CHM 304

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Third law of Thermodynamics — Entropy at absolute zero temperature and total entropy of phase changes.

Content:

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CHM 304

Introduction.

The study of solutions is of great importance because many interesting and useful chemical and biological processes occur in liquid solutions. Generally, a solution is defined as a homogeneous mixture of two or more components that form a single phase. Most solutions are liquids, although gas solutions (e.g., air) and solid solutions (e.g., solder) also exist.

This study is on the thermodynamics of ideal and nonideal solutions of nonelectrolytes — solutions that do not contain ionic species — and the colligative properties of these solutions.

Concentration Units

Any quantitative study of solutions requires that we know the amount of solute dissolved in a solvent or the concentration of the solution. Chemists employ several different concentration units. The use of the solution generally determines how we express its concentration. Examples of concentration units include percent by weight, mole fraction, molarity, and molality.

(2)

(i) **Percent by Weight**

The percent by weight (also called percent by mass) of a solute in a solution is defined as

$$\text{percent by weight} = \frac{\text{weight of solute}}{\text{weight of solute} + \text{weight of solvent}} \times 100\%$$

$$= \frac{\text{weight of solute}}{\text{weight of solution}} \times 100\% \quad \text{—— (1)}$$

(ii) **Mole fraction (x)**

We define the mole fraction of a component i of a solution, x_i, as

$$x_i = \frac{\text{number of moles of component } i}{\text{number of moles of all components}}$$

$$= \frac{n_i}{\sum_i n_i} \quad \text{—— (2)}$$

The mole fraction has no units.

(iii) **Molarity (M)**

Molarity is defined as the number of moles of solute dissolved in 1 liter of solution, ~~that~~ is

$$\text{Molarity} = \frac{\text{number of moles of solute}}{\text{liters of solution.}} \quad \text{—— (3)}$$

Thus, molarity has the units moles per liter (mol L^{-1})
By convention, we use square brackets [ ] ~~for~~ represent molarity.

(iv) Molality (m)

Molality is defined as the number of moles of solute dissolved in 1 kg (1000 g) of solvent, that is,

$$\text{Molality} = \frac{\text{number of moles of solute}}{\text{Mass of solvent in kg.}} \quad \text{——} (4)$$

Thus, molality has the units of moles per kg of solvent (mol kg^{-1}).

Ideal solution

In ideal solutions, volumes are additive

(i) Intermolecular interactions are the same for all molecules $(\Delta_{mix} H^{0})_{P,T} = 0$

(ii) Molecules have a finite volume independent of composition $(\Delta_{mix} V)_{P,T} = 0$

(iii) The solvent follows Raoult's law and the solute follows Henry's law.

(iv) The activity coefficient for all species is unity, that is, $\gamma = 1$.

(v) All mixtures are miscible (mix at all concentration) for all temperatures.

(vi) Mixing is driven only by a positive entropy change upon mixing. $\Delta_{mix} S^{\circ} > 0$

In general, solutions in the liquid phase are non-ideal. Non-ideal solutions are called real solutions.

Partial Molar Quantities

In discussing the properties of any solution, we cannot employ molar quantities; instead we use partial molar quantities.

Unlike ideal solutions, for most real solutions volumes are not additive. That is, adding 50ml of one liquid to 50ml of another does not lead to a mixture of 100ml final volume. To account for this, we introduce the concept of partial molar volume.

The partial molar volume is the change in volume upon addition of component 2 to component 1, holding all other variables — that is, P, T and moles of 1 — constant.

For example, at 298K, the molar volumes of:

water = 0.018 L

ethanol = 0.058 L.

If we mix half a mole of each liquid, we might expect the combined volume to be 0.038L, i.e

$$\frac{0.018L}{2} + \frac{0.058L}{2} = 0.038L$$

Instead, we find the volume to be only 0.036L. The shrinkage of the volume is the result of unequal intermolecular interaction between unlike molecules. Because the forces of attraction between water and ethanol molecules are greater than those between water molecules and between ethanol molecules, the total volume is less than sum of the individual volumes.

If the intermolecular forces are weaker, then expansion will occur and the final volume will be greater than the sum of the individual volumes.

Only if the interaction between like and unlike molecules are the same will volume be additive. If the final volume is equal to the sum of the separate volumes, the solution is called an ideal solution.

At constant temperature and pressure, the volume of a solution is a function of the number of moles of different substances present; that is,

$$V = V(n_1, n_2, \ldots)$$

The total change in volume for infinitesimal changes in molar composition of a binary mixture of 1 and 2 is given as

$$dV = \left(\frac{\partial V}{\partial n_1}\right)_{P,T,n_2} dn_1 + \left(\frac{\partial V}{\partial n_2}\right)_{P,T,n_1} dn_2$$

$$= \bar{V}_1 dn_1 + \bar{V}_2 dn_2 \qquad \text{------} (5)$$

Where $\bar{V}_1$ and $\bar{V}_2$ are the partial molar volumes of component 1 and 2. The partial molar volu-

[6]

me $\bar{V}_1$, for example, tells us the rate of change in volume with number of moles of component 1, at constant T, P, and component 2. The quantity $\bar{V}_2$ can be similarly interpreted.

Equation (5) can be integrated to give

$$V = n_1\bar{V}_1 + n_2\bar{V}_2 \quad \text{———} \quad (6)$$

This equation enables us to calculate the volume of the solution by summing the products of the number of moles and the partial molar volumes of each component.

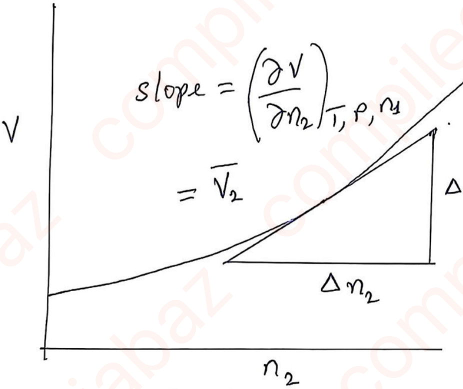

Fig 1. Determination of partial molar volume.

Figure 1 suggests a way of measuring partial molar volumes. Consider a solution composed of substances 1 and 2. To measure $\bar{V}_2$, we prepare a series of solutions at certain T, and P, all of which contains a fixed number of moles of component 1 (i.e, n_1 is fixed) but different amounts of n_2. When we plot the measured volume, V, of the solution against n_2, the slope of the curve at a particular composition of 2 gives $\bar{V}_2$ for that composition. once $\bar{V}_2$ has been measured, $\bar{V}_1$ at the same composition can be calculated using equation 6::

$$\bar{V}_1 = \frac{V - n_2\bar{V}_2}{n_1}.$$

Figure 2 shows the partial molar volume of ethanol-water solution. Note that whenever The partial molar volume of one component rises, that of the other component falls. This relationship is a characteristic of all partial molar quantities.

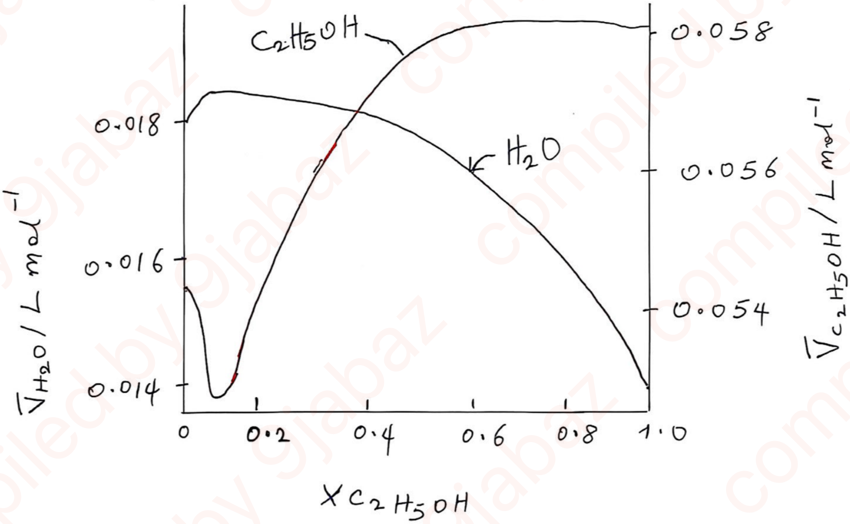

Fig. 2. The partial molar volumes of water and ethanol as a function of the mole fraction of ethanol.

Partial Molar Gibbs Energy

partial molar quantities permit us to express the total extensive properties, such as volume, energy, enthalpy, and Gibbs energy, of a solution of any composition.

The partial molar Gibbs energy of the ith component in solution $\bar{G}_i$ is given by

$$\bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j} \quad \text{———— (7)}$$

where n_j represents the number of moles of all other components present. Again we can think of $\bar{G}_i$ as the coefficient that gives the increase in the Gibbs energy of the solution upon the addition of 1 mole of component i at constant temperature and pressure to a large amount of solution of specified concentration.

partial molar Gibbs energy is also called the chemical potential (μ), so we can write

$$\bar{G}_i = \mu_i \quad \text{———— (8)}$$

The Gibbs – Duhem Equation.

The chemical potentials of two components in a binary solution are not independent. This is very important because it allows the chemical potential of a nonvolatile solute such as sucrose in a volatile solvent such as water to be determined. The differential form of the Gibbs energy is given by

$$dG = -SdT + VdP + \sum_i \mu_i dn_i \quad \text{———} \quad 9$$

where S is entropy.

For a binary solution at constant T and P, this equation reduces to

$$dG = \mu_1 dn_1 + \mu_2 dn_2 \quad \text{———} \quad 1.0$$

Imagine starting with an infinitesimally small amount of a solution at constant T and P. The amount is gradually increased at constant composition. Because of this restriction, the chemical potentials are unchanged as the size of the system is changed. Therefore, the μ_i can be taken out of the integral.

$$\int_0^G dG = \mu_1 \int_0^{n_1} dn_1 + \mu_2 \int_0^{n_2} dn_2 \quad \text{or}$$

$$G = \mu_1 n_1 + \mu_2 n_2 \quad \text{———} \quad 1.0b$$

The total differential of equation is

$$dG = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 \quad \text{———} \quad 11$$

Equation 11 differ from equation 10 because, in general, we have to take the changes of the composition of the solution into account. Therefore μ_1 and μ_2 must be regarded as variables.

Equating the expression for dG in equation 10 and 11 gives the Gibbs-Duhem equation for a binary solution, i.e;

$$\mu_1 dn_1 + \mu_2 dn_2 = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2$$

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \qquad \text{———} \; 12$$

or

$$x_1 d\mu_1 + x_2 d\mu_2 = 0$$

This equation states ~~that~~ the chemical potentials in a binary solution are not independent.

Therefore,

If the change in the chemical potential of the first component is $d\mu_1$, the change of the chemical potential of the second component is given by

$$d\mu_2 = \frac{n_1 d\mu_1}{n_2} \qquad \text{———} \; 13$$

Thermodynamics of Mixing.

The formation of solutions is generally governed by the principles of thermodynamics. Equation (106) gives the dependence of the Gibbs energy of a system on its composition, The spontaneous mixing of gases is accompanied by a change in composition; consequently, the systems's Gibbs energy decreases. The expression for the molar Gibbs energy of an ideal gas is

$$\bar{G} = \bar{G}^\circ + RT\ln\frac{P}{1\,\text{bar}}$$

In a mixture of ideal gases, the chemical potential of the ith component is given by

$$\mu_i = \mu_i^\circ + RT\ln\frac{P_i}{1\,\text{bar}} \qquad \text{———— (14)}$$

Where P_i is the partial pressure of component i in the mixture and μ_i° is the standard chemical potential of component i when its partial pressure is 1 bar.

