

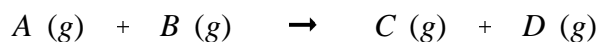
## IV. Chemical Equilibrium

### A) Law of Chemical Equilibrium

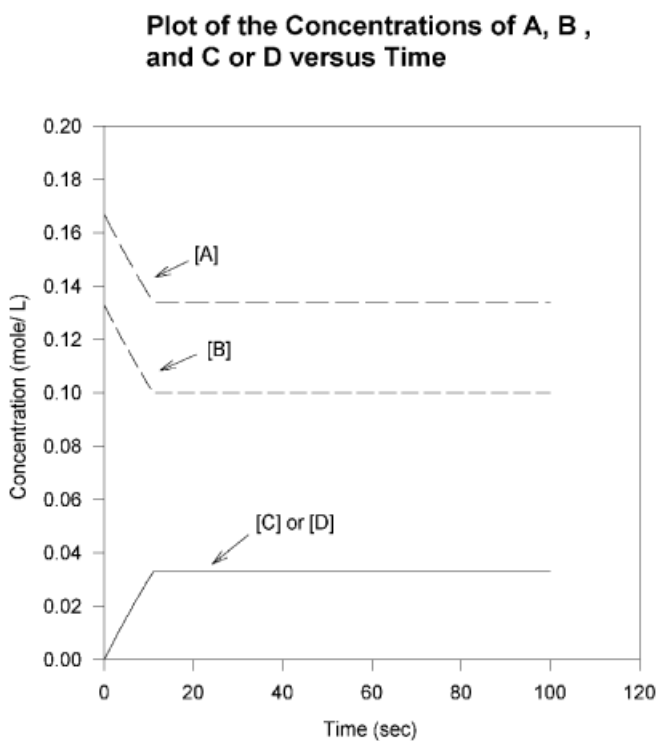
Concentration expressed as molarity

$$\text{Molarity of A} = [A] = \frac{\text{moles of A}}{\text{volume in liters}} \quad \text{units: } \frac{\text{mole}}{\text{L}} = M$$

Consider the hypothetical reaction

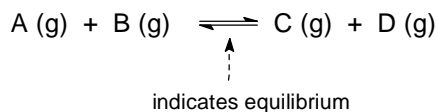


Compound A is allowed to react with B and the concentrations of the reactants and products are plotted as a function of time.



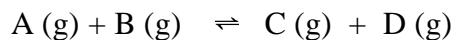
Note: After eleven seconds the concentrations do not change with time.

Chemical equilibrium is the condition that exists when the concentrations of the reactants and products no longer change with time. Chemical equilibrium is a dynamic state. It occurs when the rate of the forward reaction ( $A + B \rightarrow C + D$ ) equals the rate of the reverse reaction ( $A + B \leftarrow C + D$ ).



At equilibrium there is a specific relationship between the concentrations of the reactants and products.

Consider three experiments for the reaction



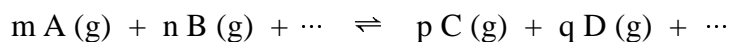
in which the initial concentrations of A and B vary from experiment to experiment.

Table of Equilibrium Concentrations				
Exp. #	$[A]_{eq}$	$[B]_{eq}$	$[C]_{eq}$	$[D]_{eq}$
1	3.00	2.00	1.00	1.00
2	9.60	10.0	4.00	4.00
3	0.500	3.00	0.500	0.500

The following relationship fits the data in each experiment.

$$\frac{[C]_{eq} [D]_{eq}}{[A]_{eq} [B]_{eq}} = 0.167 = \text{constant} = K_c$$

For the general reaction



$K_c$  is defined

$$\frac{[C]_{eq}^p [D]_{eq}^q \dots}{[A]_{eq}^m [B]_{eq}^n \dots} = K_c$$

The magnitude of the constant  $K_c$  depends on the nature of the reaction and the temperature.

The units of  $K_c$  depend on the specific reaction.

**Example:**  $A + 3 B \rightleftharpoons 2 C$

$$K_c = \frac{[C]_{eq}^2}{[A]_{eq} [B]_{eq}^3} \quad \text{units: } \frac{\left[\frac{\text{mole}}{L}\right]^2}{\left[\frac{\text{mole}}{L}\right]^4} = \left[\frac{L}{\text{mole}}\right]^2$$

**Example:**  $A + B \rightleftharpoons C + D$

$$K_c = \frac{[C]_{eq} [D]_{eq}}{[A]_{eq} [B]_{eq}} \quad \text{units: } \frac{\left[\frac{\text{mole}}{\text{L}}\right]^2}{\left[\frac{\text{mole}}{\text{L}}\right]^2} = \text{unitless}$$

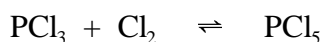
Terms:

When  $K < 1$ , then the equilibrium is said to lie to the *left*.

