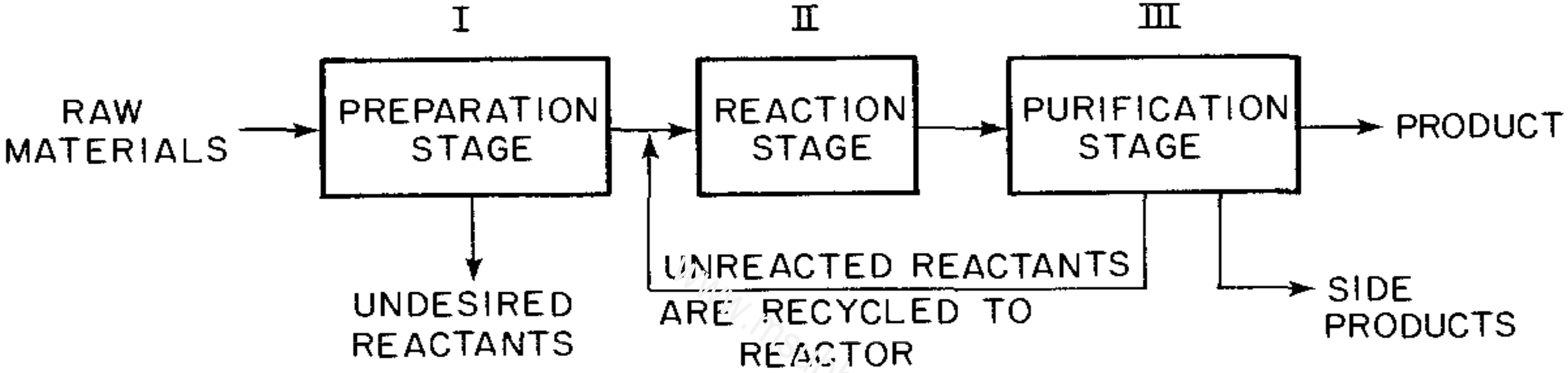


STAGES I AND III REQUIRE SEPARATION OPERATIONS (e.g., DISTILLATION, ABSORPTION, EXTRACTION). IN A TYPICAL CHEMICAL PLANT, 40-80% OF INVESTMENT IS FOR SEPARATION—OPERATION EQUIPMENT.

Typical Chemical Plant

Introduction

- Most of the materials of the real world are not pure substances with all atoms or molecules identical but rather are mixtures of one type or another.

- The pure substances from which a solution may be prepared are called *components*, or constituents, of the solution.

- Solutions are not limited to liquids: for example air, a mixture of predominantly N_2 and O_2, forms a vapor solution. Solid solutions such as the solid phase in the Si-Ge system are also common

Multicomponent Systems – Basic Relations

- Single component system:
  - Intensive properties: depends on Pressure, Temperature
  - Extensive properties: depends on Pressure, Temperature, and amount

- Multicomponent system:
  - Intensive properties: depends on Pressure, Temperature, and composition
  - Extensive properties: depends on Pressure, Temperature, amount of each component

Composition

Mole fraction

$$x_i = \frac{n_i}{\sum n_i}$$

$$\sum x_i = 1$$

For binary solution

$$x_1 + x_2 = 1$$

$$dx_1 = -dx_2$$

In dealing with dilute solutions it is convenient to speak of the component present in the largest amount as the **solvent**, while the diluted component is called the **solute**.

Other Measures of Composition

- Mass fraction – preferable where the definition of molecular weight is ambiguous (eg. Polymer molecules)
- Molarity – moles per litre of solution
- Molality – moles per kilogram of solvent. The molality is usually preferred, since it does not depend on temperature or pressure, whereas any concentration unit is so dependent.
- Volume fraction
- Mole ratio or volume ratio (for binary systems)

Properties of Solutions

- The properties of solutions are, in general, not additive properties of the pure components.
- The actual contribution to any extensive property is designated as its partial property. The term partial property is used to designate the property of a component when it is in admixture with one or more other components
- Because most chemical, biological, and geological processes occur at constant temperature and pressure, it is convenient to provide a special name for the partial derivatives of all thermodynamic properties with respect to mole number at constant pressure and temperature. They are called **partial molar properties**

Ethanol-Water System at 20^{o}C

Molar volumes:

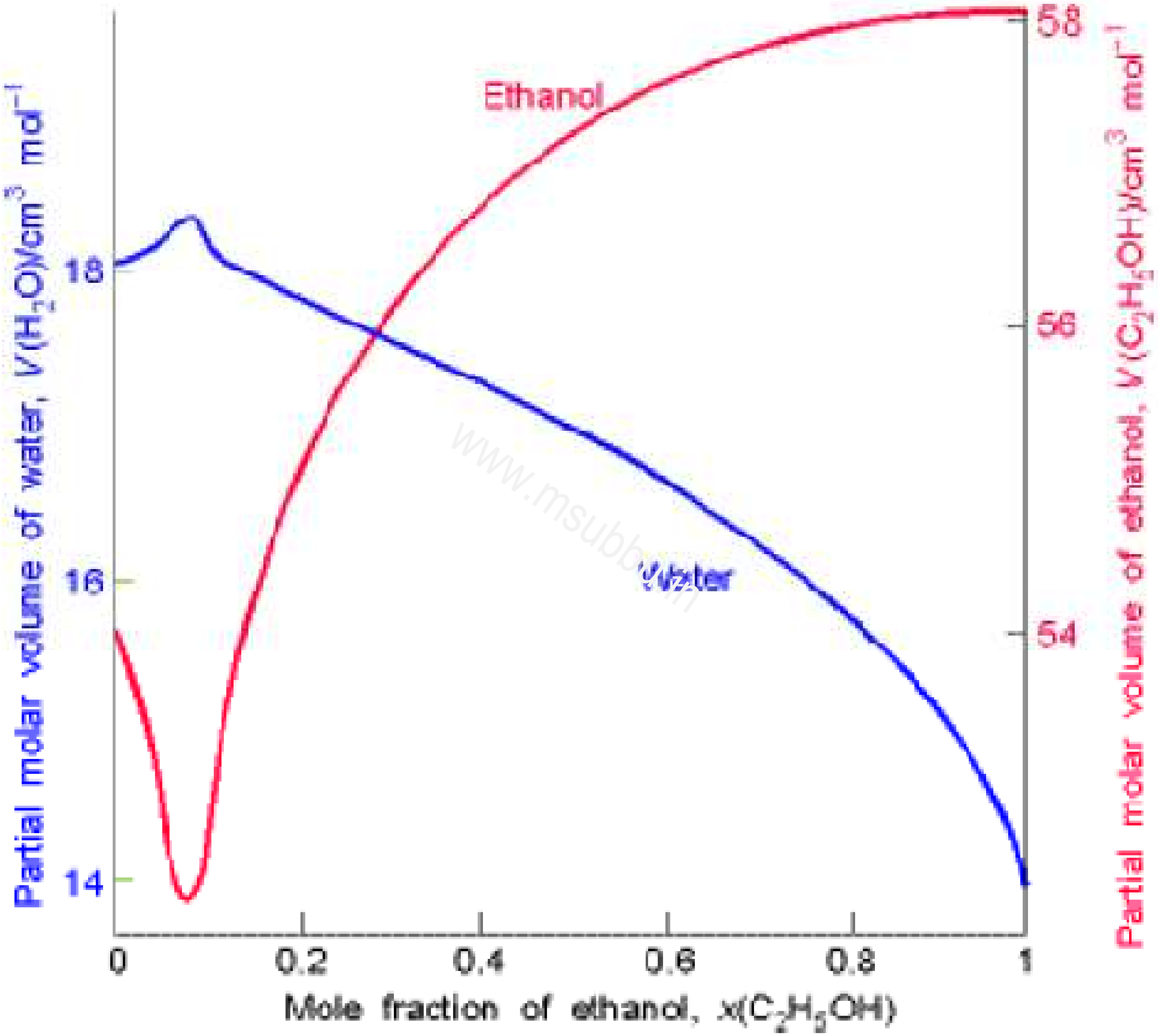
Water: 18 mL/mol
Ethanol: 58 mL/mol

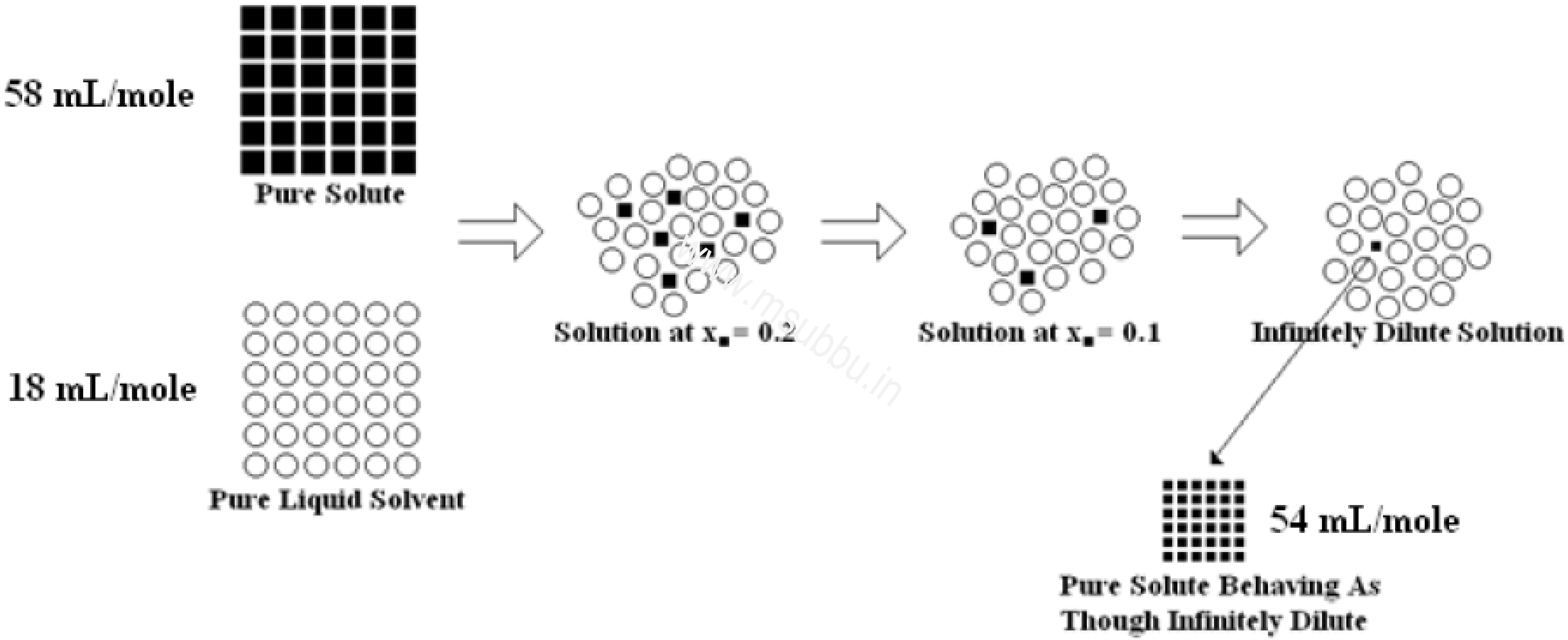
Partial molar volumes (at 50 mole% of Ethanol):