Consider the mixing n_1 moles of gas 1 at Temperature T and pressure P with n_2 moles of gas 2 at the same T and P. Before mixing, the total Gibbs energy of the system is given by equation 9, where chemical potentials are the same as molar Gibbs energies,

$$G = n_1\bar{G}_1 + n_2\bar{G}_2 = n_1\mu_1 + n_2\mu_2$$

$$G_{\text{initial}} = n_1(\mu_1^\circ + RT\ln P) + n_2(\mu_2^\circ + RT\ln P)$$

(For simplicity, we omit the term "1 bar". Note that the resulting P values are dimensionless.)

After mixing, the gases exert partial pressures P_1 and P_2, where $P_1 + P_2 = P$, and the Gibbs energy is

$$G_{\text{final}} = n_1(\mu_1^\circ + RT\ln P_1) + n_2(\mu_2^\circ + RT\ln P_2)$$

Note that $P_1 + P_2 = P$ only if there is no change in volume as a result of mixing; that is, $\Delta_{\text{mix}}V = 0$. This condition holds for ideal solutions.

The Gibbs energy of mixing, $\Delta_{mix} G$, is given by

$$\Delta_{mix} G = G_{final} - G_{initial}$$
$$= n_1 RT \ln \frac{P_1}{P} + n_2 RT \ln \frac{P_2}{P}$$
$$= n_1 RT \ln x_1 + n_2 RT \ln x_2$$

where $P_1 = x_1 P$ and $P_2 = x_2 P$ and x_1 and x_2 are the mole fractions of 1 and 2, respectively. (The standard chemical potential, μ^0 is the same in the pure state and in the mixture).

Further, from the relations

$$x_1 = \frac{n_1}{n_1 + n_2} = \frac{n_1}{n}, \text{ and}$$

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{n_2}{n}$$

where n is the total number of moles, we have

$$\Delta_{mix} G = nRT(x_1 \ln x_1 + x_2 \ln x_2) \quad \text{———} \quad (15)$$

Because both x_1 and x_2 are less than unity, $\ln x_1$ and $\ln x_2$ are negative quantities, and hence so is $\Delta_{mix} G$. This result is consistent with our expectation that the mixing of gases is a spontaneous process at constant T and P.

Now we can calculate other thermodynamic quantities of mixing.

From equation (16), we see that at constant pressure

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad \text{——— (16)}$$

Thus, the entropy of mixing is obtained by differentiating equation (15) with respect to temperature at constant pressure.

$$\left(\frac{\partial \Delta_{mix} G}{\partial T}\right)_p = nR(x_1 \ln x_1 + x_2 \ln x_2)$$

$$= -\Delta_{mix} S$$

$$\Delta_{mix} S = -nR(x_1 \ln x_1 + x_2 \ln x_2) \quad \text{——— (17)}$$

The minus sign in equation (12) makes $\Delta_{mix} S$ a positive quantity, in accord with a spontaneous process.

The enthalpy of mixing is given by

$$\Delta_{mix} H = \Delta_{mix} G + T\Delta_{mix} S$$

$$= 0$$

This result is not surprising, because molecules of ideal gases do not interact with one another so no heat is absorbed or produced as a result of mixing.

Example 1.

Calculate the Gibbs energy and entropy of mixing 1.6 moles of argon at 1 atm and 25°C with 2.6 moles of nitrogen at 1 atm and 25°C. Assume ideal behaviour.

Solution

The mole fractions of argon and nitrogen are

$$x_{Ar} = \frac{1.6}{1.6 + 2.6} = 0.38$$

$$x_{N_2} = \frac{2.6}{1.6 + 2.6} = 0.62$$

From equation (11)

$$\Delta_{mix} G = nRT(x_1 \ln x_1 + x_2 \ln x_2)$$

$$= (4.2\,\text{mol})(8.314\,\text{J K}^{-1}\text{mol}^{-1})(298\,\text{K})\,[(0.38)\ln 0.38 + (0.62)\ln 0.62]$$

$$= -6.9\,\text{kJ}$$

Because $\Delta_{mix} S = \Delta_{mix} G/T$, we write

$$\Delta_{mix} S = \frac{-6.9 \times 10^3\,\text{J}}{298\,\text{K}}$$

$$= 23\,\text{J K}^{-1}.$$

Comment

In this example, the gases are at the same temperature and pressure when they are mixed. If the initial pressures of the gases differ, then there will be two contributions to $\Delta_{mix} G$: the mixing itself and the changes in pressure.

Binary Mixture of Volatile Liquids

The results obtained for mixtures of gases also apply to ideal liquid solutions. We shall consider a solution containing two volatile liquids, that is, liquids with easily measurable vapour pressures. Let us start with a liquid in equilibrium with its vapour in a closed container. Because the the system is at equilibrium, the chemical potentials of the liquid phase and the vapour phase must be the same, that is,

$$\mu^*(l) = \mu^*(g)$$

Where the asterisk denotes a pure component. Further, from the expression for $\mu^*(g)$ for an ideal gas, i.e,

$$\mu_i = \mu_i^\circ + RT\ln\frac{P_i}{1\text{ bar}} \quad \text{———} (14)$$

We can write

$$\mu^*(l) = \mu^*(g) = \mu^\circ(g) + RT\ln\frac{P^*}{1\text{ bar}} \quad \text{———} (18)$$

Where $\mu^\circ(g)$ is the standard chemical potential at $P^* = 1$ bar. For a two-component solution at equilibrium with its vapour, the chemical potential of each component is still the same in the two phases. Thus, for component 1 we write

$$\mu(l) = \mu(g) = \mu_1^\circ(g) + RT\ln\frac{P_1}{1\text{ bar}} \quad \text{———} (19)$$

Where P_1 is the partial pressure.

Because $\mu^\circ(g) = \mu_1^\circ(g)$, we can combine the previous two equations to get

[15]

$$\mu(l) = \mu_1^{\circ}(g) + RT\ln\frac{p_1}{1\text{ bar}}$$

$$= \mu_1^{*}(l) - RT\ln\frac{p_1^{*}}{1\text{ bar}} + RT\ln\frac{p_1}{1\text{ bar}}$$

$$= \mu_1^{*}(l) + RT\ln\frac{p_1}{p_1^{*}} \quad \text{———} (20)$$

Thus, the chemical potential of component 1 in solution is expressed in terms of the chemical potential of the liquid in the pure state and the vapour pressures of the liquid in solution and in the pure state.

Raoult's Law

The french chemist François Marie Raoult's (1830 - 1901) found that for some solutions, the ratio of p_1/p_1^{*} in equation (15) is equal to the mole fraction of component 1, that is,

$$\frac{p_1}{p_1^{*}} = x_1$$

or

$$p_1 = x_1 p_1^{*} \quad \text{———} (21)$$

Equation 21 is known as Raoult's law.

Raoult's law states that the vapour pressure of a component of a solution is equal to the product of its mole fraction and the vapour pressure of the pure liquid.

Substituting equation (21) into equation (20), we obtain

$$\mu_1(l) = \mu_1^*(l) + RT\ln x_1 \qquad (22)$$

In a pure liquid

$x_1 = 1$ and $\ln x_1 = 0$

Therefore, equation (22) becomes

$$\mu_1(l) = \mu_1^*(l)$$

Solutions that obey Raoult's law are called ideal solutions.

An example of a near ideal solution is the benzene – toluene system.

The benzene – toluene system approximates ideal solution because benzene and toluene molecules have similar shapes and electronic structures.

Benzene

Toluene

Figure 3 shows a plot of the vapour pressure versus the mole fraction of benzene.

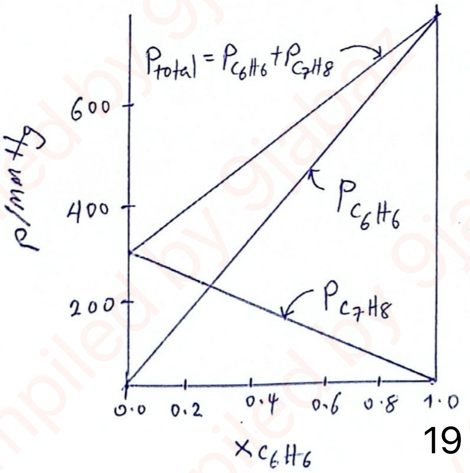

Fig. 3: Total vapour pressure of the benzene-toluene mixture as a function of the benzene mole fraction at 80.1°C.

Example 2

Liquids A and B form an ideal solution. At 45°C, The vapour pressures of pure A and pure B are 66 torr and 88 torr, respectively. Calculate the composition of the vapour in equilibrium with a solution containing 36 mole percent A at this temperature.

Solution:

Because $x_A = 0.36$

$$x_B = 1 - 0.36 = 0.64$$

According to Raoult's law

$$P_A = x_A P_A^* = 0.36 \times 66 \text{ torr} = 23.8 \text{ torr}$$

$$P_B = x_B P_B^* = 0.64 \times 88 \text{ torr} = 56.3 \text{ torr}$$

The total vapour pressure P_T, is given by

$$P_T = P_A + P_B = 23.8 \text{ torr} + 56.3 \text{ torr} = 80.1 \text{ torr}$$

Finally, The mole fraction of A and B in the vapour phase, x_A^V and x_B^V, are given by

$$x_A^V = \frac{P_A}{P_T} = \frac{23.8 \text{ torr}}{80.1 \text{ torr}} = 0.30$$

and

$$x_B^V = \frac{P_B}{P_T} = \frac{56.3 \text{ torr}}{80.1 \text{ torr}} = 0.70$$

Example 3

An ideal solution is made from 5.00 mol of benzene and 3.25 mole of toluene. Calculate ΔG_{mixing} and

ΔS_{mixing} at 298 K and 1 bar pressure. Is mixing a spontaneous process?

Solution.

The mole fractions of the components in the solution are

$$x_{benzene} = \frac{5.00}{5.00 + 3.25} = \frac{5.00}{8.25} = 0.606$$

$$x_{toluene} = \frac{3.25}{8.25} = 0.394$$

According to equation (11),

$$\Delta G_{mixing} = nRT \sum_i x_i \ln x_i$$

For a two-component solution

$$\Delta G_{mix} = nRT(x_1 \ln x_1 + x_2 \ln x_2)$$

If $x_{benzene} = x_1$, and
$x_{toluene} = x_2$, then

$$\Delta G_{mix} = 8.25 mol \times 8.314 J mol^{-1} K^{-1} \times 298 K \times (0.606 \ln 0.606 + 0.394 \ln 0.394)$$

$$= -13.7 \times 10^3 J.$$

$$\Delta S_{mix} = -nR(x_1 \ln x_1 + x_2 \ln x_2)$$

$$= -8.25 mol \times 8.314 J mol^{-1} K^{-1} \times (0.606 \ln 0.606 + 0.394 \ln 0.394)$$

$$= 46.0 JK^{-1}$$

Mixing is spontaneous because $\Delta G_{mix} < 0$ for an ideal solution

NB: If two liquids are miscible, it is always true that $\Delta G_{mix} < 0$.

Deviations from Raoult's law

1. positive deviation.

Example: Carbon disulfide – acetone system ($CS_2 - CH_3COCH_3$)

Most solutions do no behave ideally. The positive deviation corresponds to the case in which the inter-molecular forces between unlike molecules are weaker than those between like molecules, and there is a greater tendency for these molecules to leave the solution than in the case of an ideal solution. Consequently, the vapour pressure of the solution is greater than the sum of the vapour pressure for an ideal solution.

2. negative deviation

Example: Chloroform – acetone ($CHCl_3 - CH_3COCH_3$) system.

Just the opposite of positive deviation holds for a negative deviation from Raoult's law. In this case, unlike molecules attract each other more strongly than they do their own kind, and the vapour pressure of the solution is less than the sum of the vapour pressures from an ideal solution.

Henry's Law

When one solution component is present in excess (this component is called the solvent), it's vapour pressure is quite accurately described by equation (21). In contrast, the vapour pressure of the component present in small amount (this component is called the solute) does not vary with the composition of the solution, as predicted by equation (21). Still, the vapour pressure of the solute varies with concentration in a linear manner:

$$P_2 = K x_2 \qquad (23)$$

Equation (23) is known as Henry's law (after the English chemist William Henry, 1775-1836), where K, the Henry's law constant, has units of pressure.