When  $K > 1$ , then the equilibrium is said to lie to the *right*.

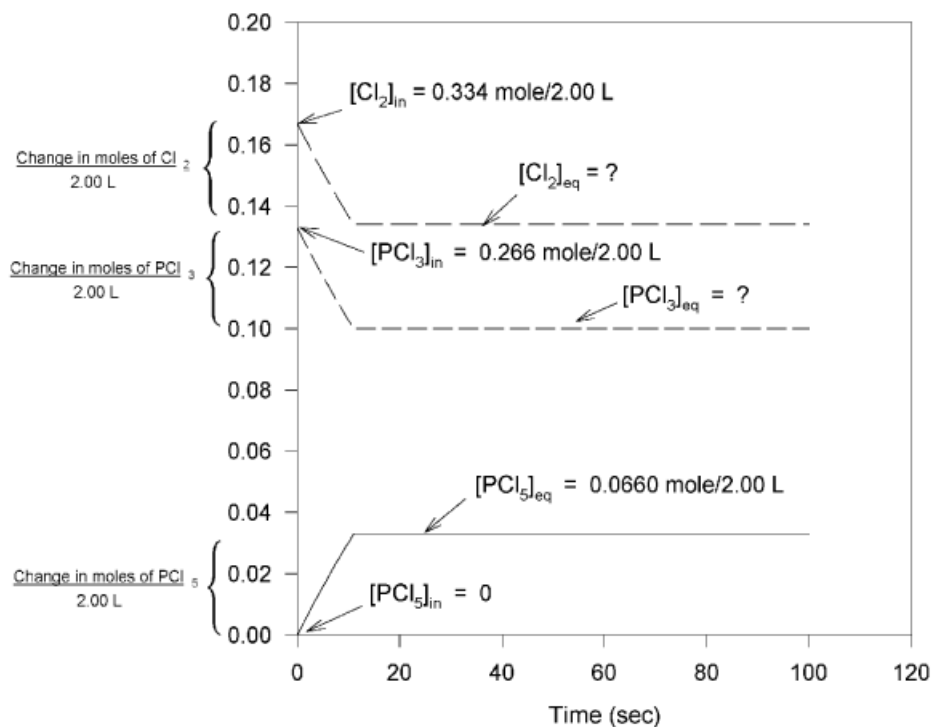
## B) Equilibrium Calculations

**Example #1:** Initially, 0.2660 mole of  $\text{PCl}_3$  and 0.3340 mole of  $\text{Cl}_2$  are placed in a 2.00 L container at  $300^\circ\text{C}$ . If the moles of  $\text{PCl}_5$  are found experimentally to be 0.0660 at equilibrium, calculate  $K_c$  for the reaction



at  $300^\circ\text{C}$ .

**Plot of the Concentrations of  $\text{PCl}_3$ ,  $\text{Cl}_2$ , and  $\text{PCl}_5$  versus Time**



where  $[A]_{in}$  is the initial (at time = 0) molarity of A and  $[A]_{eq}$  is the equilibrium molarity of A

### Important observations from the above plot

- *Initial moles of a substance + change in moles of substance = equilibrium moles of substance*

**Example:**

$$\text{initial moles of } \text{PCl}_5 + \text{change in moles of } \text{PCl}_5 = \text{equilibrium moles of } \text{PCl}_5$$

$$0.0 \text{ moles of } \text{PCl}_5 + 0.0660 \text{ moles of } \text{PCl}_5 = 0.0660 \text{ moles of } \text{PCl}_5$$

- *The changes in number of moles of reactants and products are related by **mole ratios**.*

These observations can be utilized in an Equilibrium Table to solve equilibrium problems.

