CH2351 Chemical Engineering Thermodynamics II

Unit – I, II

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Solution Thermodynamics

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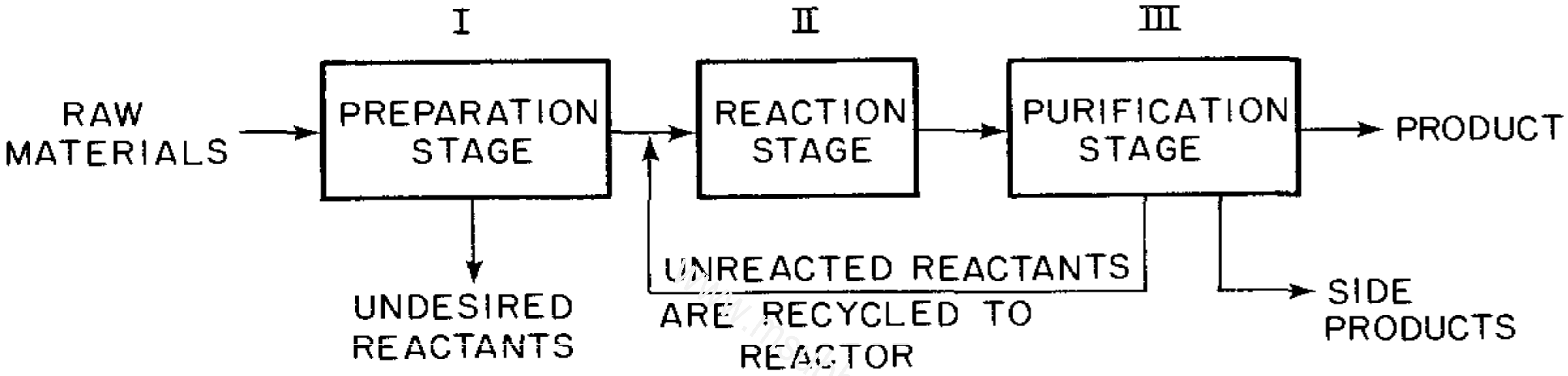
- UNIT I: PROPERTIES OF SOLUTIONS
  - Partial molar properties, ideal and non-ideal solutions, standard states definition and choice, Gibbs-Duhem equation, excess properties of mixtures.

- UNIT II: PHASE EQUILIBRIA
  - Criteria for equilibrium between phases in multi component non-reacting systems in terms of chemical potential and fugacity



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°C

Molar volumes:

