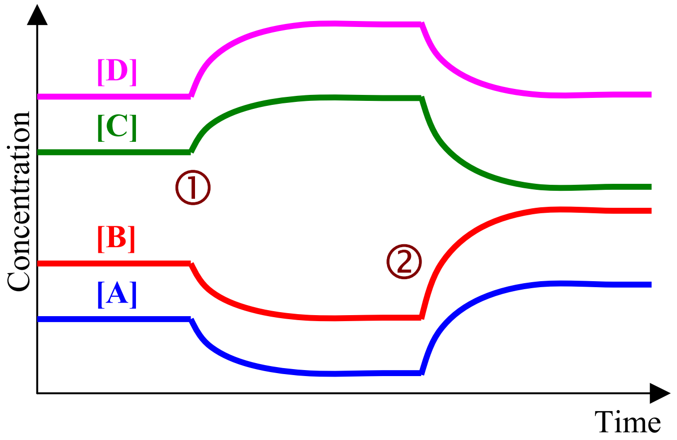
a. For an Exothermic Equilibrium System: $aA + bB \rightleftharpoons cC + dD + \textit{Energy}$

- **an Increase in Temperature will drive the system to the left ($aA + bB \overset{\longleftarrow}{\rightleftharpoons} cC + dD + \textit{Energy}$).** There is more heat added and because energy is written on the product side, the system will shift to the opposite side to re-establish equilibrium. Hence, **[A]**↑, **[B]**↑, **[C]**↓, and **[D]**↓.

- **a Decrease in Temperature will drive the system to the right ($aA + bB \overset{\longrightarrow}{\rightleftharpoons} cC + dD + \textit{Energy}$).** There is less heat overall and because energy is written on the product side, the system will shift to the products to compensate. Hence, **[A]**↓, **[B]**↓, **[C]**↑, and **[D]**↑.

Changes in Temperature on an *Exothermic*

Equilibrium System $aA + bB \rightleftharpoons cC + dD + \textit{Energy}$



① **indicates a Decrease in Temperature. As *T*↓, equilibrium shifts to the right of an exothermic system ($aA + bB \overset{\longrightarrow}{\rightleftharpoons} cC + dD + \textit{Energy}$).** Hence, **[A]**↓, **[B]**↓, **[C]**↑, and **[D]**↑.

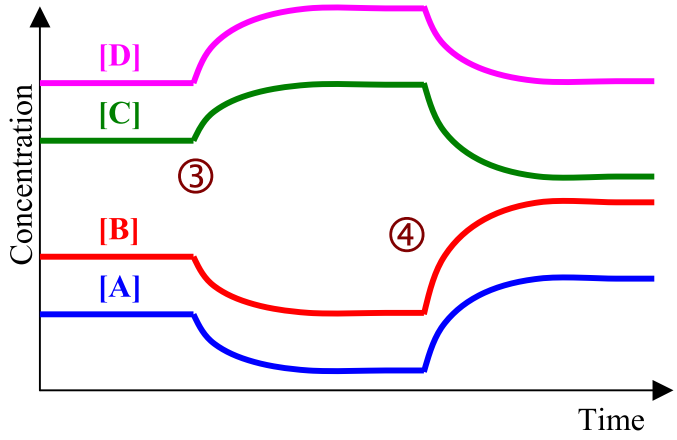
② **indicates an Increase in Temperature. As *T*↑, equilibrium shifts to the left of an exothermic system ($aA + bB \overset{\longleftarrow}{\rightleftharpoons} cC + dD + \textit{Energy}$).** Hence, **[A]**↑, **[B]**↑, **[C]**↓, and **[D]**↓.

b. For Endothermic Equilibrium System: $aA + bB + \textit{Energy} \rightleftharpoons cC + dD$

- **a Decrease in Temperature will drive the system to the left ($aA + bB + \textit{Energy} \overset{\longleftarrow}{\rightleftharpoons} cC + dD$).** There is less heat overall and because energy is written on the reactant side, the system will shift to the reactants to compensate. Hence, **[A]**↑, **[B]**↑, **[C]**↓, and **[D]**↓.

- **an Increase in Temperature will drive the system to the right ($aA + bB + \textit{Energy} \overset{\longrightarrow}{\rightleftharpoons} cC + dD$).** There is more heat added and because energy is written on the reactant side, the system will shift to the opposite side to re-establish equilibrium. Hence, **[A]**↓, **[B]**↓, **[C]**↑, and **[D]**↑.

Changes in Temperature on an *Endothermic*
Equilibrium System $aA + bB + Energy \rightleftharpoons cC + dD$



③ **indicates an Increase in Temperature. As *T*↑, equilibrium shifts to the right of an endothermic reaction ($aA + bB + Energy \overset{\longrightarrow}{\rightleftharpoons} cC + dD$).** Hence, **[A]**↓, **[B]**↓, **[C]**↑, and **[D]**↑.

④ **indicates a Decrease in Temperature. As *T*↓, equilibrium shifts to the left of an endothermic reaction ($aA + bB + Energy \overset{\longleftarrow}{\rightleftharpoons} cC + dD$).** Hence, **[A]**↑, **[B]**↑, **[C]**↓, and **[D]**↓.

Example 1: The equilibrium system, $2\ NF_{3\,(g)} + 124.9\ \text{kJ} \rightleftharpoons N_{2\,(g)} + 3\ F_{2\,(g)}$, is put under the following changes. Predict the shift of the system and the resulting concentrations of all species for each case.

a. an increase in the concentration of $F_{2\,(g)}$.

The system will shift to the LEFT.

$$2\ NF_{3\,(g)} + 124.9\ \text{kJ} \overset{\longleftarrow}{\rightleftharpoons} N_{2\,(g)} + 3\ F_{2\,(g)}\uparrow$$

Effects: $[NF_3]$↑ (increase); $[N_2]$↓ (decrease)

b. a decrease in the concentration of $N_{2\,(g)}$

The system will shift to the RIGHT.

$$2\ NF_{3\,(g)} + 124.9\ \text{kJ} \overset{\longrightarrow}{\rightleftharpoons} N_{2\,(g)}\downarrow + 3\ F_{2\,(g)}$$

Effects: $[NF_3]$↓ (decrease); $[F_2]$↑ (increase)

c. a decrease in the concentration of $NF_{3\,(g)}$.