Henry's law relates the mole fraction of the solute to its partial (vapour) pressure.

Alternatively, Henry's law can be expressed as

$$P_2 = K' m \qquad (24)$$

where m is the molality of the solution and the constant K' now has the units atm mol^{-1} kg of the solvent.

Henry's law is normally associated with solutions of gases in liquids, although it is equally applicable to solutions containing nongaseous volatile solutes.

It has great practical importance in chemical and biological systems:

(i) The effervescence observed when a drink or champagne bottle is opened is a demonstration of the decrease in gas — mostly CO_2 — solubility as its partial pressure is lowered.

(ii) The emboli (gas bubbles in the bloodstream) suffered by deep-sea divers who rise to the surface too rapidly also illustrate Henry's law.

Deviations from Henry's law

There are several types ~~of~~ of deviations from Henry's law:

(i) The law holds only for dilute solutions

(ii) If the dissolved gas interacts chemically with the solvent, then the solubility can be greatly enhanced. Gases such as CO_2, H_2S, NH_3, and HCl all have high solubilities in water because they react with the solvent

(iii) The third type of deviation is illustrated by the dissolution of oxygen in blood. Normally, oxygen is only sparingly soluble in water, but its solubility increases dramatically if the solution contains hemoglobin or myoglobin.

Example 4

Calculate the molal solubility of carbon dioxide in water at 298K and a CO_2 pressure of

[2.2]

3.3×10^{-4} atm, which corresponds to the partial pressure of CO_2 in air. The Henry's law constant, K, for CO_2 is given as 1.24×10^6 torr (K' is 29.3 atm mol^{-1} kg of water.

Solution

The mole fraction of solute (CO_2) is given as:

$$X_{CO_2} = \frac{P_{CO_2}}{K}$$

Because the number of moles of CO_2 dissolved in 1000g of water is small, we can approximate the mole fraction as follows:

$$X_{CO_2} = \frac{n_{CO_2}}{n_{CO_2} + n_{H_2O}} = \frac{n_{CO_2}}{n_{H_2O}}$$

So that

$$n_{CO_2} = \frac{P_{CO_2} n_{H_2O}}{K}$$

Finally,

$$n_{CO_2} = (3.3 \times 10^{-4} \times 760)\text{torr} \times \frac{1000g}{18.01 g mol^{-1}} \times \frac{1}{1.24 \times 10^6 \text{torr}}$$

$$= 1.12 \times 10^{-5} \text{mol}.$$

NB: 1 atm = 760 torr.

Because this is the number of moles of CO_2 in 1000g or 1 kg of H_2O, the molality is 1.12×10^{-5} mol $(kg\ H_2O)^{-1}$.

Alternatively;

We can use equation (24) and proceed as follows:

$$m = \frac{P_{CO_2}}{K'}$$

$$= \frac{3.3 \times 10^{-4} \text{ atm}}{29.3 \text{ atm mol}^{-1} \text{ kg } H_2O}$$

$$= 1.12 \times 10^{-5} \text{ mol } (\text{kg } H_2O)^{-1}$$

Example 5.

The average human with a 70 kg has a blood volume of 5.00 L. The Henry's law constant for the solubility of N_2 in H_2O is 9.04×10^4 bar at 298 K. Assume that this is also the value of the Henry's law constant for blood and that the density of blood is 1.00 kg L^{-1}.

Calculate the number of moles of nitrogen absorbed in this amount of blood in air of composition 80.% N_2 at sea level, where the pressure is 1 bar, and at pressure of 50 bar.

SOLUTION

$$\text{Density} = \frac{\text{mass}}{\text{Volume}}$$

$$\text{mass} = \text{Density} \times \text{volume}$$

$\text{Mass} = 1.00\,\text{kg L}^{-1} \times 5.00\,\text{L}$

$= 5.0\ \text{kg} = 5.0 \times 10^3\,\text{g}.$

Density of blood = Density of H_2O

$\therefore$ Mass of blood = mass of H_2O.

Because the number of moles of N_2 dissolved in 1000g of blood ($\equiv H_2O$) is small, we can approximate the mole fraction as follows:

$$x_{N_2} = \frac{P_{N_2}}{K}$$

$$= \frac{n_{N_2}}{n_{N_2} + n_{H_2O}} = \frac{n_{N_2}}{n_{H_2O}} = \frac{P_{N_2}}{K}$$

$$\therefore n_{N_2} = n_{H_2O} \frac{P_{N_2}}{K}$$

(a) $n_{H_2O} = \dfrac{\text{mass of } H_2O}{\text{Molar mass of } H_2O}$

$MM_{H_2O} = 18.02\,\text{g mol}$

$$\therefore n_{N_2} = \frac{5.0 \times 10^3\,\text{g}}{18.02\,\text{g mol}^{-1}} \times \frac{0.80\,\text{bar}}{9.04 \times 10^4\,\text{bar}}.$$

$= 2.5 \times 10^{-3}$ mol at 1 bar total pressure.

NB: P_{N_2} is taken as 0.80 bar because the air is said to be composed of 80% of N_2 at sea level, where the pressure is 1 bar.

At 50 bar, $n_{N_2} = 50 \times 25 \times 10^{-3}$ mol.

$= 0.13$ mol.

Real solutions

As pointed out earlier, most solutions do not behave ideally. One problem that immediately arises in dealing with nonideal solutions is how to write the chemical potentials for the solvent and solute components.

The solvent component

The chemical potential of the solvent in an ideal solution is given as

$$\mu(l) = \mu_1^*(l) + RT\ln x_1 \quad \text{------} \quad (22)$$

where $x_1 = P_1/P_1^*$ and P_1^* is the equilibrium vapour pressure of pure component 1 at T. The standard state is the pure liquid and is attained when $x_1 = 1$.

For nonideal solution, we write

$$\mu_1(l) = \mu_1^*(l) + RT\ln a_1 \quad \text{------} \quad (25)$$

Where a_1 is the activity of the solvent. Nonideality is the consequence of unequal intermolecular forces between solvent-solvent and solvent-solute molecules. Therefore, the extent of nonideality depends on the composition of solution, and the activity of the solvent plays the role of "effective" concentration.

The solvent's activity can be expressed in terms of vapour pressure as

$$a_1 = \frac{P_1}{P_1^*} \text{ ——— } (26)$$

Where P_1 is the partial vapour pressure of component 1 over the (nonideal) solution.

Activity is related to concentration (mole fraction) as follows:

$$a_1 = \gamma_1 x_1 \text{ ——— } (27)$$

Where γ_1 is the activity coeficient.

Equation (25) can now be written as

$$\mu_1(l) = \mu_1^*(l) + RT \ln y_1 + RT \ln x_1 \text{ —— } (28)$$

The value of γ_1 is a measure of the deviation from ideality.

In the limiting case, where $x_1 \to 1$, $\gamma_1 \to 1$ and activity and the mole fraction are identical. This condition also holds for an ideal solution at all concentrations.

The solute component

For dilute, nonideal solutions in which there is no chemical interaction, the solvent obeys Raoult's law, and the solute obeys Henry's law. Such solutions are sometimes called "ideal dilute solutions". If the solution were ideal, the chemical potential of the solute is also given by Raoult's law.

$$\mu_2(l) = \mu_2^*(l) + RT \ln x_2$$

$$= \mu_2^*(l) + RT \ln \frac{P_2}{P_2^*}$$

In an ideal dilute solution, Henry's law applies. That is $P_2 = Kx_2$ ~~that~~

$$\mu_2(l) = \mu_2^*(l) + RT \ln \frac{Kx_2}{P_2^*}$$

$$= \mu_2^*(l) + RT \ln \frac{K}{P_2^*} + RT \ln x_2$$

$$= \mu_2^\circ(l) + RT \ln x_2 \qquad \text{——— (28)}$$

Where $\mu_2^\circ(l) = \mu_2^*(l) + RT \ln (K/P_2^*)$.

Equation (28) holds only for dilute solutions.

For nonideal solutions in general (beyond the dilute solution limit) equation (28) is modified to

$$\mu_2(l) = \mu_2^\circ(l) + RT \ln a_2 \qquad \text{——— (29)}$$

where a_2 is the activity of the solute.

As in the case of the solvent component, we have $a_2 = \gamma_2 x_2$, where γ_2 is the activity coefficient of the solute.

Here we have $a_2 \to x_2$ or $\gamma_2 \to 1$ as $x_2 \to 0$.

Henry's law is now given by

$$P_2 = K a_2 \quad \text{———} \quad (30)$$

Concentrations are usually expressed in molalities (or molarities) instead of mole fractions.

In molality, equation (28) takes the form

$$\mu_2(l) = \mu_2^0(l) + RT \ln \frac{m_2}{m^0} \quad \text{———} \quad (31)$$

where $m^0 = 1 \text{ mol kg}^{-1}$ so that the ratio m_2/m^0 is dimensionless.

For nonideal solutions, equation (31) is rewritten as

$$\mu_2(l) = \mu_2^0(l) + RT \ln a_2 \quad \text{———} \quad (32)$$

where $a_2 = \gamma_2 (m_2/m^0)$.

In the limiting case of $m_2 \to 0$, we have $a_2 \to m_2/m^0$ or $\gamma_2 \to 1$.

Example 7

Calculate the activity and activity coefficient for CS_2 at $x_{CS_2} = 0.3502$; given that $P_{CS_2} = 358.3$ torr and $P^*_{CS_2}$ (vapour pressure of pure CS_2) $= 512.3$ torr.

Assume a Raoult's law standard state.

solution

$$a_{CS_2} = \frac{P_{CS_2}}{P^*_{CS_2}} = \frac{358.3 \text{ torr}}{512.3 \text{ torr}} = 0.6994$$

$$\gamma_{CS_2} = \frac{a_{CS_2}}{x_{CS_2}} = \frac{0.6994}{0.3502} = 1.997.$$

Colligative properties

Many solutions consist of nonvolatile solutes that have limited solubility in a volatile solvent. Examples are solutions of sucrose or sodium chloride in water. Important properties of these solutions, including boiling point elevation, freezing point depression and osmotic pressure are found to depend only on the solute concentration (i.e the number of solute molecules present) — not on the size or molar mass of the molecules. These properties are called colligative, or collective, properties.

If the vapour pressure of the solvent follows Raoult's law, then

$$P_1 = P_1^* x_1$$

Because $x_1 = 1 - x_2$, in the presence of a nonvolatile solute, the equation above becomes

$$P_1 = (1 - x_2) P_1^*$$

Rearranging this equation gives

$$P_1^* - P_1 = \Delta P = x_2 P_1^* \quad \text{———} \quad (33)$$

where Δp, the decrease in vapour pressure from that of the pure solvent, is directly proportional to the mole fraction of the solute.

Boiling-point Elevation

The boiling point of a solution is the temperature at which its vapour pressure is equal to the external pressure.

For a solution containing a nonvolatile solute, the boiling point elevation originates in the change in the chemical potential of the solvent due to the presence of the solute.

According to equation (22) earlier discussed; i.e

$$\mu_1(l) = \mu_1^*(l) + RT\ln x_1 \quad \text{———} \quad (22)$$

the chemical potential of the solvent in a solution is less than the chemical potential of the pure solvent by an amount equal to $RT\ln x_1$.

Fig 4 illustrates how this changes affects the boiling point of the solution.

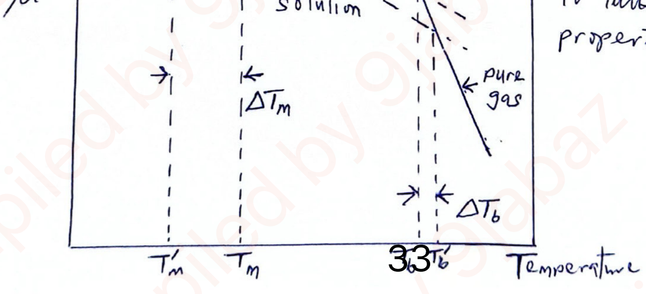

Fig 4: plot of chemical potentials versus temperature to illustrate colligative properties.

