Study materials for DII_Chem (H) students:

Short notes

1. Henry's law

Henry's law is one of the gas laws, formulated by the British chemist, William Henry, in 1803. It states that:

At a constant temperature, the amount of a given gas dissolved in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid.

Formula and Henry's constant:

A formula for Henry's law is:

$$e^p = e^{k_H}\, c$$

Where:

e is approximately 2.7182818, the base of the natural logarithm (also called Euler's number)

p is the partial pressure of the solute above the solution

c is the concentration of the solute in the solution (in one of its many units)

k_H is the Henry's law constant, which has units such as L·atm/mol, atm/mole fraction or Pa·m3/mol.

2. Nernst Distribution law

Statement- "At constant temperature, a solute distributes itself between two immiscible solvents only in a particular ratio"

This statement is a Nernst Distribution Law – i.e. The law that determines the relative distribution of a component that is soluble in two liquids, these liquids being immiscible or miscible to a limited extent. This law is one of the laws applying to ideal dilute solutions. It was discovered by W. Nernst in 1890. The Nernst distribution law states that, at equilibrium, the ratio of the concentrations of a third component in two liquid phases is constant. The law may be expressed in the form

$$c1/c2 = k$$

Where c1 and c2 are the molar equilibrium concentrations of the third component in the first and second phase, respectively; the constant k is the distribution coefficient, which is temperature dependent. The Nernst distribution law permits us to determine the most favourable conditions for the extraction of substances from solutions.

3. Ionic Products of Water

Pure water is a very weak electrolyte and ionises according to the equation

$$H_2O \rightarrow H^+ + OH^-$$

Applying law of mass action at equilibrium, the value of dissociation constant, K comes to

$$K = [H^+][OH^-]/[H_2O]$$

$$\text{or } [H^+][OH^-] = K[H_2O]$$

Since dissociation takes place to a very small extent, the concentration of undissociated

water molecules, $[H_2O]$, may be **regarded as constant**. Thus, the product $K[H_2O]$ gives

another constant which is designated as K_w.

$$\text{So, } [H^+][OH^-] = K_w$$

The constant, K_w, is **termed as ionic product of water.**

The product of concentrations of H^+ and OH^- ions in water at a particular temperature is known as ionic product of water. The value of K_w increases with the increase of temperature, i.e., the concentration of H+ and OH- ions increases with increase in temperature.

$$\boxed{\textbf{The value of } K_w \textbf{ at } 25°C \textbf{ is } 1 \times 10^{-14}}$$

4. Degree of Freedom

Degree of freedom is used to define a state of matter using different parameter. Degree of freedom tells about the input or no of parameters which are required to define a particular system. The degree of freedom is calculated by the Phase Rule which is given as following,

$$F = C + P - 2$$

Where C = No of constituents, P = Phase of material present at given condition and F = Degree of freedom.

Consider following example for degree of freedom for triple point of water at it's triple point. So, here the water is only constituent means C = 1 and Phase present are P = 3 (at triple point ice, water and vapour is present). So, according above rule degree of freedom F can be calculate as following:

$$F = 1 + 3 - 2 = 2$$

Hence, here we required two parameters to define this system at triple point.

5. Thermodynamic scale of temperature

A temperature scale in which the temperature, T, is a function of the energy possessed by matter. Thermodynamic temperature is therefore a physical quantity that can be expressed in units, termed kelvin. The zero of the scale is absolute zero. The temperature of the ice point (0 °C) is 273.15 kelvin. Thermodynamic temperature can be converted to Celsius temperature by subtracting 273.15 from the thermodynamic temperature. Any temperature scale in which the ratio of the temperatures of two reservoirs is equal to the ratio of the amount of heat absorbed from one of them by a heat engine operating in a Carnot cycle to the amount of heat rejected by this engine to the other reservoir; the Kelvin scale and the Rankine scale are examples of this type.

6. **Condensed phase and phase diagram of Ag-Pb system:**

In some systems, an equilibrium exists between solid - liquid phases and gaseous phase is practically absent. Hence the effect of pressure on such system can be neglected. Then it is necessary to take into account only two variables viz. temperature and concentration. Such system showing solid-liquid equilibrium is called condensed system and phase rule applied to such systems is as follows:

F = C – P + 1 … known as condensed phase rule.

