UNIT 5: CHEMICAL KINETICS AND EQUILIBRIUM

Chapter 14: Chemical Kinetics

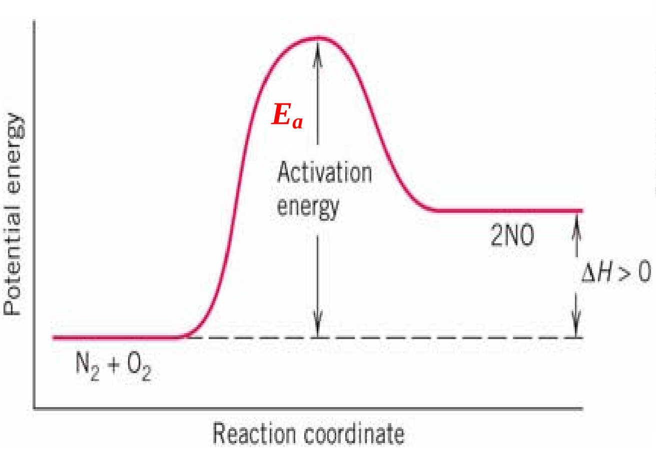
14.4 & 14.6: Activation Energy, Temperature Dependence on Reaction Rates & Catalysis

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

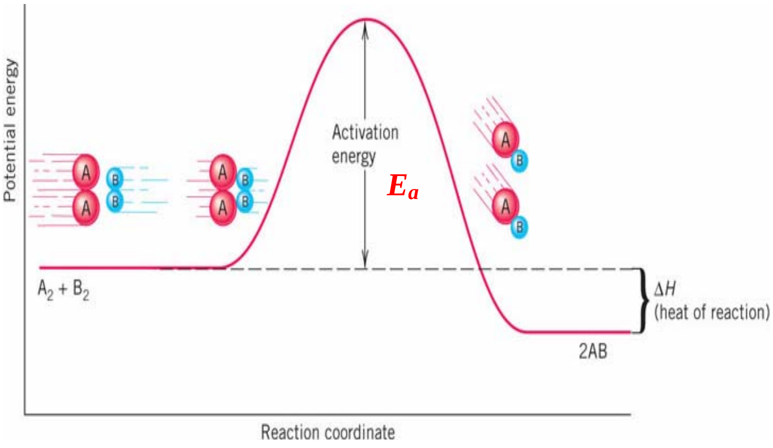
Collision Model: - a model that state for a reaction to occur, molecules must collide with each other.

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**.

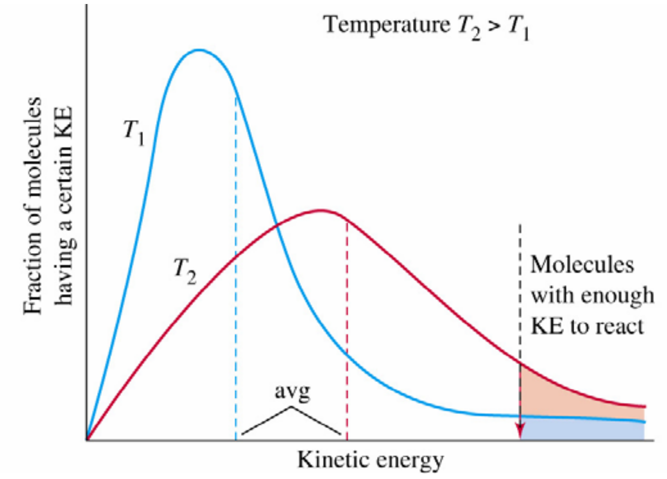


Activation Energy of an Endothermic Reaction



Activation Energy of an Exothermic Reaction

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.

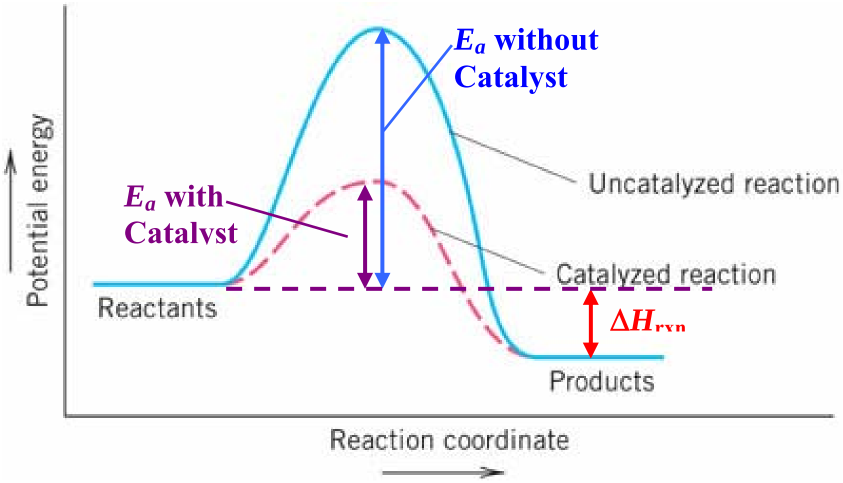
3. **Particle Size**: - the **Smaller the Particle Size (the Larger the Surface Area exposed), the Faster the Reaction Rate.**

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.



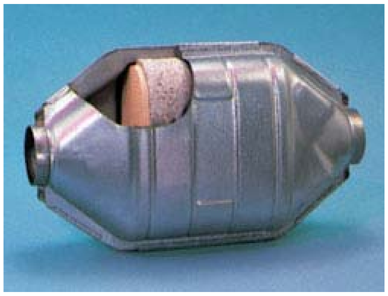
6. **Inhibitor**: - a substance that "inhibit" the function of a catalyst to speed up the reaction.
   - in general, the **Addition of an Inhibitor DECREASES the Reaction Rate**.

Example 3: Ammonia is formed from its elements using heterogeneous catalyst (catalyst in different phase compared to the reactants) such as $Pt_{(s)}$:

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

(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 $CO_{(g)}$.



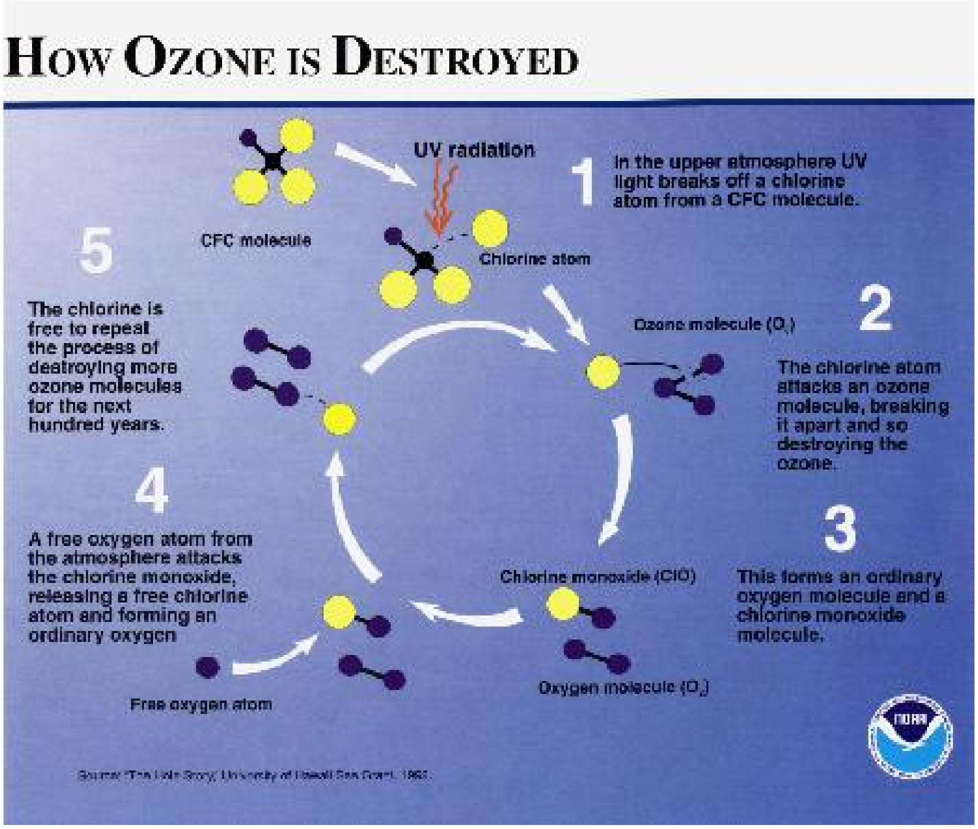
$$2\,NO_{(g)} \xrightarrow{\text{catalytic converter}} N_{2\,(g)} + O_{2\,(g)}$$
$$2\,CO_{(g)} + O_{2\,(g)} \xrightarrow{\text{catalytic converter}} 2\,CO_{2\,(g)}$$

