Physical Chemistry
Chapter 4
The Properties of Mixtures

by

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Chapter Description

- Aims
  - Determine the fugacity and fugacity coefficients for pure species using generic
  - Determine the heat of formation based on typical data by the constructional of chemical formation equation and graphical data
  - Develop and solve calculational path to determine heat transfer of mixing process

- Expected Outcomes
  - Apply basic physical chemistry principle to solve the problem

- Other related Information
  - **Problem Analysis** - Identify, formulate, research literature and analyse complex engineering problems reaching substantiated conclusions using first principles of mathematics, natural sciences and engineering sciences.

Subtopics

4.1 DEFINITION

4.2 MIXTURES AND ITS THERMODYNAMIC

  (a) Measures of concentration

  (b) Phase Stability for Pure Substance

  (c) Heat Work Changes

4.3 COLLIGATIVE PROPERTIES

  (a) Modification of boiling and freezing points

  (b) Osmosis

4.1 Definitions

- ***Solution*** - homogenous mixture of 2 or more substances.
- ***Solute*** - substance(s) present in the smaller amount(s)
- ***Solvent*** - substance present in the larger amount
- ***Non-electrolyte solution*** - solute is not present as ions.

4.2 MIXTURES AND ITS THERMODYNAMIC
(a) Measures of Concentration

- Concentration is a quantitative study of a solution.

Types of concentration unit
Molar concentration (Molarity), M
Molality, m The number of moles of solute dissolved in 1 kg of solvent
Mole fraction, x

$$[\mathrm{J}] = C_J = \frac{n_\mathrm{J}}{\mathrm{V}}$$

unit; mol dm^{-3} (M) or mol L^{-1}

where;

n_J is amount of moles of J(solute)

V is the volume of solution (dm^{3}or L)

$$b_J = \frac{n_J}{m_{solvent}}$$

unit : mol/kg

where;

n_J is amount of moles of J

$m_{solvent}$ is the mass of the solvent (kg)

$$x_J = \frac{n_J}{n}$$

where;

n_J is amount of moles of J

n is the total amount of molecules (mol)

(b) Phase Stability for Pure Substance

https://en.wikipedia.org/wiki/Water

The difference of Molar Gibbs energy between water and ice.

Source: https://pixabay.com/en/drop-of-water-water-drip-close-1905122/

(c) Heat-Work Changes

$$G_m(P_f) = G_m(P_i) + V_m(P_f - P_i)$$

$$G_m(P_f) = G_m(P_i) + RT \ln \frac{P_f}{P_i}$$

(d) Partial Molar Properties

- The contribution that a substance makes to an overall property of a mixture.
  - (i) Partial molar volume
  - (ii) Partial molar Gibbs energy

d (i)Partial molar volume, V_J

$$V = \int V_A dn_A + \int V_B dn_B$$

$$= V_A \int_0^{n_A} dn_A + V_B \int_0^{n_B} dn_B$$

$$= n_A V_A + n_B V_B$$

Is the mixing to form an ideal solution spontaneous?

- Gibbs energy change, ΔG (The calculation is the same as for mixing of two perfect gas)

$$\Delta G = nRT\left[x_A \ln x_A + x_B \ln x_B\right]$$

  - For spontaneous mixing, $\Delta G < 0$.
  - X_A and X_B less than 1, so $\ln x < 0$, $\Delta G < 0$ at all composition.

$$\begin{aligned}&\text{At constant temperature}\\&\Delta H = 0\\&\Delta S = -nR\left[x_A \ln x_A + x_B \ln x_B\right]\end{aligned}$$

Henry’s Law vs Raoult’s Law

- In a dilute solution the solvent molecules are in environment very much like the one they have in pure liquid.
- In contrast, the solute molecules are surrounded by solvent molecules, which is entirely different from their environment when pure.
- The solvents behaves like slightly modified pure liquid.
- But the solute behaves entirely differently from its pure state.

Henry’s law (molar concentration)

$$p_J = K_H[J]$$

p_J = partial pressure
K_H = Henry’s constant (kPa.m^3/mol)
[J] = molar concentration of substances

Applications;
Oxygen concentration in natural water;
Carbon dioxide Concentration in plasma blood.