**Equilibrium Table**

	$\text{PCl}_3$	+	$\text{Cl}_2$	$\rightleftharpoons$	$\text{PCl}_5$	
initial:	0.2660		0.3340		0.0	mole
change:	-0.0660		-0.0660		0.0660	mole
equil:	0.2000		0.2680		0.0660	mole

Change in moles of  $\text{PCl}_5$  = (equilibrium moles  $\text{PCl}_5$ ) - (initial moles of  $\text{PCl}_5$ )

Negative sign indicates moles of  $\text{Cl}_2$  are consumed

Change in moles of  $\text{Cl}_2$  = (change in moles  $\text{PCl}_5$ )(1 mole  $\text{Cl}_2$  / 1 mole  $\text{PCl}_5$ )

Equilibrium moles of  $\text{Cl}_2$  = (initial moles  $\text{Cl}_2$ ) + (change in moles  $\text{Cl}_2$ )

Substituting the equilibrium moles into the equilibrium expression

$$K_c = \frac{[\text{PCl}_5]_{eq}}{[\text{PCl}_3]_{eq} [\text{Cl}_2]_{eq}} = \frac{\left[\frac{0.0660 \text{ mole}}{2.00 \text{ L}}\right]}{\left[\frac{0.200 \text{ mole}}{2.00 \text{ L}}\right] \left[\frac{0.268 \text{ mole}}{2.00 \text{ L}}\right]} = 2.46 \frac{\text{L}}{\text{mole}}$$

**Example #2:** Initially, 3.00 moles of  $\text{PCl}_3$  and 3.00 moles of  $\text{Cl}_2$  are placed in a 5.00 L container at  $300^\circ\text{C}$ . Calculate the equilibrium concentration of  $\text{PCl}_5$ ,  $[\text{PCl}_5]_{eq}$ .  $K_c$  is 2.46 L/mole.

Unknown:  $[\text{PCl}_5]_{eq}$ , Let  $x$  = moles of  $\text{PCl}_5$  at equilibrium.

Knowns: initial moles of  $\text{PCl}_3$  = 3.00 mole, initial moles of  $\text{Cl}_2$  = 3.00 mole, volume of container =

$$5.00\text{L}, K_c = 2.46 \text{ L/mole}$$

Concepts: chemical equilibrium, molarity

Substitute known values into equilibrium table.

	$\text{PCl}_3$	+	$\text{Cl}_2$	$\rightleftharpoons$	$\text{PCl}_5$	
initial	3.00		3.00		0	mole
<u>change</u>						<u>mole</u>
equil					x	mole

Use the concepts presented above to fill in the table.

	$\text{PCl}_3$	+	$\text{Cl}_2$	$\rightleftharpoons$	$\text{PCl}_5$	
initial	3.00		3.00		0	mole
<u>change</u>	- x		- x		x	<u>mole</u>
equil	3.00 - x		3.00 - x		x	mole

Substituting equilibrium moles into the equilibrium expression

$$K_c = \frac{[\text{PCl}_5]_{eq}}{[\text{PCl}_3]_{eq} [\text{Cl}_2]_{eq}} = \frac{\left[\frac{x}{5.00\text{L}}\right]}{\left[\frac{3.00-x}{5.00\text{L}}\right] \left[\frac{3.00-x}{5.00\text{L}}\right]} = 2.46 \frac{\text{L}}{\text{mole}}$$

$$2.46x^2 - 19.76x + 22.14 = 0$$

For the quadratic equation

$$ax^2 + bx + c = 0$$

the solutions are

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Substituting

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(-19.76) \pm \sqrt{(-19.76)^2 - 4(2.46)(22.14)}}{2(2.46)}$$

$$x = 1.35, 6.67$$

Although both roots (1.35 and 6.67) are mathematically correct, only one root satisfies the physical constraints of the problem and that root is 1.35. If root 6.67 is used, then the moles of  $\text{PCl}_3$  and  $\text{Cl}_2$  at equilibrium would be - 3.67 (3.00 - 6.67) and the equilibrium concentrations of  $\text{PCl}_3$  and  $\text{Cl}_2$  would be - 0.734 M. A negative or zero equilibrium concentration for reactants or products is physically impossible.

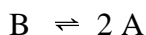
$$x = 1.35 \text{ mole} = \text{moles of } PCl_5 \text{ at equilibrium}$$

$$[PCl_5]_{eq} = \frac{x}{5.00L} = \frac{1.35 \text{ mole}}{5.00L}$$

$$[PCl_3]_{eq} = \frac{(3.00-x)}{5.00L} = \frac{(3.00-1.35)}{5.00L} = \frac{1.65 \text{ mole}}{5.00L}$$

$$[Cl_2]_{eq} = \frac{1.65 \text{ mole}}{5.00L}$$

The degree of dissociation,  $\alpha$ , of B



is defined as

$$\alpha = \frac{\text{change in moles of } B}{\text{initial moles of } B}$$

and the percent dissociation is  $(\alpha)(100)$ .

**Example #3:** If 3.00 moles of B are placed in a 1.00 L flask at 25°C, calculate the degree of dissociation,  $\alpha$ , of B.  $K_c$  for B at 25°C is 0.100 mole/L.