Water: 16.9 mL/mol
Ethanol: 57.4 mL/mol

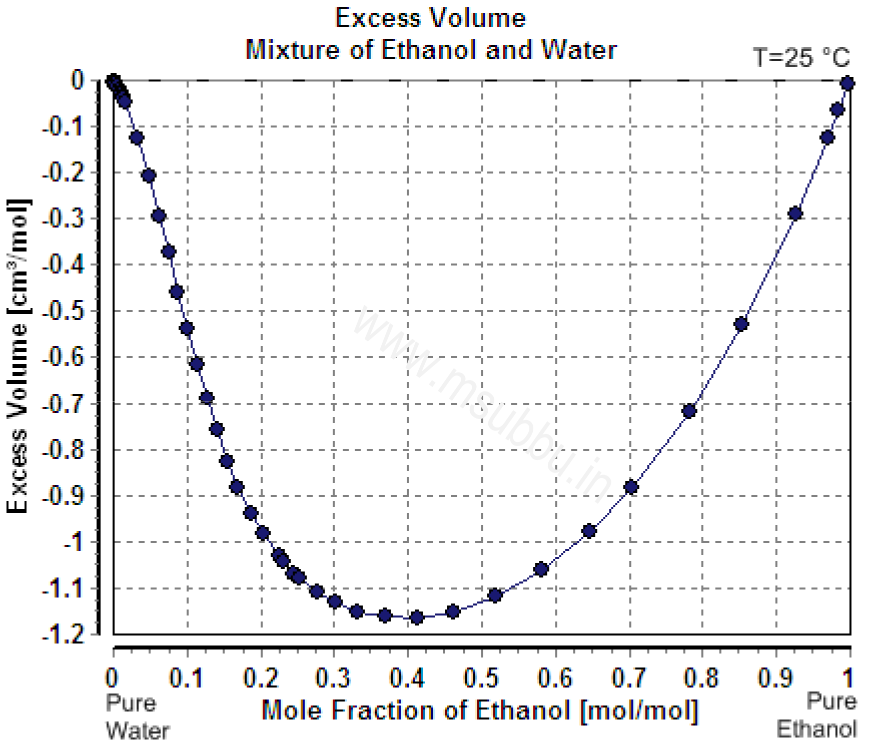
Volume before mixing = (1 mole) (18.0 mL/mole) + (1 mole) (58.0 mL/mole) = 76 mL

