Lecture 17
Thermodynamics of Solutions
The Ideal and Nonideal Solutions

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Today's Topics

☐ The ideal solutions and the Raoult's law

☐ Deviation from ideality and the non-ideal solutions

☐ The concept of fugacity

☐ The concept of activity and activity coefficient

The Ideal Solutions

Question:
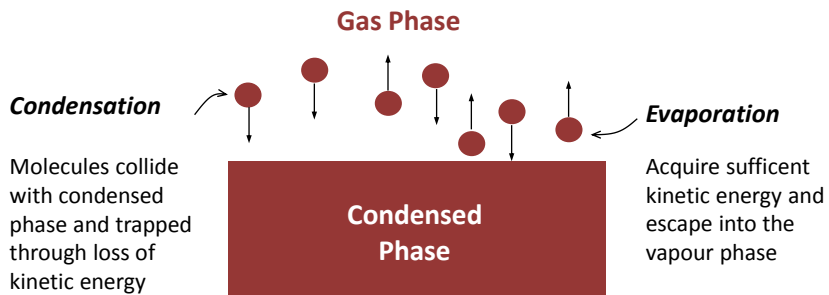
How does the wet cloth dry at room temperature ?

Answer:

- Every pure substance in liquid or solid state has a definite **vapour pressure** at any given temperature

- Pure solid or liquid, when placed in a closed, initially evacuated chamber will **evaporate spontaneously** until the vapour phase and the solid or the liquid phase comes to a dynamic equilibrium.

- At any temperature, every substance in liquid or solid state has been in equilibrium with its vapour phase and has a definite vapour pressure.

Pure Metal	Approx. Vapour Pressure at 1600 C (atm)
Mg	> 20
Mn	0.07
Al	0.006
Fe	0.0007
Ni	0.0001

Kinetic View

Gas Phase

Condensation

Evaporation

Molecules collide with condensed phase and trapped through loss of kinetic energy

Condensed Phase

Acquire sufficent kinetic energy and escape into the vapour phase

At equilibrium,

Rate of evaporation, r_e = Rate of condensation, r_c

In case of a pure condensed phase A

The evaporation rate, r_e (A)

☐ Depends upon the magnitude of the mutual attraction of A particles

The condensation rate, r_c (A)

☐ Proportional to the number of A atoms in the vapour phase which strike the liquid surface in unit time

☐ This, for a fixed temperature, is proportional to the pressure of the vapour, that is, r_c (A) = $k\,p_A$

At Equilibrium

$$r_e \text{ (A)} \; = \; r_c \text{ (A)} \; = \; k \cdot p^0_A$$

p^0_A = standard vapour pressure of A

When a small quantity of B is added to A

☐ Some fraction of the surface area (X_A) of liquid A will be occupied by B

☐ The rate of evaporation of liquid A will be reduced by a factor X_A.

☐ The new evaporation rate will be $r_e(A) . X_A$

☐ The equilibrium vapour pressure exerted by A is decreased from p^0_A to p_A

☐ At equilibrium, for A containing small quantity of B

$$r_e(A). X_A = k.p^0_A . X_A = k . p_A$$

$$r_e(A) . X_A = k.p^0_A . X_A = k . p_A$$
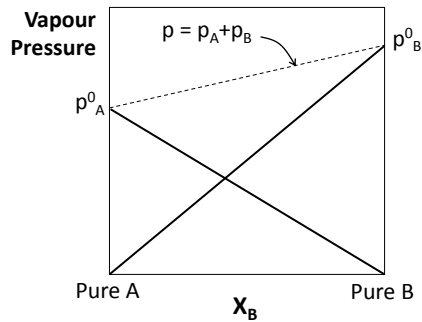
$$p_A = p^0_A X_A$$

$$p_B = p^0_B X_B$$

☐ These equations are known as the **Raoult's Law**:

> The **vapour pressure** exerted by a component k in a solution **is directly proportional to the mole fraction** of k in the solution and the proportionality constant is the saturated vapour pressure of component k at the temperature of the solution

☐ A solution that obeys Raoult's Law is called an **ideal solution**, and such behaviour of a solution is called the **Raoultian behaviour**.

$$p_A = p^0_A X_A$$

☐ Addition of solute
- **the solute itself also exerts its own vapour pressure.**
- **lowers the vapour pressure of solvent**

☐ The vapour pressure of the solution is the sum of the separate vapour pressures of solvent and solute.

Vapour Pressure

$p = p_A + p_B$ p^0_B

p^0_A

Pure A X_B Pure B

Alternate Formulation of Raoult's Law

$$p_A = p^0_A \cdot X_A = p^0_A \cdot (1 - X_B)$$

$$\frac{p^0_A - p_A}{p^0_A} = X_B$$

The relative lowering of vapour pressure of solvent due to addition of solute is equal to the mole fraction of solute in the solution.
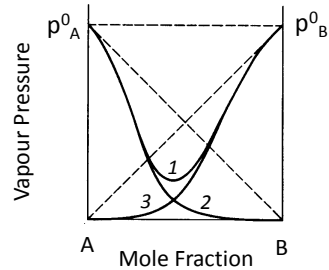

The Non-ideal Solutions

☐ The Raoult's law presupposes that

- The intrinsic evaporation rates of A and B be independent of the composition of the solution.