Raoult’s Law

- The vapour pressure obtained from Henry’s law can also be used to determine the chemical potential of the solute;

$$\mu_B = \mu_B^* + RT\ln x_B$$

$$where$$

$$\mu_B^* \text{ is the vapour pressure; reffered as } p_B^* \text{ in Henry's law}$$

$$\mu_B = \mu_B^{o} + RT\ln\left[B\right]$$

4.3 Colligative Properties

- **Colligative properties** are properties that depend only on the **number of solute** particles in solution and **not** on the **nature** of the solute particles.
- The origin of colligative properties is the lowering of chemical potential of the solvent by the presence of a solute.
- Non-volatile solute has three main effects:
  - Raise the boiling point of a solution
  - Lower the freezing point
  - Raise the osmotic pressure

- The elevation of boiling point, ΔT_B

$$\Delta T_B = K_B b_B$$

where

K_B is the ebullioscopic constant

b_B is molality of the solute B

(a)Modification of freezing points

- The depression of freezing point, ΔT_f

$$\Delta T_f = K_f b_B$$

$$where$$

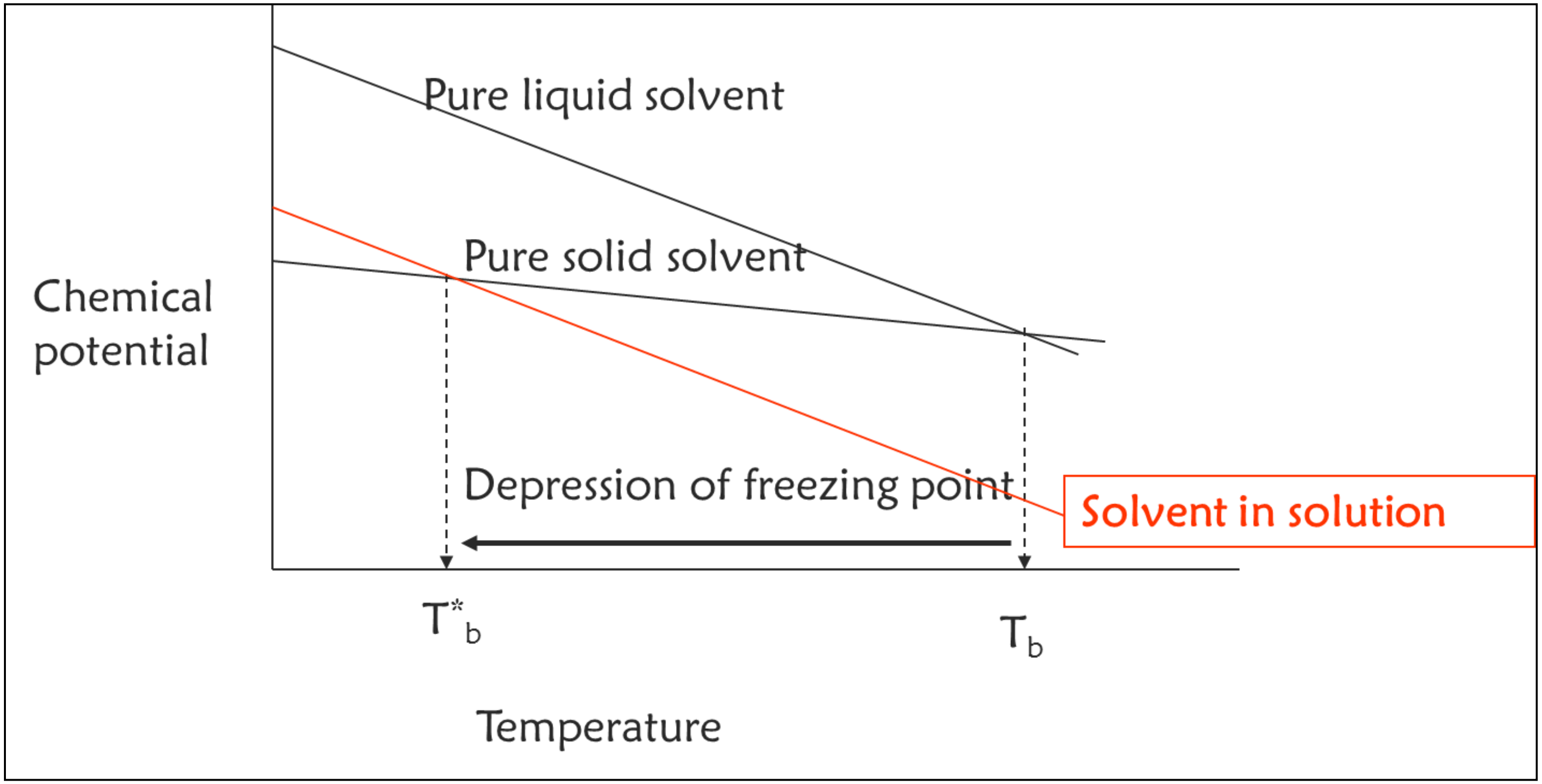
$$K_f \text{ is cryoscopic constant}$$

$$b_B \text{ is the molality of the solute B}$$

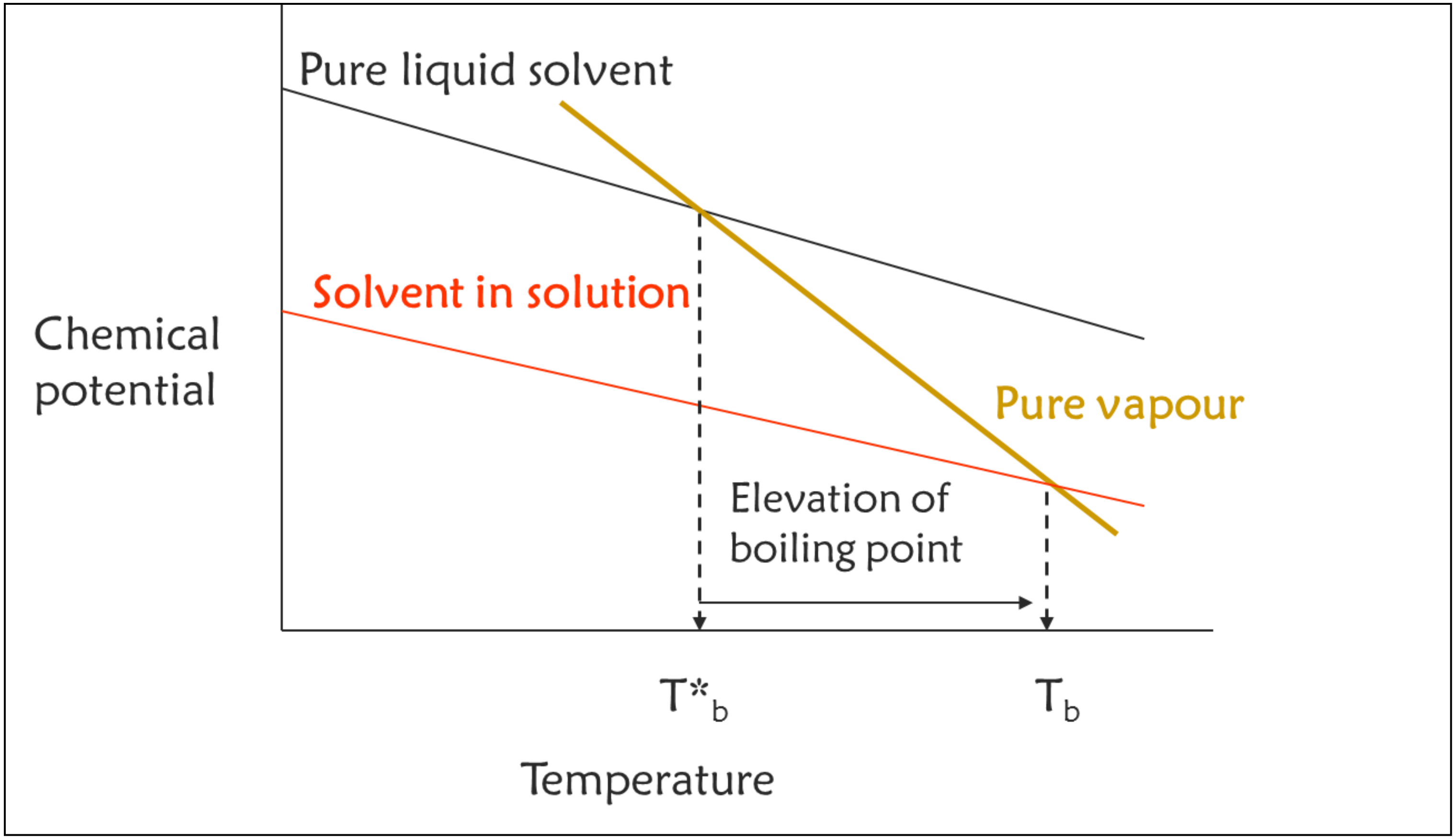
- Two assumptions:
  - The solute is not volatile, thus not presence in the vapour phase.
  - The solute is insoluble in the solid solvent, (not presence in solid phase)
- Presence of solute lowers the chemical potential of the liquid, but because the vapour and solid remain pure, chemical potential remain unchanged. (*e.g: sucrose solution*)