Volume after mixing = (1 mole) (16.9 mL/mole) + (1 mole) (57.4 mL/mole) = 74.3 mL


Ethanol
Water
18
16
14
58
56
54
0
0.2
0.4
0.6
0.8
1
Mole fraction of ethanol, $x(C_2H_5OH)$
Partial molar volume of water, $V(H_2O)/cm^3\ mol^{-1}$
Partial molar volume of ethanol, $V(C_2H_5OH)/cm^3\ mol^{-1}$


58 mL/mole
Pure Solute
18 mL/mole
Pure Liquid Solvent
Solution at $x_■$ = 0.2
Solution at $x_■$ = 0.1
Infinitely Dilute Solution
54 mL/mole
Pure Solute Behaving As Though Infinitely Dilute

$$\bar{V}^E = \Delta\bar{V}_{mxg} - \Delta\bar{V}_{mxg,Id} = \Delta\bar{V}_{mxg}$$



Data taken from Dortmund Data Bank

1 liter of ethanol and 1 liter of water are mixed at constant temperature and pressure. What is the expected volume of the resultant mixture ?

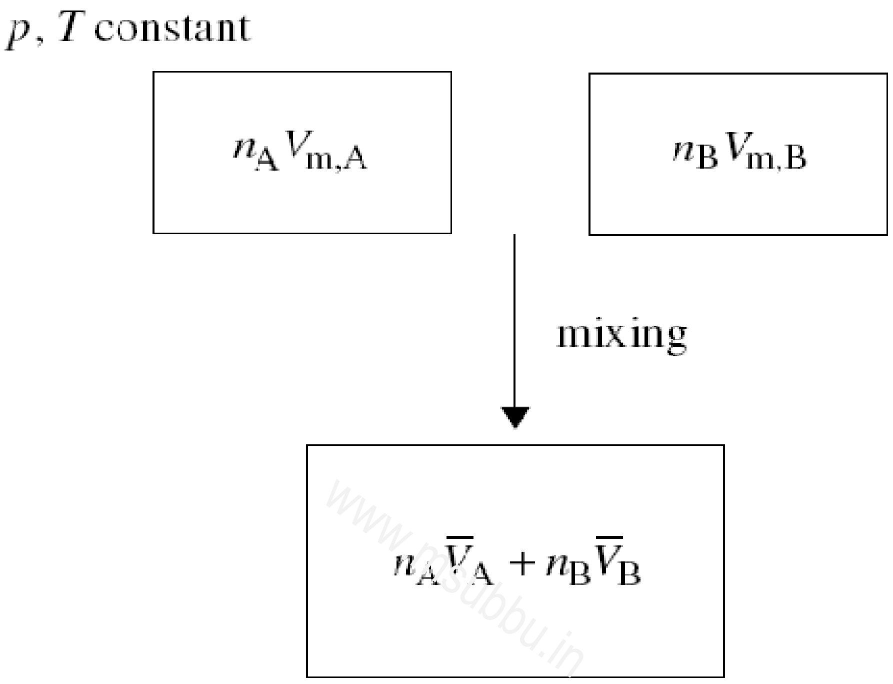


Figure 3.1 Mixing of n_A moles of A and n_B moles of B at constant p and T. The molar volumes of pure A and B are V_A and V_B. The partial molar volumes of A and B in the solution are $\overline{V}_A$ and $\overline{V}_B$, respectively.

$$V(\text{before}) = n_A V_{m,A} + n_B V_{m,B}$$

where $V_{m,A}$ and $V_{m,B}$ are the molar volumes of pure A and B.

$$V(\text{after}) = n_A \overline{V}_A + n_B \overline{V}_B$$

where $\overline{V}_A$ and $\overline{V}_B$ represent the partial molar volumes of A and B in the solution.