- This requires that the magnitudes of A-A, B-B, and A-B interactions be identical (i.e., no preferential mixing or bond formation).

☐ In order to do that, the following **three conditions must be satisfied**:

1. Atoms of A and B of the solution must be of **same size**,
2. Atoms of A and B must be **inert to each other**, and
3. The **vapours** of A and B should **behave like ideal gas**.

☐ If a solution violates one or more of the above conditions, Raoult's is not obeyed, and the solution is termed as the **non-ideal solution**.

Case I: Existence of attraction/repulsion between components

- vapours behave as ideal gas
- molecules are of similar size
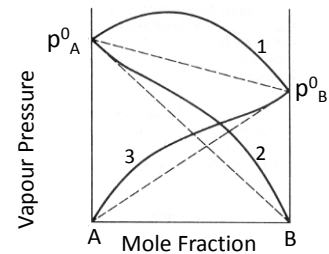- not inert to each other (A-B bond $\neq$ A-A / B-B bond)

A-B attraction   >> A-A / B-B attractions

☐ **Negative deviation** from Raoult's Law

Example: Fe – 50 wt%Ni solution at 1600 °C
(p_{Ni} is roughly three-quarter of its ideal value)

A-B attraction   << A-A / B-B attractions

☐ **Positive deviation** from Raoult's Law

Example: Fe – 1 wt.% Cu solution at 1550 °C
(p_{Cu} is about 10 times higher than its ideal value)

☐ Fe – Mn solution is virtually an **ideal solution** at 1600 °C.

Case II: Components are of different sizes

☐ A difference in size in atoms of the components of a solution will affect the distance between the centres of adjacent particles, and consequently, there **exists a mutual attraction or repulsion** between them.

Case III: Vapour phases do not behave ideally

☐ At high pressures or low temperatures (approaching the critical temperature of the gas), the pressure exerted by gases are not equal to their vapour pressure, p.

☐ In such cases the **ideal gas law, pV = nRT, is no longer obeyed** by the gas phase.

The Concept of Fugacity

☐ At higher pressures or low temperatures, the gases no longer obey the ideal gas law, PV = nRT.

☐ Also, the linear relationship between Gibbs free energy, G, and the vapour pressure, p, becomes complicated.

☐ For such conditions, G. N. Lewis introduced the quantity **fugacity**, Φ, so that, under all conditions, the equation of state remains the familiar form, and ensure the linear relation between G and Φ in any state for all gas.

$$\Phi V = RT$$

☐ Using fugacity the Raoult's law can then be restated as: $\Phi_k = \Phi^0_k X_k$

☐ This equation is valid for all **ideal solutions with imperfect gases**.

The Concept of Activity

☐ Real solutions do not obey $\Phi_k = \Phi^0_k X_k$

☐ Thus the fugacity of a component is **not proportional** to its mole fraction.

☐ For real solutions, another thermodynamic quantity, **activity**, is defined

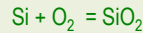$$a_k = \Phi_k / \Phi^0_k \qquad or, \qquad \Phi_k = \Phi^0_k a_k$$

☐ If the vapour above the solution is ideal, then $\Phi = p$, and

$$a_k = p_k / p^0_k = X_k$$

☐ This is an alternate and more commonly used expression of Raoult's law.

- In real solutions, the activity of a component can be considered as the **active mass** of the component in the solution, ie. a **measure of its availability** for reaction, perhaps with another phase.

- Activity of a component is the fraction of molar concentration that is available for reaction.

  Example: Removal of Si in steelmaking process

  $$Si + O_2 = SiO_2$$

  - The rate of reaction is not proportional to $X_{Si}.p_{O2}$ but to $a_{Si}.p_{O2}$ (assuming oxygen to behave as an ideal gas at 1600 °C)

  Reason:
  - Silicon in solution does not behave as if it were pure silicon dissolved in ideal solution in iron. This is because the Fe-Si bond is very strong.
  - Thus, the activity of silicon is less than its mole fraction (a –ve deviation).
  - In fact, the activity of silicon in a 1 wt.% solution in iron at 1600 °C is about 1/60 of its mole fraction.

- For ideal solutions, interactions between components do not exist and, therefore, activity equals mole fraction, i.e., $a_k = X_k$

The Standard State

- The numerical value of activity depends on the concentration, temperature and pressure of the solution as well as on the choice of the standard state.

- The activity is meaningless unless it is accompanied by a detailed description of the standard state to which it refers.

- There are may standard states used to refer activity.

- For liquid and solid solutions, one standard state commonly used is that of **pure substance** at the temperature and pressure of the system.

- For pure substance, $\gamma_k = 1$ and $X_k = 1$ so that $a_k = 1$.

The Concept of Activity Coefficient

☐ For non-ideal/actual/real solution, activities of the components are not equal to their mole fractions, i.e., $a_k \neq X_k$

☐ The **Raoultian activity coefficient** of a component in a solution is defined as the ratio of the activity of the component to its mole fraction

$$\gamma_k \;=\; \frac{a_k}{X_k} \;=\; \frac{\Phi_k}{\Phi^0_k \, X_k}$$

☐ For an ideal solution, $\gamma_k = 1$.
- $\gamma_k >$ for positive deviation
- $\gamma_k <$ for negative deviation

Next Class

Lecture 18

Thermodynamics of Solutions
Measurement of Activity