

1. ΔG , Q , K

For a chemical reaction or physical process



as reaction happens, the amount of A, B, C, D will change, so the free energy G for each species A, B, C, D will change $\rightarrow \Delta G = (G_{\text{products}} - G_{\text{reactants}})$ occurs
(note: we could not get absolute values of G though)

How could ΔG help us?

- (1) Direction: if $\Delta G < 0$ reaction goes forward $A+B \rightarrow C+D$
 $\Delta G > 0$ reaction goes backward $A+B \leftarrow C+D$
 $\Delta G = 0$ equilibrium

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

-	-	+	reaction \rightarrow
+	+	-	\leftarrow

+	+	}	ΔG could be +, - and $\Delta G = 0$
-	-		

- (2) Extent: $\Delta G^\circ \sim K$ (later)
 if ΔG° is very very negative (absolute value large) \rightarrow at equilibrium,
 Most of A and B will be converted to C and D (products favored)

Describe the amount of a substance

Activity: unitless number as referenced to a standard state

gas $a_i = \frac{P_i}{P^\circ}$

$$P^\circ = 1 \text{ atm}$$

solution $a_i = \frac{[i]}{c^\circ}$

$$c^\circ = 1 \text{ M}$$

$a_i = 1$ (pure solid or liquid)

Note: pure solid/liquid \neq elemental substance

$\text{MgO}(s)$ $\text{CaCO}_3(s)$ $\text{H}_2\text{O}(l)$ all have activity as 1

pure solid/liquid means that we do not have impurity in it, we do not have a mixture of 2 or more compounds.

We already have concentration to track the amount of substance, why introduce activity? (model closer to reality)

$\text{H}^+(aq)$ dissolved H^+ in water

acid $a_{\text{H}^+} = \frac{[\text{H}^+]}{1M} \gamma_{\text{H}^+}$ \rightarrow to modify the concentration

γ_{H^+} : activity coefficient, to account for deviation from ideal solution as in real solution, interactions between molecules of different species are different.

But in our class, we assume γ_s as 1.

No need to worry about this.

Describe the state (composition, progress) of the system



Mass action expression $\frac{a_c^c \cdot a_d^d}{a_A^a \cdot a_B^b} = Q$ reaction quotient

We can write Q in 2 versions

concentration $\frac{[C]^c [D]^d}{[A]^a [B]^b} = Q_c$ use molarity (mol/L)

pressure $\frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b} = Q_p$ use partial pressure (atm)

Q describes the composition of the mixture at any point

specially @ equilibrium $Q = K$ equilibrium constant K_c, K_p

Conversion between K_p and K_c

$$PV = nRT \quad P = CRT \quad C = \frac{P}{RT}$$

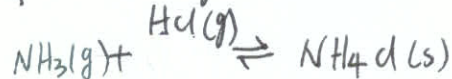


$$K_c = \frac{[\text{O}_2][\text{HCl}]^4}{[\text{Cl}_2]^2[\text{H}_2\text{O}]^2} = \frac{\left(\frac{P_{\text{O}_2}}{RT}\right) \left(\frac{P_{\text{HCl}}}{RT}\right)^4}{\left(\frac{P_{\text{Cl}_2}}{RT}\right)^2 \left(\frac{P_{\text{H}_2\text{O}}}{RT}\right)^2} = \frac{\left(\frac{1}{RT}\right)^{1+4-2} \cdot P_{\text{O}_2} \cdot P_{\text{HCl}}^4}{P_{\text{Cl}_2}^2 \cdot P_{\text{H}_2\text{O}}^2} = \left(\frac{1}{RT}\right)^1 K_p$$

$$K_c = \left(\frac{1}{RT}\right)^{\Delta n} K_p \quad \Delta n = (\text{\# of moles of gaseous products}) - (\text{\# of moles of gaseous reactants})$$

Example problems

1. The correct units for the equilibrium constant K_p for the reaction

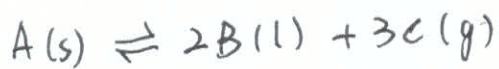


are

1. atm^{-1}
2. None (unitless) ✓
3. atm
4. atm^2

K is defined by activity. Activity has no unit. So equilibrium constant K_p is dimensionless.