Unknown: change in moles of B. Let  $x$  = change in moles of B

Knowns: initial moles of B = 3.00 mole, volume of flask = 1.00 L,  $K_c = 0.100$  mole/L

Concepts: chemical equilibrium, degree of dissociation

Substitute known values into the equilibrium table.

	B	$\rightleftharpoons$	2 A	
initial	3.00		0	mole
<u>change</u>	<u>- x</u>			<u>mole</u>
equil				mole

The reaction must go to the right in order to produce A. Moles of B will be consumed and thus, the change in moles of B will be -x.

Use the concepts presented above to fill in the table.

	B	$\rightleftharpoons$	2 A	
initial	3.00		0	mole
<u>change</u>	<u>- x</u>		<u>2 x</u>	<u>mole</u>
equil	3.00 - x		2 x	mole

Substitute equilibrium moles into the equilibrium expression.

$$K_c = \frac{[A]_{eq}^2}{[B]_{eq}} = \frac{\left[\frac{2x}{1.00L}\right]^2}{\left[\frac{3.00-x}{1.00L}\right]} = 0.100 \frac{\text{mole}}{L}$$

$$4.00x^2 + 0.100x - 0.300 = 0$$

$$x = 0.261, -0.287$$

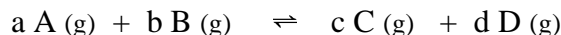
$$x = 0.261 \text{ mole} = \text{change in moles of B}$$

$$\alpha = \frac{\text{change in moles of B}}{\text{initial moles of B}} = \frac{x}{3.00 \text{ mole}} = \frac{0.261 \text{ mole}}{3.00 \text{ mole}} = 8.70 \cdot 10^{-2}$$

### C) Factors Affecting Equilibrium Concentrations at Constant Temperature

Le Châtelier's principle - when a system is in equilibrium, a change in any one of the factors upon which the equilibrium depends will cause the equilibrium to shift in such a way as to diminish the effect of the change.

To determine if the reaction



will go to the left or to the right to reestablish the equilibrium,  $Q$  is defined as

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

If  $Q < K_c$ , then the reaction will go to the *right* to reestablish the equilibrium. Moles of reactants A and B will be consumed and moles of products C and D will be produced.

If  $Q > K_c$ , then the reaction will go to the *left* to reestablish the equilibrium. Moles of products C and D will be consumed and moles of reactants A and B will be produced.

#### 1) Addition or Removal of Moles of Reactants or Products

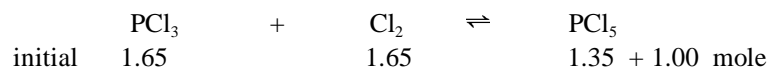
**Example #4:** If 1.00 mole of  $\text{PCl}_5$  is added to the equilibrium in Example #2, what will be the NEW equilibrium concentration of  $\text{PCl}_5$ ?

Unknown: new equilibrium molarity of  $\text{PCl}_5$  after the addition of 1.00 mole of  $\text{PCl}_5$

Knowns: *equilibrium* moles of  $\text{PCl}_3$ ,  $\text{Cl}_2$ , and  $\text{PCl}_5$  (1.65, 1.65, and 1.35 mole) *before* the addition of 1.00 mole of  $\text{PCl}_5$  (see Example #2);  $K_c = 2.46 \text{ L/mole}$ ; volume of the container = 5.00 L

Concepts: chemical equilibrium, Q, molarity

*Step #1: Evaluate Q and determine whether the reaction will go to the left or right to reestablish the equilibrium.*



The moles in the table are the equilibrium values from **Example #2** and the 1.00 mole of PCl<sub>5</sub> added.

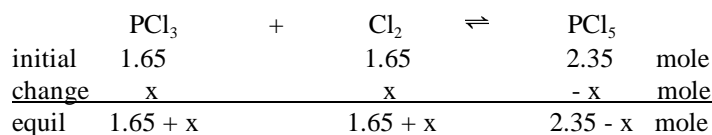
$$Q = \frac{[PCl_5]_{in}}{[PCl_3]_{in} [Cl_2]_{in}} = \frac{\left[\frac{(2.35 \text{ mole})}{5.00L}\right]}{\left[\frac{(1.65 \text{ mole})}{5.00L}\right] \left[\frac{(1.65 \text{ mole})}{5.00L}\right]} = 4.31 \frac{L}{\text{mole}}$$

$$Q = 4.31 \frac{L}{\text{mole}} > 2.46 \frac{L}{\text{mole}} = K_c$$

Since  $Q > K_c$ , the reaction will go to the left to reestablish the equilibrium. Moles of PCl<sub>5</sub> will be consumed and moles of PCl<sub>3</sub> and Cl<sub>2</sub> will be produced.