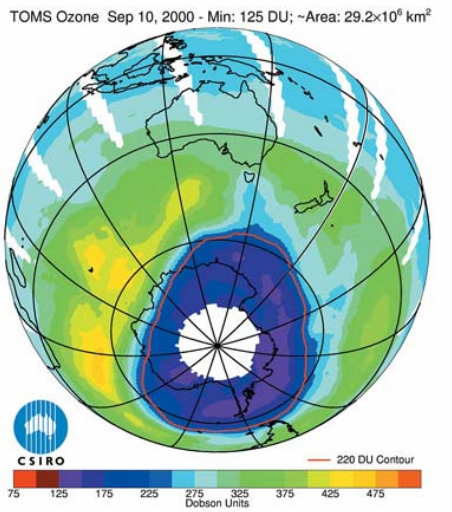
(Left): A catalytic converter for most modern vehicle. Leaded gasoline, an inhibitor, deactivates catalytic converter. Hence, it is not legally used in vehicles

Example 5: The destruction of ozone in upper atmosphere can be attributed to $NO_{(g)}$ and CFCs acting as homogeneous catalysts (catalysts in the same phases as the reactants). $NO_{(g)}$ 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.

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

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





(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

14.4 & 14.6: pg. 489−491 #27, 30, 31, 49 to 52, 75a, 75c, 76

Chapter 15: Chemical Equilibrium

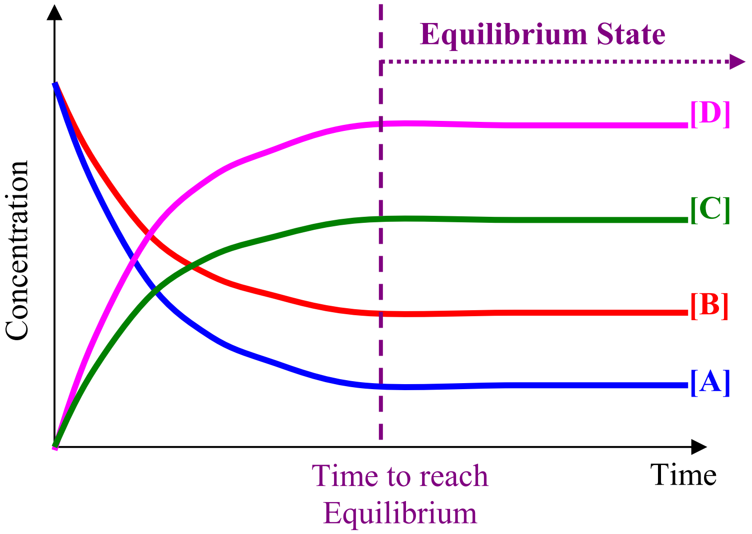
15.1: The Concept of Equilibrium and the Equilibrium Constant

Chemical Equilibrium: - the state at which the concentrations of all reactants and products remain constant with time (**the Forward Reaction Rate = Reverse Reaction Rate**).

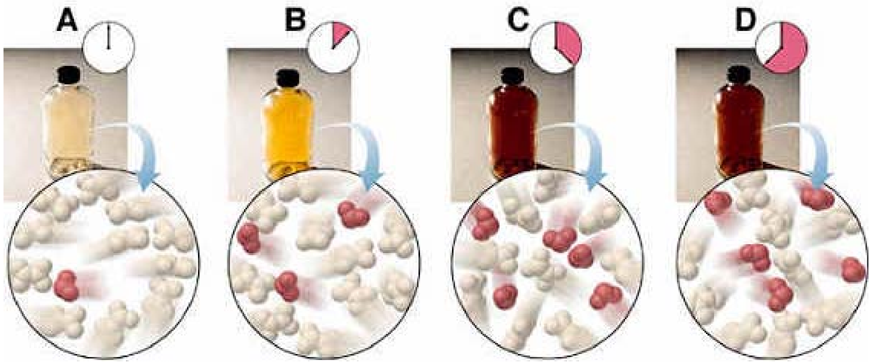
- **the equilibrium state is dynamic (not static).** Chemical species are continuously converting from reactants to products and vice versa. It appears that the reaction has stopped only because the rate of consumption = rate of production.
- **if an equilibrium state is disturbed** (changing concentrations 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.mhhe.com/physsci/chemistry/animations/chang_7e_esp/kim2s2_5.swf)



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).

Law of Mass Action: - a reversible reaction at equilibrium and a constant temperature, a certain ratio of reactant and product concentrations (**Equilibrium Expression**) has a constant value, ***K* – equilibrium constant**.

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**.

Equilibrium Expression and Constant of a Reaction

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

$$K = \left.\frac{[C]^c[D]^d}{[A]^a[B]^b}\right\} \longleftarrow \text{Equilibrium Expressions}$$

***a* and *b*: Coefficients of reactant species A and B**
***c* and *d*: Coefficients of product species C and D**
[A], [B], [C] & [D] = Equilibrium Concentrations of Chemicals
***K* = Equilibrium Constant (Concentrations)**

Assignment
15.1 pg. 520 #1 to 4

15.2: Ways of Expressing Equilibrium Constants

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

Equilibrium Constant (***K***): - the symbol for equilibrium constant when the expression deals with **concentrations** is simply K or K_c. When the expression deals with pressures, it is symbolized as K_P.
- for equilibrium of an ideal system, the activity of a substance is the ratio of its concentration or partial pressure to a standard value of 1 M or 1 atm. The procedure eliminates all units but does not alter the numerical value of the concentrations and pressures. Therefore, ***K* has no units**.

