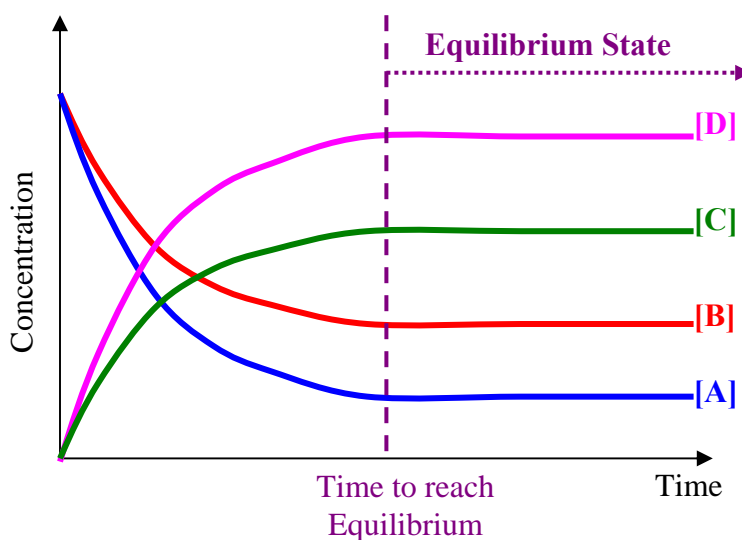
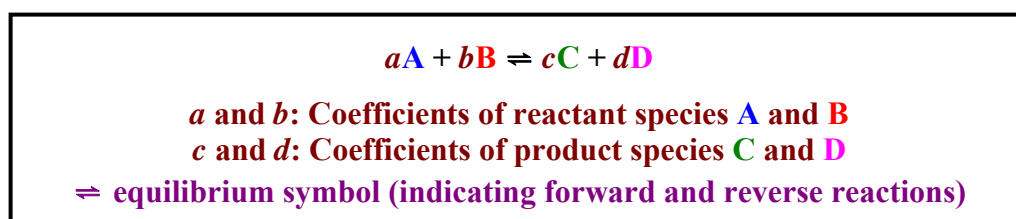


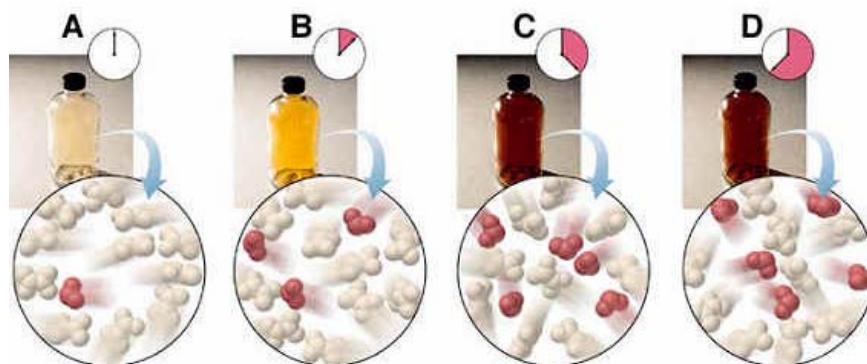
Chapter 14: Chemical Equilibrium

14.1: 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**.



(Check out Video at http://www.saskschools.ca/curr_content/chem30/swf/equilgraph.swf)



The $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ 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**.

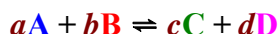
Equilibrium Expression: - an expression **relating the concentrations or pressures of the reactants and products when they are at the state of equilibrium**.

- 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



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

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

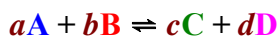
14.1 pg. 633 #1 to 4

14.2: Writing Equilibrium Constant Expressions

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

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

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

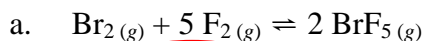
[A], [B], [C] & [D] = [A]_{eq}, [B]_{eq}, [C]_{eq} & [D]_{eq} = Equilibrium Concentrations of Chemicals (mol/L)

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)

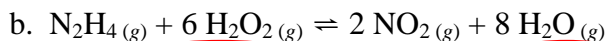
K or K_c = Equilibrium Constant (Concentrations) **K_P = Equilibrium Constant (Pressures)**

Both K_c and K_P are Unitless

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



$$K = \frac{[\text{BrF}_5]^2}{[\text{Br}_2][\text{F}_2]^5} \quad K_P = \frac{P_{\text{BrF}_5}^2}{P_{\text{Br}_2} P_{\text{F}_2}^5}$$



$$K = \frac{[\text{NO}_2]^2 [\text{H}_2\text{O}]^8}{[\text{N}_2\text{H}_4] [\text{H}_2\text{O}_2]^6} \quad K_P = \frac{P_{\text{NO}_2}^2 P_{\text{H}_2\text{O}}^8}{P_{\text{N}_2\text{H}_4} P_{\text{H}_2\text{O}_2}^6}$$

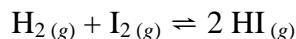
Equilibrium Position: - the **concentrations or pressures of all chemical species at equilibrium state.**

- **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 are 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.



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

- Write the equilibrium expression for the formation of HI_(g).
- Calculate the equilibrium constant for each experiment, and average them for an overall value.

a. Equilibrium Expression: $K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$

b. Equilibrium Constant:

Experiment 1: $K_1 = \frac{[\text{HI}]_{eq}^2}{[\text{H}_2]_{eq}[\text{I}_2]_{eq}} = \frac{(0.156)^2}{(0.0222)(0.0222)}$ Experiment 2: $K_2 = \frac{[\text{HI}]_{eq}^2}{[\text{H}_2]_{eq}[\text{I}_2]_{eq}} = \frac{(0.280)^2}{(0.0350)(0.0450)}$

$K_1 = 49.4$

$K_2 = 49.8$

Experiment 3: $K_3 = \frac{[\text{HI}]_{eq}^2}{[\text{H}_2]_{eq}[\text{I}_2]_{eq}} = \frac{(0.100)^2}{(0.0150)(0.0135)}$ Experiment 4: $K_4 = \frac{[\text{HI}]_{eq}^2}{[\text{H}_2]_{eq}[\text{I}_2]_{eq}} = \frac{(0.311)^2}{(0.0442)(0.0442)}$

$K_3 = 49.3$

$K_4 = 49.5$

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

$K_{avg} = 49.5$

Converting K_c to K_p :

$PV = nRT$ (Ideal Gas Law)

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

$K_P = \frac{P_C^c P_D^d}{P_A^a P_B^b}$ (Equilibrium Expression and Constant for $aA + bB \rightleftharpoons cC + dD$)

Substituting pressures for each chemical species into the equilibrium expression:

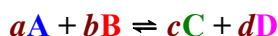
$(P_A = [A]RT ; P_B = [B]RT ; P_C = [C]RT ; \text{ and } P_D = [D]RT)$

$K_P = \frac{([C]RT)^c ([D]RT)^d}{([A]RT)^a ([B]RT)^b} = \frac{[C]^c (RT)^c [D]^d (RT)^d}{[A]^a (RT)^a [B]^b (RT)^b}$ (Combine exponents on common base RT using Laws of Exponents)

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

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

Conversion between Concentration and Pressure Equilibrium Constants



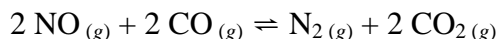
$K_P = K_c (RT)^{\Delta n}$

where $\Delta n = \Sigma \text{Coefficients of Products} - \Sigma \text{Coefficients of Reactants} = (c + d) - (a + b)$

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

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 $\text{NO}_{(g)}$ from the exhaust of an internal combustion engine is to cause it to react with $\text{CO}_{(g)}$ in the presence of suitable catalyst.



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

$$K = K_c = 2.2 \times 10^{59}$$

$$R = 0.08206 \text{ K}^{-1}$$

$$T = 575 \text{ K}$$

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

$$K_P = (2.2 \times 10^{59})[(0.08206 \text{ K}^{-1})(575 \text{ K})]^{-1}$$

$$K_P = (2.2 \times 10^{59})[47.1845]^{-1}$$

$$\Delta n = \sum n_{\text{products}} - \sum n_{\text{reactants}}$$

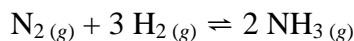
$$\Delta n = (1 + 2) - (2 + 2) = 3 - 4$$

$$\Delta n = -1$$

$$K_P = ?$$

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

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.



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

a. **Equilibrium Expression:** $K_P = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3}$ **Equilibrium Constant:** $K_P = \frac{(0.1024)^2}{(2.8084)(0.0102)^3}$

b. $K_P = 3.52 \times 10^3$

$$R = 0.08206 \text{ K}^{-1} \quad T = 400 \text{ K}$$

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

$$K_c = \frac{K_P}{(RT)^{\Delta n}} = \frac{(3.52 \times 10^3)}{[(0.08206 \text{ K}^{-1})(400 \text{ K})]^{-2}}$$

$$K_c = 3.79 \times 10^7$$

$$\Delta n = \sum n_{\text{products}} - \sum n_{\text{reactants}}$$

$$\Delta n = (2) - (1 + 3) = 2 - 4$$

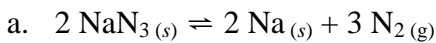
$$\Delta n = -2$$

$$K_P = ?$$

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.