Because the solute is nonvolatile, it does not vaporise; therefore, the curve for the vapour phase is the same as that for the pure vapour. On the other hand, because the liquid contains a solute, the chemical potential of the solvent decreases. The points where the curve for the vapour intersects the curves for the liquid (pure and solution) correspond to the boiling points of the pure solvent and the solution, respectively. From the plot, we see that the boiling point of the solution (T'_b) is higher than that of the pure solvent (T_b).

At the boiling point the solvent vapour is in equilibrium with the solvent in solution, so that

$$\mu_1(g) = \mu_1(l) = \mu_1^*(l) + RT\ln x_1$$

or

$$\Delta\mu_1 = \mu_1(g) - \mu_1^*(l) = RT\ln x_1 \quad \text{——— (34)}$$

where $\Delta\mu_1$ is the Gibbs energy change associated with the evaporation of 1 mole of solvent from the solution at temperature, T, its boiling point. Thus, we can write

$$\Delta\mu_1 = \Delta_{vap}\overline{G}.$$

Dividing equation (34) by T, we obtain

$$\frac{\Delta_{vap}\overline{G}}{T} = \frac{\mu_1(g) - \mu_1^*(l)}{T} = R\ln x_1$$

According to the Gibbs-Helmholtz equation; i.e

$$\left[\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right]_P = -\frac{\Delta H}{T^2} \quad \text{——— (35)}$$

we write

$$\frac{d(\Delta G/T)}{dT} = -\frac{\Delta H}{T^2} \quad \text{(at constant p)}$$

or

$$\frac{d(\Delta_{vap}\bar{G}/T)}{dT} = \frac{-\Delta_{vap}\bar{H}}{T^2} = R\frac{d(\ln x_1)}{dT}$$

where $\Delta_{vap}\bar{H}$ is the molar enthalpy of vaporization of the solvent from the solution.

Because the solution is dilute, $\Delta_{vap}\bar{H}$ is taken to be the same as the molar enthalpy of vaporization of the pure solvent.

Rearranging the last equation gives

$$d\ln x_1 = -\frac{\Delta_{vap}\bar{H}}{RT^2}dT \qquad (36)$$

Integration of equation (36) between the limits T_b' and T_b; and because the mole fraction of the solvent is x_1 at T'_b and 1 at T_b, we write

$$\int_{\ln 1}^{\ln x_1} d\ln x_1 = \int_{T_b}^{T'_b} -\frac{\Delta_{vap}\bar{H}}{RT^2}dT$$

$$\ln x_1 = -\frac{\Delta_{vap}\bar{H}}{R}\left(\frac{1}{T'_b} - \frac{1}{T_b}\right)$$

$$= -\frac{\Delta_{vap}\bar{H}}{R}\left(\frac{T'_b - T_b}{T'_b T_b}\right)$$

$$= -\frac{\Delta_{vap}\bar{H}}{R}\cdot\frac{\Delta T}{T_b^2} \qquad (37)$$

where $\Delta T = T'_b - T_b$.

To arrive at equation (37) two assumptions were made, both of which are based on the fact that T'_b and T_b differ only by a small amount (a few degrees).

(i) we assumed $\Delta_{vap}\bar{H}$ to be temperature independent

(ii) $T'_b \approx T_b$, so that $T'_b T_b \approx T_b^2$.

If we express the concentration in terms of the amount of solute present, we write

$$\ln x_1 = \ln(1-x_2) = \frac{-\Delta_{vap}\bar{H}}{R}\frac{\Delta T}{T_b^2}$$

where, by Maclaurin's series,

$$\ln(1-x_2) = -x_2 - \frac{x_2^2}{2} - \frac{x_2^3}{3} \cdots$$

$$\approx -x_2 \quad (x_2 \ll 1)$$

we now have

$$\Delta T = \frac{RT_b^2}{\Delta_{vap}\bar{H}} x_2$$

To convert the mole fraction x_2 into a more practical concentration unit, such as molality (m_2), we write

$$x_2 = \frac{n_2}{n_1+n_2} \approx \frac{n_2}{n_1} = \frac{n_2}{W_1/M_1} \qquad (n_1 \gg n_2)$$

where w_1 is the mass of the solvent in kg and M_1 is the molar mass of the solvent in kgmol^{-1}, respectively.

NB: $\dfrac{n_2}{W_1/M_1} = \dfrac{n_2}{w_1} M_1$

where $\frac{n_2}{W_1}$ gives the molality of the solution, m_2.

$\therefore x_2 = M_1 m_2$, and thus,

$$\Delta T = \frac{R T_b^2 M_1}{\Delta_{vap}\overline{H}} m_2 \qquad (38)$$

Note that all the quantities in the first term on the right of equation (38) are constants for a given solvent, and so we have

$$K_b = \frac{R T_b^2 M_1}{\Delta_{vap}\overline{H}} \qquad (39)$$

where K_b is called the molal boiling-point-elevation constant. The units of K_b are $K\,mol^{-1}\,kg$.

finally,

$$\Delta T = K_b m_2 \qquad (40)$$

Figure 5 shows the phase diagrams of pure water and an aqueous solution. Upon the addition of non-volatile solute, the vapour pressure of the solution decreases at every temperature. Consequently, the boiling point of the solution at 1 atm will be greater than 373.15K.

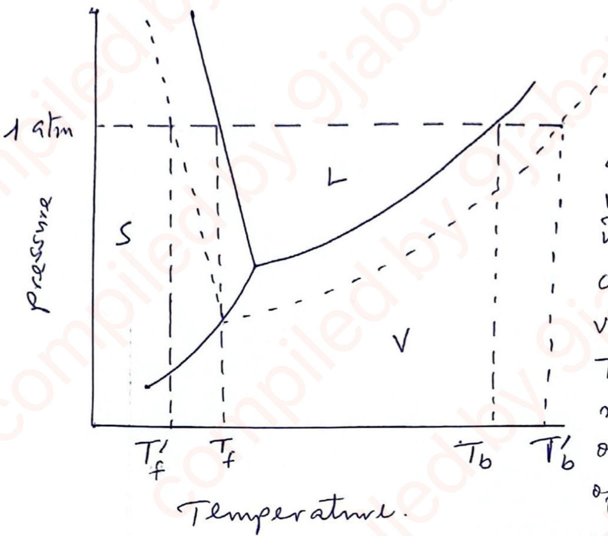

Fig 5: phase diagrams of pure water and of water in an aqueous solution containing a non volatile solid. T_f', T_f, T_b and T_b' represent freezing point of solution, freezing point of solvent, boiling point of solvent and boiling point of solution, respectively.

Freezing-point Depression

The thermodynamic analysis of freezing-point depression is similar to that of boiling point elevation. If we assume that when a solution freezes, the solid that separates from the solution contains only the solvent, then the curve for the chemical potential of the solid does not change (Fig. 4). Consequently, the solid curve for the solid and the dashed curve for the solvent in solution now intersect at a point (T_f') below the freezing point of the pure solvent (T_f).

By following the same procedure as that for the boiling-point elevation, we can show that the drop in freezing-point, ΔT, (i.e; $T_f - T_f'$) is

$$\Delta T = K_f m_2 \quad \text{——} \quad (41)$$

where K_f is the molal freezing-point-depression constant given by

$$K_f = \frac{RT_f^2 M_1}{\Delta_{fus}\bar{H}} \quad \text{———} \quad (42)$$

where $\Delta_{fus}\bar{H}$ is the enthalpy of fusion of the solvent.

Application of freezing-point depression phenomenon

The freezing point depression phenomenon has many examples in everyday life and in biological systems.

(i) Salts, such as sodium chloride (NaCl) and calcium chloride ($CaCl_2$) are used to melt ice on roads and sidewalks. Ice on winter roads and sidewalks melts readily when sprinkled with salt. This method of thawing depresses the freezing-point of water.

(ii) The organic compound ethylene glycol [$CH_2(OH)CH_2(OH)$] is the common automobile antifreeze. It is also employed to de-ice airplanes.

Example 8

For a solution of 45.20g of sucrose ($C_{12}H_{22}O_{11}$) in 316.0g of water, calculate (a) the boiling point and (b) the freezing point. K_b and K_f for water are 0.51 K mol^{-1}kg and 1.86 K mol^{-1}kg, respectively.

Solution

(a) The molality of the solution is given by

Class Notes/Jottings With Questions

(i) Application of thermodynamic concept to mixture and solution

(ii) Entropy, Enthalpy and free energy of mixing

(iii) Open system and chemical potential

(iv) Chemical potential of ideal gas mixture or solution

(v) Fugacity function

(vi) Partial molar quantities - Gibbs-Duhem equation

(vii) Gibbs Phase rule and phase Diagram

(viii) Ideal binary mixtures - Raoult's and Henry's laws.

(ix) Solubility and pressure

(x) Solubility and temperature

(xi) Solutions of involatile solutes - The Colligative properties

(xii) Colligative properties of electrolyte

Some of Quantities Used

Percent by Weight ⇒ $\dfrac{\text{Weight of Solute}}{\text{Weight of Solute + solvent}} \times 100\%$

$= \dfrac{\text{Weight of Solute}}{\text{Weight of Solution}} \times 100\%$

Mole Fraction (x) – Is defined by no of moles of

$\dfrac{\text{no of moles of Component i}}{\text{no of moles of all components}}$

$= \dfrac{n_i}{\Sigma_i n}$ ...... ②

⇒ The mole fraction has no unit.

Molarity – It expresses the amount of mole in 1L. It is the no of moles of solute dissolved in 1L of solution.

$M = \dfrac{\text{no of moles of Solute}}{\text{1 litre of solution.}}$ (mol L^{-1})

Molality – No of mole of solute dissolved in 1kg (1000g) of solvent.

$\text{Molality} = \dfrac{\text{no of moles of solute}}{\text{Mass of solvent}}$ (mol kg^{-1})

Ideal Solution.

Propeties

① Intermolecular Interactions are the same for all molecules

$(\Delta_{mix} H^\circ)_{P,T} = 0$

② Molecules have finite Volume Independent of composition.

$(\Delta_{mix} V)_{T,P} = 0$

③ The solvent follows Raoult's law & the ~~Solute~~ Solute follows Henry's law.

④ The activity coefficient for all Species is Unity

$\gamma = 1$

⑤ All mixtures are miscible i.e they mix at all Concentrations and temperature.

⑥ Mixing is driven by a positive entropy change upon mixing. $(\Delta_{mix} S^\circ)_{T,P} > 0$.

However, In general Solution in the liquid phase are non-ideal. Non-Ideal solutions are called real Solution

Partial Molar Quantities.