Equilibrium Expression and Constant of a Reaction

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

$$K = K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad K_P = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

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_c = Equilibrium Constant (Concentrations) **K_P = Equilibrium Constant (Pressures)**

Both K_c and K_P are Unitless

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

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

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

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

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

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 2: 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

Initial	Equilibrium
$[H_2]_0 = 0.100$ M	$[H_2]_{eq} = 0.0222$ M
$[I_2]_0 = 0.100$ M	$[I_2]_{eq} = 0.0222$ M
$[HI]_0 = 0$ M	$[HI]_{eq} = 0.156$ M

Experiment 2

Initial	Equilibrium
$[H_2]_0 = 0$ M	$[H_2]_{eq} = 0.0350$ M
$[I_2]_0 = 0.0100$ M	$[I_2]_{eq} = 0.0450$ M
$[HI]_0 = 0.350$ M	$[HI]_{eq} = 0.280$ M

Experiment 3

Initial	Equilibrium
$[H_2]_0 = 0.00150$ M	$[H_2]_{eq} = 0.0150$ M
$[I_2]_0 = 0$ M	$[I_2]_{eq} = 0.0135$ M
$[HI]_0 = 0.127$ M	$[HI]_{eq} = 0.100$ M

Experiment 4

Initial	Equilibrium
$[H_2]_0 = 0$ M	$[H_2]_{eq} = 0.0442$ M
$[I_2]_0 = 0$ M	$[I_2]_{eq} = 0.0442$ 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:** $\boxed{K = \dfrac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]}}$

b. **Equilibrium Constant:**

Experiment 1: $K_1 = \dfrac{[\mathrm{HI}]_{eq}^{\ 2}}{[\mathrm{H_2}]_{eq}[\mathrm{I_2}]_{eq}} = \dfrac{(0.156)^2}{(0.0222)(0.0222)}$ $\boxed{K_1 = 49.4}$

Experiment 2: $K_2 = \dfrac{[\mathrm{HI}]_{eq}^{\ 2}}{[\mathrm{H_2}]_{eq}[\mathrm{I_2}]_{eq}} = \dfrac{(0.280)^2}{(0.0350)(0.0450)}$ $\boxed{K_2 = 49.8}$

Experiment 3: $K_3 = \dfrac{[\mathrm{HI}]_{eq}^{\ 2}}{[\mathrm{H_2}]_{eq}[\mathrm{I_2}]_{eq}} = \dfrac{(0.100)^2}{(0.0150)(0.0135)}$ $\boxed{K_3 = 49.3}$

Experiment 4: $K_4 = \dfrac{[\mathrm{HI}]_{eq}^{\ 2}}{[\mathrm{H_2}]_{eq}[\mathrm{I_2}]_{eq}} = \dfrac{(0.311)^2}{(0.0442)(0.0442)}$ $\boxed{K_4 = 49.5}$

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

Converting K_c to K_P:

$PV = nRT$ **(Ideal Gas Law)**

$P = \left(\dfrac{n}{V}\right)RT = CRT$ **(Solving for P and let $\dfrac{n}{V}$ = Concentration)**

$K_P = \dfrac{P_\mathrm{C}^c P_\mathrm{D}^d}{P_\mathrm{A}^a P_\mathrm{B}^b}$ **(Equilibrium Expression and Constant for $a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$)**

Substituting pressures for each chemical species into the equilibrium expression:
($P_\mathrm{A} = [\mathrm{A}]RT$; $P_\mathrm{B} = [\mathrm{B}]RT$; $P_\mathrm{C} = [\mathrm{C}]RT$; and $P_\mathrm{D} = [\mathrm{D}]RT$)

$$K_P = \frac{([\mathrm{C}]RT)^c([\mathrm{D}]RT)^d}{([\mathrm{A}]RT)^a([\mathrm{B}]RT)^b} = \frac{[\mathrm{C}]^c(RT)^c[\mathrm{D}]^d(RT)^d}{[\mathrm{A}]^a(RT)^a[\mathrm{B}]^b(RT)^b}$$

(Combine exponents on common base RT using Laws of Exponents)

$$K_P = \frac{[\mathrm{C}]^c[\mathrm{D}]^d(RT)^{c+d}}{[\mathrm{A}]^a[\mathrm{B}]^b(RT)^{a+b}} = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}(RT)^{(c+d)-(a+b)}$$

(Replace $\dfrac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$ with K_c)

$$K_P = K_c(RT)^{(c+d)-(a+b)}$$

Conversion between Concentration and Pressure Equilibrium Constants

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$$

$$K_P = K_c(RT)^{\Delta n}$$

where Δn = Σ Coefficients of Products – Σ Coefficients of Reactants = $(c + d) - (a + b)$

$R = 0.08206\ \mathrm{K}^{-1}$ T = Temperature in K

R has a unit of K^{-1} to cancel out with the Kelvin from Temperature only, therefore K calculated will remain unitless

Example 3: One possible way of removing NO $_{(g)}$ from the exhaust of an internal combustion engine is to cause it to react with CO $_{(g)}$ in the presence of suitable catalyst.

$$2\ \mathrm{NO}_{(g)} + 2\ \mathrm{CO}_{(g)} \rightleftharpoons \mathrm{N}_{2\,(g)} + 2\ \mathrm{CO}_{2\,(g)}$$

At 575 K, the reaction has $K = 2.2 \times 10^{59}$. What is K_P of the same reaction at 575 K?

$K = K_c = 2.2 \times 10^{59}$
$R = 0.08206\ \mathrm{K}^{-1}$
$T = 575\ \mathrm{K}$

$\Delta n = \Sigma n_{\text{products}} - \Sigma n_{\text{reactants}}$
$\Delta n = (1 + 2) - (2 + 2) = 3 - 4$
$\Delta n = -1$

$K_P = ?$

$K_P = K_c(RT)^{\Delta n}$
$K_P = (2.2 \times 10^{59})[(0.08206\ \cancel{\mathrm{K}^{-1}})(575\ \cancel{\mathrm{K}})]^{-1}$
$K_P = (2.2 \times 10^{59})[47.1845]^{-1}$

$$\boxed{K_P = 4.7 \times 10^{57}}$$

Example 4: The German's Haber-Bosch process developed in 1913 utilizes an iron surface that contains traces of aluminium 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.

$$\mathrm{N}_{2\,(g)} + 3\ \mathrm{H}_{2\,(g)} \rightleftharpoons 2\ \mathrm{NH}_{3\,(g)}$$

a. At 400 K, $P_{\mathrm{NH}_3} = 0.1024$ atm, $P_{\mathrm{N}_2} = 2.8084$ atm and $P_{\mathrm{H}_2} = 0.0102$ atm. Write the equilibrium expression in terms of pressure and calculate K_P.
b. Convert the calculated K_P above to K.

a. **Equilibrium Expression:** $\boxed{K_P = \dfrac{P^2_{\mathrm{NH}_3}}{P_{\mathrm{N}_2} P^3_{\mathrm{H}_2}}}$ **Equilibrium Constant:** $K_P = \dfrac{(0.1024)^2}{(2.8084)(0.0102)^3}$

$$\boxed{K_P = 3.52 \times 10^3}$$

b. $K_P = 3.52 \times 10^3$
$R = 0.08206\ \mathrm{K}^{-1}$ $T = 400\ \mathrm{K}$

$\Delta n = \Sigma n_{\text{products}} - \Sigma n_{\text{reactants}}$
$\Delta n = (2) - (1 + 3) = 2 - 4$
$\Delta n = -2$

$K_P = ?$

$K_P = K_c(RT)^{\Delta n}$

$$K_c = \frac{K_P}{(RT)^{\Delta n}} = \frac{(3.52 \times 10^3)}{[(0.08206\ \cancel{\mathrm{K}^{-1}})(400\ \cancel{\mathrm{K}})]^{-2}} \qquad \boxed{K_c = 3.79 \times 10^7}$$

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

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

(NaN_3 and Na are Pure Solids)

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

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

(H_2NCONH_2 is a Pure Solid)

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

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

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

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

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

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

Multiple Equilibria: - the overall equilibrium constant of a multi-steps systems is the ***product*** of all the equilibrium constants of the individual steps involved.