The system will shift to the LEFT.

$$2\ NF_{3\,(g)}\downarrow + 124.9\ \text{kJ} \overset{\longleftarrow}{\rightleftharpoons} N_{2\,(g)} + 3\ F_{2\,(g)}$$

Effect: $[N_2]$↓ (decrease); $[F_2]$↓ (decrease)

d. a decrease in Temperature.

The system will shift to the LEFT.

$$2\ NF_{3\,(g)} + 124.9\ \text{kJ}\downarrow \overset{\longleftarrow}{\rightleftharpoons} N_{2\,(g)} + 3\ F_{2\,(g)}$$

Effect: $[NF_3]$↑ (increase); $[N_2]$↓ (decrease); $[F_2]$↓ (decrease)

e. an addition of $He_{(g)}$.

There will be NO SHIFT on the system.

$$2\ NF_{3\,(g)} + 124.9\text{ kJ} \rightleftharpoons N_{2\,(g)} + 3\ F_{2\,(g)}$$

(He is an inert gas and does not involve with the equilibrium system)

Effect: $[PF_3]$, $[N_2]$ and $[F_2]$ remain the same.

f. an increase in volume.

The system will shift to the RIGHT.

→

$$\mathbf{2}\ NF_{3\,(g)} + 124.9\text{ kJ} \rightleftharpoons N_{2\,(g)} + \mathbf{3}\ F_{2\,(g)}$$

(There are more gaseous molecules on the product side – 4 moles of $N_{2\,(g)}$ and $F_{2\,(g)}$ versus 2 moles of $NF_{3\,(g)}$)

Effect: $[NF_3]\downarrow$ (decrease); $[N_2]\uparrow$ (increase); $[F_2]\uparrow$ (increase)

Example 2: The Haber-Bosch process, $N_{2\,(g)} + 3\ H_{2\,(g)} \rightleftharpoons 2\ NH_{3\,(g)} + 92\text{ kJ}$ is essentially an equilibrium system. A chemical engineer would like the highest yield of ammonia. List all the possible method of production that will ensure maximum amount of $NH_{3\,(g)}$ produced.

$$N_{2\,(g)} + 3\ H_{2\,(g)} \rightleftharpoons 2\ NH_{3\,(g)} + 92\text{ kJ}$$

(Desire Effect: $[NH_3]\uparrow$, which means driving the system forward.)

1. **Increase the concentrations of $N_{2\,(g)}$ or $H_{2\,(g)}$ or both will drive the system forward.**
2. **Decrease the concentration of $NH_{3\,(g)}$ as it is produced will shift the system forward.**
3. **Lower the Temperature will drive the system to the product side.**
4. **Decrease the Volume of the system will shift the system to the right due to smaller number of gaseous molecules on the product side.**

Assignment

19.2A: pg. 544 #6 and 7; pg. 548 #14 and 16;
pg. 572 #44 to 47; pg. 573 #67, 70 and 76; pg. 575 #3

19.2B: Equilibrium Constants, Concentrations and Pressures

Equilibrium Expression: - an expression **relating the concentrations or pressures of the reactants and products when they are at the state of equilibrium**.
- it takes the form of the individual products raised to the power of their respective coefficients divided by the individual reactants raised to the power of their respective coefficients.
- **the equilibrium expression is unique for each reaction**, but **it is the same for that particular reaction regardless of temperature**.

Equilibrium Constant (***K***): - the **unitless numerical value of the equilibrium expression**.
- **the equilibrium constant is the same for a particular reaction if it remains at the same temperature**.
- the symbol for equilibrium constant when the expression deals with **concentrations** is simply K or K_{eq}. When the expression deals with pressures, it is symbolized as K_P.
- **reversing equilibrium reaction will cause the reciprocate the equilibrium constant (1/*K*)**

Equilibrium Expression and Constant of a Reaction

$$aA + bB \rightleftharpoons cC + dD$$

$$K = K_{eq} = \frac{[C]^c_{eq}[D]^d_{eq}}{\underbrace{[A]^a_{eq}[B]^b_{eq}}} \qquad K_P = \frac{P^c_{C,eq}P^d_{D,eq}}{\underbrace{P^a_{A,eq}P^b_{B,eq}}}$$

Equilibrium Expressions

a and b: Coefficients of reactant species A and B **c and d: Coefficients of product species C and D**

$[A]$, $[B]$, $[C]$ & $[D]$ = $[A]_{eq}$, $[B]_{eq}$, $[C]_{eq}$ & $[D]_{eq}$ = Equilibrium Concentrations of Chemicals (mol/L)

P_A, P_B, P_C & P_D = $P_{A,\,eq}$, $P_{B,\,eq}$, $P_{C,\,eq}$ & $P_{D,\,eq}$ = Equilibrium Pressures of Chemicals (atm)

K or K_{eq} = Equilibrium Constant (Concentrations) **K_P = Equilibrium Constant (Pressures)**

Both K_{eq} and K_P are Unitless

Reversing Equilibrium Reaction

$$aA + bB \rightleftharpoons cC + dD \;\rightarrow\; cC + dD \rightleftharpoons aA + bB$$

$$K' = \frac{[A]^a[B]^b}{[C]^c[D]^d} = \left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right)^{-1} = K^{-1} = \frac{1}{K}$$

K' = Reverse Equilibrium Constant

Example 1: Write the equilibrium expression of the following reactions.

a. $Br_{2\,(g)} + 5\,F_{2\,(g)} \rightleftharpoons 2\,BrF_{5\,(g)}$

$$K = \frac{[BrF_5]^2}{[Br_2][F_2]^5} \qquad K_P = \frac{P^2_{BrF_5}}{P_{Br_2}\,P^5_{F_2}}$$

b. $N_2H_{4\,(g)} + 6\,H_2O_{2\,(g)} \rightleftharpoons 2\,NO_{2\,(g)} + 8\,H_2O_{(g)}$

$$K = \frac{[NO_2]^2[H_2O]^8}{[N_2H_4][H_2O_2]^6} \qquad K_P = \frac{P^2_{NO_2}\,P^8_{H_2O}}{P_{N_2H_4}\,P^6_{H_2O_2}}$$