Partial Molar Properties

- The partial molar property of a given component in solution is defined as the differential change in that property with respect to a differential change in the amount of a given component under conditions of constant pressure and temperature, and constant number of moles of all components other than the one under consideration.

$$\boxed{\bar{M}_i = \left[\frac{\partial(nM)}{\partial n_i}\right]_{T,P,n_j\neq i}}$$

where M is any thermodynamic property.

- The concept of **partial molar quantity** can be applied to **any extensive state function**

Partial Molar Volume

- **Benzene-Toluene:** Benzene and toluene form an ideal solution. The volume of 1 mole pure benzene is 88.9 ml; the volume of 1 mole pure toluene is 106.4 ml. 88.9 ml benzene mixed with 106.4 ml toluene results in 88.9 ml + 106.4 ml, or 195.3 ml of solution. (**ideal solution**)

- **Ethanol-Water:**
  - The volume of 1 mole pure ethanol is 58.0 ml and the volume of 1 mole pure water is 18.0 ml. However, 1 mole water mixed with 1 mole ethanol does not result in 58.0 ml + 18.0 ml, or 76.0 ml, but rather 74.3 ml.
  - When the mole fraction is 0.5, the partial molal volume of ethanol is 57.4 ml and the partial molal volume of water is 16.9 ml. **(non-ideal solution)**

Fundamental Equations of Solution Thermodynamics

For any extensive thermodynamic property nM with a molar value of M, the partial molar property $\bar{M}_i$ is defined as

$$\boxed{\bar{M}_i = \left[\frac{\partial(nM)}{\partial n_i}\right]_{T,P,n_j \neq i}} \tag{1}$$

Thermodynamic properties of homogeneous phase are functions of pressure, temperature, and the number of moles of the individual species which comprise the phase. Therefore, for a thermodynamic property M, we can write

$$nM = \mathcal{M}(P, T, n_1, n_2, n_3, \ldots) \tag{2}$$

The total differential of nM is,

$$d(nM) = \left[\frac{\partial(nM)}{\partial P}\right]_{T,n} dP + \left[\frac{\partial(nM)}{\partial T}\right]_{P,n} dT + \sum_i \left[\frac{\partial(nM)}{\partial n_i}\right]_{P,T,n_j} dn_i$$

At constant number of moles (n), the composition of the solution x is constant. Hence the above equation can be simplified as

$$d(nM) = n\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + n\left(\frac{\partial M}{\partial T}\right)_{P,x} dT + \sum_i \bar{M}_i dn_i \qquad (4)$$

From the definition of mole fraction,

$$n_i = x_i n$$

Differentiating this,

$$dn_i = x_i dn + n dx_i \qquad (5)$$

And

$$d(nM) = n dM + M dn \qquad (6)$$

Using Eqns.(5) and (6) in Eqn.(4), we get

$$ndM+Mdn = n\left(\frac{\partial M}{\partial P}\right)_{T,x} dP+n\left(\frac{\partial M}{\partial T}\right)_{P,x} dT+\sum \bar{M}_i(x_i dn+ndx_i)$$

Rearranging the above equation, we get

$$\left[dM - \left(\frac{\partial M}{\partial P}\right)_{T,x} dP - \left(\frac{\partial M}{\partial T}\right)_{P,x} dT - \sum \bar{M}_i dx_i\right] n+\left(M - \sum \bar{M}_i x_i\right) dn = 0 \tag{7}$$

In application, one is free to choose a system of any size n, and its variation dn. Thus, n and dn are arbitrary and independent.

Hence for the left-hand side of above equation to be zero, both the quantities enclosed in brackets to be zero. Therefore, we have:

$$dM = \left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \left(\frac{\partial M}{\partial T}\right)_{P,x} dT + \sum \bar{M}_i dx_i \tag{8}$$

and

Taking derivative of Eqn.(9), we get

$$dM = \sum x_i d\bar{M}_i + \sum \bar{M}_i dx_i \tag{10}$$

From Eqns.(8) and (10), we get

$$\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \left(\frac{\partial M}{\partial T}\right)_{P,x} dT = \sum x_i d\bar{M}_i$$

i.e.,

$$\boxed{\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \left(\frac{\partial M}{\partial T}\right)_{P,x} dT - \sum x_i d\bar{M}_i = 0} \tag{11}$$

This equation is known as ***Gibbs-Duhem equation***. At constant T and P, the above equation becomes,

$$\boxed{\sum x_i d\bar{M}_i = 0} \tag{12}$$