Consider the following multiple equilibria:

Step 1: A + B ⇌ C + D $\qquad K_1 = \frac{[C][D]}{[A][B]}$

Step 2: C + D ⇌ E + F $\qquad K_2 = \frac{[E][F]}{[C][D]}$

A + B ⇌ E + F $\qquad K = \frac{[E][F]}{[A][B]} = \frac{[\cancel{C}][\cancel{D}]}{[A][B]} \times \frac{[E][F]}{[\cancel{C}][\cancel{D}]}$

$$K = K_1 \times K_2$$

Multiple Equilibria

$$K = K_1 \times K_2 \times K_3 \times \ldots$$

Working with Equilibrium Constant and Equations:

- **reversing equilibrium reaction will cause the reciprocate the equilibrium constant (1/*K*)**
- **multiplying the equation by a multiple *n* will result in raising the *K* by the power of *n*.**

Reversing Equilibrium Reaction	**Multiplying Equilibrium Reaction by a Factor of *n***
$aA + bB \rightleftharpoons cC + dD \ \rightarrow\ cC + dD \rightleftharpoons aA + bB$	$n(aA + bB \rightleftharpoons cC + dD) \ \rightarrow\ naA + nbB \rightleftharpoons ncC + ndD)$
$K' = \frac{[A]^a[B]^b}{[C]^c[D]^d} = \left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right)^{-1} = K^{-1} = \frac{1}{K}$	$K'' = \frac{[C]^{nc}[D]^{nd}}{[A]^{na}[B]^{nb}} = \left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right)^n = K^n$
K' = Reverse Equilibrium Constant	**K'' = New Equilibrium Constant**

Example 6: 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 $[NH_3]_{eq} = 0.250$ M $[O_2]_{eq} = 0.350$ M
$[C_3H_3N]_{eq} = 2.50$ M $[H_2O]_{eq} = 3.00$ 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.

$$2\ C_3H_3N\,_{(g)} + 6\ H_2O\,_{(g)} \rightleftharpoons 2\ C_3H_6\,_{(g)} + 2\ NH_3\,_{(g)} + 3\ O_2\,_{(g)}$$

c. Write the equilibrium expression and find the equilibrium constant for the following reaction with the same equilibrium concentrations.

$$C_3H_6\,_{(g)} + NH_3\,_{(g)} + \frac{3}{2}\,O_2\,_{(g)} \rightleftharpoons C_3H_3N\,_{(g)} + 3\ H_2O\,_{(g)}$$

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

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

$$K = 6.80 \times 10^6$$

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

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

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

$$K' = 1.47 \times 10^{-7}$$

c. **Equilibrium Expression:** $$K'' = \frac{[C_3H_3N][H_2O]^3}{[C_3H_6][NH_3][O_2]^{\frac{3}{2}}}$$ **(All Coefficients Multiplied by ½)**

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

$$K'' = \left(6.80 \times 10^6\right)^{\frac{1}{2}}$$

$$K'' = 2.61 \times 10^3$$

Assignment
15.2 pg. 520 #5 to 9

15.3: What Does the Equilibrium Constant Tell Us?

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).***
5. The **Size of K depends mainly on Temperature (T)**.

Reaction Quotient (Q): - the mass action expression under any set of conditions (*not necessarily equilibrium*).
- **its magnitude relative to K determines the direction in which the reaction must occur to establish equilibrium**.

$$Q = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$

a. **When $Q > K$, the system shifts to the reactants. *At a specific condition, Q indicates that there are too much products.* Therefore, the system has to shift back to the left.**

b. **When $Q < K$, the system shifts to the products. At a specific condition, *Q indicates that there are not enough products*. Therefore, the system has to shift forward to the right.**

c. **When $Q = K$, the system is at equilibrium. *At a specific condition, Q indicates that all concentrations are that of the equilibrium state*. Therefore, there will be no shifting.**

Example 1: The reaction, 2 $NO_{(g)}$ + $O_{2\,(g)}$ $\rightleftharpoons$ 2 $NO_{2\,(g)}$ has an equilibrium constant of K = 29.54 at 600 K. Indicate the direction in which the system will shift to reach equilibrium when the $[NO]_0$ = 0.300 M, $[O_2]_0$ = 0.250 M, and $[NO_2]_0$ = 0.500 M.

$[NO]_0$ = 0.300 M
$[O_2]_0$ = 0.250 M
$[NO_2]_0$ = 0.500 M

Q = ?

$$Q = \frac{[NO_2]_0^2}{[NO]_0^2[O_2]_0} = \frac{(0.500)^2}{(0.300)^2(0.250)} \qquad \boxed{Q = 11.1}$$

Since $Q < K$ (11.1 < 29.54), *the system will shift to the product* (NO_2). There are not enough NO_2 at the initial conditions.

Example 2: 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 3: 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 shift to the left 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:

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

Example 4: The reaction, $2\,NO_{2\,(g)} \rightleftharpoons NO_{3\,(g)} + NO_{(g)}$ has $K = 31.7$ at 700 K. A 2.50 L flask at 700 K has 1.00 mol of each species initially. Calculate the concentrations of all species at equilibrium.

$K = 31.7$

$$[NO_2]_0 = \frac{1.00 \text{ mol}}{2.50 \text{ L}} = 0.400 \text{ M}$$

$$[NO_3]_0 = \frac{1.00 \text{ mol}}{2.50 \text{ L}} = 0.400 \text{ M}$$

$$[NO]_0 = \frac{1.00 \text{ mol}}{2.50 \text{ L}} = 0.400 \text{ M}$$

$[NO_2]_{eq} = ?$
$[NO_3]_{eq} = ?$
$[NO]_{eq} = ?$

First, we must determine Q and the direction of the shift.

$$Q = \frac{[NO_3]_0[NO]_0}{[NO_2]_0^2} = \frac{(0.400)(0.400)}{(0.400)^2} \qquad Q = 1.00$$

Since $Q < K$ (1.00 < 31.7), *the system will shift to the products* (NO_3 and NO). There are not enough products at the initial conditions. Hence, the change to the NO_2 is negative, and the changes to the NO_3 and NO would be positive.

Let x = amount of change per mole, since there are 2 moles of NO_2 reacted; NO_2 will be lowered by $2x$. Similarly, NO_3 and NO will be increased by $1x$ each.

	$2\,NO_{2\,(g)}$	$\rightleftharpoons$	$NO_{3\,(g)}$	+	$NO_{(g)}$
Initial	0.400 M		0.400 M		0.400 M
Change	$-\,2x$		$+\,x$		$+\,x$
Equilibrium	**$(0.400 - 2x)$ M**		**$(0.400 + x)$ M**		**$(0.400 + x)$ M**

Next, we set up the equilibrium expression, substitute the above mathematical expressions and solve for x.

(Since we have a set of common exponents we can group it and square root both sides.)

$$K = \frac{[NO_3]_{eq}[NO]_{eq}}{[NO_2]_{eq}^2} \qquad 31.7 = \frac{(0.4+x)(0.4+x)}{(0.4-2x)^2} = \frac{(0.4+x)^2}{(0.4-2x)^2} = \left[\frac{(0.4+x)}{(0.4-2x)}\right]^2$$

$$\sqrt{31.7} = \sqrt{\left[\frac{(0.4+x)}{(0.4-2x)}\right]^2}$$

$$5.630275304 = \frac{(0.4+x)}{(0.4-2x)}$$

$$5.630275304\,(0.4 - 2x) = 0.4 + x$$
$$2.252110122 - 11.26055061x = 0.4 + x$$
$$-12.26055061x = -1.852110122$$
$$x = \frac{-1.852110122}{-12.26055061}$$
$$\mathbf{x = 0.15106}$$

Finally, substitute x back into the mathematical expressions.

$$[NO_2]_{eq} = 0.400 - 2x = 0.400 - 2(0.15106)$$
$$\boxed{[NO_2]_{eq} = 0.0979 \text{ M}}$$

$$[NO_3]_{eq} = 0.400 + x = 0.400 + (0.15106)$$
$$\boxed{[NO_3]_{eq} = 0.551 \text{ M}}$$

$$[NO]_{eq} = 0.400 + x = 0.400 + (0.15106)$$
$$\boxed{[NO]_{eq} = 0.551 \text{ M}}$$

Verify with K:

$$K = \frac{[NO_3]_{eq}[NO]_{eq}}{[NO_2]_{eq}^2} = \frac{(0.551)(0.551)}{(0.0979)^2} \qquad K = 31.7$$

This matches with the K given in the question.