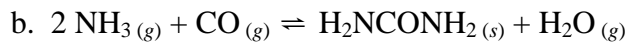
Example 5: Write the equilibrium expression for the following systems.



$$K = [\text{N}_2]^3$$

$$K_P = P_{\text{N}_2}^3$$

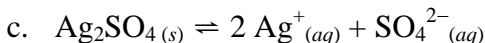
(NaN_3 and Na are Pure Solids)



$$K = \frac{[\text{H}_2\text{O}]}{[\text{NH}_3]^2 [\text{CO}]}$$

$$K_P = \frac{P_{\text{H}_2\text{O}}}{P_{\text{NH}_3}^2 P_{\text{CO}}}$$

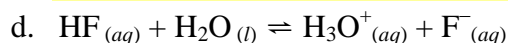
(H_2NCONH_2 is a Pure Solid)



$$K = [\text{Ag}^+]^2 [\text{SO}_4^{2-}]$$

(Ag_2SO_4 is a Pure Solid)

(No K_P because there are no gases.)



$$K = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]}$$

(H_2O is a Pure Liquid)

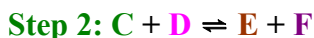
(No K_P because there are no gases.)

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

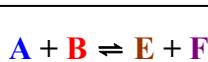
Consider the following multiple equilibria:



$$K_1 = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]}$$



$$K_2 = \frac{[\text{E}][\text{F}]}{[\text{C}][\text{D}]}$$



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

$$K = K_1 \times K_2$$

Multiple Equilibria

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

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



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

K' = Reverse Equilibrium Constant

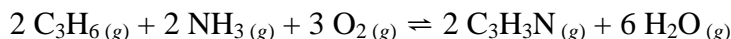
Multiplying Equilibrium Reaction by a Factor of n



$$K'' = \frac{[\text{C}]^{nc} [\text{D}]^{nd}}{[\text{A}]^{na} [\text{B}]^{nb}} = \left(\frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \right)^n = K^n$$

K'' = New Equilibrium Constant

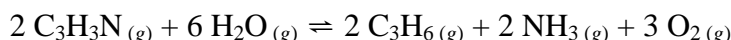
Example 6: For the following reaction and the equilibrium concentrations at 300 K.



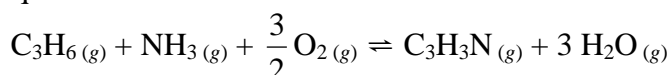
$$[\text{C}_3\text{H}_6]_{eq} = 0.500 \text{ M} \quad [\text{NH}_3]_{eq} = 0.250 \text{ M} \quad [\text{O}_2]_{eq} = 0.350 \text{ M}$$

$$[\text{C}_3\text{H}_3\text{N}]_{eq} = 2.50 \text{ M} \quad [\text{H}_2\text{O}]_{eq} = 3.00 \text{ M}$$

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



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



a. **Equilibrium Expression:** $K = \frac{[\text{C}_3\text{H}_3\text{N}]^2 [\text{H}_2\text{O}]^6}{[\text{C}_3\text{H}_6]^2 [\text{NH}_3]^2 [\text{O}_2]^3}$

Equilibrium Constant: $K = \frac{[\text{C}_3\text{H}_3\text{N}]^2 [\text{H}_2\text{O}]^6}{[\text{C}_3\text{H}_6]^2 [\text{NH}_3]^2 [\text{O}_2]^3} = \frac{(2.50)^2 (3.00)^6}{(0.500)^2 (0.250)^2 (0.350)^3} \quad K = 6.80 \times 10^6$

b. **Equilibrium Expression:** $K' = \frac{[\text{C}_3\text{H}_6]^2 [\text{NH}_3]^2 [\text{O}_2]^3}{[\text{C}_3\text{H}_3\text{N}]^2 [\text{H}_2\text{O}]^6}$ (Reverse Equilibrium)

Equilibrium Constant: $K' = \frac{[\text{C}_3\text{H}_6]^2 [\text{NH}_3]^2 [\text{O}_2]^3}{[\text{C}_3\text{H}_3\text{N}]^2 [\text{H}_2\text{O}]^6} = \left(\frac{[\text{C}_3\text{H}_3\text{N}]^2 [\text{H}_2\text{O}]^6}{[\text{C}_3\text{H}_6]^2 [\text{NH}_3]^2 [\text{O}_2]^3} \right)^{-1} = K^{-1}$

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

c. **Equilibrium Expression:** $K'' = \frac{[\text{C}_3\text{H}_3\text{N}] [\text{H}_2\text{O}]^3}{[\text{C}_3\text{H}_6] [\text{NH}_3] [\text{O}_2]^{\frac{3}{2}}}$ (All Coefficients Multiplied by $\frac{1}{2}$)

Equilibrium Constant: $K'' = \frac{[\text{C}_3\text{H}_3\text{N}] [\text{H}_2\text{O}]^3}{[\text{C}_3\text{H}_6] [\text{NH}_3] [\text{O}_2]^{\frac{3}{2}}} = \left(\frac{[\text{C}_3\text{H}_3\text{N}]^2 [\text{H}_2\text{O}]^6}{[\text{C}_3\text{H}_6]^2 [\text{NH}_3]^2 [\text{O}_2]^3} \right)^{\frac{1}{2}} = K^{\frac{1}{2}}$

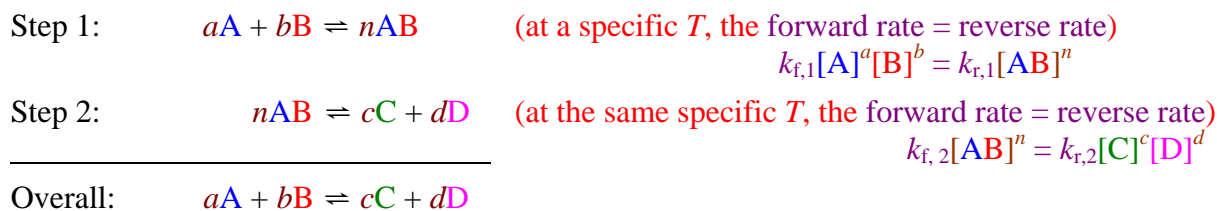
$K'' = (6.80 \times 10^6)^{\frac{1}{2}} \quad K'' = 2.61 \times 10^3$

Assignment

14.2 pg. 633–635 #5 to 11, 13, 14, 16, 18, 20, 22 to 24, 26 to 28, 30 to 32; pg. 639 #92

14.3: The Relationship Between Chemical Kinetics and Chemical Equilibrium

Suppose we have the following elementary steps of an overall system, $aA + bB \rightleftharpoons cC + dD$



Equilibrium Constant (K) can be written as the ratio of rate constants of the forward and reverse reactions.

For Step 1, we have $K_1 = \frac{k_{f,1}}{k_{r,1}} = \frac{[AB]^n}{[A]^a[B]^b}$. Similarly, for Step 2, we have $K_2 = \frac{k_{f,2}}{k_{r,2}} = \frac{[C]^c[D]^d}{[AB]^n}$.

From what we have learned about multiple equilibria (section 14.2), $K = K_1 \times K_2$. Therefore,

$$K = \frac{k_{f,1}}{k_{r,1}} \times \frac{k_{f,2}}{k_{r,2}} \longrightarrow K = \frac{[AB]^n}{[A]^a[B]^b} \times \frac{[C]^c[D]^d}{[AB]^n}$$

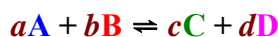
Now, the overall reaction of, $aA + bB \rightleftharpoons cC + dD$, would have an equilibrium expression of $K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$.

Since the **rate constant is dependent on temperature**, and **equilibrium constant is a ratio of rate constants**,

Equilibrium Constant (K) is highly dependent on temperature (T).

Assignment

14.3 pg. 635 #33 and 34

14.4: What Does the Equilibrium Constant Tell Us?**Important Notes Regarding the Size of the Equilibrium Constant (K):**

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

- When $K \gg 1$, 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 $P_{D,eq} \gg [A]_{eq}$ and $[B]_{eq}$ or $P_{A,eq}$ and $P_{B,eq}$)
- When $K \ll 1$, 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 $P_{B,eq} \gg [C]_{eq}$ and $[D]_{eq}$ or $P_{C,eq}$ and $P_{D,eq}$)
- 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 $P_{B,eq}$)
- 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).
- The **Size of K depends on Free Energy (G) and 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.