*Step #2: Solve the equilibrium problem.*

Let  $x$  = change in moles of PCl<sub>5</sub>. Since the reaction goes to the left to reestablish the equilibrium, moles of PCl<sub>5</sub> will be consumed and the entry for PCl<sub>5</sub> in the row labeled “change” of the equilibrium table will be  $-x$ .



$$K_c = \frac{[PCl_5]_{eq}}{[PCl_3]_{eq} [Cl_2]_{eq}} = \frac{\left[\frac{2.35 - x}{5.00L}\right]}{\left[\frac{1.65 + x}{5.00L}\right] \left[\frac{1.65 + x}{5.00L}\right]} = 2.46 \frac{L}{\text{mole}}$$

$$0.492x^2 - 2.624x + 1.010 = 0$$

$$x = 0.361 \text{ mole} = \text{change in moles of PCl}_5$$

$$[PCl_5]_{eq} = \frac{(2.35 \text{ mole} - x)}{5.00 \text{ L}} = \frac{(2.35 \text{ mole} - 0.36 \text{ mole})}{5.00 \text{ L}} = \frac{1.99 \text{ mole}}{5.00 \text{ L}}$$

## 2) Change in Volume of the Container

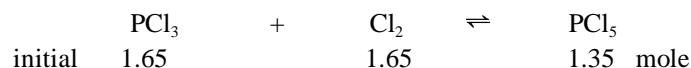
**Example #5:** If the volume of the container in Example #2 is decreased from 5.00 L to 2.00 L, will the moles of  $PCl_5$  at the NEW equilibrium be greater or less than the moles of  $PCl_5$  in Example #2?

Unknown: new equilibrium moles of  $PCl_5$  after the volume of the container in Example #2 is reduced to 2.00 L

Knowns: equilibrium moles of  $PCl_3$ ,  $Cl_2$  and  $PCl_5$  in Example #2, new volume = 2.00 L,  $K_c = 2.46 \text{ L/mole}$

Concept:  $Q$ , molarity

### Step #1



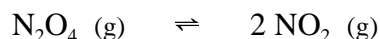
$$Q = \frac{[PCl_5]_{in}}{[PCl_3]_{in} [Cl_2]_{in}} = \frac{\left[\frac{1.35 \text{ mole}}{2.00 \text{ L}}\right]}{\left[\frac{1.65 \text{ mole}}{2.00 \text{ L}}\right] \left[\frac{1.65 \text{ mole}}{2.00 \text{ L}}\right]} = 0.992 \frac{\text{L}}{\text{mole}}$$

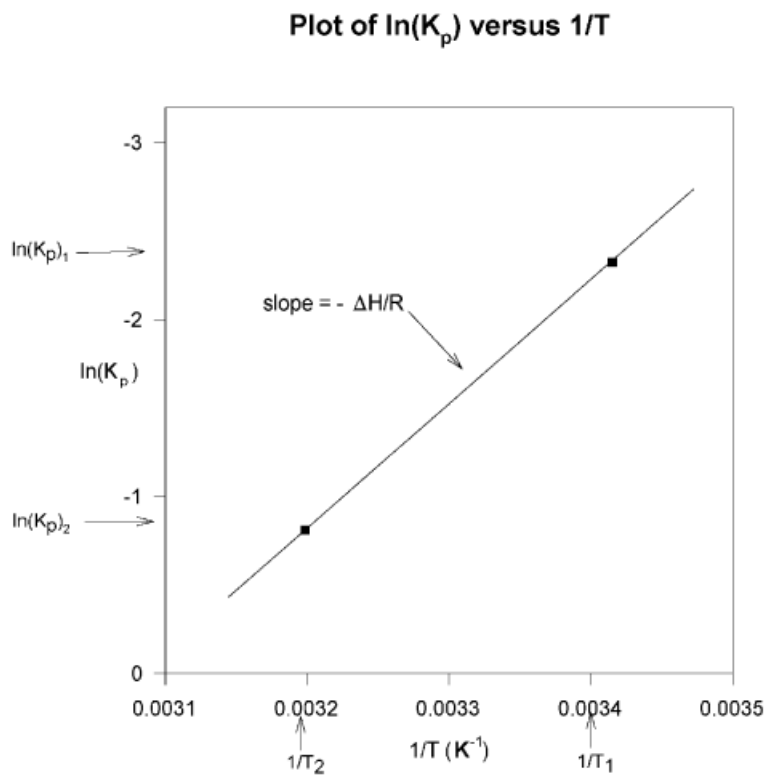
$$Q = 0.992 \frac{\text{L}}{\text{mole}} < 2.46 \frac{\text{L}}{\text{mole}} = K_c$$