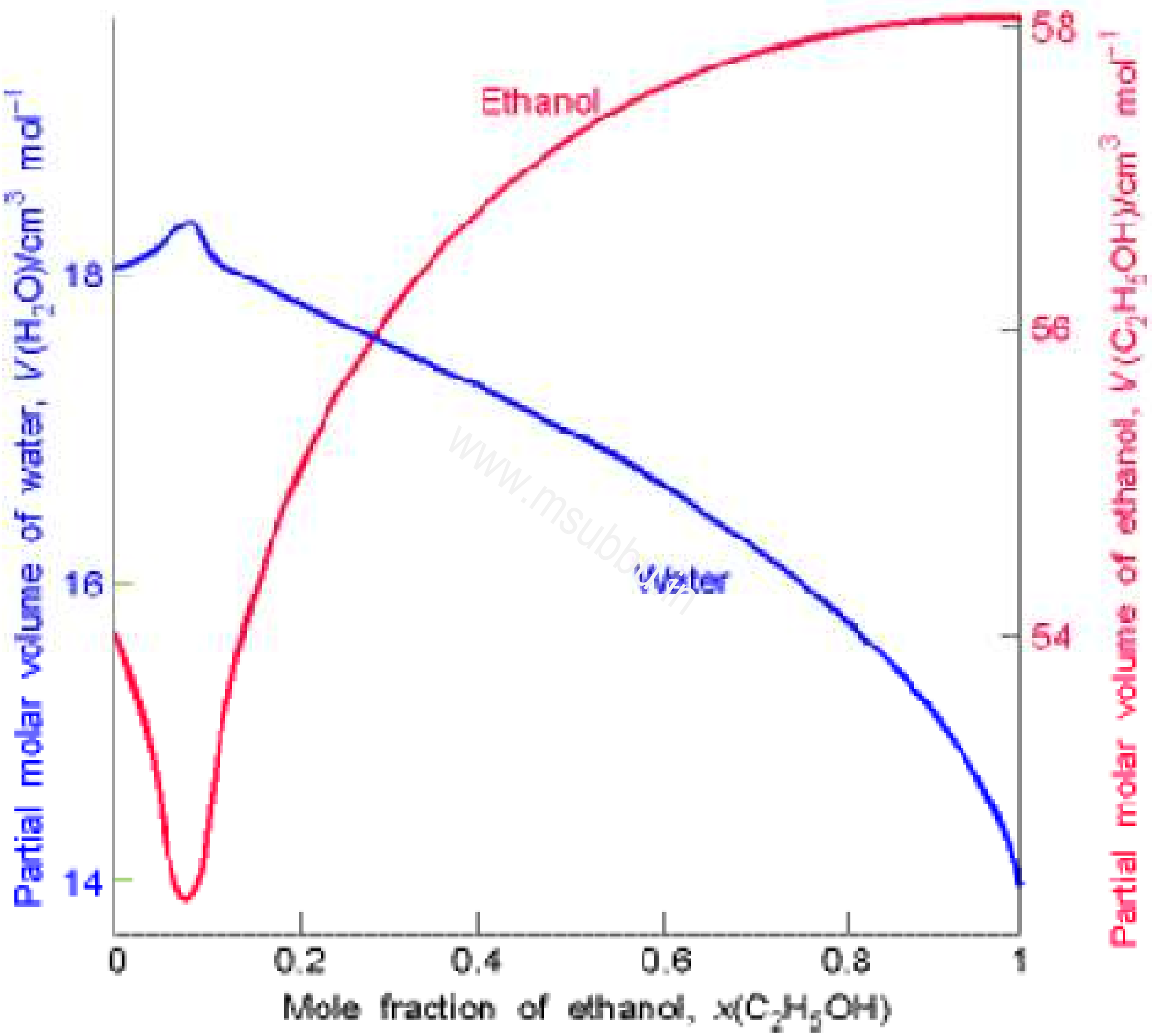
Water: 18 mL/mol
Ethanol: 58 mL/mol

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

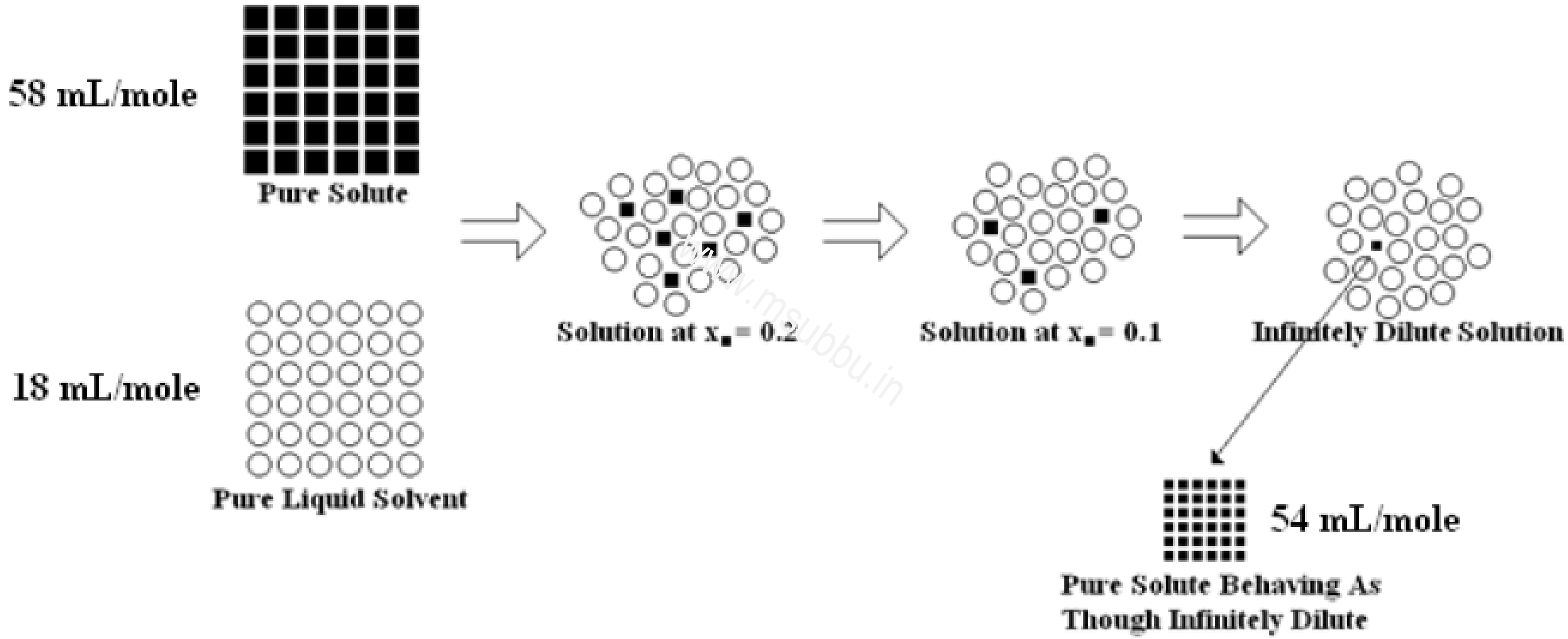
Water: 16.9 mL/mol
Ethanol: 57.4 mL/mol

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

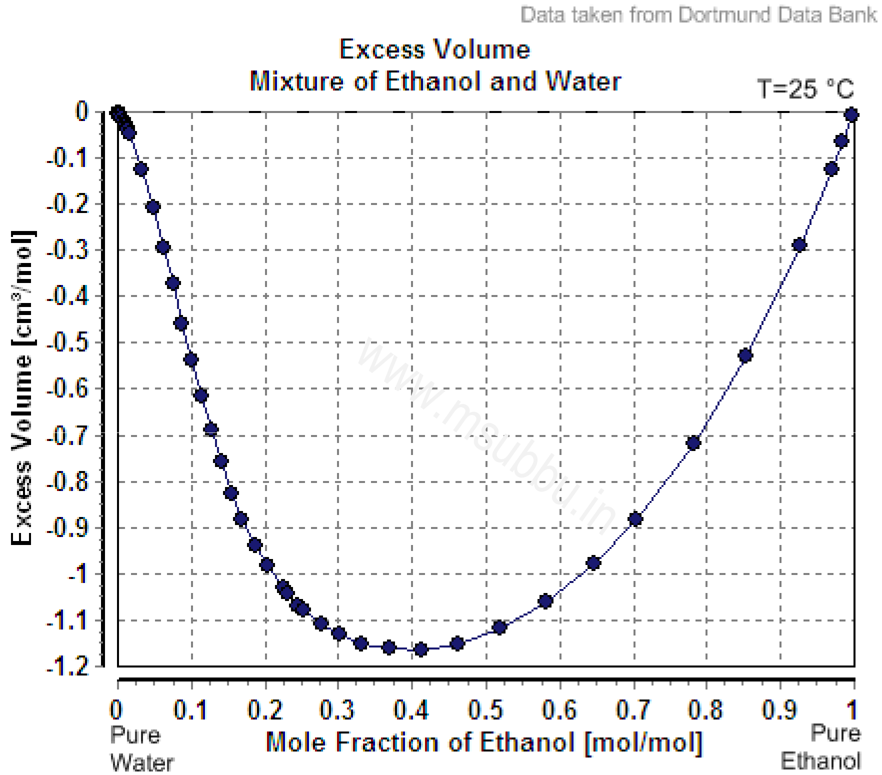
Volume after mixing = (1 mole) (16.9 mL/mole) + (1 mole) (57.4 mL/mole) = 74.3 mL



Ethanol
Water
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}
Mole fraction of ethanol, $x(C_2H_5OH)$