Where F is degree of freedom, C = no. of components and P is the no. of phases in the system.

Phase diagram of Ag-Pb system:
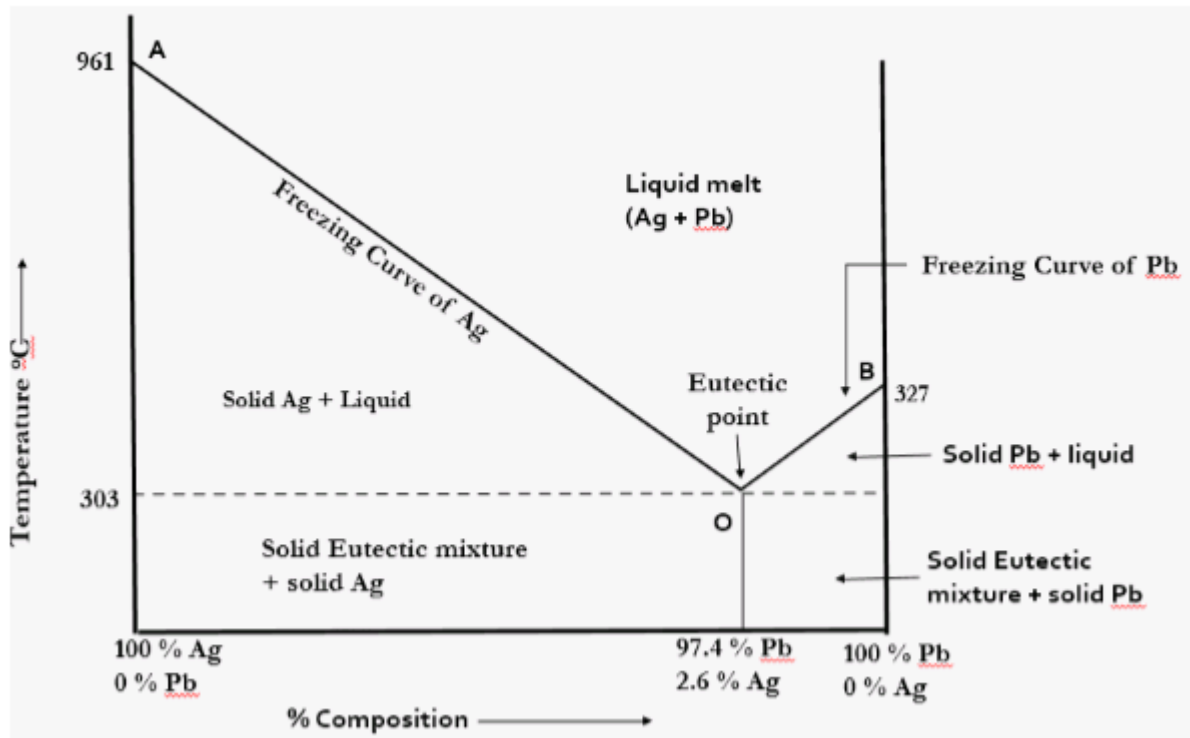
In two component systems there are four possible phases- solid Ag, solid Pb, solution of Ag, + Pb and vapour. Since the pressure has no effect on equilibrium so the system can be represented by temperature concentration diagram at constant atmospheric pressure. As pressure is neglected the phase rule is called condensed phase rule.

1) Curve AO:

It is a freezing point curve of Ag. Ag Co exists as solid and liquid. Melting point of Ag falls gradually on adding Pb till the lowest point is reached. The solution gets saturated with respective to lead.

2) Curve BO:

It is a freezing point curve of Pb. At this curve the melting point gradually falls on the addition of Ag till lowest point it reach.

3) Point O:

It is *eutectic point.* Here 3 phases co-exists and point O represents a fixed composition and system is in variant.

Below the temperature line of eutectic temperature, we have two regions:

➤ The region marked eutectic plus solid Ag in which crystalline silver and solid eutectic are stable.

➤ The region marked eutectic plus solid Pb in which crystalline lead and solid eutectic are stable.

4) Area AOB:

It represents solution of Pb and Ag. On lowering temperature the lead begins to separate out till the point O is reached.