Using the TI-Graphing Calculator to Solve Higher Degree Equations:

Sometimes we may encounter equations with higher degrees when solving for equilibrium pressures or concentrations. In some cases, we may be able to use the quadratic formula, but for cubic and higher degrees equations, they can become quite difficult. The TI-Graphing Calculator has a SOLVE function to aide the determination of the roots.

Example: Solve for the final concentrations of both products in the following equilibrium system when the initial concentration of the reactant is 0.400 mol/L, and $K = 2.4 \times 10^{-2}$.

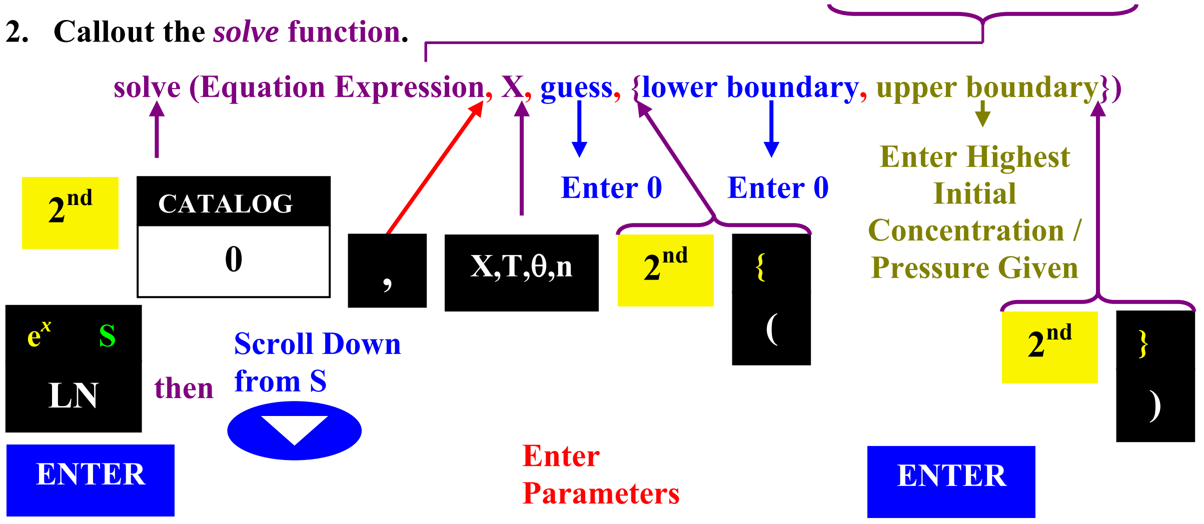
$$A_{(g)} \rightleftharpoons B_{(g)} + C_{(g)}$$

	$A_{(g)}$	$\rightleftharpoons$	$B_{(g)}$	+	$C_{(g)}$
Initial	0.400 M		0 M		0 M
Change	$-x$		$+x$		$+x$
Equilibrium	**$(0.400 - x)$ M**		**x M**		**x M**

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

Example: $2.4 \times 10^{-2} = \frac{x^2}{(0.4 - x)}$ becomes $0 = \frac{x^2}{(0.4 - x)} - 2.4 \times 10^{-2}$

2. Callout the *solve* function.



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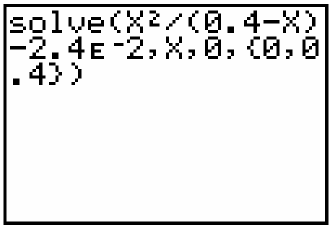

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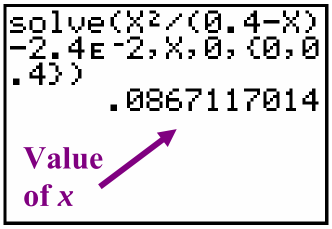
solve(X²/(0.4-X)
-2.4ᴇ-2,X,0,{0,0
.4})
```



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

Value of x

Therefore, the concentrations of the products are:

$$x = [B]_{eq} = [C]_{eq} = 0.0867 \text{ mol/L}$$

Example 5: The reaction, $SO_{2\,(g)} + Cl_{2\,(g)} \rightleftharpoons SO_2Cl_{2\,(g)}$, has an equilibrium constant of 0.486 at 500 K. Determine the equilibrium concentrations of all species if there are 2.00 mol of each species in 10.0 L container at 500 K.

$K = 0.486$

$$[SO_2]_0 = \frac{2.00\text{ mol}}{10.0\text{ L}} = 0.200\text{ M}$$

$$[Cl_2]_0 = \frac{2.00\text{ mol}}{10.0\text{ L}} = 0.200\text{ M}$$

$$[SO_2Cl_2]_0 = \frac{2.00\text{ mol}}{10.0\text{ L}} = 0.200\text{ M}$$

$[SO_2]_{eq}$ = ?
$[Cl_2]_{eq}$ = ?
$[SO_2Cl_2]_{eq}$ = ?

First, we must determine Q and the direction of the shift.

$$Q = \frac{[SO_2Cl_2]_0}{[SO_2]_0[Cl_2]_0} = \frac{(0.200)}{(0.200)(0.200)} \qquad \mathbf{Q = 5.00}$$

Since $Q > K$ (5.00 > 0.486), *__the system will shift to the reactants__* (SO_2 and Cl_2). There is too much product at the initial conditions. Hence, the changes to the SO_2 and Cl_2 are positive, and the change to the SO_2Cl_2 would be negative.

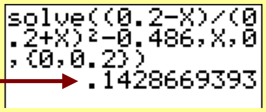
Let x = amount of change per mole, since there is 1 mole of SO_2 reacted; SO_2 will increase by 1x. Similarly, Cl_2 will increase by 1x. SO_2Cl_2, on the other hand, will decrease by 1x.

	$SO_{2\,(g)}$	+	$Cl_{2\,(g)}$	$\rightleftharpoons$	$SO_2Cl_{2\,(g)}$
Initial	0.200 M		0.200 M		0.200 M
Change	$+x$		$+x$		$-x$
Equilibrium	**$(0.200 + x)$ M**		**$(0.200 + x)$ M**		**$(0.200 - x)$ M**

Next, we set up the equilibrium expression, substitute the above mathematical expressions and solve for x. (Since we don't have any common exponent, we have to expand the denominator.)

$$K = \frac{[SO_2Cl_2]_{eq}}{[SO_2]_{eq}[Cl_2]_{eq}} \qquad 0.486 = \frac{(0.2-x)}{(0.2+x)(0.2+x)} = \frac{(0.2-x)}{(0.04+0.4x+x^2)} \qquad \text{or} \qquad 0 = \frac{(0.2-x)}{(0.2+x)^2} - 0.486$$

x →