The partial molar Volume is the change In Volume upon addition of component 2 to component 1 holding all other Variables i.e P, T and moles of 1 constant. Unlike Ideal solutions, ~~Volumes are not additive~~ Real Solution Volumes are not ADDITIVE

$$V = V(n_1, n_2)$$

$$dV = \left(\frac{\partial V}{\partial n_1}\right)_{T, P, n_2} dn_1 + \left(\frac{\partial V}{\partial n_2}\right)_{T, P, n_1} dn_2$$

[Note: Const. T & const. P]

$$dV = \bar{V}_1 dn_1 + \bar{V}_2 dn_2$$

$$\int_0 dV = \bar{V}_1 \int_0^{n_1} dn_1 + \bar{V}_2 \int_0^{n_2} dn_2$$

$$V = \bar{V}_1 n_1 + \bar{V}_2 n_2$$

[$\bar{V}_2$ = Molar Volume of 2]

$$\boxed{\bar{V}_2 = \frac{V - \bar{V}_1 n_1}{n_2}} \qquad \boxed{\bar{V}_1 = \frac{V - \bar{V}_2 n_2}{n_1}}$$

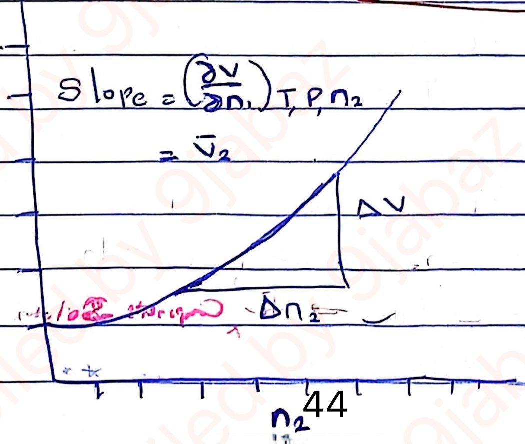

Fig 1

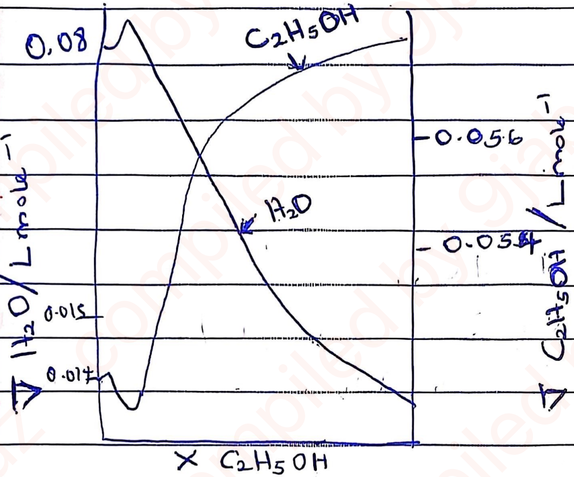

Fig 2.

Partial Molar Gibb's Energy.

Partial molar quantities permit us to express the total extensive properties such as volume, energy, enthalpy & Gibbs energy.

i = Component will are considering

j = All other Components present

$$\overline{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j}$$

i = Component will are considering

j = All other Components

The Gibbs - Duhem Equation.

[μ = chemical potential]

$$dG = -SdT + Vdp + \Sigma_i \mu_i dn_i$$

$dG = \Sigma_i \mu_i dn_i \Rightarrow$ for 2 Components Solution

$dG = \mu_1 dn_1 + \mu_2 dn_2$ ... etc

Gibbs - ~~[illegible]~~ Duhem Equation.

It simply the chemical potential in two binary solutions are not Independent.

$$dG = \mu_1 dn_1 + \mu_2 dn_2.$$

$$\int_0^G dG = \mu_1 \int_0^{n_1} dn_1 + \mu_2 \int_0^{n_2} dn_2$$

[If addition of the two is -ve It is Spontaneous]

$$\Rightarrow G = \mu_1 n_1 + \mu_2 n_2 \ldots\ldots ** $$

$$dG = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 \quad --**$$

$$\mu_1 \cancel{dn_1} + \cancel{\mu_2 dn_2} = \mu_1 \cancel{dn_1} + n_1 d\mu_1 + \mu_2 \cancel{dn_2} + n_2 d\mu_2$$

$$\boxed{\begin{gathered} n_1 d\mu_1 + n_2 d\mu_2 = 0 \\ x_1 d\mu_1 + x_2 d\mu_2 = 0. \end{gathered}} \Leftarrow \text{Gibbs - Duhem equation.}$$

If the (chemical potential of the first component is $d\mu_1$

$$\therefore x_1 d\mu_1 = -x_2 d\mu_2.$$

Thermodynamics of Mixing.

(The one in large quantity = Solvent)

For a gaseous system,

$$\bar{G} = \bar{G}^{*} + RT \ln \frac{P^{*}}{1\,\text{bar}}$$

[G^{*} = Molar free mixing energy of the solution]

In a mixture of ideal gases, the chemical potential of the ~~bright~~ i component is given.

$$\bar{G}_i = \mu_i$$

$$\mu_i = \mu_i^{\circ} + RT \ln \frac{P_i}{1\,\text{bar}}$$

Where P_i = partial pressure of component "i" in the mixture.

μ_i^0 = Standard Chemical potential of Component i when its standard partial pressure is 1 bar.

Gaseous System

$$\mu_i = \mu_i \bar{G}_i + \mu_2 \bar{G}_2 = \bar{G}_i$$

The ~~Standard chemical~~

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$$\bar{G} = \bar{G}^{\circ} + RT \ln \frac{P}{1\,\text{bar}}$$

$$\bar{G}^{\circ} = \mu^0$$

Already written

$$\boxed{\bar{G} = \mu_i^0 + RT \ln \frac{P}{1\,\text{bar}}} \quad \ldots *$$

And: $G = \mu_1 n_1 + \mu_2 n_2$ ... **

$$G = \bar{G}_1 n_1 + \bar{G}_2 n_2$$

Hint. You can substitute $\bar{G}_1$ in ** to *

Recall: $\overline{G} = \overset{\Uparrow}{G_1^\circ} + RT\ln\frac{P_1}{1bar} = \mu_1^\circ + RT\ln\frac{P_1}{1bar}$

Note: $G = \overline{G}n_1 + \overline{G_2}n_2$

$$G_{initial} = n_1\left(\mu_1^\circ + RT\ln\frac{P_1}{1bar}\right) + n_2\left(\mu_2^\circ + RT\ln\frac{P_2}{1bar}\right)$$

Note: $P_1 + P_2 = P$ only if there is no change in Volume as a result of mixing, that is: $\Delta_{mix}V = 0$.

This condition holds for Ideal solns

$$G_{initial} = n_1(\mu_1^\circ + RT\ln P) + n_2(\mu_2^\circ + RT\ln P)$$

$$G_{final} = n_1(\mu_1^\circ + RT\ln P_1) + n_2(\mu_2^\circ + RT\ln P_2)$$

$$\Delta_{mix}G = G_{final} - G_{initial}$$
$$= n_1RT\ln\frac{P_1}{P} + n_2RT\ln\frac{P_2}{P}$$

$$= n_1RT\ln x_1 + n_2RT\ln x_2 \quad \text{......} \ast\ast\ast\ast$$

Where, $P_1 = x_1p$ and $P_2 = x_2p$

x_1 & x_2 are the mole fractions of 1 and 2 respectively. [The standard chemical potential μ° is the same in the pure state and in the mixture).

$$x_1 = \frac{n_1}{n_1+n_2} = \frac{n_1}{n} \qquad \boxed{\text{If } n_1 + n_2 = n}$$

$$x_2 = \frac{n_2}{n_1+n_2} = \frac{n_2}{n}$$

$n_1 = x_1 n$, $n_2 = x_2 n$.

Subtituting into equation ★★★

$n_1 RT\ln x_1 + n_2 RT\ln x_2$.

$nx_1 RT\ln x_1 + nx_2 RT\ln x_2$.

$nRT[x_1\ln x_1 + x_2\ln x_2]$.

$$\boxed{\Delta_{mix}G = nRT(x_1\ln x_1 + x_2\ln x_2)} \quad \ldots (i)$$

When we have the change in Gibb's free energy with Temperature;

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\boxed{\Delta_{mix}S = -\frac{\Delta_{mix}G}{T}}$$

From ...(i)

$$\left(\frac{\partial \Delta_{mix}G}{\partial T}\right)_p = -\Delta_{mix}S = nR(x_1\ln x_1 + x_2\ln x_2)$$

$$\Delta_{mix}S = -nR(x_1\ln x_1 + x_2\ln x_2).$$ — Entropy //

Now for Enthalpy;

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

$$\Delta_{mix}G = \Delta_{mix}H - T\Delta_{mix}S.$$

$$\Delta_{mix}H = \Delta_{mix}G + T\Delta_{mix}S.$$

$= 0$ Why? Because molecules of ideal gases do not interact with one another so no heat is absorbed / produced as a result of mixing

Example 1: Calculate the Gibbs Energy and entropy of mixing 1.6 moles of Argon at 1 atm and 25°C with 2.6 moles of nitrogen at 1 atm and 25°C. Assume Ideal behaviour.

Solution.

Using: $\Delta_{mix} G = nRT(x_1 \ln x_1 + x_2 \ln x_2)$.

Ar = 1.6 moles   Nitrogen = 2.6 moles.

$x_{Ar} = \dfrac{n_{Ar}}{n_{Ar} + n_{N_2}} = \dfrac{1.6}{1.6 + 2.6} = 0.38$ [has no Unit].

$x_{N_2} = \dfrac{2.6}{1.6 + 2.6} = 0.62$

$T ~~= 273°C~~$ $T = 273 + 25 = 298\,K$.

$R = 8.314\ J mol^{-1} K^{-1}$; $n = n_1 + n_2 = 4.2$ moles

$\Delta_{mix} G = (4.2\ moles) \times 8.314\ J mol^{-1} K^{-1} \times 298K (0.38 \ln 0.38 + 0.62 \times \ln 0.62)$

$\Delta_{mix} G = -6.9\,kJ.$

Mistake: (Take note of "−")

$\Delta_{mix} S = -\dfrac{\Delta_{mix} G}{T} ~~=~~ -\left(\dfrac{-6.9\,kJ}{298\,K}\right) = +23.15\,J/K$

$\Delta G = -ve$ = Spontaneous.

For reaction to proceed, there must be $\Delta S = +ve$

Binary Mixture Of Volatile Liquid

The chemical potential for the liquid must be the same for a gaseous state.

$$\mu^*_{(l)} = \mu^*_{(g)}$$

i = for a Particular Specie)

$$\mu_i = \mu_i^0 + RT \ln \frac{P}{1\,\text{bar}}$$

$$\mu^0_{(l)} = \mu^0_{(g)} = \mu_i^0 + RT \ln \frac{P^*}{1\,\text{bar}}$$

[P^* = Standard presu

(μ^0 = Standard chemical potential at 1bar)

For a two Component System (Liquid & gas)

$$\mu^0_{(l)} = \mu^0_{(g)} = \mu_1^0 + RT \ln \frac{P_1}{1\,\text{bar}}$$

$$\mu^0_{(l)} = \mu^0_{(g)} = \mu_2^0 + RT \ln \frac{P_2}{1\,\text{bar}}$$

$$\mu_{(l)} = \mu^0_{(l)} + RT \ln \frac{P_1}{P^*}$$

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$$\mu^*_{(l)} = \mu^*_{g} = \mu^\circ_{(g)} + RT \ln \frac{p^*}{1\,bar}$$

$$\boxed{\mu^*_{(l)} = \mu^*_{(g)}}$$

$$\mu_{(l)} = \mu_{(g)} = \mu^\circ_{(g)} + RT \ln \frac{P_1}{1\,bar}$$

$$\mu^*_{(l)} = \mu^*_{(g)} + RT \ln \frac{p^*}{1\,bar}$$

$$\mu_{(g)} = \mu^*_{(l)} - RT \ln \frac{p^*}{1\,bar} \quad \ldots\ldots \text{(iii)}$$

$$\mu_{(l)} = \mu^*_{(l)} - RT \ln \frac{p^*}{1\,bar} + RT \ln \frac{P_1}{1\,bar}$$

$$\mu_{(l)} = \mu^*_{(l)} - RT \left(\ln \frac{p^*}{1\,bar} - \ln \frac{P_1}{1\,bar} \right)$$

$$= \mu^*_{(l)} + RT \left(\ln \frac{P_1}{1\,bar} - \ln \frac{p^*}{1\,bar} \right)$$

$$\mu_{(l)} = \mu^*_{(l)} + RT \ln \frac{P_1}{p^*} \quad \ldots\ldots \text{(iv)}$$

Raoult Law

$$\frac{P_1}{p^*} = x_1$$

$$\boxed{P_1 = x_1 p^*} \quad \text{— Raoult law}$$

The partial vapour pressure of a component of a solution is equal to the product of the mole fraction of the component and pressure of the free solution.

equation (v) into (iii)

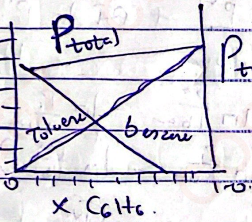
$\mu_{(l)} = \mu^*_{(l)} + RT\ln x_1$

In pure liquid,

$x_1 = 1$ then $\ln x_1 = 0$

$\therefore \mu_{(l)} = \mu^*_{(l)}$ only for an ideal solution.