18
16
14
58
56
54
0
0.2
0.4
0.6
0.8
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

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



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 ?

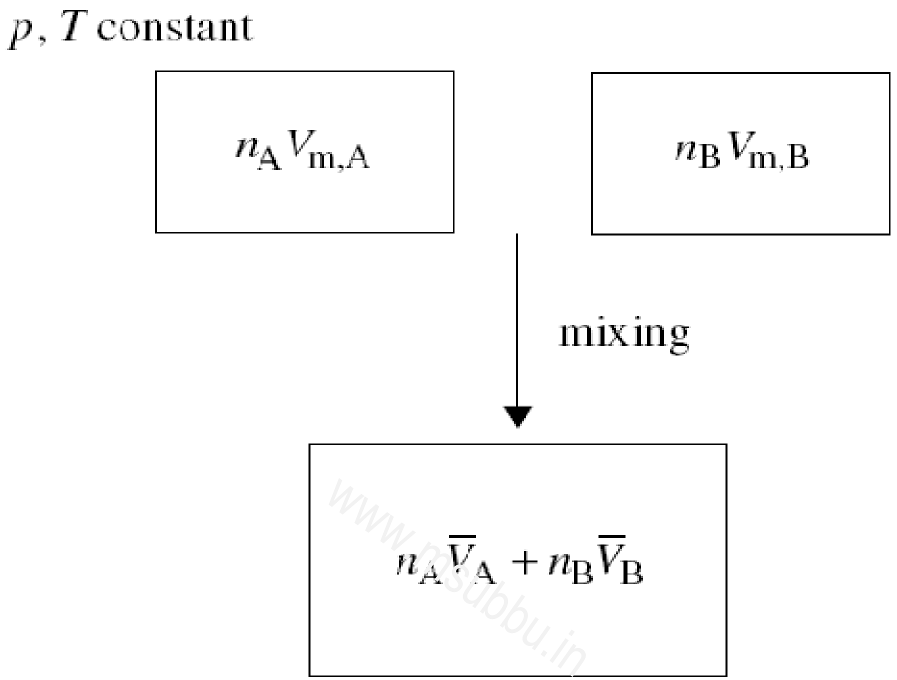


Figure 3.1 Mixing of n_A moles of A and n_B moles of B at constant p and T. The molar volumes of pure A and B are V_A and V_B. The partial molar volumes of A and B in the solution are $\overline{V}_A$ and $\overline{V}_B$, respectively.