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

- 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.
- 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.
- 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, $2 \text{NO}_{(g)} + \text{O}_{2(g)} \rightleftharpoons 2 \text{NO}_{2(g)}$ 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 $[\text{NO}]_0 = 0.300 \text{ M}$, $[\text{O}_2]_0 = 0.250 \text{ M}$, and $[\text{NO}_2]_0 = 0.500 \text{ M}$.

$$\begin{aligned} [\text{NO}]_0 &= 0.300 \text{ M} \\ [\text{O}_2]_0 &= 0.250 \text{ M} \\ [\text{NO}_2]_0 &= 0.500 \text{ M} \end{aligned}$$

$$Q = \frac{[\text{NO}_2]_0^2}{[\text{NO}]_0^2 [\text{O}_2]_0} = \frac{(0.500)^2}{(0.300)^2 (0.250)}$$

$$Q = 11.1$$

$$Q = ?$$

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, $\text{Cl}_2(\text{g}) + 3 \text{F}_2(\text{g}) \rightleftharpoons 2 \text{ClF}_3(\text{g})$ at 350 K has $K = 50.2$. If the equilibrium concentrations of $\text{Cl}_2(\text{g})$ and $\text{ClF}_3(\text{g})$ are 0.149 M and 0.205 M respectively, what is the equilibrium concentration of $\text{F}_2(\text{g})$?

$$\begin{aligned} [\text{Cl}_2]_{eq} &= 0.149 \text{ M} \\ [\text{ClF}_3]_{eq} &= 0.205 \text{ M} \\ K &= 50.2 \end{aligned}$$

$$K = \frac{[\text{ClF}_3]_{eq}^2}{[\text{Cl}_2]_{eq} [\text{F}_2]_{eq}^3} \quad 50.2 = \frac{(0.205)^2}{(0.149)[\text{F}_2]_{eq}^3}$$

$$[\text{F}_2]_{eq} = ?$$

$$[\text{F}_2]_{eq}^3 = \frac{(0.205)^2}{(50.2)(0.149)}$$

$$[\text{F}_2]_{eq} = \sqrt[3]{\frac{(0.205)^2}{(50.2)(0.149)}}$$

$$[\text{F}_2]_{eq} = 0.178 \text{ M}$$

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 $\text{HCl}(\text{g})$ from its elements, $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{HCl}(\text{g})$ has $K = 0.404$ at 250 K. A 5.00 L flask at 250 K contained an initial concentration of 3.00 mol of $\text{HCl}(\text{g})$ and 3.85 mol of $\text{H}_2(\text{g})$. When the system reached equilibrium, it was found that there were 0.860 mol of $\text{Cl}_2(\text{g})$. Determine the concentrations of $\text{H}_2(\text{g})$ and $\text{HCl}(\text{g})$ at equilibrium.

$$K = 0.404$$

$$[\text{H}_2]_0 = \frac{3.85 \text{ mol}}{5.00 \text{ L}} = 0.770 \text{ M}$$

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

$$[\text{Cl}_2]_0 = 0 \text{ M}$$

$$[\text{Cl}_2]_{eq} = \frac{0.860 \text{ mol}}{5.00 \text{ L}} = 0.172 \text{ M}$$

$$[\text{H}_2]_{eq} = ?$$

$$[\text{HCl}]_{eq} = ?$$

The system must **shift to the left** because initially, we are missing **one reactant** ($[\text{Cl}_2]_0 = 0 \text{ M}$). 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).

	$\text{H}_2(\text{g})$	+	$\text{Cl}_2(\text{g})$	\rightleftharpoons	$2 \text{HCl}(\text{g})$
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 :

$$K = \frac{[\text{HCl}]_{eq}^2}{[\text{H}_2]_{eq} [\text{Cl}_2]_{eq}} = \frac{(0.256)^2}{(0.942)(0.172)}$$

$$K = 0.404$$

This matches with K given in the question.

Therefore, the equilibrium concentrations are:

$$[\text{H}_2]_{eq} = 0.942 \text{ M}, [\text{Cl}_2]_{eq} = 0.172 \text{ M} \text{ and } [\text{HCl}]_{eq} = 0.256 \text{ M}$$

Example 4: The reaction, $2 \text{NO}_2(\text{g}) \rightleftharpoons \text{NO}_3(\text{g}) + \text{NO}(\text{g})$ 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.

$$K = 31.7$$

$$[\text{NO}_2]_0 = \frac{1.00 \text{ mol}}{2.50 \text{ L}} = 0.400 \text{ M}$$

$$[\text{NO}_3]_0 = \frac{1.00 \text{ mol}}{2.50 \text{ L}} = 0.400 \text{ M}$$

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

$$[\text{NO}_2]_{eq} = ?$$

$$[\text{NO}_3]_{eq} = ?$$

$$[\text{NO}]_{eq} = ?$$

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

$$Q = \frac{[\text{NO}_3]_0 [\text{NO}]_0}{[\text{NO}_2]_0^2} = \frac{(0.400)(0.400)}{(0.400)^2} \quad Q = 1.00$$

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.

	$2 \text{NO}_2(\text{g})$	\rightleftharpoons	$\text{NO}_3(\text{g})$	+	$\text{NO}(\text{g})$
Initial	0.400 M		0.400 M		0.400 M
Change	$-2x$		$+x$		$+x$
Equilibrium	$(0.400 - 2x) \text{ M}$		$(0.400 + x) \text{ M}$		$(0.400 + x) \text{ M}$

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.)

$$K = \frac{[\text{NO}_3]_{eq} [\text{NO}]_{eq}}{[\text{NO}_2]_{eq}^2} \quad 31.7 = \frac{(0.4+x)(0.4+x)}{(0.4-2x)^2} = \frac{(0.4+x)^2}{(0.4-2x)^2} = \left[\frac{(0.4+x)}{(0.4-2x)} \right]^2$$

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

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

$$5.630275304(0.4-2x) = 0.4+x$$

$$2.252110122 - 11.26055061x = 0.4+x$$

$$-12.26055061x = -1.852110122$$

$$x = \frac{-1.852110122}{-12.26055061}$$

$$x = 0.15106$$

Verify with K :

$$K = \frac{[\text{NO}_3]_{eq} [\text{NO}]_{eq}}{[\text{NO}_2]_{eq}^2} = \frac{(0.551)(0.551)}{(0.0979)^2} \quad K = 31.7$$

This matches with the K given in the question.

Finally, substitute x back into the mathematical expressions.

$$[\text{NO}_2]_{eq} = 0.400 - 2x = 0.400 - 2(0.15106)$$

$$[\text{NO}_2]_{eq} = 0.0979 \text{ M}$$

$$[\text{NO}_3]_{eq} = 0.400 + x = 0.400 + (0.15106)$$

$$[\text{NO}_3]_{eq} = 0.551 \text{ M}$$

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

$$[\text{NO}]_{eq} = 0.551 \text{ M}$$

Example 5: The reaction, $\text{SO}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2\text{Cl}_2(\text{g})$, 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.

$$K = 0.486$$

$$[\text{SO}_2]_0 = \frac{2.00 \text{ mol}}{10.0 \text{ L}} = 0.200 \text{ M}$$

$$[\text{Cl}_2]_0 = \frac{2.00 \text{ mol}}{10.0 \text{ L}} = 0.200 \text{ M}$$

$$[\text{SO}_2\text{Cl}_2]_0 = \frac{2.00 \text{ mol}}{10.0 \text{ L}} = 0.200 \text{ M}$$

$$[\text{SO}_2]_{eq} = ?$$

$$[\text{Cl}_2]_{eq} = ?$$

$$[\text{SO}_2\text{Cl}_2]_{eq} = ?$$

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

$$Q = \frac{[\text{SO}_2\text{Cl}_2]_0}{[\text{SO}_2]_0[\text{Cl}_2]_0} = \frac{(0.200)}{(0.200)(0.200)} \quad Q = 5.00$$

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 $1x$.

	$\text{SO}_2(\text{g})$	+	$\text{Cl}_2(\text{g})$	\rightleftharpoons	$\text{SO}_2\text{Cl}_2(\text{g})$
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.)

$$K = \frac{[\text{SO}_2\text{Cl}_2]_{eq}}{[\text{SO}_2]_{eq}[\text{Cl}_2]_{eq}} \quad 0.486 = \frac{(0.2 - x)}{(0.2 + x)(0.2 + x)} = \frac{(0.2 - x)}{(0.04 + 0.4x + x^2)}$$

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

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

$$0.486x^2 + 1.1944x - 0.18056 = 0 \quad (\text{Quadratic Equation: Apply the Quadratic Formula!})$$

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

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

$$x = 0.14287 \quad x = -2.6005 \text{ (omit negative } x)$$

Verify with K :

$$K = \frac{[\text{SO}_2\text{Cl}_2]_{eq}}{[\text{SO}_2]_{eq}[\text{Cl}_2]_{eq}} = \frac{(0.0571)}{(0.343)(0.343)} \quad K = 0.485$$

This matches closely with the K given in the question.