Example 2: For the following reaction and the equilibrium concentrations at 300 K.

$$2\,C_3H_{6\,(g)} + 2\,NH_{3\,(g)} + 3\,O_{2\,(g)} \rightleftharpoons 2\,C_3H_3N_{(g)} + 6\,H_2O_{(g)}$$

$[C_3H_6]_{eq} = 0.500$ M $\quad [NH_3]_{eq} = 0.250$ M $\quad [O_2]_{eq} = 0.350$ M
$[C_3H_3N]_{eq} = 2.50$ M $\quad [H_2O]_{eq} = 3.00$ M

a. Write the equilibrium expression and determine the equilibrium constant.
b. Write the equilibrium expression and calculate the equilibrium constant for the following reaction with the same equilibrium concentrations.

$$2\,C_3H_3N_{(g)} + 6\,H_2O_{(g)} \rightleftharpoons 2\,C_3H_{6\,(g)} + 2\,NH_{3\,(g)} + 3\,O_{2\,(g)}$$

a. **Equilibrium Expression:** $K = \dfrac{[C_3H_3N]^2[H_2O]^6}{[C_3H_6]^2[NH_3]^2[O_2]^3}$

Equilibrium Constant: $K = \dfrac{[C_3H_3N]^2[H_2O]^6}{[C_3H_6]^2[NH_3]^2[O_2]^3} = \dfrac{(2.50)^2(3.00)^6}{(0.500)^2(0.250)^2(0.350)^3}$ $\quad$ $K = 6.80 \times 10^6$

b. **Equilibrium Expression:** $K' = \dfrac{[C_3H_6]^2[NH_3]^2[O_2]^3}{[C_3H_3N]^2[H_2O]^6}$ **(Reverse Equilibrium)**

Equilibrium Constant: $K' = \dfrac{[C_3H_6]^2[NH_3]^2[O_2]^3}{[C_3H_3N]^2[H_2O]^6} = \left(\dfrac{[C_3H_3N]^2[H_2O]^6}{[C_3H_6]^2[NH_3]^2[O_2]^3}\right)^{-1} = K^{-1}$

$K' = (6.80 \times 10^6)^{-1}$ $\quad$ $K' = 1.47 \times 10^{-7}$

Example 3: The German's Haber-Bosch process developed in 1913 utilizes an iron surface that contains traces of aluminum and potassium oxide as a catalyst to manufacture ammonia from nitrogen and hydrogen. It is an important process as ammonia is commonly used in fertilizer and ammunition. In 1918, the scientist Fritz Haber won the Nobel Prize in chemistry for his contribution.

$$N_{2\,(g)} + 3\,H_{2\,(g)} \rightleftharpoons 2\,NH_{3\,(g)}$$

At 400 K, $P_{NH_3} = 0.1024$ atm, $P_{N_2} = 2.8084$ atm and $P_{H_2} = 0.0102$ atm. Write the equilibrium expression in terms of pressure and calculate K_P.

Equilibrium Expression: $K_P = \dfrac{P^2_{NH_3}}{P_{N_2}\,P^3_{H_2}}$

Equilibrium Constant: $K_P = \dfrac{(0.1024)^2}{(2.8084)(0.0102)^3}$ $\quad$ $K_P = 3.52 \times 10^3$

Equilibrium Position: - the **concentrations or pressures of all chemical species at equilibrium state**.
- **depends strongly on the Initial Concentrations of the chemical species**. (In contrast, ***K* does NOT depend on initial concentrations**, only on temperature and the specific reaction.)
- since there all many possible initial concentrations for any one reaction, **there are infinite number of equilibrium position for a particular reaction**.

***Note*: Do NOT confuse initial concentrations $[A]_0$ with equilibrium concentration $[A]_{eq}$!! We only use Equilibrium Concentrations to calculate *K* by substituting them into the equilibrium expression.**

Example 4: The formation of HI $_{(g)}$ is an equilibrium reaction. Several experiments are performed at 710 K using different initial concentrations.

$$H_{2\,(g)} + I_{2\,(g)} \rightleftharpoons 2\ HI_{(g)}$$

Experiment 1		**Experiment 2**	
Initial	**Equilibrium**	**Initial**	**Equilibrium**
$[H_2]_0 = 0.100$ M	$[H_2]_{eq} = 0.0222$ M	$[H_2]_0 = 0$ M	$[H_2]_{eq} = 0.0350$ M
$[I_2]_0 = 0.100$ M	$[I_2]_{eq} = 0.0222$ M	$[I_2]_0 = 0.0100$ M	$[I_2]_{eq} = 0.0450$ M
$[HI]_0 = 0$ M	$[HI]_{eq} = 0.156$ M	$[HI]_0 = 0.350$ M	$[HI]_{eq} = 0.280$ M

Experiment 3		**Experiment 4**	
Initial	**Equilibrium**	**Initial**	**Equilibrium**
$[H_2]_0 = 0.00150$ M	$[H_2]_{eq} = 0.0150$ M	$[H_2]_0 = 0$ M	$[H_2]_{eq} = 0.0442$ M
$[I_2]_0 = 0$ M	$[I_2]_{eq} = 0.0135$ M	$[I_2]_0 = 0$ M	$[I_2]_{eq} = 0.0442$ M
$[HI]_0 = 0.127$ M	$[HI]_{eq} = 0.100$ M	$[HI]_0 = 0.400$ M	$[HI]_{eq} = 0.311$ M

a. Write the equilibrium expression for the formation of HI $_{(g)}$.
b. Calculate the equilibrium constant for each experiment, and average them for an overall value.