2. If more solid A is added to the reaction



at equilibrium,

1. the amount of A will decrease
2. the amount of B will remain unchanged
3. C will increase
4. the partial pressure of C will increase
5. the amount of B will increase

Describe the state of the system @ equilibrium using equilibrium constant K

$$K = \frac{a_B^2 \cdot a_C^3}{a_A}$$

$$a_A = a_B = 1 \quad (\text{pure solid / liquid})$$

$$K = a_C^3$$
$$\boxed{K} = \boxed{P_C^3}$$

K remains constant, so P_C is constant. The added solid A does not affect equilibrium.

Note: A, B, C do not have to be elemental substances.

K is dependent on temperature. When temperature is kept constant, K is constant.

Exam 1

#12 The vapor pressure of a pure liquid depends on which of the following

- I the volume of the liquid
- II the volume of the gas
- III the surface area of the liquid
- IV the temperature

$$P_{\text{vap}} \propto e^{\frac{-\Delta H_{\text{vap}}}{RT}}$$

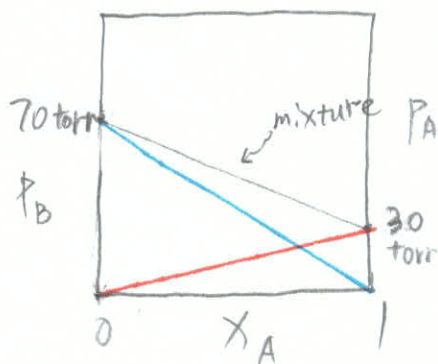
Vapor pressure of a pure liquid only depends on T .

STP: 0°C and 1 atm

SATP: 25°C and 1 bar

Exam 1

#16 Consider the following vapor pressure diagram for a binary liquid containing solvents A and B



If 3 moles of A and 2 moles of B are mixed, what is the vapor pressure of the solution?

Which line is corresponding to A, which one is corresponding to B?

When $X_A = 1$, we have pure A in the system, the vapor pressure should be 30 torr rather than 0 torr. Or think it this way, when we increase X_A , the partial pressure of A should increase (according to Raoult's law $P_A^{\uparrow} = P_{\text{vap}} \cdot X_A^{\uparrow}$), so as we are moving from $0 \rightarrow 1$ in terms of X_A , we should expect a line with positive slope. \Rightarrow orange line A Blue line B

Look at the line for the mixture

$$P_{\text{total}} = P_{\text{vap},A} \cdot X_A + P_{\text{vap},B} \cdot X_B$$

$$P_{\text{total}} = P_{\text{vap},A} \cdot X_A + P_{\text{vap},B} \cdot (1 - X_A)$$

when $X_A = 0$

$$P_{\text{total}} = P_{\text{vap},B} = 70 \text{ torr}$$

when $X_A = 1$

$$P_{\text{total}} = P_{\text{vap},A} = 30 \text{ torr}$$

Back to the problem

$$\text{mole fraction of A} : X_A = \frac{\text{mol A}}{\text{total mol}} = \frac{3}{2+3} = 0.6$$

$$P_{\text{total}} = P_{\text{vap},A} \cdot X_A + P_{\text{vap},B} \cdot (1 - X_A)$$

$$= 30 \cdot 0.6 + 70 \cdot 0.4$$

$$= 46 \text{ Torr}$$

Note: 46 torr is a small number compared to atmospheric pressure, because:

★ Raoult's law is valid only for systems at low to moderate pressures, and in general, only for systems comprised of chemically similar species.

Responding to suggestion on more problems:

1. What is the main driving force for any spontaneous reaction or change?
Consider only the reaction system, not the surroundings.

1. To minimize electrostatic interactions
2. To obey the law of gravity
3. To maximize entropy
4. To lower the available free energy
5. To release heat

Reaction moves toward equilibrium, minimizing G . The system always seeks for lower free energy state.

2. At 300°C , the equilibrium constant for the reaction



is 2.8. Calculate the equilibrium constant for the reaction



1. 1.2

2. 0.36

3. -1.7

4. 0.60

5. 1.6

At a given temperature, $K_{\text{reverse}} = \frac{1}{K_{\text{original}}}$

If reaction is multiplied by n , K becomes K^n

So $\frac{C(g) + 2B(l) \rightarrow 2A(s)}{2.8} \quad K = \frac{1}{2.8}$

$\frac{1}{2}C(g) + B(l) \rightarrow A(s) \quad n = \frac{1}{2} \quad K^{\frac{1}{2}} = \sqrt{\frac{1}{2.8}} = 0.6$