Since  $Q < K_c$ , the reaction will go to the right to reestablish the equilibrium. Moles of  $PCl_3$  and  $Cl_2$  will be consumed and moles of  $PCl_5$  will be produced. The moles of  $PCl_5$  at the NEW equilibrium will be greater than the moles of  $PCl_5$  in Example #2.

## D) Dependency of K on Temperature

Plot of  $\ln(K_p)$  versus  $1/T$  for the reaction





Equation for a straight line is

$$y = (\text{slope})x + (\text{intercept})$$

$$\ln(K_p) = \left[ \frac{-\Delta H}{R} \right] \left[ \frac{1}{T} \right] + C$$

where C is a constant.

Consider  $K_2$  at  $T_2$  and  $K_1$  at  $T_1$  for a specific reaction, then

$$\ln(K_p)_2 = \left[ \frac{-\Delta H}{R} \right] \left[ \frac{1}{T_2} \right] + C$$

$$-\left[ \ln(K_p)_1 = \left[ \frac{-\Delta H}{R} \right] \left[ \frac{1}{T_1} \right] + C \right]$$

$$\ln(K_p)_2 - \ln(K_p)_1 = \left[ \frac{-\Delta H}{R} \right] \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

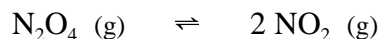
Rearranging

$$\ln(K_p)_2 = \left[ \frac{\Delta H}{R} \right] \left[ \frac{T_2 - T_1}{T_2 T_1} \right] + \ln(K_p)_1$$

When  $\Delta H > 0$ , heat is absorbed and the reaction is said to be *endothermic*.

When  $\Delta H < 0$ , heat is evolved and the reaction is said to be *exothermic*.

**Example:** If  $K_p = 0.09823$  at  $20^\circ\text{C}$  and  $0.4554$  at  $40^\circ\text{C}$ , calculate  $\Delta H$  for the reaction.



$$\ln(K_p)_2 = \left[ \frac{\Delta H}{R} \right] \left[ \frac{T_2 - T_1}{T_2 T_1} \right] + \ln(K_p)_1$$

Rearranging

$$\Delta H = R \ln \left[ \frac{(K_p)_2}{(K_p)_1} \right] \left[ \frac{T_2 T_1}{T_2 - T_1} \right] = (8.314 \frac{\text{J}}{\text{K}}) \ln \left[ \frac{(0.4554)}{(0.09823)} \right] \left[ \frac{(313\text{K})(293\text{K})}{20\text{K}} \right] = 5.85 \cdot 10^4 \text{J}$$

E) Entropy and Free Energy

The thermodynamic function *entropy*,  $S$ , is a measure of the disorder or randomness of a system. *Entropy is a state function.*

The second law of thermodynamics states that an increase in entropy of the universe is associated with every spontaneous process. The change in entropy of the universe is the sum of the changes in the entropy of the system and surroundings.

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \quad (1)$$

For a process to proceed spontaneously  $\Delta S_{univ}$  must be a positive number. If  $\Delta S_{univ}$  is a negative number, then the process will proceed spontaneously in the reverse direction and when  $\Delta S_{univ} = 0$ , then the system is at equilibrium.

The change in the entropy of the surroundings,  $\Delta S_{surr}$ , is dependent on the heat that is transferred between the system and the surroundings. For a constant pressure and constant temperature process

$$\Delta S_{surr} = \frac{q_{surr}}{T} = \frac{-(q_p)_{sys}}{T} = \frac{-\Delta H}{T} \quad (2)$$

As an example consider the reaction



The change in the entropy of the surroundings with the formation of two moles of  $\text{NH}_3$  is

$$\Delta S_{surr} = \frac{-\Delta H}{T} = \frac{-(-92.4 \text{kJ}) \left[ \frac{1000 \text{J}}{1 \text{kJ}} \right]}{298 \text{K}} = 310 \frac{\text{J}}{\text{K}}$$

and the change in the entropy of the universe is

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = -198.5 \frac{\text{J}}{\text{K}} + 310 \frac{\text{J}}{\text{K}} = 111 \frac{\text{J}}{\text{K}}$$

The entropy of the system,  $\Delta S^\circ = -198.5 \text{ J/K}$ , decreases primarily because there are fewer product molecules than reactant molecules. The reduction in number of molecules results in a lowering of the positional disorder. Although  $\Delta S^\circ$  for the reaction is a negative number,  $\Delta S_{univ} > 0$  due to the large increase in the entropy of the surroundings and the reaction proceeds spontaneously to the right.