Solution that OBEY RAOULT law are called ideal solution e.g benzene & Toluene.



$P_{total} = P_{C_6H_6} + P_{C_7H_8}$

Question

liquid A & B form an ideal solution at 45°C, the Vapour pressure of pure A & B are 66 torr & 88 torr respectively. Calculate the composition of the Vapour in equilibrium with a solution containing 36% mole at the temperature.

Solution

liq A $\longrightarrow$ 66 torr, P_A^*

liq B $\longrightarrow$ 88 torr; P_B^*

Solution = 36 mole percent A.

$\frac{36}{100} = 0.36$

$X_A \Rightarrow$ mole fraction of A in the solution = 0.36

$X_B \Rightarrow$ mole fraction of B in the Solution = $1 - X_A$

$X_B = 1 - 0.36 = 0.64$

$P_A = 66$ torr, $P_B = 88$ torr, $X_A = 0.36$, $X_B = 0.64$

Partial pressure of A $(P_A^*) = X_A P_A^*$, ~~$P_B = X$~~

$P_B^* = X_B P_B^*$

$P^*_A = X_A P_A^*$

$P^*_A = 0.36 \times 66 = 23.6$ torr.

$P^*_B = 0.64 \times 88 = 56.3$ torr

$P_T = P_A + P_B = 23.6 + 56.3 = P_T = 79.9$ torr.

$$x_A^v = \frac{P_A}{P_A + P_B} = \frac{P_A}{P_T} = \frac{23.6}{(23.6 + 56.3)\text{ torr}} = 0.3$$

$x_A^v = 0.3$

$$x_B^v = \frac{56.3}{(23.6 + 56.3)\text{ torr}} = 0.70 \qquad x^v_B = 0.70$$

An ideal solution made from 5 moles of benzene and 3.25 mole of toluene. Calculate ΔG of mixing and ΔS of mixing at 298 K and 1 bar pressure

Is the mixing a spontaneous process

$$x_{benzene} = \frac{5}{5+3.25} = 0.606$$

$$x_{toluene} = \frac{3.25}{5+3.25} = 0.394$$

$$n = 5 + 3.25 = 8.25$$

$$\Delta_{mix} G = nRT(x_{benzene} \ln x_{benzene} + x_{toluene} \ln x_{toluene})$$

$$\Delta_{mix} G = 8.25 \times 8.314 \times 298 (0.606 \ln 0.606 + 0.394 \ln 0.394)$$

$$= -13.623 \text{ kJ}$$

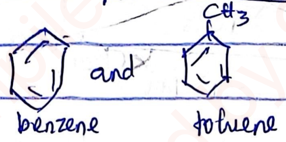
$$\Delta_{mix} S = -\frac{\Delta_{mix} G}{T} = -\left(\frac{-13624}{298}\right)$$

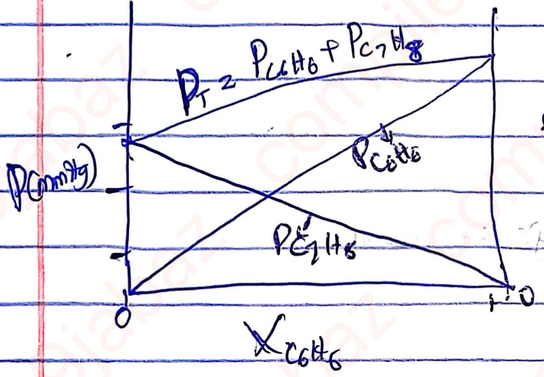
$$\Delta_{mix} S = 45.72 \text{ J/K}$$

Yes, the mixing is a spontaneous process. ($\Delta G < 0$, $\Delta S > 0$)

Deviations from Raoult's Law

(i) Ideal situation

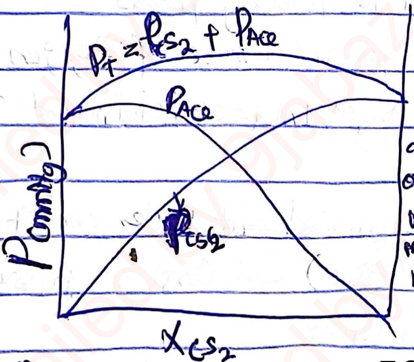




exact raoult law

+ve

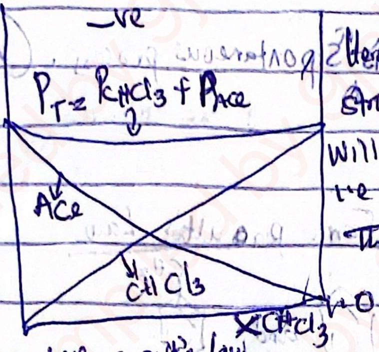
(ii)



Positive raoult's law

Force of attraction is weaker than the one of (benzene + toluene). Therefore, the addition of CS_2 and ACE_2 will be more than the normal additive number (e.g say 20ml of CS_2 and 20mL of Ace, the total which is supposed to be 40ml will be more than 40mL, i.e there will be increase in number of ml

(iii)



negative raoult's law

Here, the force of attraction is stronger, due to IMFs, there ~~negative raoult law~~ will be decrease in the volume, i.e the volume shrinks. Therefore total P will be less than the addition of both

Henry's law

$P_2 = K x_2$

K = Henry's law constant

$P_2 = KM$

Examples

Calculate the ΔS for the following process

(a) mixing of 1 mole of Nitrogen and 1 mole of Oxygen

(b) Mixing of 2 moles of Argon, 1 mole of Helium and 3 moles of hydrogen.

Both a and b are carried out under condition of constant temperature (298K) and constant pressure

Assume ideal behaviour

Nto In note

Calculate the change in entropy for the following processes:

ⓐ Mixing of 1 mole of N_2 & 1 mole of O_2.

ⓑ Mixing of two moles of Ar, 1 mole of He & three moles of H.

Both A & B are carried out under conditions of constant temperature 298K & constant pressure assume ideal behaviour.

Questn 4)

Henry's law

1. Calculate the molar solubility of Carbondioxide in H_2O water at 298K and CO_2 pressure of 3.30×10^{-4} atm which corresponds to the partial pressure of CO_2 in air. The [Henry's law Constant (K) for CO_2 = 1.24×10^{6} torr].

$[K' = 29.3 \text{ atm } mol^{-1} kg]$

Henry's law

Solution ⇒ Solute + Solvent.

1 2.

$P_2 = Kx_2$. ; K = Henry's law constant.

~~P~~

$P_2 = K'm$. $P_1 = x_1 P_1^*$ m = molality.

Solution to questn ①

$P_{CO_2} = Kx_{CO_2}$ ⇒ Henry's law

$$x_{CO_2} = \frac{P_{CO_2}}{K}$$

$\boxed{n_{CO_2} << n_{H_2O}}$

$$x_{CO_2} = \frac{n_{CO_2}}{n_{CO_2} + n_{H_2O}} = \frac{n_{CO_2}}{n_{H_2O}}$$

$$\frac{n_{CO_2}}{n_{H_2O}} = \frac{P_{CO_2}}{K}$$

$$n_{CO_2} = \frac{n_{H_2O} P_{CO_2}}{K}$$ ⇒ 1 atm = 760 torr

$$n_{CO_2} = (760 \text{ torr} \times 3.3 \times 10^{-4}) \times \frac{1000g}{18 g mol^{-1}} \times \frac{1}{1.24 \times 10^6 \text{ torr}}$$

$$= 1.12 \times 10^{-5} \text{ mol}$$

$$m = 1.12 \times 10^{-5} \text{ mol} (kg H_2O)^{-1}$$

$$n_{H_2O} = \frac{m_{H_2O}}{Mm_{H_2O}}$$

$$= \frac{1000g}{18 g/mol}$$

OR

$$P_2 = k'm$$

$$m = \frac{P_2}{k'} = \frac{3.3\times10^{-6}\,\cancel{atm}}{29.3\,\cancel{atm}\,mol^{-1}\,Kg} =$$

*

② The average human with a 70kg ~~Pass~~ has a blood volume of 5.00L. The Henry's law constant for the solubility of N_2 in water is 9.04×10^{4} bar at 298K. Assume that this is also the value of the Henry's Law Constant for blood and that the density of blood is 1.0kg/L. Calculate the no of moles of nitrogen absorbed in this amount of blood in air of composition of 80% N_2 at sea-level where the pressure is 1 bar and at pressure of 50 bar.

Solution.

$$x_{N_2} = \frac{P_{N_2}}{K}$$

Where - The partial pressure

$$x_{N_2} = \frac{n_{N_2}}{n_{N_2} + n_{H_2O}}$$

total pressure = 1 bar.

N_2 is 80% of air

$$P_T\,(1\,bar) = \boxed{P_{N_2}} + P_{other}$$ ✓

$$\text{Density} = \frac{\text{mass}}{\text{Volume}}$$

$$m = DV = 1\,kg\,\cancel{L^{-1}} \times 5.00\,\cancel{L} = 5\,kg.$$

$K = 9.04 \times 10^4$ bar

Volume = 5.00L.

$\rho = 1.0 \text{kg/L}$ ~~of~~ of blood = ρ of H_2O.

Mass of H_2O = mass of water why?

$m_{ass_{bld}} = \rho_{bld} \times V_{bld} = 5.0 \times 10^3 g$ (bld = blood)

$$P_{N_2} = K x_{N_2}$$

$$x_{N_2} = \frac{P_{N_2}}{K}$$

$$x_{N_2} = \frac{n_{N_2}}{n_{N_2} + n_w} = \frac{n_{N_2}}{n_w}$$

$$n_w \gg n_{N_2}$$

$$\frac{n_{N_2}}{n_w} = \frac{P_{N_2} n_w}{K}$$

Note: 80% of 1bar
80% of 50 bar

$$n_w = \frac{5000g}{18.02 g\,mol^{-1}} = \frac{mass}{molar\ mass}$$

$m = 5000g.$

$$n_{N_2} = \frac{5 \times 10^3 g}{18.02 g\,mol^{-1}} \times \underline{0.8 bar} = 2.5 \times 10^{-3} mol$$

Pressure at 50bar = 2.5×10^{-3} mol $\times 50$

Real Solutions

Note: Ideal Solution DOES NOT EXIST.

Recap: Ideal solution $\mu(l) = \mu^*(l) + RT\ln x_1$

Real solution $\mu(l) = \mu^*(l) + RT\ln a_1$

Ideal situation: Solvent $\Rightarrow$ Raoult's law

Solute $\Rightarrow$ Henry's law

$$x_1 = \frac{P_1}{P_1^*}$$

P_1: Partial pressure of one solution

P_2: Partial pressure of free solvn

For any liquid; if $x_1 \to 1$, $\underset{\text{activity}}{a_1} \to 1$

$$a_1 = \frac{P_1}{P_1^*}$$

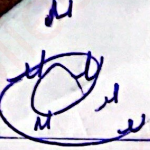
$a_1 = \gamma_1 x_1 \Rightarrow$ γ_1 = activity coefficient

x_1 = solvent component

For Real solution:

$$\mu(l) = \mu^*(l) + RT\ln a_1$$

$$\mu(l) = \mu^*(l) + RT\ln \gamma_1 x_1 \quad =$$



$$\boxed{\mu_{(l)} = \mu^*_{(l)} + RT\ln \gamma_1 + RT\ln x_1}$$

For Solute

$$a_2 = \frac{P_2}{P_2^*}$$

$$\mu_{(l)} = \mu^*_{(l)} + RT\ln\left(\frac{P_2}{P_2^*}\right)$$

$$\mu_{(l)} = \mu^*_{(l)} + RT\ln\left(\frac{Kx_2}{P_2^*}\right)$$

$$\mu_{(l)} = \mu^*_{(l)} + RT\ln\frac{K}{P_2^*} + RT\ln x_2$$

$$= \mu^*_{(l)} + RT\ln\frac{K}{P_2^*} = \mu^\circ_{(l)}$$

$$P_2 = Kx_2.$$

$$\mu_{(l)} = \mu^\circ + RT\ln x_2.$$

Question

Calculate an activity coefficient for Carbon disulphide at $x_{CS_2} = 0.3502$ Given that:

i $P_{CS_2} = 358.3$ torr ⇒ Partial pressure of ~~Cs~~ CS_2

(ii) $P^*_{CS_2} = 512.3$ torr ⇒ Vapour pressure of Carbon disulphide is 512.3 torr

Solution

$$a_{CS_2} = \frac{P_{CS_2}}{P^*_{CS_2}} = \frac{358.3 \text{ torr}}{512.3 \text{ torr}} = 0.6994.$$

$$\gamma_{CS_2} = \frac{a_{CS_2}}{x} = \frac{0.6994}{0.3502} = 1.997$$

Quiz

* With the aid of Sketches, and with specific examples, briefly explain positive and negative deviation for Raoult's law

Ques.