a. **Equilibrium Expression:** $\boxed{K = \frac{[HI]^2}{[H_2][I_2]}}$

b. **Equilibrium Constant:**

Experiment 1: $K_1 = \frac{[HI]_{eq}^{\ 2}}{[H_2]_{eq}[I_2]_{eq}}$

$K_1 = \frac{(0.156)^2}{(0.0222)(0.0222)}$ $\boxed{K_1 = 49.4}$

Experiment 2: $K_2 = \frac{[HI]_{eq}^{\ 2}}{[H_2]_{eq}[I_2]_{eq}}$

$K_2 = \frac{(0.280)^2}{(0.0350)(0.0450)}$ $\boxed{K_2 = 49.8}$

Experiment 3: $K_3 = \frac{[HI]_{eq}^{\ 2}}{[H_2]_{eq}[I_2]_{eq}}$

$K_3 = \frac{(0.100)^2}{(0.0150)(0.0135)}$ $\boxed{K_3 = 49.3}$

Experiment 4: $K_4 = \frac{[HI]_{eq}^{\ 2}}{[H_2]_{eq}[I_2]_{eq}}$

$K_4 = \frac{(0.311)^2}{(0.0442)(0.0442)}$ $\boxed{K_4 = 49.5}$

Average $K = \frac{49.4 + 49.8 + 49.3 + 49.5}{4}$ $\boxed{K_{avg} = 49.5}$

Homogeneous Equilibria: - an equilibrium system where all chemical species are in the same phase.

Heterogeneous Equilibria: - an equilibrium system where some chemical species are in different phase compare to the others.

- **chemical species that are Pure Solid or Pure Liquid are NOT Included in the Equilibrium Expression.** This is due to the fact that pure solids and liquids do not have concentrations.

Example 5: Write the equilibrium expression for the following systems.

a. $2\ NaN_{3\,(s)} \rightleftharpoons 2\ Na_{(s)} + 3\ N_{2\,(g)}$

$$\boxed{K = [N_2]^3} \qquad \boxed{K_P = P_{N_2}^3}$$

(NaN_3 and Na are Pure Solids)

b. $2\ NH_{3\,(g)} + CO_{(g)} \rightleftharpoons H_2NCONH_{2\,(s)} + H_2O_{(g)}$

$$\boxed{K = \frac{[H_2O]}{[NH_3]^2[CO]}} \qquad \boxed{K_P = \frac{P_{H_2O}}{P_{NH_3}^2 P_{CO}}}$$

(H_2NCONH_2 is a Pure Solid)

c. $Ag_2SO_{4\,(s)} \rightleftharpoons 2\ Ag^+_{(aq)} + SO_4^{2-}{}_{(aq)}$

$$\boxed{K = [Ag^+]^2[SO_4^{2-}]}$$

(Ag_2SO_4 is a Pure Solid)
(No K_P because there are no gases.)

d. $HF_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)}$

$$\boxed{K = \frac{[H_3O^+][F^-]}{[HF]}}$$

(H_2O is a Pure Liquid)
(No K_P because there are no gases.)

Important Notes Regarding the Size of the Equilibrium Constant (K):

$$aA + bB \rightleftharpoons cC + dD$$

$$K = K_c = \frac{[C]_{eq}^c[D]_{eq}^d}{[A]_{eq}^a[B]_{eq}^b} \qquad K_P = \frac{P_{C,eq}^c P_{D,eq}^d}{P_{A,eq}^a P_{B,eq}^b}$$

1. When **$K >> 1$**, the equilibrium **system favours the products**. ***There are more products than reactants at the state of equilibrium.*** ($[C]_{eq}$ and $[D]_{eq}$ or $P_{C,\,eq}$ and $P_{D,\,eq}$ >> $[A]_{eq}$ and $[B]_{eq}$ or $P_{A,\,eq}$ and $P_{B,\,eq}$)

2. When **$K << 1$**, the equilibrium **system favours the reactants**. ***There are less products than reactants at the state of equilibrium.*** ($[A]_{eq}$ and $[B]_{eq}$ or $P_{A,\,eq}$ and $P_{B,\,eq}$ >> $[C]_{eq}$ and $[D]_{eq}$ or $P_{C,\,eq}$ and $P_{D,\,eq}$)

3. When **$K \approx 1$**, the equilibrium system **favours neither the products nor the reactants**. ***There are roughly the same amount of products and reactants at the state of equilibrium.*** ($[C]_{eq}$ and $[D]_{eq}$ or $P_{C,\,eq}$ and $P_{D,\,eq}$ $\approx$ $[A]_{eq}$ and $[B]_{eq}$ or $P_{A,\,eq}$ and $P_{B,\,eq}$)

4. The **Size of K has NO Relationship with the Rate of Reaction** to reach the state of equilibrium. ***Reaction Rate is dependent on Activation Energy and Temperature (T) (NOT K).***

Example 6: The reaction, $Cl_{2\,(g)} + 3\,F_{2\,(g)} \rightleftharpoons 2\,ClF_{3\,(g)}$ at 350 K has $K = 50.2$, If the equilibrium concentrations of $Cl_{2\,(g)}$ and $ClF_{3\,(g)}$ are 0.149 M and 0.205 M respectively, what is the equilibrium concentration of $F_{2\,(g)}$?

$[Cl_2]_{eq} = 0.149$ M
$[ClF_3]_{eq} = 0.205$ M
$K = 50.2$

$[F_2]_{eq} = ?$

$$K = \frac{[ClF_3]^2_{eq}}{[Cl_2]_{eq}[F_2]^3_{eq}}$$

$$50.2 = \frac{(0.205)^2}{(0.149)[F_2]^3_{eq}}$$

$$[F_2]^3_{eq} = \frac{(0.205)^2}{(50.2)(0.149)}$$

$$[F_2]_{eq} = \sqrt[3]{\frac{(0.205)^2}{(50.2)(0.149)}}$$

$$\boxed{[F_2]_{eq} = 0.178 \text{ M}}$$

ICE Box: - stands for **Initial, Change, and Equilibrium**. It is a table that organizes information to calculate final equilibrium concentrations given the equilibrium constant and initial concentration.

Example 7: The formation of $HCl_{(g)}$ from its elements, $H_{2\,(g)} + Cl_{2\,(g)} \rightleftharpoons 2\,HCl_{(g)}$ has $K = 0.404$ at 250 K. A 5.00 L flask at 250 K contained an initial concentration of 3.00 mol of $HCl_{(g)}$ and 3.85 mol of $H_{2\,(g)}$. When the system reached equilibrium, it was found that there were 0.860 mol of $Cl_{2\,(g)}$. Determine the concentrations of $H_{2\,(g)}$ and $HCl_{(g)}$ at equilibrium.