For a constant pressure and constant temperature process, eq 2 can be substituted into eq 1.

$$\Delta S_{univ} = \Delta S_{sys} + \frac{-\Delta H}{T} = \Delta S + \frac{-\Delta H}{T} \quad (3)$$

Multiply eq 3 by  $-T$  and rearrange.

$$-T\Delta S_{univ} = \Delta H - T\Delta S \quad (4)$$

Gibbs free energy,  $G$ , is defined as

$$G \equiv H - TS$$

For a constant pressure and constant temperature process

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

Comparing eqs 4 and 5

$$\Delta G = -T\Delta S_{univ}$$

A constant pressure and constant temperature process will be spontaneous when  $\Delta S_{univ} > 0$  or  $\Delta G < 0$ .

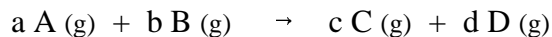
**Example:** Calculate  $\Delta G^\circ$  at  $25^\circ\text{C}$  for the following reaction?



$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 436 \text{ kJ} - (298 \text{ K})(98.5 \frac{\text{J}}{\text{K}}) \left[ \frac{1 \text{ kJ}}{1000 \text{ J}} \right] = 407 \text{ kJ}$$

## F) Reaction Free Energy

For the generic reaction



the reaction free energy,  $\Delta G$ , is defined as

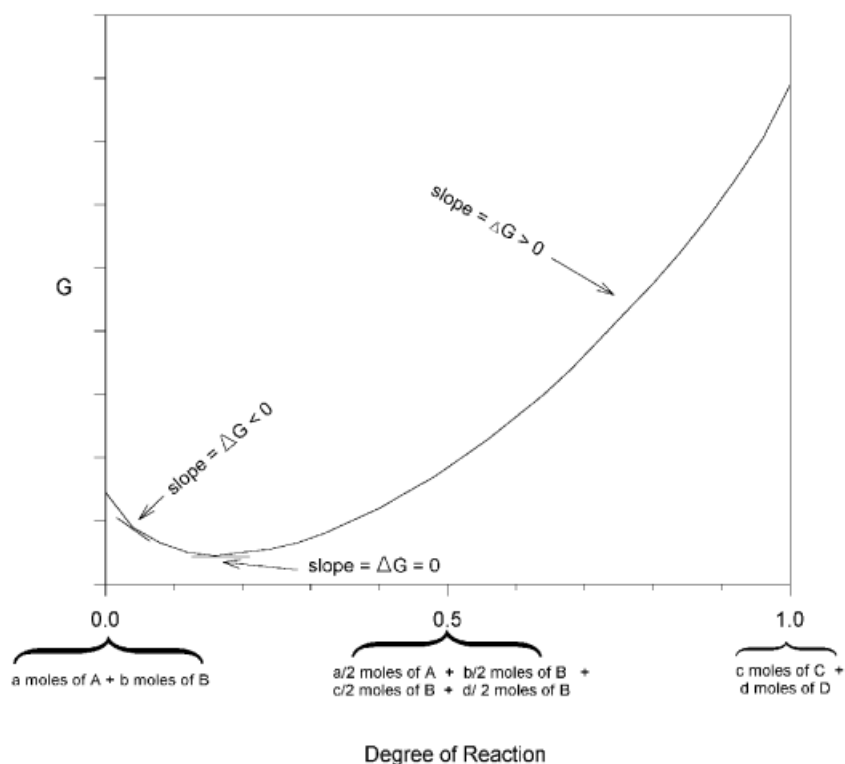
$$\Delta G = \Delta G^\circ + RT \ln \left\{ \frac{P_C^c P_D^d}{P_A^a P_B^b} \right\}$$

Diagram illustrating the equation for reaction free energy ( $\Delta G$ ) and its components:

- $\Delta G$  is labeled as **Reaction Free Energy**.
- $\Delta G^\circ$  is labeled as **Standard Reaction Free Energy**.
- $R$  is labeled as **Ideal Gas Constant**.
- $T$  is labeled as **Absolute Temp**.
- The logarithmic term is defined by the partial pressures of the gases:
  - $P_C$  and  $P_D$  are labeled as **Partial Pressure of Gas C** and **Partial Pressure of Gas D** respectively.
  - $P_A$  and  $P_B$  are labeled as **Partial Pressure of Gas A** and **Partial Pressure of Gas B** respectively.