Finally, substitute x back into the mathematical expressions.

$$[\text{SO}_2]_{eq} = 0.200 + x = 0.200 + (0.14287)$$

$$[\text{SO}_2]_{eq} = 0.343 \text{ M}$$

$$[\text{Cl}_2]_{eq} = 0.200 + x = 0.200 + (0.14287)$$

$$[\text{Cl}_2]_{eq} = 0.343 \text{ M}$$

$$[\text{SO}_2\text{Cl}_2]_{eq} = 0.200 - x = 0.200 - (0.14287)$$

$$[\text{SO}_2\text{Cl}_2]_{eq} = 0.0571 \text{ M}$$

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, $\text{C}_2\text{H}_6(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{C}_2\text{H}_5\text{Cl}(\text{s}) + \text{HCl}(\text{g})$, at 283 K is 0.100. If we had 6.00 mol of $\text{C}_2\text{H}_6(\text{g})$, 6.00 mol of $\text{Cl}_2(\text{g})$ and 6.00 mol $\text{HCl}(\text{g})$ originally in a 3.00 L container at 283 K, determine the equilibrium concentrations for all species.

$$K = 0.100$$

$$[\text{C}_2\text{H}_6]_0 = \frac{6.00 \text{ mol}}{3.00 \text{ L}} = 2.00 \text{ M}$$

$$[\text{Cl}_2]_0 = \frac{6.00 \text{ mol}}{3.00 \text{ L}} = 2.00 \text{ M}$$

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

$$[\text{C}_2\text{H}_6]_{\text{eq}} = ?$$

$$[\text{Cl}_2]_{\text{eq}} = ?$$

$$[\text{HCl}]_{\text{eq}} = ?$$

First, we must determine Q and the direction of the shift. (Be careful! This is a heterogeneous system. $\text{C}_2\text{H}_5\text{Cl}$ is a pure solid and it is not involved in the equilibrium expression.)

$$Q = \frac{[\text{HCl}]_0}{[\text{C}_2\text{H}_6]_0[\text{Cl}_2]_0} = \frac{(2.00)}{(2.00)(2.00)} \quad Q = 0.500$$

Since $Q > K$ ($0.500 > 0.100$), the system will shift to the reactants (C_2H_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 $1x$. Similarly, Cl_2 will increase by $1x$. HCl , on the other hand, will decrease by $1x$.

	$\text{C}_2\text{H}_6(\text{g})$	+	$\text{Cl}_2(\text{g})$	\rightleftharpoons	$\text{C}_2\text{H}_5\text{Cl}(\text{s})$	+	$\text{HCl}(\text{g})$
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.)

$$K = \frac{[\text{HCl}]_0}{[\text{C}_2\text{H}_6]_0[\text{Cl}_2]_0} \quad 0.100 = \frac{(2-x)}{(2+x)(2+x)} = \frac{(2-x)}{(4+4x+x^2)}$$

$$0.100(4+4x+x^2) = (2-x)$$

$$0.4 + 0.4x + 0.1x^2 = 2 - x$$

$$0.1x^2 + 1.4x - 1.6 = 0$$

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

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

$$x = 1.062258 \quad x = -15.06226 \text{ (omit negative } x)$$

Finally, substitute x back into the mathematical expressions.

$$[\text{C}_2\text{H}_6]_{eq} = 2.00 + x = 2.00 + (1.062257748)$$

$$[\text{C}_2\text{H}_6]_{eq} = 3.06 \text{ M}$$

$$[\text{Cl}_2]_{eq} = 2.00 + x = 2.00 + (1.062257748)$$

$$[\text{Cl}_2]_{eq} = 3.06 \text{ M}$$

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

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

Verify with K :

$$K = \frac{[\text{HCl}]_0}{[\text{C}_2\text{H}_6]_0[\text{Cl}_2]_0} = \frac{(0.938)}{(3.06)(3.06)} \quad K = 0.100$$

This matches closely with the K given in the question.

Example 7: The reaction of $\text{CO}_{(g)} + \text{Cl}_2_{(g)} \rightleftharpoons \text{COCl}_2_{(g)}$ has an equilibrium constant of $K_P = 0.289$ at 450 K. The initial pressures of $\text{CO}_{(g)}$, $\text{Cl}_2_{(g)}$ and $\text{COCl}_2_{(g)}$ 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.

$$K_P = 0.289$$

$$P_{\text{CO},0} = 0.800 \text{ atm}$$

$$P_{\text{Cl}_2,0} = 0.900 \text{ atm}$$

$$P_{\text{COCl}_2,0} = 0.150 \text{ atm}$$

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

$$Q_P = \frac{P_{\text{COCl}_2,0}}{P_{\text{CO},0}P_{\text{Cl}_2,0}} = \frac{(0.150)}{(0.800)(0.900)} \quad Q_P = 0.208$$

Since $Q < K$ ($0.208 < 0.289$), *the system will shift to the product* (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.

$$P_{\text{CO},eq} = ?$$

$$P_{\text{Cl}_2,eq} = ?$$

$$P_{\text{COCl}_2,eq} = ?$$

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

	CO _(g)	+	Cl _{2(g)}	⇌	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.)

$$K_P = \frac{P_{\text{COCl}_2,eq}}{P_{\text{CO},eq}P_{\text{Cl}_2,eq}} \quad 0.289 = \frac{(0.15+x)}{(0.8-x)(0.9-x)} = \frac{(0.15+x)}{(0.72-1.7x+x^2)}$$

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

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

$$0.289x^2 - 1.4913x + 0.05808 = 0 \quad (\text{Quadratic Equation: Apply the Quadratic Formula!})$$

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

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

$$x = 5.120963266 \text{ (omit larger value - bigger than 0.800 atm and 0.900 atm)}$$

$$x = 0.0392443468$$

Verify with K :

$$K_P = \frac{P_{\text{COCl}_2,eq}}{P_{\text{CO},eq}P_{\text{Cl}_2,eq}} = \frac{(0.189)}{(0.761)(0.861)}$$

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

Finally, substitute x back into the mathematical expressions.

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

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

$$P_{\text{Cl}_2,eq} = 0.900 - x = 0.900 - (0.0392443468)$$

$$P_{\text{Cl}_2,eq} = 0.861 \text{ atm}$$

$$P_{\text{COCl}_2,eq} = 0.150 + x = 0.150 + (0.0392443468)$$

$$P_{\text{COCl}_2,eq} = 0.189 \text{ M}$$

Assignment

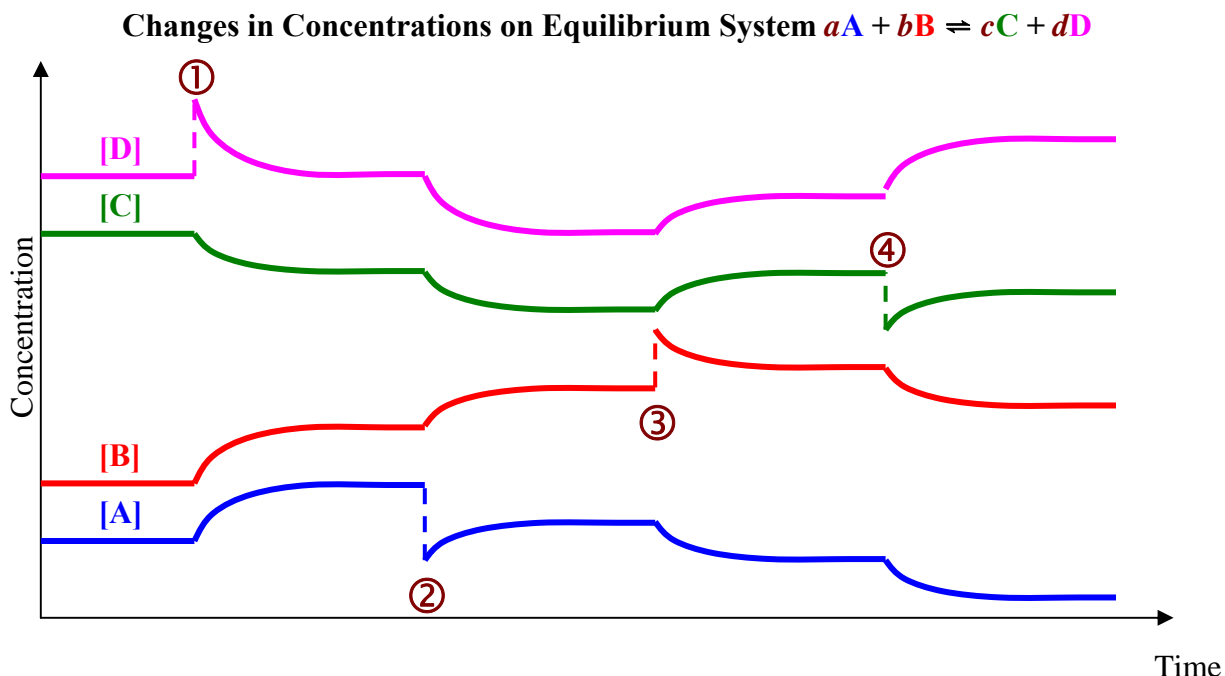
14.4 pg. 635–636 #37 to 48; pg. 637–641 #64, 70 to 78 (even), 82, 84, 108

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:

- 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.)
- 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.)