$K = 0.404$

$$[H_2]_0 = \frac{3.85 \text{ mol}}{5.00 \text{ L}} = 0.770 \text{ M}$$

$$[HCl]_0 = \frac{3.00 \text{ mol}}{5.00 \text{ L}} = 0.600 \text{ M}$$

$[Cl_2]_0 = 0$ M

$$[Cl_2]_{eq} = \frac{0.860 \text{ mol}}{5.00 \text{ L}} = 0.172 \text{ M}$$

$[H_2]_{eq} = ?$
$[HCl]_{eq} = ?$

The system must <u>shift to the left</u> because initially, we are missing one reactant ($[Cl_2]_0 = 0$ M). Hence, the change to the H_2 is positive, and the change to the HCl would be negative.

Since there is 0.172 M of Cl_2 at equilibrium, it means 0.172 M of H_2 is added (1:1 mol ratio between Cl_2 and H_2). It also means that there is 2(0.172 M) less HCl (2:1 mol ratio between Cl_2 and HCl).

	$H_{2\,(g)}$	+	$Cl_{2\,(g)}$	$\rightleftharpoons$	$2\,HCl_{(g)}$
Initial	0.770 M		0 M		0.600 M
Change	+ 0.172 M		+ 0.172 M		−2(0.172 M)
Equilibrium	**0.942 M**		**0.172 M**		**0.256 M**

Verify with K:

$$K = \frac{[HCl]^2_{eq}}{[H_2]_{eq}[Cl_2]_{eq}} = \frac{(0.256)^2}{(0.942)(0.172)}$$

$K = 0.404$ (This matches with K given in the question.)

Therefore, the equilibrium concentrations are:

$$\boxed{[H_2]_{eq} = 0.942 \text{ M},\ [Cl_2]_{eq} = 0.172 \text{ M and } [HCl]_{eq} = 0.256 \text{ M}}$$

Assignment

19.2B: pg. 545 #8; pg. 546 #9 and 10; pg. 547 #11 and 12; pg. 548 #13, 15, 17 to 19; pg. 572 #48 to 50; pg. 573 #71 and 72; pg. 575 #1

19.2C: Equilibrium Calculation with Initial Concentrations and Pressures

Procedure to calculate Equilibrium Concentrations/Pressures from Initial Concentrations/Pressures:

1. **Balance** the Equilibrium Chemical **Equation** (if needed).
2. Set up the **ICE Box** and the **equilibrium expression**.
3. **Find the Initial Concentrations or Pressures.**
4. **Decide on which way the system will shift.**
5. Using **mole ratios**, fill out the **Change row using x as 1 mole** of reactant and/or product used/produced.
6. Write out the expressions for the Equilibrium row of the ICE Box.
7. **Substitute** these **Final Concentrations** into the Equilibrium Expressions.
8. **Solve for x** using the **Solve Function** of your calculator.
9. Calculate the actual equilibrium concentrations of all chemical species.

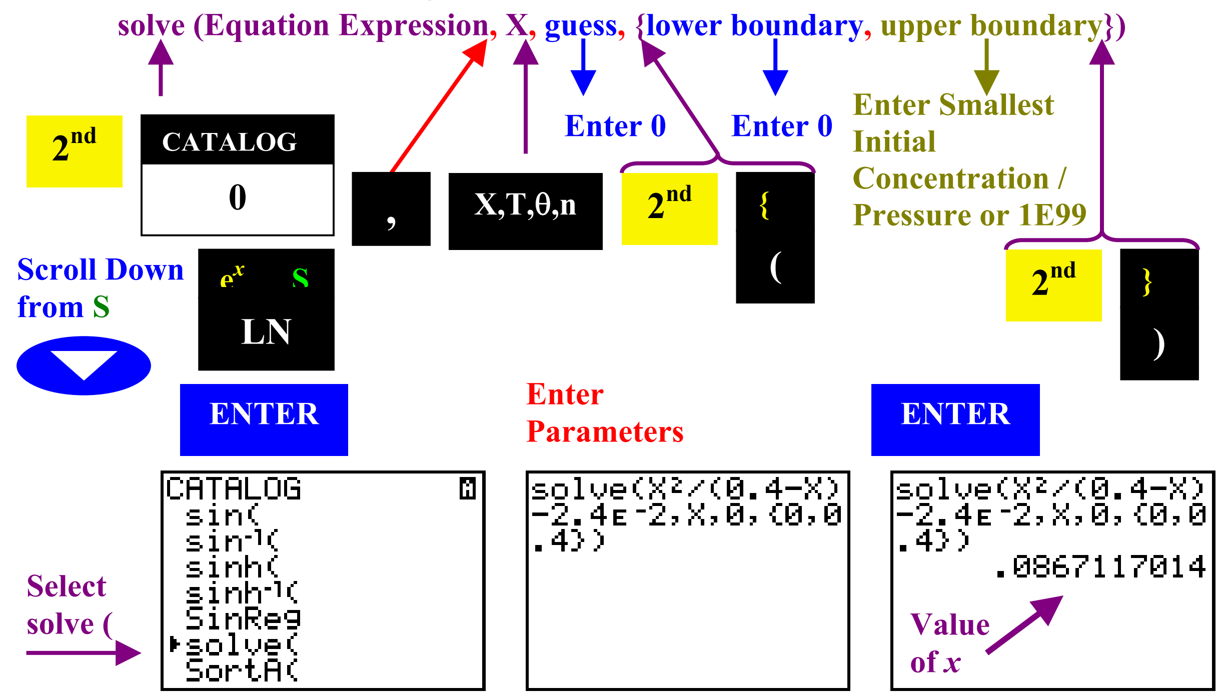
Using the *SOLVE* function of the TI-83 Plus Calculator:

1. **Manipulate the Equation so one-side is equal to 0.**

Example: $2.4\times10^{-2} = \frac{x^2}{(0.4-x)}$ becomes $0 = \underbrace{\frac{x^2}{(0.4-x)} - 2.4\times10^{-2}}$