A plot of  $G$  for the above reaction versus the extent of reaction yields

Plot of G versus Degree of Reaction



The *degree of reaction* is a measure of the extent to which the reaction has advanced from the left to right.

The slope of the above curve at any point is equal to the reaction free energy,  $\Delta G$ . When the degree of reaction is 0, only the reactants A and B are present,  $\Delta G < 0$ , and the reaction will *proceed spontaneously to the right*. When the degree of reaction is 1.0, only the products are present,  $\Delta G > 0$ , and the reaction will *proceed spontaneously to the left*. When the degree of reaction is 0.16,  $\Delta G = 0$  and the reaction is at equilibrium.

**At equilibrium,  $\Delta G = 0$  and**

$$\Delta G = 0 = \Delta G^\circ + RT \ln \left[ \frac{(P_C)_{eq}^c (P_D)_{eq}^d}{(P_A)_{eq}^a (P_B)_{eq}^b} \right] \quad (6)$$

$K_p$  is defined as

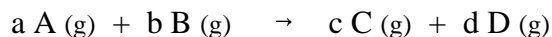
$$K_p = \left[ \frac{(P_C)_{eq}^c (P_D)_{eq}^d}{(P_A)_{eq}^a (P_B)_{eq}^b} \right] \quad (7)$$

Substituting eq 7 into eq 6 and rearranging

$$\Delta G^\circ = -RT \ln(K_p) \quad \text{or} \quad K_p = \exp\left[\frac{-\Delta G^\circ}{RT}\right]$$

Relationship between  $K_c$  and  $K_p$

For the generic reaction



$$K_p = \left[ \frac{(P_C)_{eq}^c (P_D)_{eq}^d}{(P_A)_{eq}^a (P_B)_{eq}^b} \right]$$

Assuming ideal gas behavior

$$P_A = \left[\frac{n_A}{V}\right]RT = [A]RT; \quad P_B = [B]RT; \quad P_C = [C]RT; \quad P_D = [D]RT$$

Substituting

$$K_p = \left[ \frac{(P_C)_{eq}^c (P_D)_{eq}^d}{(P_A)_{eq}^a (P_B)_{eq}^b} \right] = \left[ \frac{([C]RT)_{eq}^c ([D]RT)_{eq}^d}{([A]RT)_{eq}^a ([B]RT)_{eq}^b} \right] = \left[ \frac{[C]_{eq}^c [D]_{eq}^d}{[A]_{eq}^a [B]_{eq}^b} \right] (RT)^{c+d-a-b}$$

and

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

where  $\Delta n = c + d - a - b$ .

## G) Standard Reaction Free Energy and Standard Absolute Entropy

1)  $\Delta G^\circ$

The free energy change for the formation of a compound in its standard state from its elements (most stable form) in their standard states is called the standard free energy of formation,  $\Delta G_f^\circ$ .

**Example:**



By definition  $\Delta G_f^\circ$  for elements in their most stable form is zero.

A table of  $\Delta G_f^\circ$  is found in the text. See example below.

To calculate the standard reaction free energy,  $\Delta G^\circ$ , from the standard free energies of formation

$$\Delta G_{\text{reaction}}^\circ = \sum v_{\text{product}} \Delta G_f^\circ (\text{product}) - \sum v_{\text{reactant}} \Delta G_f^\circ (\text{reactant})$$

where  $v$ , called the *mole number*, is the stoichiometric coefficient in the thermochemical equation.

2)  $S^\circ$

The third law of thermodynamics states that the entropy for all pure, perfectly ordered, crystalline substances is zero at absolute zero (0 K). Consequently the absolute entropies,  $S^\circ$ , of all compounds and elements in their most stable form can be determined. Some of these entropies are listed in a table of thermodynamic data found in the text.

**Example:** Table of Selected Thermodynamic Data

Substance	$\Delta G_f^\circ$ (kJ/mole)	$S^\circ$ (J/mole-K)
CO <sub>2</sub> (g)	-394.4	213.6
H <sub>2</sub> O (l)	-237.2	70.0
H <sub>2</sub> (g)	0.0	130.5
H (g)	203.3	115

To calculate the change in the standard entropy for a reaction

$$\Delta S_{\text{reaction}}^\circ = \sum v_{\text{product}} S^\circ (\text{product}) - \sum v_{\text{reactant}} S^\circ (\text{reactant})$$