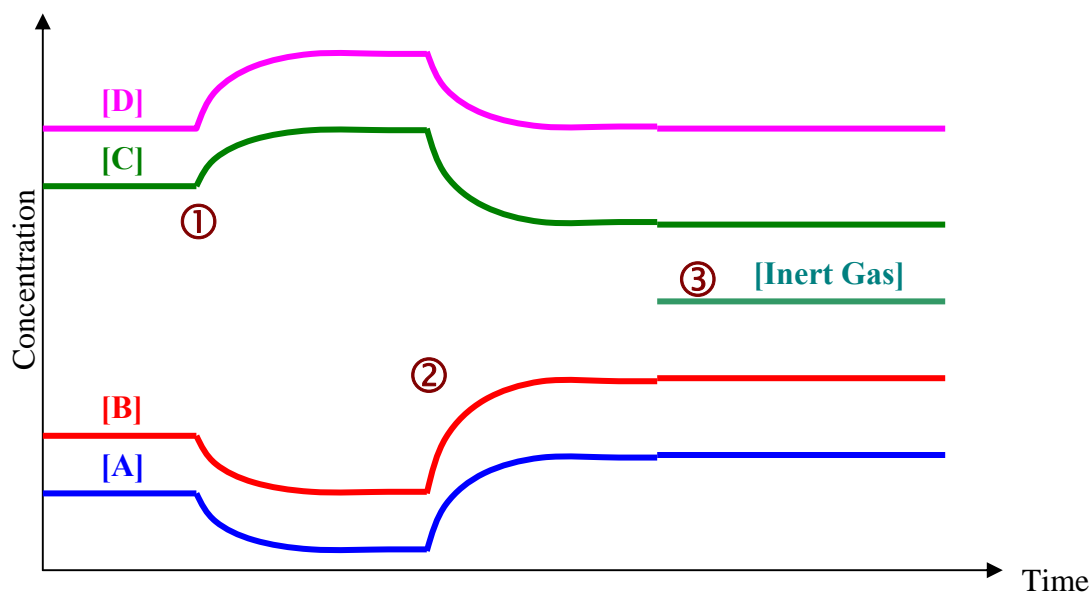


- ① **indicates an Increase in [D].** As $[D] \uparrow$, equilibrium shifts to the left ($aA + bB \rightleftharpoons cC + dD$). Hence, $[A] \uparrow$, $[B] \uparrow$, and $[C] \downarrow$.
- ② **indicates a Decrease in [A].** As $[A] \downarrow$, equilibrium shifts to the left ($aA + bB \rightleftharpoons cC + dD$). Hence, $[B] \uparrow$, $[C] \downarrow$, and $[D] \downarrow$.
- ③ **indicates an Increase in [B].** As $[B] \uparrow$, equilibrium shifts to the right ($aA + bB \rightleftharpoons cC + dD$). Hence, $[A] \downarrow$, $[C] \uparrow$, and $[D] \uparrow$.
- ④ **indicates a Decrease in [C].** As $[C] \downarrow$, equilibrium shifts to the right ($aA + bB \rightleftharpoons cC + dD$). Hence, $[A] \downarrow$, $[B] \downarrow$, and $[D] \uparrow$.

2. Effects of a Change in Pressure:

- 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.
- 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.
- 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.
- 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 $V \uparrow$, equilibrium shifts to the right ($aA + bB \rightleftharpoons cC + dD$) since there are more gaseous molecules on the product side $[(c + d) > (a + b)]$. Hence, $[A] \downarrow$, $[B] \downarrow$, $[C] \uparrow$, and $[D] \uparrow$.
- ② **indicates a Decrease in Volume.** As $V \downarrow$, equilibrium shifts to the left ($aA + bB \rightleftharpoons cC + dD$) since there are LESS gaseous molecules on the reactant side $[(c + d) > (a + b)]$. Hence, $[A] \uparrow$, $[B] \uparrow$, $[C] \downarrow$, and $[D] \downarrow$.
- 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:**

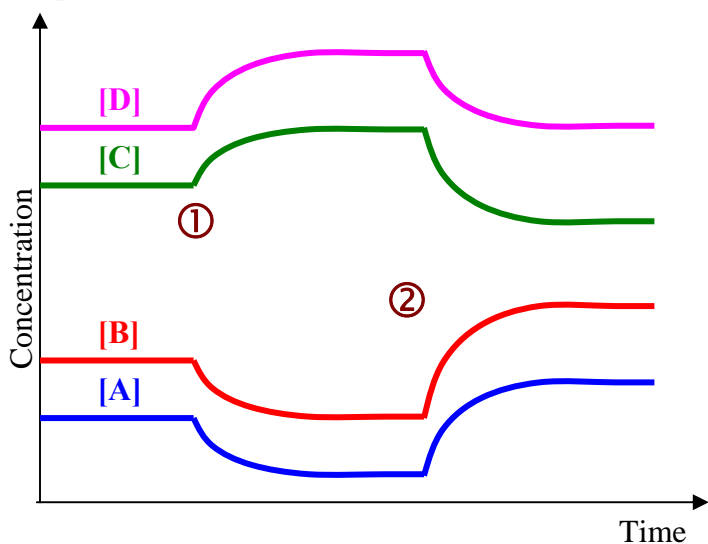


- an **Increase in Temperature** will drive the system to the left ($aA + bB \rightleftharpoons cC + dD + \text{Energy}$). There is more heat added and because energy is written on the product side, the system will shift to the opposite side to re-establish equilibrium. Hence, $[A] \uparrow$, $[B] \uparrow$, $[C] \downarrow$, and $[D] \downarrow$.
- a **Decrease in Temperature** will drive the system to the right ($aA + bB \rightleftharpoons cC + dD + \text{Energy}$). There is less heat overall and because energy is written on the product side, the system will shift to the products to compensate. Hence, $[A] \downarrow$, $[B] \downarrow$, $[C] \uparrow$, and $[D] \uparrow$.

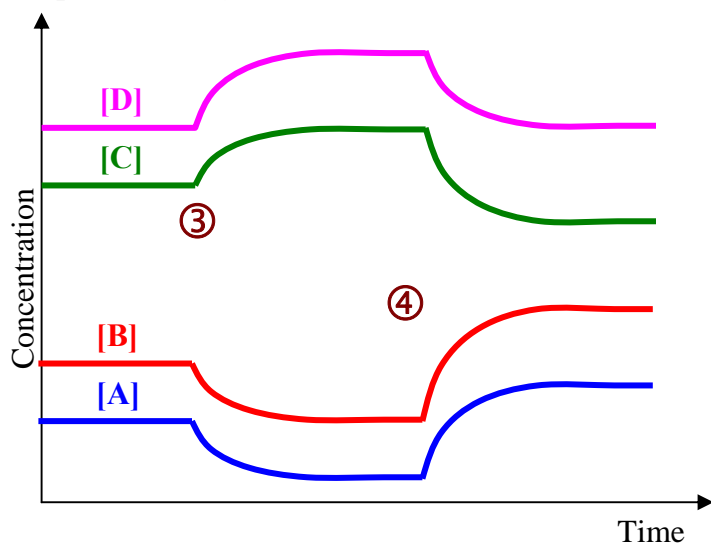
b. For **Endothermic Equilibrium System**: $aA + bB + \text{Energy} \rightleftharpoons cC + dD$

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

Changes in Temperature on an **Exothermic** Equilibrium System $aA + bB \rightleftharpoons cC + dD + \text{Energy}$



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



- ① **indicates a Decrease in Temperature.** As $T\downarrow$, equilibrium shifts to the right of an exothermic system ($aA + bB \rightleftharpoons cC + dD + \text{Energy}$). Hence, $[A]\downarrow$, $[B]\downarrow$, $[C]\uparrow$, and $[D]\uparrow$.
- ② **indicates an Increase in Temperature.** As $T\uparrow$, equilibrium shifts to the left of an exothermic system ($aA + bB \rightleftharpoons cC + dD + \text{Energy}$). Hence, $[A]\uparrow$, $[B]\uparrow$, $[C]\downarrow$, and $[D]\downarrow$.
- ③ **indicates an Increase in Temperature.** As $T\uparrow$, equilibrium shifts to the right of an endothermic reaction ($aA + bB + \text{Energy} \rightleftharpoons cC + dD$). Hence, $[A]\downarrow$, $[B]\downarrow$, $[C]\uparrow$, and $[D]\uparrow$.
- ④ **indicates a Decrease in Temperature.** As $T\downarrow$, equilibrium shifts to the left of an endothermic reaction ($aA + bB + \text{Energy} \rightleftharpoons cC + dD$). Hence, $[A]\uparrow$, $[B]\uparrow$, $[C]\downarrow$, and $[D]\downarrow$.