① The vapor pressure of n-propanol ~~at 298K~~ and water at 298K are 21.8 and 23.8 mmHg respectively. In a solution in which the mole fraction of water is 0.20, their partial pressure are 17.8 and 13.4 mmHg respectively, Calculate the activity (a_i) and activity Coefficients (γ_i) of the two components in each solution.

② The mole fraction of a non-volatile solute in water is 0.01 If the equilibrium vapour pressure of pure water at 293K is 2.334 KPa and that of the solution is 2.269 KPa, Calculate the activity and activity coefficient of water.

ⓑ Is the water in this solution acting ideally or close? Give a reason for your answer..

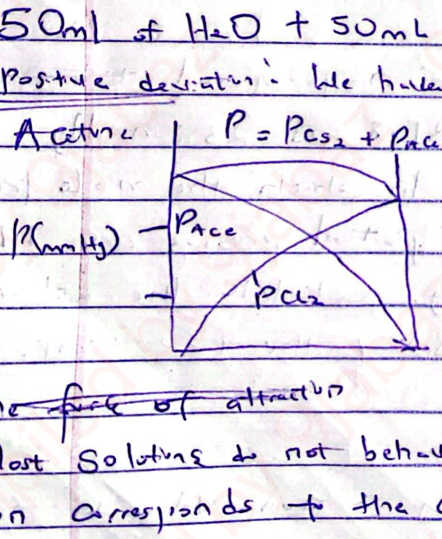
Deviations From Raoult's law

In an Ideal Solution, because molecules are alike then there is no Intermolecular attraction, Then the molecules are additive.

Example:

50ml of H_2O + 50mL (Ethanol).

For positive deviation: We have below: e.g Carbondisulphide and Acetone



This is for Acetone and CS_2

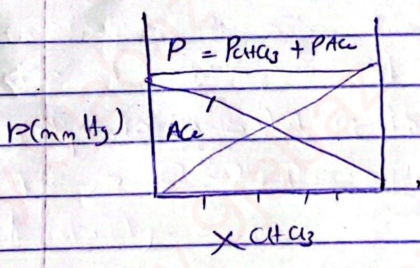
The ~~force of~~ attraction

Most Solutions do not behave ideally. The positive deviation corresponds to the case in which the intermolecular forces between unlike molecules are weaker than those between like molecules and there is a greater tendency for those molecules to leave the solution than in the case of an ideal solution. Consequently, the vapour pressure of the solution is greater than the sum of the vapour pressure for an ideal solution

Negative Deviation

Example: Chloroform — Acetone [$CHCl_3 - CH_3COCH_3$]

Just the opposite of positive deviation, holds for a negative deviation from Raoult's law. In this case, unlike molecules attract each other more strongly than they do their own kind, and the vapour pressure of the solution is less than the sum of the vapour pressure from an ideal solution



Note: Since there is a stronger force of attraction, there will be a shrink in volume then a decrease in pressure.

Example: class:

Calculate the change in entropy of the following processes:

(a) Mixing of 1 mole of N_2 and 1 mole of O_2

(b) Mixing of 2 moles of Argon, 1 mole of Helium & 3 moles of Hydrogen.

Both A & B are carried out under conditions of constant temperature i.e 298K & constant pressure. Assume Ideal behaviour!

Note :- Henry's law is only applicable to dilute solutions. They can mix and form chemical bond. (but each of the components cannot be gotten as solute from the solution).

Example 4: Calculate the molar solubility of carbon dioxide in water at 298K and CO_2 pressure of 3.3×10^{-4} atm, which corresponds to the partial pressure of CO_2 in air. The Henry's law constant, K for CO_2 is given as 1.24×10^{6} torr (K' is 29.3 atm mol^{-1} kg of water)

Solution

The mole fraction of solute CO_2 is given as!

$$X_{CO_2} = \frac{P_{CO_2}}{K}$$

Because the no of moles of CO_2 dissolved in 1000g of water is small, we can approximate the mole fraction as follow!

$$X_{CO_2} = \frac{n_{CO_2}}{n_{CO_2} + n_{H_2O}} = \frac{n_{CO_2}}{n_{H_2O}}$$

$$n_{CO_2} = \frac{P_{CO_2} n_{H_2O}}{K}$$ ✓

Finally,

$$n_{CO_2} = (3.3 \times 10^{-4} \times 760)\text{torr} \times \frac{1000g}{18.01\,g\,mol^{-1}} \times \frac{1}{1.24 \times 10^{6}\text{torr}}$$

$$= 1.12 \times 10^{-5}\,mol.$$

Note: 1 atm = 760 torr

Because this is the no of moles of CO_2 in 1000g or 1kg of H_2O, the molality is:

$$1.12 \times 10^{-5}\,mol\,(kg\,H_2O)^{-1}$$

Alternatively

We can use equation (24) and proceed as follows:

$$m = \frac{P_{CO_2}}{K'} = \frac{3.3 \times 10^{-4}\,atm}{29.3\,atm\,mol^{-1}\,kg\,H_2O} = 1.12 \times 10^{-5}\,mol\,kg(H_2O)^{-1}$$

Example 5: Done ✓.

12-05-2025

Colligative Properties

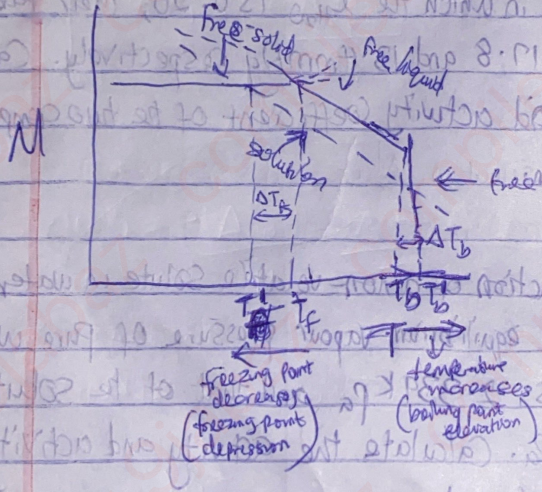
i. Boiling - point elevation

ii. Freezing - point depression

iii. Osmotic pressure

$\mu(l) = \mu^*(l) + RT \ln x_1 \Rightarrow \mu(l) - \mu^*(l) = RT \ln x_1$

$\Delta\mu(l) = RT \ln x_1$



$x_1 = \frac{p_1}{p_1^*} \Rightarrow x_1 + x_2 = 1$

$x_1 = 1 - x_2$

$x_1 = 1 - x_2 = \frac{p_1}{p_1^*}$

$p_1 = p_1^*(1 - x_2)$

$p_1 = p_1^* - x_2 p_1^* \Rightarrow p_1 - p_1^* = -x_2 p_1^*$

$P_1^{sln} = P_1$ [illegible]

$$\boxed{\Delta P_1 = x_2 P_1^*}$$

$\Delta T_b =$ [illegible]

$\Delta T_f =$ [illegible] $P\,d$

$\mu_{1(l)} = \mu^*_{1(l)} + RT \ln x_1$

$\mu_{1(l)} = \mu_{1(g)} = \mu^*_{(l)} + RT \ln x_1$

$\mu_{1(g)} - \mu^*_{(l)} = RT \ln x_1$

$\Delta \mu_1 = RT \ln x_1$

$\Delta \mu_1 = \Delta_{vap} \bar{G}$

$\Rightarrow$ ~~$\Delta_{vap} \bar{G} = RT \ln x_1 T$~~

$\Rightarrow \Delta_{vap} \bar{G} = \mu_{1(g)} - \mu^*_{(l)} = RT \ln x_1$

Dividing by T

$$\frac{\Delta_{vap} \bar{G}}{T} = \frac{\mu_{1(g)} - \mu^*_{(l)}}{T} = R \ln x_1$$

Gibbs - Helmholtz Equation

$$\left[\frac{\partial \left(\frac{\Delta G}{T}\right)}{\partial T}\right]_P = \frac{-\Delta H}{T^2}$$

$$\frac{d\,(\Delta G/T)}{dT} = \frac{-\Delta H}{T^2} \quad (\text{at constant } p)$$

$$\frac{d\,(\Delta_{vap}\bar{G}/T)}{dT} = \frac{-\Delta_{vap}\bar{H}}{T^2} = R\,\frac{d(\ln x_1)}{dT}$$

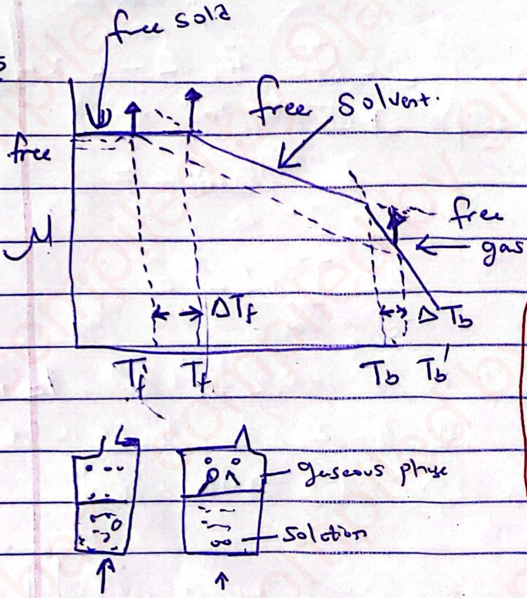
$$\int_{\ln 1}^{\ln x_1} d\ln x_1 = \int_{T_b}^{T'_b} -\frac{\Delta_{vap}\bar{H}}{RT^2}\,dT$$

$$\ln x_1 = -\frac{\Delta_{vap}\bar{H}}{R}\,\frac{\Delta T}{T_b^2}$$

where

$$\Delta T = T'_b - T_b$$

13/05/2025



ΔTf = freezing point depression !.