```
solve((0.2-X)/(0
.2+X)²-0.486,X,0
,{0,0.2})
     .1428669393
```

$$0.486\,(0.04 + 0.4x + x^2) = (0.2 - x)$$

$$0.01944 + 0.1944x + 0.486x^2 = 0.2 - x$$

$$0.486x^2 + 1.1944x - 0.18056 = 0$$

(Quadratic Equation: Apply the Quadratic Formula!)

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \qquad a = 0.486 \qquad b = 1.1944 \qquad c = -0.18056$$

$$x = \frac{-(1.1944) \pm \sqrt{(1.1944)^2 - 4(0.486)(-0.18056)}}{2(0.486)}$$

$x = 0.14287$ $\qquad x = -2.6005$ (omit negative x)

Finally, substitute x back into the mathematical expressions.

$[SO_2]_{eq} = 0.200 + x = 0.200 + (0.14287)$

$$\boxed{\mathbf{[SO_2]_{eq} = 0.343\text{ M}}}$$

$[Cl_2]_{eq} = 0.200 + x = 0.200 + (0.14287)$

$$\boxed{\mathbf{[Cl_2]_{eq} = 0.343\text{ M}}}$$

$[SO_2Cl_2]_{eq} = 0.200 - x = 0.200 - (0.14287)$

$$\boxed{\mathbf{[SO_2Cl_2]_{eq} = 0.0571\text{ M}}}$$

Verify with K:

$$K = \frac{[SO_2Cl_2]_{eq}}{[SO_2]_{eq}[Cl_2]_{eq}} = \frac{(0.0571)}{(0.343)(0.343)} \qquad \mathbf{K = 0.485}$$

This matches closely with the K given in the question.

Steps to Solve Equilibrium Problems:

1. **Write the Balanced Chemical Equation for the system.** This **includes all the correct states** for all species.
2. **Write the Equilibrium Expression and equate it to *K* value given.**
3. **List the Initial Concentrations.**
4. **Determine *Q* and compare it to *K* to determine the direction of the shift** to equilibrium.
5. **Construct the ICE Box and define the change amount of change per mole as *x***. Using the coefficients and the direction of the shifts, state the mathematical expressions of each species at equilibrium.
6. **Solve for *x* after substituting the mathematical expressions into the equilibrium expression**. (Look for methods of simplifying like common exponents if they exist. Otherwise, the quadratic equation will be needed to solve for *x*.)
7. **Calculate the equilibrium concentrations** of each species and **verify that they indeed give the value of *K*.**
8. **For equilibrium involving pressures, the procedure is the same as above**.

Example 6: The equilibrium constant for the system, $C_2H_{6\,(g)} + Cl_{2\,(g)} \rightleftharpoons C_2H_5Cl_{\,(s)} + HCl_{\,(g)}$, at 283 K is 0.100. If we had 6.00 mol of $C_2H_{6\,(g)}$, 6.00 mol of $Cl_{2\,(g)}$ and 6.00 mol $HCl_{\,(g)}$ originally in a 3.00 L container at 283 K, determine the equilibrium concentrations for all species.

$K = 0.100$

$$[C_2H_6]_0 = \frac{6.00\text{ mol}}{3.00\text{ L}} = 2.00\text{ M}$$

$$[Cl_2]_0 = \frac{6.00\text{ mol}}{3.00\text{ L}} = 2.00\text{ M}$$

$$[HCl]_0 = \frac{6.00\text{ mol}}{3.00\text{ L}} = 2.00\text{ M}$$

$[C_2H_6]_{eq}$ = ?
$[Cl_2]_{eq}$ = ?
$[HCl]_{eq}$ = ?

First, we must determine *Q* and the direction of the shift. (Be careful! This is a heterogeneous system. C_2H_5Cl is a pure solid and it is not involved in the equilibrium expression.

$$Q = \frac{[HCl]_0}{[C_2H_6]_0[Cl_2]_0} = \frac{(2.00)}{(2.00)(2.00)} \qquad Q = 0.500$$

Since $Q > K$ (0.500 > 0.100), *the system will shift to the reactants* (C_3H_6 and Cl_2). There are too much products at the initial conditions. Hence, the changes to the C_2H_6 and Cl_2 are positive, and the change to the HCl would be negative.

Let *x* = amount of change per mole, since there is 1 mole of C_2H_6 reacted; C_2H_6 will increase by 1*x*. Similarly, Cl_2 will increase by 1*x*. HCl, on the other hand, will decrease by 1*x*.

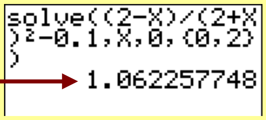
	$C_2H_{6\,(g)}$	+	$Cl_{2\,(g)}$	$\rightleftharpoons$	$C_2H_5Cl_{\,(s)}$	+	$HCl_{\,(g)}$
Initial	2.00 M		2.00 M		------		2.00 M
Change	$+x$		$+x$		------		$-x$
Equilibrium	**$(2.00 + x)$ M**		**$(2.00 + x)$ M**		**------**		**$(2.00 - x)$ M**

Next, we set up the equilibrium expression, substitute the above mathematical expressions and solve for *x*. (Since we have a set of common exponents we can group it and square root both sides.)

$$K = \frac{[\mathrm{HCl}]_0}{[\mathrm{C_2H_6}]_0[\mathrm{Cl_2}]_0} \qquad 0.100 = \frac{(2-x)}{(2+x)(2+x)} = \frac{(2-x)}{(4+4x+x^2)} \qquad \text{or} \qquad 0 = \frac{(2-x)}{(2+x)^2} - 0.100$$

$$0.100\ (4 + 4x + x^2) = (2 - x)$$
$$0.4 + 0.4x + 0.1x^2 = 2 - x$$
$$0.1x^2 + 1.4x - 1.6 = 0$$

x →



```
solve((2-X)/(2+X
)²-0.1,X,0,{0,2}
)
        1.062257748
```

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \qquad a = 0.1 \qquad b = 1.4 \qquad c = -1.6$$

$$x = \frac{-(1.4) \pm \sqrt{(1.4)^2 - 4(0.1)(-1.6)}}{2(0.1)}$$

$\boldsymbol{x = 1.062258}$

$x = -15.06226$ (omit negative x)

Finally, substitute *x* back into the mathematical expressions.

$[\mathrm{C_2H_6}]_{eq} = 2.00 + x = 2.00 + (1.062257748)$

$\boxed{[\mathrm{C_2H_6}]_{eq} = 3.06\ \mathrm{M}}$

$[\mathrm{Cl_2}]_{eq} = 2.00 + x = 2.00 + (1.062257748)$

$\boxed{[\mathrm{Cl_2}]_{eq} = 3.06\ \mathrm{M}}$

$[\mathrm{HCl}]_{eq} = 2.00 - x = 2.00 - (1.062257748)$

$\boxed{[\mathrm{HCl}]_{eq} = 0.938\ \mathrm{M}}$

Verify with *K*:

$$K = \frac{[\mathrm{HCl}]_0}{[\mathrm{C_2H_6}]_0[\mathrm{Cl_2}]_0} = \frac{(0.938)}{(3.06)(3.06)} \qquad \boldsymbol{K = 0.100}$$

This matches closely with the *K* given in the question.

Example 7: The reaction of $CO_{(g)} + Cl_{2\,(g)} \rightleftharpoons COCl_{2\,(g)}$ has an equilibrium constant of $K_P = 0.289$ at 450 K. The initial pressures of $CO_{(g)}$, $Cl_{2\,(g)}$ and $COCl_{2\,(g)}$ are 0.800 atm, 0.900 atm and 0.150 atm respectively. They are all mixed in a 7.50 L flask at 450 K. Find the equilibrium pressures.

$K_P = 0.289$
$P_{CO,\,0} = 0.800$ atm
$P_{Cl_2,\,0} = 0.900$ atm
$P_{COCl_2,\,0} = 0.150$ atm

$\boldsymbol{P_{CO,\,eq} = ?}$
$\boldsymbol{P_{Cl_2,\,eq}} = ?$
$\boldsymbol{P_{COCl_2,\,eq}} = ?$

First, we must determine *Q* and the direction of the shift.

$$Q_P = \frac{P_{COCl_2,0}}{P_{CO,0}P_{Cl_2,0}} = \frac{(0.150)}{(0.800)(0.900)} \qquad \boldsymbol{Q_P = 0.208}$$

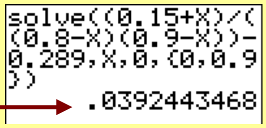
Since <u>*Q* < *K*</u> (0.208 < 0.289), *<u>the system will shift to the product</u>* ($COCl_2$). There is too little product at the initial conditions. Hence, the changes to the CO and Cl_2 are negative, and the change to the $COCl_2$ would be positive.

Let *x* = amount of change per mole, since there is 1 mole of CO reacted; CO will decrease by 1*x*. Similarly, Cl_2 will decrease by 1*x*. $COCl_2$, on the other hand, will increase by 1*x*.

	$CO_{(g)}$	+	$Cl_{2\,(g)}$	$\rightleftharpoons$	$COCl_{2\,(g)}$
Initial	0.800 atm		0.900 atm		0.150 atm
Change	$-x$		$-x$		$+x$
Equilibrium	**(0.800 – *x*) atm**		**(0.900 – *x*) atm**		**(0.150 + *x*) M**

Next, we set up the equilibrium expression, substitute the above mathematical expressions and solve for *x*. (Since we don't have any common exponent, we have to expand the denominator.)

$$K_P = \frac{P_{\mathrm{COCl_2},eq}}{P_{\mathrm{CO},eq}P_{\mathrm{Cl_2},eq}} \qquad 0.289 = \frac{(0.15+x)}{(0.8-x)(0.9-x)} = \frac{(0.15+x)}{(0.72-1.7x+x^2)} \quad \text{or} \quad 0 = \frac{(0.15+x)}{(0.8-x)(0.9-x)} - 0.289$$