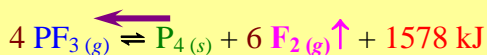
4. **Effects of Adding a Catalyst:** - *has NO CHANGE on the equilibrium system.*

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

Example 1: The equilibrium system, $4 \text{PF}_3(\text{g}) \rightleftharpoons \text{P}_4(\text{s}) + 6 \text{F}_2(\text{g}) + 1578 \text{ kJ}$, 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 $\text{F}_2(\text{g})$.

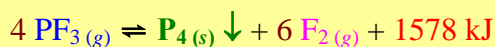
The system will shift to the LEFT.



Effect: $[\text{PF}_3] \uparrow$ (increase)

b. a decrease in the concentration of $\text{P}_4(\text{s})$

There will be NO SHIFT on the system.

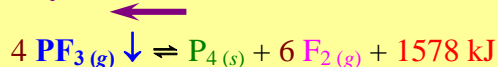


(P_4 is a pure solid and does not involve with the equilibrium system)

Effect: $[\text{PF}_3]$ and $[\text{F}_2]$ remain the same.

c. a decrease in the concentration of $\text{PF}_3(\text{g})$.

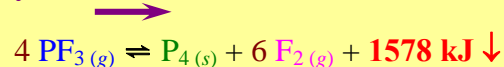
The system will shift to the LEFT.



Effect: $[\text{F}_2] \downarrow$ (decrease)

d. a decrease in Temperature.

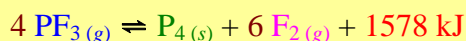
The system will shift to the RIGHT.



Effect: $[\text{PF}_3] \downarrow$ (decrease) and $[\text{F}_2] \uparrow$ (increase)

e. an addition of $\text{He}(\text{g})$.

There will be NO SHIFT on the system.

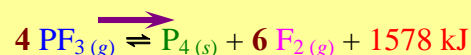


(He is an inert gas and does not involve with the equilibrium system)

Effect: $[\text{PF}_3]$ and $[\text{F}_2]$ remain the same.

f. an increase in volume.

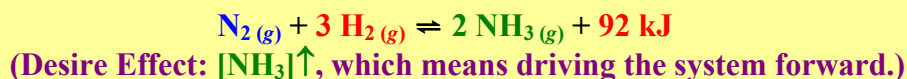
The system will shift to the RIGHT.



(There are more gaseous molecules on the product side – 6 moles of $\text{F}_2(\text{g})$ versus 4 moles of $\text{PF}_3(\text{g})$)

Effect: $[\text{PF}_3] \downarrow$ (decrease) and $[\text{F}_2] \uparrow$ (increase)

Example 2: The Haber-Bosch process, $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g}) + 92 \text{ kJ}$ 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 $\text{NH}_3(\text{g})$ produced.



1. Increase the concentrations of $\text{N}_2(\text{g})$ or $\text{H}_2(\text{g})$ or both will drive the system forward.
2. Decrease the concentration of $\text{NH}_3(\text{g})$ 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

14.5 pg. 636–640 #49 to 52, 56 to 62 (even), 65 to 69, 90, 98, 106

18.6: Free Energy and Chemical Equilibrium

Relationship between Free Energy and Pressure: - the free energy of a gas at any pressure, G , can be calculated when comparing it to the free energy at standard pressures (1 atm), G° , along with the stated temperature in Kelvin and the gas constant.

Relationship between Free Energy and Pressure

$$G = G^\circ + RT \ln(P)$$

G = Free Energy (J) of the gas at Pressure of P atm

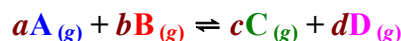
G° = Free Energy (J) of gas at Standard Pressure of 1 atm

R = Gas Constant 8.314 J/K

T = Temperature in K

P = Pressure of Gas in atm

When $P = 1$ atm, then $G = G^\circ + RT \ln(1)$ and $G = G^\circ$ because $\ln(1) = 0$

Calculating the ΔG of a System with Gaseous Products and Reactants at any Pressure, P :

$$\Delta G = cG_C + dG_D - aG_A - bG_B \quad (\Delta G = \Sigma nG_{\text{products}} - \Sigma nG_{\text{reactants}})$$

$$\Delta G = c[G^\circ_C + RT \ln(P_C)] + d[G^\circ_D + RT \ln(P_D)] - a[G^\circ_A + RT \ln(P_A)] - b[G^\circ_B + RT \ln(P_B)]$$

(Expand each term using $G = G^\circ + RT \ln(P)$)

$$\Delta G = cG^\circ_C + cRT \ln(P_C) + dG^\circ_D + dRT \ln(P_D) - aG^\circ_A - aRT \ln(P_A) - bG^\circ_B - bRT \ln(P_B)$$

(Multiply moles into each brackets)

$$\Delta G = [cG^\circ_C + dG^\circ_D - aG^\circ_A - bG^\circ_B] + cRT \ln(P_C) + dRT \ln(P_D) - aRT \ln(P_A) - bRT \ln(P_B)$$

(Collect G° terms: $[cG^\circ_C + dG^\circ_D - aG^\circ_A - bG^\circ_B] = \Delta G^\circ$)

$$\Delta G = \Delta G^\circ + RT [c \ln(P_C) + d \ln(P_D) - a \ln(P_A) - b \ln(P_B)]$$

(Take out common factor RT from other terms)

$$\Delta G = \Delta G^\circ + RT [\ln(P_C^c) + \ln(P_D^d) - \ln(P_A^a) - \ln(P_B^b)]$$

(Apply law of logarithm: $n \log x = \log x^n$)

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{P_C^c P_D^d}{P_A^a P_B^b} \right)$$

[Apply logarithm laws: $\log m + \log n = \log(mn)$ and $\log m - \log n = \log(m/n)$]

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

[Substitute Reaction Q as $\left(\frac{P_C^c P_D^d}{P_A^a P_B^b} \right)$]

Free Energy and Pressures of Gaseous System $aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

ΔG = Free Energy (J) of the gas at Pressure of P atm

ΔG° = Free Energy (J) of gas at Standard Pressure of 1 atm

R = Gas Constant 8.314 J/K

T = Temperature in K

$$Q = \text{Reaction Quotient of Gaseous Species} = \left(\frac{P_C^c P_D^d}{P_A^a P_B^b} \right)$$

When $Q = 1$, then $\Delta G = \Delta G^\circ + RT \ln(1)$ and $\Delta G = \Delta G^\circ$ because $\ln(1) = 0$

Example 1: At 25°C, the system, $2 \text{NO}_{(g)} + \text{Cl}_{2(g)} \rightleftharpoons 2 \text{NOCl}_{(g)}$ has the following partial pressures of $\text{NO}_{(g)}$, $\text{Cl}_{2(g)}$, and $\text{NOCl}_{(g)}$ are 2.40 atm, 5.30 atm and 3.25 atm respectively. Determine the change in free energy for the system at the partial pressures indicated. (G° of $\text{NO}_{(g)} = 87 \text{ kJ/mol}$, G° of $\text{Cl}_{2(g)} = 0 \text{ kJ/mol}$ and G° of $\text{NOCl}_{(g)} = 66 \text{ kJ/mol}$)

$$G^\circ_{\text{NO}} = 87 \text{ kJ/mol}$$

$$G^\circ_{\text{Cl}_2} = 0 \text{ kJ/mol}$$

$$G^\circ_{\text{NOCl}} = 66 \text{ kJ/mol}$$

$$P_{\text{NO}} = 2.40 \text{ atm}$$

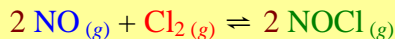
$$P_{\text{Cl}_2} = 5.30 \text{ atm}$$

$$P_{\text{NOCl}} = 3.25 \text{ atm}$$

$$T = 25^\circ\text{C} = 298.15 \text{ K}$$

$$\Delta G^\circ = ? \quad Q = ?$$

$$\Delta G = ?$$



$$\Delta G^\circ = \sum G^\circ_{\text{products}} - \sum G^\circ_{\text{reactants}}$$

$$\Delta G^\circ = [(2 \text{ mol})(66 \text{ kJ/mol})] - [(2 \text{ mol})(87 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJ/mol})]$$

$$\Delta G^\circ = -42 \text{ kJ} = -4.2 \times 10^4 \text{ J} \quad (\Delta G^\circ < 0; \text{Forward Reaction is Spontaneous})$$

$$Q = \frac{P_{\text{NOCl}}^2}{P_{\text{NO}}^2 P_{\text{Cl}_2}} = \frac{(3.25)^2}{(2.40)^2 (5.30)} \quad Q = 0.3459938417$$