Note: Initial = T_f'
final = T_f

Initial = T_b
final = T_b'

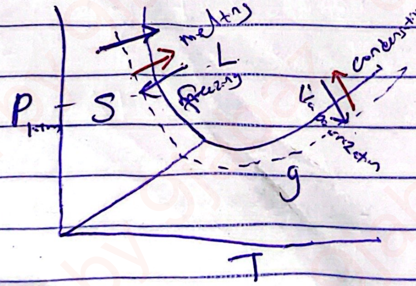
In a Solution, At boiling point you see equilibrium

ΔTb = Boiling point depression

for example: Show that: $\Delta T_b = K m_2$

: $\Delta T_f = K m_2$

Note: $\Delta \mu_1 = \Delta \bar{G}$ from: $\mu_i = \bar{G}_i$



S-G

~~Condens~~

Sublimation

Solid - liquid = melting

Liquid - gas ⇒ Vaporation

$$\Delta \mu = \Delta_{vap} \bar{G}$$

$$\Delta \bar{G} = \mu_{(g)} - \mu^{*}(l) = RT \ln x_1$$

$$\frac{\Delta G}{T} = \frac{\mu_1(g) - \mu^{*}(l)}{T} = R \ln x_1$$

Gibb's Helmoltz equatn.

$$\left[\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right]_P = \frac{-\Delta H}{T^2} \quad ; \text{ At constant P}$$

$$\left[\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right]_P = \frac{R \partial \ln x_1}{\partial T} = R\frac{\partial \ln x_1}{\partial T}$$

$$d\left[\frac{\partial\left(\frac{\Delta G}{T}\right)}{dT}\right] = -\frac{\Delta \bar{H}}{T^2}$$

$$-\frac{\Delta_{vap} \bar{H}}{T^2} = \frac{R \ln x_1}{dT}$$

$$d \ln x_1 = -\frac{\Delta_{vap} \bar{H}\, dT}{RT^2}$$

$$\int_{\ln 1}^{\ln x_1} d \ln x_1 = -\int_{T_b}^{T_b'} \frac{\Delta_{vap} \bar{H}\, dT}{RT^2}$$

$$\ln x_1 = \frac{\Delta_{vap} \bar{H}}{R}\left(\frac{1}{T_b'} - \frac{1}{T_b}\right)$$

$$\ln x_1 = -\frac{\Delta_{vap}\bar{H}}{R}\left(\frac{T_b' - T_b}{T_b' T_b}\right)$$

$$= -\frac{\Delta_{vap}\bar{H}}{R}\frac{\Delta T}{T_b' T_b}$$

$$= -\frac{\Delta_{vap}\bar{H}}{R}\frac{\Delta T}{T_b^2}$$

$x_1 = 1 \Rightarrow$ In a free state

$x_1 + x_2 = 1$; $x_1 = (1 - x_2)$

$$\ln x_1 = \ln(1 - x_2) = -\frac{\Delta_{vap}\bar{H}}{R}\frac{\Delta T}{T_b^2}$$

Maclaurin's Series:

$$\ln(1 - x_2) = -x_2 - \frac{x_2^2}{2} - \frac{x_2^3}{3} \Rightarrow = -x_2.$$

$$(x_2 << 1)$$

$$\ln(1 - x_2) = -x_2 = -\frac{\Delta_{vap}\bar{H}}{R}\frac{\Delta T}{T_b^2}$$

$$x_2 = \frac{\Delta_{vap}\bar{H}}{R}\frac{\Delta T}{T_b^3}$$

$$\Delta T = \frac{R T_b^2 x_2}{\Delta_{vap}\bar{H}}$$

$$x_2 = \frac{n_2}{n_1 + n_2} \simeq \frac{n_2}{n_1}$$

$x_2 = \frac{n_2}{n_1} = \frac{n_2}{w_1/M_1}$ Hint $\left[w_1/M_1 = \frac{\text{Mass}}{\text{Molar mass}} \right]$

$\frac{n_2}{n_1} = n_2 \frac{M_1}{w_1} = \frac{n_2}{w_1} M_1$

Note: Molality = $\frac{\text{no of mole of solute}}{\text{~~Mass of~~ solvent In Kg}}$,

∴ $\frac{n_2}{w_1}$ = Molality. = m_2 $\left[\text{where } m_2 = \text{molality}\right]$

$x_2 = \frac{n_2}{n_1} = m_2 M_1$

$x_2 = \boxed{\frac{n_2}{n_1} = m_2 M_1}$

$\Delta T = \frac{RT_b^2}{\Delta_{vap}\bar{H}} m_2 M_1$

∴ $\Delta T = \frac{RT_b^2}{\Delta_{vap}\bar{H}} M_1 m_2.$

$\Rightarrow \cancel{\frac{RT_b^2}{\Delta H_{xtal}}}, \Rightarrow \frac{RT_b^2}{\Delta_{vap}\bar{H}} M_1 = K$

∴ $\Delta T = K m_2$

$\Delta T = K_b m_2.$

You can be asked!!

For freezing Point depression

$$\Delta T = \frac{RT_f^2 M_1 m_2}{\Delta_{freez}\overline{H}} = K_f m_2$$

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Note $\boxed{x_1 < 1}$

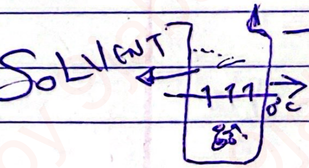
$$\mu_1 = \mu^*(l) + RT\ln x_1$$

$$x_1 + x_2 + x_3 \dots + x_n = 1$$

$$\frac{n_1}{\Sigma n} + \frac{n_2}{\Sigma n} \dots + \frac{n_z}{\Sigma_z} = 1.$$ [For A Solution]

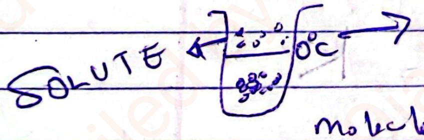
For Only one Component;

$$\mu(l) = \mu^*(l) + RT\ln(1)$$

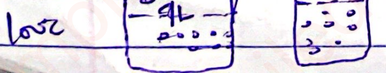


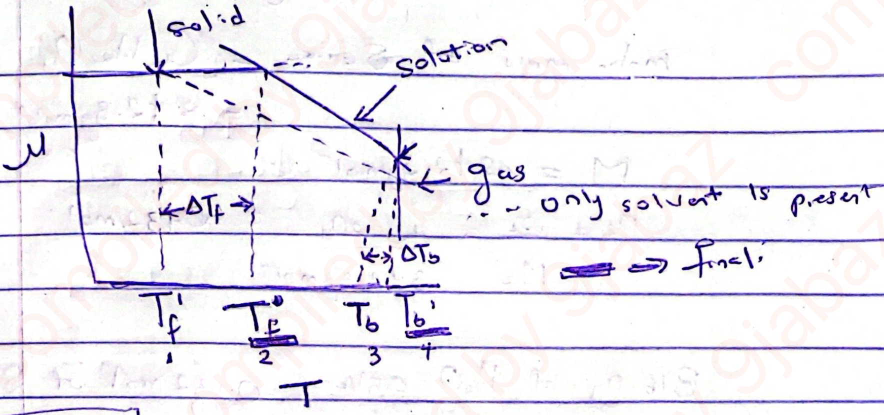
→ Only solvent molecules are present at the exact boiling point.

→ Interface → A kind of equilibrium



→ When Solute is present at the boiling point, because there is a molecule of the solid and it also close to the Interface, It will not allow freezing at that particular temperature.





$\boxed{\Delta T_f = -1}$ ΔT_f = freezing point depression

$T_f' - T_f = 1 - 2 = -1$ ⇒ Decrease

$\Delta T_b = T_b' - T_b$

eg: $4 - 3 = 1$.

Question

For a solution of 45.20g of sucrose in 316.0g of water. Calculate:

ⓐ The boiling point

ⓑ The freezing point

$(K_b \; \& \; K_f)_{water} = 0.51 \, K mol^{-1} kg \; \& \; 1.86 \, K mol^{-1} kg$ respectively.

Solution

$$\Delta T = K_b m_2$$

w_1 = mass of H_2O = 316.0g

w_2 = mass of Sucrose = 45.20g

$K_b = 0.51 \, K mol^{-1} kg$

$K_f = 1.86 \, K mol^{-1} kg$.

molar mass of Sucrse = $C_{12}H_{22}O_{11}$

$= 342.3 g mol^{-1}$

$M = 342.3 g mol^{-1}$

$n_2 = \frac{w_2}{M_2} = \frac{45.20g}{342.3 g mol^{-1}} = 0.132 mol$

316.0g of H_2O contains 0.132 mol of Sucose

1000g of H_2O $\longrightarrow$ x

~~$x = \frac{1000g \times 0.132 mol}{316.0g}$~~

$x = \frac{1000g/kg \times 0.132 mol}{316.0g}$

$x = 0.4178 mol/kg$ of H_2O

$\therefore m_2 = 0.418 mol/kg$ of H_2O.

$\Delta T = 0.51 K \cancel{mol^{-1}} \cancel{kg} \times 0.418 \cancel{mol} kg^{-1}$

$\Delta T = 0.213 K$

Note: water boils at 100°C = 373K

$0°C = 273.15K$

$\Delta T = T_b' - T_b$

$T_b' = \Delta T + T_b = 373.15K + 0.213K$

$T_b' = 373.363K.$ 4

$\Delta T = K_f m_2$

$\Delta T = T_f' - T_f.$

$T_f' = T_f + \Delta T \Rightarrow$

$\Delta T = 1.861 K \cancel{mol^{-1} kg} \times 0.418 \cancel{mol^{-1} kg^{-1}}$

$\Delta T = 0.777K.$

$T_f' = \Delta T + T_f.$

$= -273.15K - 0.777K$

$= -272.32K$

19th May, 2025

Osmotic Pressure

The dissolution of a 4.5g substance in 25g of CCl_4 leads to an elevation of 0.650K. calculate

(a) The freezing point depression

(b) The molar mass of the substance

(c) The factor by which the vapour pressure to which CCl_4 is lowered. ($K_f = 30\ Kmol^{-1}kg$, $K_b = 4.95\ Kmol^{-1}kg$

Solution

$W_2 = 4.5g$, $W_1 = 25g$ (CCl_4), $\Delta T_b = 0.650K$

$M_1 = 153.8 gmol^{-1}$ $\Delta T_f = ?$

(a) $\Delta T_b = K_b m_2$

$$m_2 = \frac{\Delta T_b}{K_b}$$

$$\Delta T_f = K_f m_2$$

$$m_2 = \frac{\Delta T_f}{K_f}$$

$$m_2 = \frac{\Delta T_b}{K_b} = \frac{\Delta T_f}{K_f}$$

$$\Delta T_f = \frac{\Delta T_b K_f}{K_b}$$

$$\Delta T_f = \frac{-0.650K \times 30\ Kmol^{-1}Kg}{4.95\ Kmol^{-1}kg}$$

$\Delta T_f = -3.94K$

(b) $m_2 = \frac{n_2}{1kg\ CCl_4}$

m_2 = molality, w_2 = mass of solute

n_1 = no of mole of solvent

w_1 = mass of solvent

M_1 = molar mass of CCl_4

$$m_2 = \frac{n_2}{w_1(kg)} = \frac{\frac{w_2}{M_2}}{w_1}$$

$$m_2 = \frac{w_2}{M_2 w_1} \Rightarrow \frac{\Delta T_b}{K_b} = \frac{w_2}{M_2 w_1}$$

$$\Rightarrow \Delta T_b = K_b\left(\frac{w_2}{M_2 w_1}\right)$$

$$M_2 = \frac{K_b w_2}{\Delta T_b w_1}$$

$$M_2 = \frac{4.95\,K\,mol^{-1}\,kg \times 4.50g}{0.125kg \times 0.650K}$$

$M_2 = 274\ g\,mol^{-1}$

ⓒ We are to calculate the mole fraction

$x_1 = \frac{P_1}{P_1^*}$ x_1 is higher in a free solvent than in solution.

$x_1 + x_2 = 1$

$x_1 = 1 - x_2$

$x_2 = \frac{n_2}{n_1 + n_2}$

$\cancel{x_2 = \frac{n_2}{n_1 + n_2}}$ $(1 - x_2) = \left(1 - \frac{n_2}{n_1 + n_2}\right)$

$\boxed{x_1 = 1 - x_2}$

$x_1 = 1 - \frac{n_2}{n_1 + n_2}$

$\cancel{x_1 = 1 - \frac{w_2}{M_2}}$ $x_1 = 1 - \frac{\frac{w_2}{M_2}}{\frac{w_1}{M_1} + \frac{w_2}{M_1}}$

$\Rightarrow x_1 = 1 - \frac{\frac{4.50g}{274\,gmol^{-1}}}{\left(\frac{125g}{183.8\,gmol^{-1}}\right) + \left(\frac{4.50g}{274\,gmol^{-1}}\right)}$

$x_1 = 0.980$