```
solve((0.15+X)/(
(0.8-X)(0.9-X))-
0.289,X,0,{0,0.9
})
      .0392443468
```

x →

$$0.289\,(0.72 - 1.7x + x^2) = (0.15 + x)$$

$$0.20808 - 0.4913x + 0.289x^2 = 0.15 + x$$

$$0.289x^2 - 1.4913x + 0.05808 = 0$$

(Quadratic Equation: Apply the Quadratic Formula!)

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \qquad a = 0.289 \qquad b = -1.4913 \qquad c = 0.05808$$

$$x = \frac{-(-1.4913) \pm \sqrt{(-1.4913)^2 - 4(0.289)(0.05808)}}{2(0.289)}$$

$x = 5.120963266$ (omit larger value – bigger than 0.800 atm and 0.900 atm)

$\mathbf{x = 0.0392443468}$

Verify with *K*:

$$K_P = \frac{P_{\mathrm{COCl_2},eq}}{P_{\mathrm{CO},eq}P_{\mathrm{Cl_2},eq}} = \frac{(0.189)}{(0.761)(0.861)}$$

$\mathbf{K_P = 0.288}$ **(This matches closely with the K_P given in the question.)**

Finally, substitute *x* back into the mathematical expressions.

$P_{\mathrm{CO},eq} = 0.800 - x = 0.800 - (0.0392443468)$

$$\boxed{P_{\mathrm{CO},eq} = 0.761 \text{ atm}}$$

$P_{\mathrm{Cl_2},eq} = 0.900 - x = 0.900 - (0.0392443468)$

$$\boxed{P_{\mathrm{Cl_2},eq} = 0.861 \text{ atm}}$$

$P_{\mathrm{COCl_2},eq} = 0.150 + x = 0.150 + (0.0392443468)$

$$\boxed{P_{\mathrm{COCl_2},eq} = 0.189 \text{ M}}$$

Assignment

15.3 pg. 520–525 #11 to 26, 27 to 38, 54, 58, 60, 62, 78

14.5: Factors That Affect Chemical Equilibrium

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**.

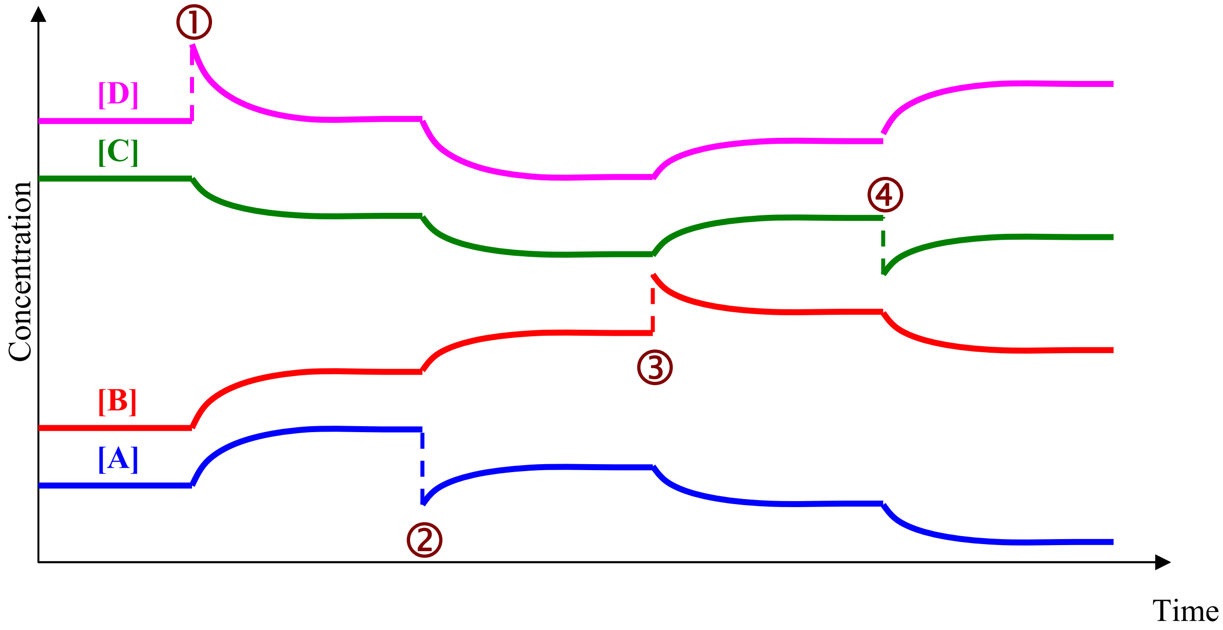
- ***the equilibrium will shift in the direction that minimizes the change imposed on the system.***

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 ($a\text{A} + \overleftarrow{b\text{B} \rightleftharpoons c\text{C}} + d\text{D}$).** Hence, **[A]↑**, **[B]↑**, and **[C]↓**.

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

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

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

2. Effects of a Change in Pressure:

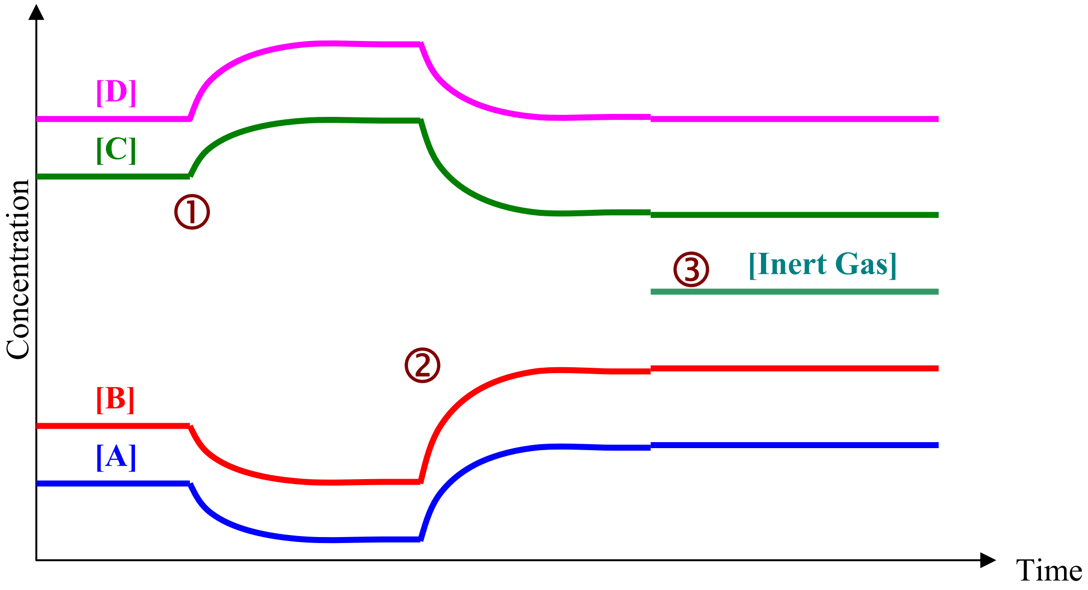
a. ***Adding an Inert Gas has NO CHANGE on the equilibrium system***. This is because an inert gas does not participate in the forward or reverse reaction.

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 $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$ when $(c + d) > (a + b)$



① **indicates an Increase in Volume. As V↑, equilibrium shifts to the right ($a\text{A} + b\text{B} \overset{\longrightarrow}{\rightleftharpoons} c\text{C} + d\text{D}$) 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 ($a\text{A} + b\text{B} \overset{\longleftarrow}{\rightleftharpoons} c\text{C} + d\text{D}$) 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. ($a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$) 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:** $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D} + \textit{Energy}$

   - **an Increase in Temperature will drive the system to the left ($a\text{A} + b\text{B} \overset{\longleftarrow}{\rightleftharpoons} c\text{C} + d\text{D} + \textit{Energy}$).** 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]↓.

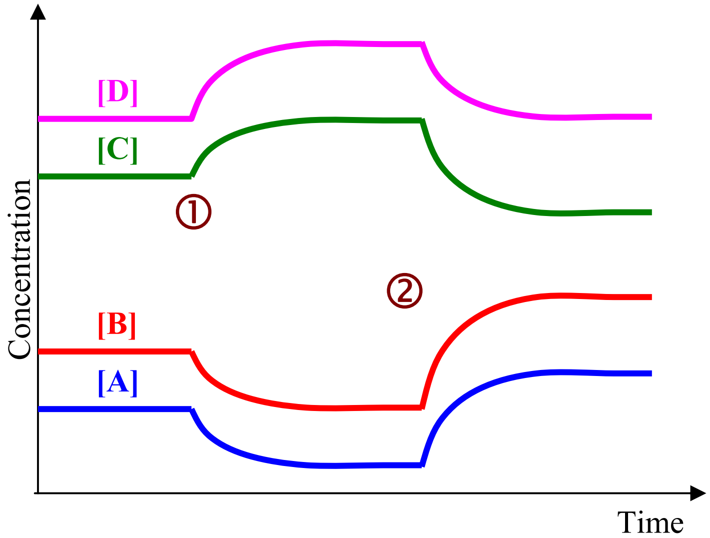
   - **a Decrease in Temperature will drive the system to the right ($a\text{A} + b\text{B} \overset{\longrightarrow}{\rightleftharpoons} c\text{C} + d\text{D} + \textit{Energy}$).** There is less heat overall and because energy is written on the product side, the system will shift to the products to compensate.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