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

$$\Delta G = (-4.2 \times 10^4 \text{ J}) + (8.314 \text{ J/K})(298.15 \text{ K}) \ln(0.3459938417)$$

$$\Delta G = -44630.85574 \text{ J}$$

$$\Delta G = -45 \text{ kJ}$$

(It became **more spontaneous towards the product side**. This probably means that $Q < K$ or $K > 0.346$)

Example 2: At 25°C, the system, $\text{H}_2\text{O}_{(g)} + \text{Cl}_2\text{O}_{(g)} \rightleftharpoons 2 \text{HOCl}_{(g)}$ has the following partial pressures of $\text{H}_2\text{O}_{(g)}$, $\text{Cl}_2\text{O}_{(g)}$, and $\text{HOCl}_{(g)}$ are 0.350 atm, 0.220 atm and 0.860 atm respectively. Determine the change in free energy for the system at the partial pressures indicated. (G° of $\text{H}_2\text{O}_{(g)} = -229 \text{ kJ/mol}$, G° of $\text{Cl}_2\text{O}_{(g)} = 98 \text{ kJ/mol}$ and G° of $\text{HOCl}_{(g)} = 0 \text{ kJ/mol}$)

$$G^\circ_{\text{H}_2\text{O}} = -229 \text{ kJ/mol}$$

$$G^\circ_{\text{Cl}_2\text{O}} = 98 \text{ kJ/mol}$$

$$G^\circ_{\text{HOCl}} = 0 \text{ kJ/mol}$$

$$P_{\text{H}_2\text{O}} = 0.350 \text{ atm}$$

$$P_{\text{Cl}_2\text{O}} = 0.220 \text{ atm}$$

$$P_{\text{HOCl}} = 0.860 \text{ atm}$$

$$T = 25^\circ\text{C} = 298.15 \text{ K}$$

$$\Delta G^\circ = ? \quad Q = ?$$

$$\Delta G = ?$$



$$\Delta G^\circ = \sum G^\circ_{\text{products}} - \sum G^\circ_{\text{reactants}}$$

$$\Delta G^\circ = [(2 \text{ mol})(0 \text{ kJ/mol})] - [(1 \text{ mol})(-229 \text{ kJ/mol}) + (1 \text{ mol})(98 \text{ kJ/mol})]$$

$$\Delta G^\circ = 131 \text{ kJ} = 1.31 \times 10^5 \text{ J} \quad (\Delta G^\circ > 0; \text{Forward Reaction is Non-spontaneous})$$

$$Q = \frac{P_{\text{HOCl}}^2}{P_{\text{H}_2\text{O}} P_{\text{Cl}_2\text{O}}} = \frac{(0.860)^2}{(0.350)(0.220)} \quad Q = 9.605194805$$

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

$$\Delta G = (1.31 \times 10^5 \text{ J}) + (8.314 \text{ J/K})(298.15 \text{ K}) \ln(9.605194805) = 136608.1798 \text{ J}$$

$$\Delta G = 137 \text{ kJ}$$

(It became **more spontaneous towards the reactants (even more non-spontaneous towards the product side)**. This probably means that $Q > K$ or $K < 9.605194805$)

- Equilibrium Point:** - the point where the system attains **thermodynamic equilibrium** – *the lowest value of free energy available to the equilibrium system.*
- this occurs when $Q = K_P$ and $\Delta G = 0$ at certain partial pressures.
 - we can use equilibrium point to calculate the value of the equilibrium constant K from ΔG°

Equilibrium Point ($Q = K_P$ and $\Delta G = 0$) of a Gaseous System $aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$

$$0 = \Delta G^\circ + RT \ln(K) \quad \text{or} \quad \Delta G^\circ = -RT \ln(K)$$

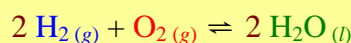
$\Delta G^\circ =$ Free Energy (J) of gas at **Standard Pressure of 1 atm** $R =$ Gas Constant 8.3145 J/K

$$K_P = \text{Equilibrium Constant of Gaseous System} = \left(\frac{P_{C,eq}^c P_{D,eq}^d}{P_{A,eq}^a P_{B,eq}^b} \right) \quad T = \text{Temperature in K}$$

Qualitative Relationship between ΔG and K_P : $\Delta G^\circ = -RT \ln(K_P)$

$K_P > 1$	$\ln(K_P) > 0$ (Positive)	$\Delta G^\circ < 0$ (Negative)	Products are favoured over the Reactants (Forward Reaction is Spontaneous)
$K_P = 1$	$\ln(K_P) = 0$	$\Delta G^\circ = 0$	Products and Reactants are Equally favoured
$K_P < 1$	$\ln(K_P) < 0$ (Negative)	$\Delta G^\circ > 0$ (Positive)	Reactants are favoured over the Products (Reverse Reaction is Spontaneous)

Example 3: Calculate the equilibrium constant of the formation of water at 25.0°C. (G° of $H_{2(g)}$ = 0 kJ/mol, G° of $O_{2(g)}$ = 0 kJ/mol and G° of $H_2O_{(l)}$ = -237 kJ/mol)



$$\Delta G^\circ = \sum G^\circ_{\text{products}} - \sum G^\circ_{\text{reactants}}$$

$$\Delta G^\circ = [(2 \text{ mol})(-237 \text{ kJ/mol})] - [(2 \text{ mol})(0 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJ/mol})]$$

$$\Delta G^\circ = -474 \text{ kJ} = -4.74 \times 10^5 \text{ J} \quad (\Delta G^\circ < 0; \text{Forward Reaction is Spontaneous})$$

$\Delta G^\circ = -RT \ln(K_P)$ at thermodynamic equilibrium

$$\ln(K_P) = -\frac{\Delta G^\circ}{RT} = \frac{-(-4.74 \times 10^5 \text{ J})}{(8.3145 \text{ J/K})(298.15 \text{ K})} = 191.2085862$$

$$K_P = e^{191.2085862}$$

$$K_P = 1.10 \times 10^{83}$$

Since $K_P \gg 1$, the equilibrium is **extremely favourable towards the product** at 25°C. This is in agreement with the conclusion made using the thermodynamic quantity of $\Delta G^\circ \ll 0$.

Example 4: Given that $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$ has the following thermodynamic values, calculate ΔG° and K_P of the given equilibrium at 25.0°C .

Chemicals	H° (kJ/mol)	S° [J/(K • mol)]
$\text{N}_2(\text{g})$	0	192
$\text{H}_2(\text{g})$	0	131
$\text{NH}_3(\text{g})$	-46	193

$$\Delta H^\circ = \sum H^\circ_{\text{products}} - \sum H^\circ_{\text{reactants}} = [(2 \text{ mol})(-46 \text{ kJ/mol})] = -92 \text{ kJ}$$

$$\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

$$\Delta S^\circ = [(2 \text{ mol})(193 \text{ J/(K • mol)})] - [(1 \text{ mol})(192 \text{ J/(K • mol)}) + (3 \text{ mol})(131 \text{ J/(K • mol)})] = -199 \text{ J/K}$$

$$\Delta H^\circ = -92 \text{ kJ} = -92000 \text{ J}$$

$$\Delta S^\circ = -199 \text{ J/K}$$

$$T = 25.0^\circ\text{C} = 298.15 \text{ K}$$

$$\Delta G^\circ = ?$$



$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = (-92000 \text{ J}) - (298.15 \text{ K})(-199 \text{ J/K}) = -32668.15 \text{ J}$$

$$\Delta G^\circ = -3.3 \times 10^4 \text{ J at } 25.0^\circ\text{C}$$

Since $\Delta G^\circ < 0$, the **Forward Reaction is Spontaneous**

$$R = 8.3145 \text{ J/K}$$

$$\Delta G^\circ = -32.66815 \text{ kJ} = -32668.15 \text{ J}$$

$$K_P = ?$$

$$\Delta G^\circ = -RT \ln(K_P) \text{ at thermodynamic equilibrium}$$

$$\ln(K_P) = -\frac{\Delta G^\circ}{RT} = \frac{-(-32668.15 \text{ J})}{(8.3145 \text{ J/K})(298.15 \text{ K})}$$

$$\ln(K_P) = 13.178124$$

$$K_P = e^{13.178124} = 528672.2741$$

$$K_P = 5.3 \times 10^5$$

As we can see $K_P \gg 1$, which indicates the equilibrium is **favouring the product** at 25°C . This is in agreement with the conclusion made using the thermodynamic quantity of $\Delta G^\circ < 0$.