2. **Callout the *solve* function.**

solve (Equation Expression, X, guess, {lower boundary, upper boundary})



```
CATALOG
 sin(
 sin⁻¹(
 sinh(
 sinh⁻¹(
 SinReg
▸solve(
 SortA(
```

```
solve(X²/(0.4-X)
-2.4ᴇ-2,X,0,{0,0
.4})
```

```
solve(X²/(0.4-X)
-2.4ᴇ-2,X,0,{0,0
.4})
           .0867117014
```

Example 1: The equilibrium between dinitrogen textraoxide and nitrogen dioxide, $N_2O_{4\,(g)} \rightleftharpoons 2\ NO_{2\,(g)}$ has $K = 4.66 \times 10^{-3}$ at 22°C. If 1.40 mol of $N_2O_{4\,(g)}$ is injected into a 2.00 L container at 22°C, determine the concentrations of both gases at equilibrium.

$$K = \frac{[NO_2]^2_{eq}}{[N_2O_4]_{eq}} = 4.66 \times 10^{-3}$$

The system must shift to the right because initially, we are missing the product ($[NO_2]_0 = 0$ M). Hence, the change to the NO_2 is positive, and the change to the HCl would be negative.

$$[N_2O_4]_0 = \frac{1.40\text{ mol}}{2.00\text{ L}} = 0.700\text{ M}$$

$[NO_2]_0 = 0$ M

$[N_2O_4]_{eq} = ?$

$[NO_2]_{eq} = ?$

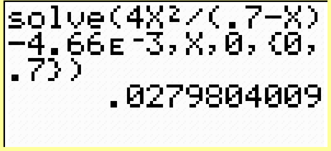
Since the mole ratio is 1:1 mol ratio between N_2O_4 and NO_2, for every x mol of N_2O_4 used, $2x$ mol of NO_2 is produced.

	$N_2O_{4\,(g)}$	$\rightleftharpoons$	$2\ NO_{2\,(g)}$
Initial	0.700 M		0 M
Change	$-\ x$ M		$+\ 2x$ M
Equilibrium	**$(0.700 - x)$ M**		**$2x$ M**

Substitute equilibrium concentrations into the equilibrium expression.

$$K = \frac{[NO_2]^2_{eq}}{[N_2O_4]_{eq}} \qquad 4.66 \times 10^{-3} = \frac{(2x)^2}{(0.700 - x)} \qquad \text{or} \qquad \underbrace{0 = \frac{4x^2}{(0.700 - x)} - 4.66 \times 10^{-3}}$$

Using the *SOLVE* function of the TI-83 Plus Calculator. ($0 \le x \le 0.700$)



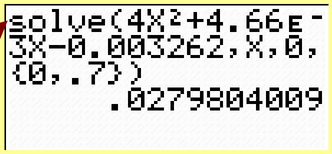
```
solve(4X²/(.7-X)
-4.66E-3,X,0,{0,
.7})
         .0279804009
```

$x = 0.02798$ mol/L

$[N_2O_4]_{eq} = (0.700 - 0.02798)$ **$[N_2O_4]_{eq} = 0.672$ mol/L**

$[NO_2]_{eq} = 2(0.02798)$ **$[NO_2]_{eq} = 0.0560$ mol/L**

or



```
solve(4X²+4.66E-
3X-0.003262,X,0,
{0,.7})
         .0279804009
```

Or expanding the original equation

$$4.66 \times 10^{-3}\,(0.7 - x) = 4x^2$$
$$0.003262 - (4.66 \times 10^{-3})\,x = 4x^2$$
$$0 = 4x^2 + (4.66 \times 10^{-3})\,x - 0.003262$$

(Quadratic Equation: Apply the Quadratic Formula!)

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \qquad a = 4 \qquad b = 4.66 \times 10^{-3} \qquad c = -0.003262$$

$$x = \frac{-(4.66 \times 10^{-3}) \pm \sqrt{(4.66 \times 10^{-3})^2 - 4(4)(-0.003262)}}{2(4)}$$

$x = 0.0279804009$ $x = -0.0291454009$ (omit negative x)

Verify with K:

$$K = \frac{[NO_2]^2_{eq}}{[N_2O_4]_{eq}} = \frac{(0.0560)^2}{(0.672)}$$

$K = 0.00467 = 4.67 \times 10^{-3}$ (This matches with K given in the question.)

Therefore, the equilibrium concentrations are:

$[N_2O_4]_{eq} = 0.672$ mol/L, and $[NO_2]_{eq} = 0.0560$ mol/L

Example 2: The equilibrium, $2\ N_2O_{(g)} \rightleftharpoons 2\ N_2{}_{(g)} + O_2{}_{(g)}$ has $K_P = 84.1$ at 25°C. If 1.50 atm of $N_2{}_{(g)}$ and 1.80 atm of $O_2{}_{(g)}$ are injected into a flask at 25°C, determine the equilibrium pressures of all gases.

$$K = \frac{\left(P_{N_2}\right)^2_{eq}\left(P_{O_2}\right)_{eq}}{\left(P_{N_2O}\right)^2_{eq}} = 84.1$$

$\left(P_{N_2O}\right)_0 = 0$ atm

$\left(P_{N_2}\right)_0 = 1.50$ atm

$\left(P_{O_2}\right)_0 = 1.80$ atm

$\left(P_{N_2O}\right)_{eq} = ?$

$\left(P_{N_2}\right)_{eq} = ?$

$\left(P_{O_2}\right)_{eq} = ?$

The system must <u>shift to the left</u> because initially, we are missing the reactant ($\left(P_{N_2O}\right)_0 = 0$ atm). Hence, the change to the N_2O is positive, and the change to the N_2 and O_2 would be negative.

Since the mole ratio is 1:2:1 mol ratio between N_2O_4, N_2, and O_2, for every x mol of N_2O_4 produced; $2x$ mol of N_2 and x mol of O_2 is used.