b. For Endothermic Equilibrium System: $a\text{A} + b\text{B} + Energy \rightleftharpoons c\text{C} + d\text{D}$

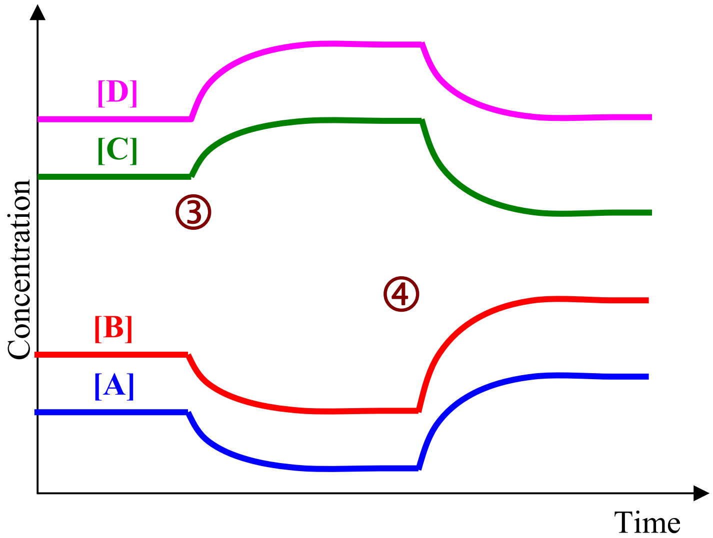
- **a Decrease in Temperature will drive the system to the left (**$a\text{A} + b\text{B} + Energy \overset{\longleftarrow}{\rightleftharpoons} c\text{C} + d\text{D}$**).** There is less heat overall and because energy is written on the reactant side, the system will shift to the reactants to compensate.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

- **an Increase in Temperature will drive the system to the right (**$a\text{A} + b\text{B} + Energy \overset{\longrightarrow}{\rightleftharpoons} c\text{C} + d\text{D}$**).** 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 *Exothermic* Equilibrium System $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D} + Energy$



Changes in Temperature on an *Endothermic* Equilibrium System $a\text{A} + b\text{B} + Energy \rightleftharpoons c\text{C} + d\text{D}$



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

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

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

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

4. Effects of Adding a Catalyst: - *has NO CHANGE on the equilibrium system.*

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

Example 1: The equilibrium system, $4\,PF_{3\,(g)} \rightleftharpoons P_{4\,(s)} + 6\,F_{2\,(g)} + 1578\text{ kJ}$, 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.

$4\,PF_{3\,(g)} \overset{\longleftarrow}{\rightleftharpoons} P_{4\,(s)} + 6\,F_{2\,(g)}\uparrow + 1578\text{ kJ}$

Effect: $[PF_3]\uparrow$ (increase)

b. a decrease in the concentration of $P_{4\,(s)}$

There will be NO SHIFT on the system.

$4\,PF_{3\,(g)} \rightleftharpoons P_{4\,(s)}\downarrow + 6\,F_{2\,(g)} + 1578\text{ kJ}$

(P_4 is a pure solid and does not involve with the equilibrium system)

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

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

The system will shift to the LEFT.

$4\,PF_{3\,(g)}\downarrow \overset{\longleftarrow}{\rightleftharpoons} P_{4\,(s)} + 6\,F_{2\,(g)} + 1578\text{ kJ}$

Effect: $[F_2]\downarrow$ (decrease)

d. a decrease in Temperature.

The system will shift to the RIGHT.

$4\,PF_{3\,(g)} \overset{\longrightarrow}{\rightleftharpoons} P_{4\,(s)} + 6\,F_{2\,(g)} + 1578\text{ kJ}\downarrow$

Effect: $[PF_3]\downarrow$ (decrease) and $[F_2]\uparrow$ (increase)

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

There will be NO SHIFT on the system.

$4\,PF_{3\,(g)} \rightleftharpoons P_{4\,(s)} + 6\,F_{2\,(g)} + 1578\text{ kJ}$

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

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

f. an increase in volume.

The system will shift to the RIGHT.

$4\,PF_{3\,(g)} \overset{\longrightarrow}{\rightleftharpoons} P_{4\,(s)} + 6\,F_{2\,(g)} + 1578\text{ kJ}$

(There are more gaseous molecules on the product side – 6 moles of $F_{2\,(g)}$ versus 4 moles of $PF_{3\,(g)}$)

Effect: $[PF_3]\downarrow$ (decrease) and $[F_2]\uparrow$ (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

15.4 pg. 522–523 #39 to 52