Temperature Dependence on K_P :

$$-RT \ln(K_P) = \Delta G^\circ$$

(Start with Free Energy Formula with Equilibrium Constant)

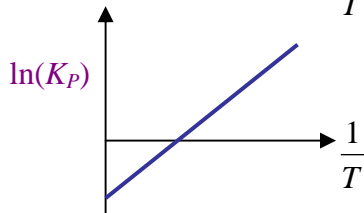
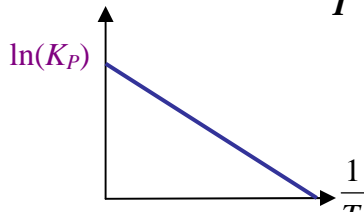
$$-RT \ln(K_P) = \Delta H^\circ - T\Delta S^\circ$$

(Substitute ΔG° with $\Delta H^\circ - T\Delta S^\circ$)

$$\ln(K_P) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

(Divide both sides by $-RT$ and simplify)

Graphs of $\ln(K_P)$ versus $\frac{1}{T}$



$$\ln(K_P) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R}$$

\uparrow \uparrow \uparrow \uparrow
 y m x b

When $\ln(K_P)$ is graphed against $(1/T)$:

$$\Delta H^\circ = -\text{slope} \times R$$

$$\Delta S^\circ = (\text{y-intercept}) \times R$$

$m < 0$ when $\Delta H^\circ > 0$ (negative slope if system is endothermic)

$m > 0$ when $\Delta H^\circ < 0$ (positive slope if system is exothermic)

$b < 0$ when $\Delta S^\circ < 0$ (negative y-int if system becomes less random)

$b > 0$ when $\Delta S^\circ > 0$ (positive y-int if system becomes more random)

Example 5: The equilibrium constant of the system, $2 \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$, is allowed to varied with the change in temperature. The experimental data are shown below.

Temperature	Equilibrium Constant (K_P)
373 K	0.067
273 K	58
195 K	1.4×10^6
77 K	3.8×10^{29}

- Complete the table below.
- Graph $\ln(K_P)$ versus $1/T$. Determine the slope and y-intercept of the graph using linear regression of your graphing calculator.
- Calculate the ΔH° and ΔS° of this equilibrium system.
- Comment on the thermodynamic spontaneity of the equilibrium system at various temperatures.

Temperature	Equilibrium Constant (K_P)	$1/T$ (K^{-1})	$\ln(K_P)$
373 K	0.067		
273 K	58		
195 K	1.4×10^6		
77 K	3.8×10^{29}		

a. Using the TI-83 Plus Calculator, we can enter the experimental results in the STATS Editor and quickly manipulate the data.

1. Enter Values in the L_1 and L_2 Columns of Stats Editor

STAT

ENTER

L1	L2	L3	2
373	.067	-----	
273	58	-----	
195	1.4E6	-----	
77	3.8E29	-----	
-----	-----	-----	

L2(5) =

2. Enter " $1/L_1$ " in the heading of L_3 .
Enter " $\ln(L_2)$ " in the heading of L_4 .

L1	L2	L3	3
373	.067	.00268	
273	58	.00366	
195	1.4E6	.00513	
77	3.8E29	.01299	
-----	-----	-----	

L3 = "1/L1"

Cursor must be on the column heading before entering formula

L2	L3	L4	4
.067	.00268	-2.703	
58	.00366	4.0604	
1.4E6	.00513	14.152	
3.8E29	.01299	68.11	
-----	-----	-----	

L4 = "ln(L2)"

" must be used to enter formula

ALPHA

MEM "

+

To access L_2 , press

2nd

L2

2

3. Fill in the Table

Temperature	Equilibrium Constant (K_P)	$1/T$ (K^{-1})	$\ln(K_P)$
373 K	0.067	0.00268	-2.703
273 K	58	0.00366	4.0604
195 K	1.4×10^6	0.00513	14.152
77 K	3.8×10^{29}	0.01299	68.110

b. Graph $\ln(K_p)$ versus $1/T$. Determine the **slope** and **y-intercept** of the graph using linear regression of your graphing calculator.

1. Turn On STATS PLOT

2nd STAT PLOT ENTER

Y=

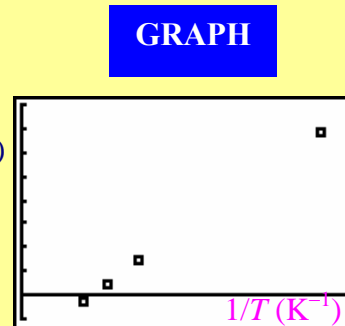
To access L₃, press 2nd L3 3

To access L₄, press 2nd L4 4

2. Set WINDOW

WINDOW x: [0, 0.014, 0.002] y: [-10, 80, 10]

3. Graph



$\ln(K_p)$ versus $(1/T)$ Graph forms a Straight Line.

We can use the linear regression function of the calculator to find the value of the **slope** and **y-intercept** for calculating ΔH° and ΔS° respectively.

1. Turn Diagnostic On

2nd CATALOG 0

ENTER

Again

ENTER

Select DiagnosticOn

Note: After **DiagnosticOn** is selected; it will remain ON even when the calculator is turned Off. However, resetting the calculator will turn the Diagnostic Off (factory setting).

2. Obtain LinReg ($ax + b$) L₃, L₄, Y₁. Copy Equation to Y= Screen, and Graph Least Square Line on Scatter Plot.

STAT Select CALC, use

ENTER 2nd L3 3

To access Y₁, press VARS

Select Option 1 for Y₁

Choose Option 4 Linear Regression ($ax + b$)

2nd L4 4

ENTER

ENTER

```
DiagnosticOn Done
LinReg(ax+b) L3,
L4, Y1
```

```
LinReg
y=ax+b
a=6869.828267
b=-21.10277046
r^2=.9999996856
r=.9999998428
```

Y= Be Sure Plot1 is On

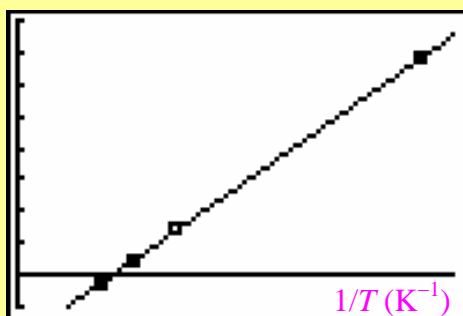
```
Y1=6869.8282669
823x+ -21.1027704
55077
Y2=
Y3=
Y4=
Y5=
```

When r is extremely close to ± 1 , it indicates the line has a linear relationship.

GRAPH

$\ln(K_P)$

x: [0, 0.014, 0.002]
y: [-10, 80, 10]



$$y = 6869.8282669823x - 21.102770455077$$

compares to

$$\ln(K_P) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R}$$

$$\text{slope} = 6869.8282669823 \text{ K}$$

$$\text{y-intercept} = -21.102770455077$$

c. Calculate the ΔH° and ΔS° of this equilibrium system.

$$-\frac{\Delta H^\circ}{R} = \text{slope}$$

$$\Delta H^\circ = -(\text{slope})R = -(6869.8282669823 \text{ K})(8.3145 \text{ J/K}) = -57119.18713 \text{ J}$$

$$\Delta H^\circ = -57 \text{ kJ}$$

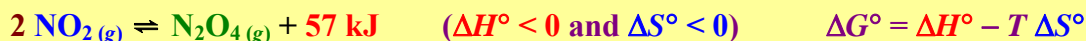
$$\frac{\Delta S^\circ}{R} = \text{y-intercept}$$

$$\Delta S^\circ = (\text{y-int})R = (-21.102770455077)(8.3145 \text{ J/K}) = -175.4589849 \text{ J/K}$$

$$\Delta S^\circ = -0.18 \text{ kJ/K}$$

For the equilibrium system, $2 \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$, it makes sense that $\Delta S^\circ < 0$ because it is proceeding from two molecules of gas to one molecule of gas.

d. Comment on the thermodynamic spontaneity of the equilibrium system at various temperatures.



At LOW Temperature, $\Delta G^\circ < 0$ (Spontaneous Forward Reaction) because $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$ ($- = (-) - \text{small } (-)$). This agrees with the fact that $K_P \gg 1$ at Low Temperature, which indicates that the system favors the product side. (Applying *Le Châtelier's Principle* will conclude that that at Low Temperature, $[\text{N}_2\text{O}_4] \uparrow$ and $[\text{NO}_2] \downarrow$)

At HIGH Temperature, $\Delta G^\circ > 0$ (Spontaneous Reverse Reaction) because $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$ ($- = (-) - \text{big } (-)$). This agrees with the fact that $K_P < 1$ at High Temperature, which indicates that the system favors the reactant side. (Applying *Le Châtelier's Principle* will conclude that at High Temperature, $[\text{N}_2\text{O}_4] \downarrow$ and $[\text{NO}_2] \uparrow$)

Assignment

18.6 pg. 811–814 #21, 22, 24, 26 to 32, 49, 64, 66, 76, 80