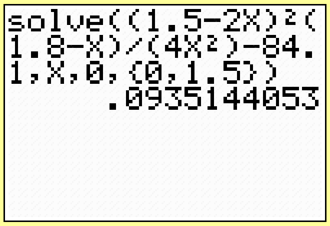
	$2\ N_2O_{(g)}$	$\rightleftharpoons$	$2\ N_2{}_{(g)}$	+	$O_2{}_{(g)}$
Initial	0 atm		1.50 atm		1.80 atm
Change	$+\ 2x$ atm		$-\ 2x$ atm		$-\ x$ atm
Equilibrium	**$2x$ atm**		**$(1.50 - 2x)$ atm**		**$(1.80 - x)$ atm**

Substitute equilibrium concentrations into the equilibrium expression.

$$K = \frac{\left(P_{N_2}\right)^2_{eq}\left(P_{O_2}\right)_{eq}}{\left(P_{N_2O}\right)^2_{eq}} \qquad 84.1 = \frac{(1.50-2x)^2(1.80-x)}{(2x)^2} \qquad \text{or} \qquad 0 = \underbrace{\frac{(1.5-2x)^2(1.8-x)}{(4x^2)} - 84.1}$$

Using the *SOLVE* function of the TI-83 Plus Calculator. ($0 \le x \le 1.50$)

$x = 0.0935144053$ atm



```
solve((1.5-2X)²(
1.8-X)/(4X²)-84.
1,X,0,{0,1.5})
      .0935144053
```

$\left(P_{N_2O}\right)_{eq} = 2(0.0935144053)$ — **$\left(P_{N_2O}\right)_{eq} = 0.187$ atm**

$\left(P_{N_2}\right)_{eq} = 1.50 - 2(0.0935144053)$ — **$\left(P_{N_2}\right)_{eq} = 1.31$ atm**

$\left(P_{O_2}\right)_{eq} = 1.80 - (0.0935144053)$ — **$\left(P_{O_2}\right)_{eq} = 1.71$ atm**

or

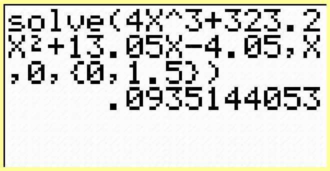
Or expanding the original equation:

$$336.4x^2 = (2.25 - 6x + 4x^2)(1.8 - x)$$

$$336.4x^2 = 4.05 - 2.25x - 10.8x + 6x^2 + 7.2x^2 - 4x^3$$

$4x^3 + 323.2x^2 + 13.05x - 4.05 = 0$ ⟶

(Use the *SOLVE* function instead of solving a cubic function by hand!)



```
solve(4X^3+323.2
X²+13.05X-4.05,X
,0,{0,1.5})
      .0935144053
```

Verify with *K*:

$$K = \frac{\left(P_{N_2}\right)^2_{eq}\left(P_{O_2}\right)_{eq}}{\left(P_{N_2O}\right)^2_{eq}} = \frac{(1.31)^2(1.71)}{(0.187)^2}$$

$K = 83.9$ (This is a very close match with K given in the question.)

Therefore, the equilibrium pressures are:

$$\boxed{\left(P_{N_2O}\right)_{eq} = 0.187 \text{ atm},\ \left(P_{N_2}\right)_{eq} = 1.31 \text{ atm, and } \left(P_{O_2}\right)_{eq} = 1.71 \text{ atm}}$$

<u>Assignment</u>

19.2C: Equilibrium Calculations Worksheet

Equilibrium Calculations Worksheet

1. Given: $A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)} + 2\ D_{(g)}$. One mole of A and one mole of B are placed in a 0.400 L container. After equilibrium has been established, 0.20 mole of C is present in the container. Calculate the equilibrium constant, K_c, for the reaction.

2. $NO_{(g)}$ and $O_{2\,(g)}$ are mixed in a container of fixed volume and kept at 1000 K. Their initial concentrations are 0.0200 mol/L and 0.0300 mol/ L, respectively. When the reaction, $2\ NO_{(g)} + O_{2\,(g)} \rightleftharpoons 2\ NO_{2\,(g)}$ has come to equilibrium, the concentration of $NO_{2\,(g)}$ is 2.1×10^{-3} mol/L. Calculate

- **a.** the concentration of $NO_{(g)}$ at equilibrium,
- **b.** the concentration of $O_{2\,(g)}$ at equilibrium, and
- **c.** the equilibrium constant, K_c, for the reaction.

3. For the reaction, $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2\,(g)} + H_{2\,(g)}$, the value of the equilibrium constant, K_c, is 1.845 at a given temperature. If 0.500 mole $CO_{(g)}$ and 0.500 mole $H_2O_{(g)}$ are placed in a 1.00-L container at this temperature, and allow the reaction to reach equilibrium, what will be the equilibrium concentrations of all substances present?

4. The equilibrium constant for the reaction, $2\ SO_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2\ SO_{3\,(g)}$ is $K_c = 279$ at a given high temperature.

- **a.** What is the value of the equilibrium constant for the reaction, $2\ SO_{3\,(g)} \rightleftharpoons 2\ SO_{2\,(g)} + O_{2\,(g)}$ at this temperature?
- **b.** 4.00 mol of $SO_{2\,(g)}$ and 3.00 mol of $O_{2\,(g)}$ are initially injected into a 2.00 L flask. What are the equilibrium concentrations for all species?

5. At 448°C, the reaction indicated by the equation, $H_{2\,(g)} + I_{2\,(g)} \rightleftharpoons 2\ HI_{(g)}$ has an equilibrium constant, K_P, equal to 50.5. If 2.00 atm of $H_{2\,(g)}$ and 1.00 atm of $I_{2\,(g)}$ were present initially, what is the equilibrium pressures for all species?

6. The reaction $2\ NO_{(g)} + Cl_{2\,(g)} \rightleftharpoons 2\ NOCl_{(g)}$, has an equilibrium constant, K_P, equal to 0.262 at 700 K. What are the equilibrium pressures for all species if initially 0.650 atm of $NO_{(g)}$ and 1.45 atm of $NOCl_{(g)}$ were placed in a container with fixed volume?

7. For the reaction, $Cl_{2\,(g)} + F_{2\,(g)} \rightleftharpoons 2\ ClF_{(g)}$, $K_P = 19.9$. Determine the finial pressures of all gases if the pressures for chlorine gas and fluorine gas were 4.50 atm and 3.25 atm respectively.