$$\mu_A = \mu_A^* + RT \ln x_A$$

Depression of freezing points



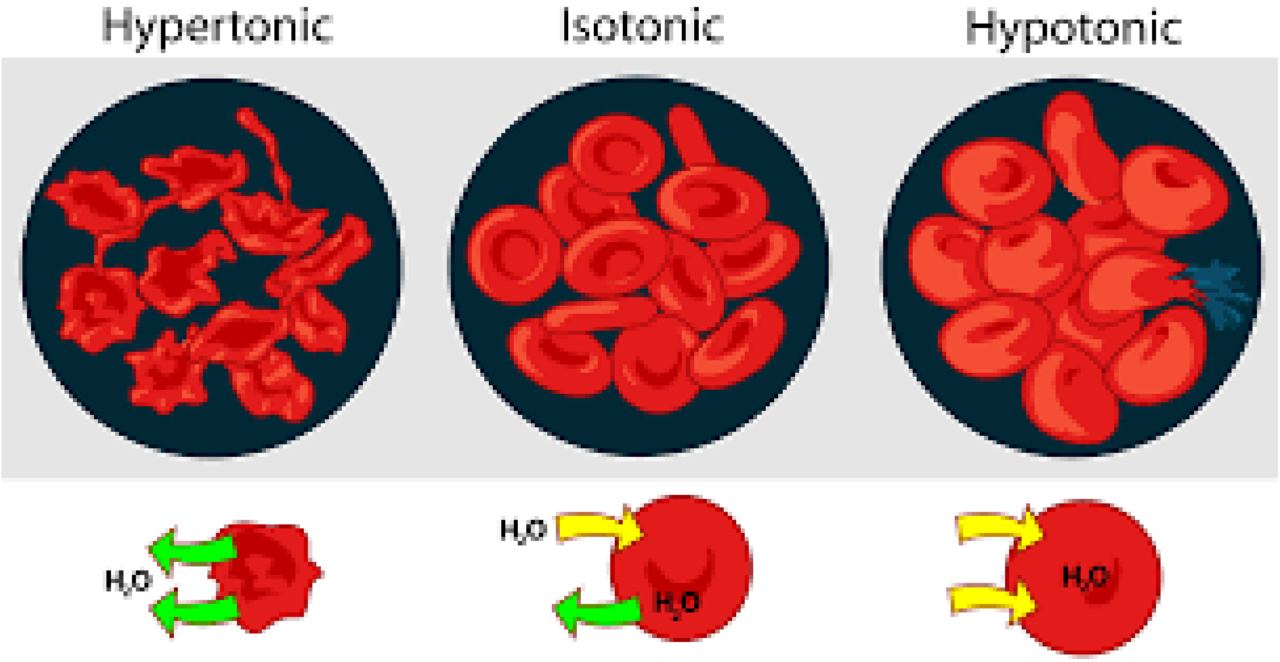
Elevation of boiling points



4.3 (b) Osmosis

- **Osmosis** is the selective passage of solvent molecules through a porous membrane from a dilute solution to a more concentrated one.
- A **semipermeable membrane** allows the passage of solvent molecules but blocks the passage of solute molecules.
- **Osmotic pressure (π)** is the pressure required to stop osmosis.

A cell in ….



Source:https://en.wikipedia.org/wiki/Osmotic_pressure

Using Colligative properties to Determine molar mass (Freezing-point depression & Osmotic pressure)

- Freezing-point depression and osmotic pressure data from the experiment,
- For instance: osmometry to determine the osmotic pressure of solution. We can calculate the molality or molarity of the solution
  - Know the mass of the solute
  - Can readily determine its molar mass

Conclusion

- Conclusion
  1. Determine the fugacity and fugacity coefficients for pure species using generic cubic equation of state, virial coefficients and generalized correlations
  2. Determine the heat of formation based on typical data by the constructional of chemical formation equation and graphical data
  3. Develop and solve calculational path to determine heat transfer of mixing process

Authors Information

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