8. For the reaction described by the equation, $N_{2\,(g)} + C_2H_{2\,(g)} \rightleftharpoons 2\ HCN_{(g)}$, $K_c = 2.30 \times 10^4$ at 300°C. What is the equilibrium concentration of hydrogen cyanide if the initial concentrations of N_2 and acetylene (C_2H_2) were 5.25 mol/L and 7.00 mol/ L respectively?

9. At 373 K, $K_P = 0.416$ for the equilibrium, $2\ NOBr_{(g)} \rightleftharpoons 2\ NO_{(g)} + Br_{2\,(g)}$. If the original pressures of $NOBr_{(g)}$ and $Br_{2\,(g)}$ were 0.760 atm and 0.450 atm respectively, what is the equilibrium pressures for all species?

10. The equilibrium constant, K_c, for $2\ BrF_{(g)} \rightleftharpoons Br_{2\,(g)} + F_{2\,(g)}$, is 0.0181. What are the equilibrium concentrations of all these gases if the initial concentration of $Br_{2\,(g)}$ and $F_{2\,(g)}$ was both 0.300 M?

11. At 218°C, $K_P = 4.83 \times 10^{-3}$ for the equilibrium, $NH_4HS_{(s)} \rightleftharpoons NH_{3\,(g)} + H_2S_{(g)}$. Calculate the equilibrium pressures for all gases if an excess amount of $NH_4HS_{(s)}$ and 1.25 atm of $NH_{3\,(g)}$ were initially placed in a closed container?

12. $K_c = 96.2$ at 400 K for the reaction, $PCl_{3\,(g)} + Cl_{2\,(g)} \rightleftharpoons PCl_{5\,(g)}$. What are the equilibrium concentrations of all species if the initial concentrations were 0.250 mol/L for PCl_5 and 6.00 mol/L for Cl_2?

13. For the equilibrium, $2\ IBr_{(g)} \rightleftharpoons I_{2\,(g)} + Br_{2\,(g)}$, $K_P = 8.53 \times 10^{-3}$ at 150°C. If 0.685 atm of $I_{2\,(g)}$ and 0.234 atm of $IBr_{(g)}$ were placed in a closed container, what are the equilibrium pressures of all gases?

14. The reaction of iron and water vapor results in an equilibrium, $3\ Fe_{(s)} + 4\ H_2O_{(g)} \rightleftharpoons Fe_3O_{4\,(s)} + 4\ H_{2\,(g)}$, and an equilibrium constant, K_c, of 4.60 at 850°C. What are the equilibrium concentrations of all gaseous species if the reaction is initiated with

a. 30.0 g of $H_2O_{(g)}$ and excess Fe in a 10.0 L container?

b. 10.0 g of $H_{2\,(g)}$ and excess iron oxide, Fe_3O_4, in a 16.0 L container?

15. The dissociation of calcium chromate, $CaCrO_{4\,(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CrO_4^{2-}{}_{(aq)}$, has a $K_c = 7.2 \times 10^{-4}$. What are the equilibrium concentrations of Ca^{2+} and CrO_4^{2-} in a saturated solution of $CaCrO_4$?

16. The dissociation of calcium fluoride, $CaF_{2\,(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2\ F^-_{(aq)}$, has a $K_c = 3.9 \times 10^{-11}$. What are the equilibrium concentrations of Ca^{2+} and F^- in a saturated solution of CaF_2?

Answers:

1. $K_c = 0.125$ **2a.** 0.0179 mol/L **b.** 0.0290 mol/L **c.** $K_c = 8.83 \times 10^{-3}$

3. $[CO]_{eq} = [H_2O]_{eq} = 0.212$ mol/L; $[CO_2]_{eq} = [H_2]_{eq} = 0.288$ mol/L

4a. $K_c' = 3.58 \times 10^{-3}$ **b.** $[SO_2]_{eq} = 0.147$ mol/L; $[O_2]_{eq} = 0.573$ mol/L; $[SO_3]_{eq} = 1.85$ mol/L

5. $\left(P_{H_2}\right)_{eq} = 1.065$ atm; $\left(P_{I_2}\right)_{eq} = 0.0650$ atm; $(P_{HI})_{eq} = 1.87$ atm

6. $(P_{NO})_{eq} = 1.56$ atm; $\left(P_{Cl_2}\right)_{eq} = 0.455$ atm; $(P_{NOCl})_{eq} = 0.539$ atm

7. $\left(P_{Cl_2}\right)_{eq} = 1.93$ atm; $\left(P_{F_2}\right)_{eq} = 0.684$ atm; $(P_{ClF})_{eq} = 5.13$ atm

8. $[N_2]_{eq} = 0.00273$ mol/L; $[C_2H_2]_{eq} = 1.75$ mol/L; $[HCN]_{eq} = 10.5$ mol/L

9. $(P_{NOBr})_{eq} = 0.418$ atm; $(P_{NO})_{eq} = 0.342$ atm; $\left(P_{Br_2}\right)_{eq} = 0.621$ atm

10. $[BrF]_{eq} = 0.473$ mol/L; $[Br_2]_{eq} = [F_2]_{eq} = 0.0636$ mol/L

11. $\left(P_{NH_3}\right)_{eq} = 1.25$ atm; $\left(P_{H_2S}\right)_{eq} = 3.85 \times 10^{-3}$ atm

12. $[PCl_3]_{eq} = 4.32 \times 10^{-4}$ mol/L; $[Cl_2]_{eq} = 6.00$ mol/L; $[PCl]_{eq} = 0.250$ mol/L

13. $(P_{IBr})_{eq} = 0.233$ atm; $\left(P_{I_2}\right)_{eq} = 0.686$ atm; $\left(P_{Br_2}\right)_{eq} = 6.73 \times 10^{-4}$ atm

14a. $[H_2O]_{eq} = 0.0676$ mol/L; $[H_2]_{eq} = 0.0989$ mol/L **b.** $[H_2O]_{eq} = 0.126$ mol/L; $[H_2]_{eq} = 0.184$ mol/L

15. $[Ca^{2+}] = [CrO_4^{2-}] = 0.027$ mol/L **16.** $[Ca^{2+}] = 2.1 \times 10^{-4}$ mol/L; $[F^-] = 4.3 \times 10^{-4}$ mol/L