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

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

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

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

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

The total differential of nM is,

$$d(nM) = \left[\frac{\partial(nM)}{\partial P}\right]_{T,n} dP + \left[\frac{\partial(nM)}{\partial T}\right]_{P,n} dT + \sum_i \left[\frac{\partial(nM)}{\partial n_i}\right]_{P,T,n_j} dn_i \qquad (3)$$

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

$$d(nM) = ndM + Mdn \qquad (6)$$

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

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

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

$$M = \sum \bar{M}_i x_i \tag{9}$$

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,

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

Gibbs-Duhem Equation

- This equation is very useful in deriving certain relationships between the partial molar quantity for a solute and that for the solvent.

- Partial Molar Properties in Binary Solutions

$$M = \sum_i x_i \bar{M}_i \quad (11.11)$$

Binary system ($x_1 + x_2 = 1$) →

$$M = x_1\bar{M}_1 + x_2\bar{M}_2 \quad \text{(A)}$$

Whence, $dM = x_1 d\bar{M}_1 + \bar{M}_1 dx_1 + x_2 d\bar{M}_2 + \bar{M}_2 dx_2$ (B)

The Gibbs/Duhem Equation at const (T, P) for binary solutions is:

$$x_1 d\bar{M}_1 + x_2 d\bar{M}_2 = 0 \quad \text{(C)}$$

Substituting (C) into (B) and noting that $x_1 + x_2 = 1$ and $dx_1 = - dx_2$, yield:

$$\frac{dM}{dx_1} = \bar{M}_1 - \bar{M}_2 \quad \text{(D)}$$

Two equivalent forms of Eq. (A), noting that $x_1 + x_2 = 1$, are:

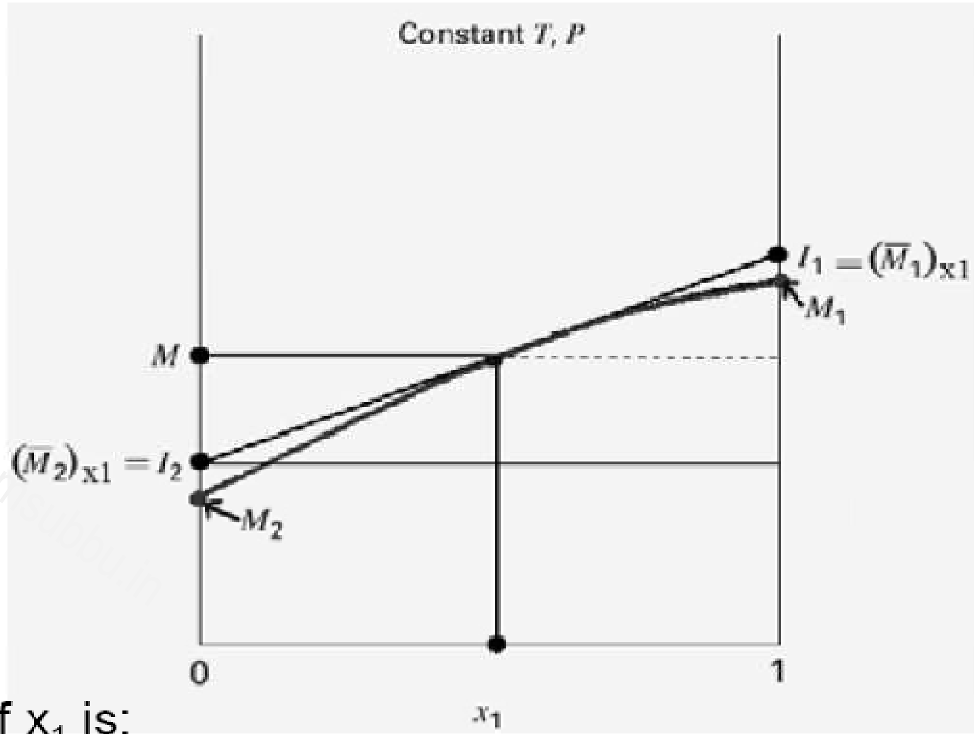
$$M = \bar{M}_1 - x_2(\bar{M}_1 - \bar{M}_2) \quad \text{and} \quad M = \bar{M}_2 + x_1(\bar{M}_1 - \bar{M}_2)$$

Substituting Eq. (D) into the above two eqs. we have the following equations used for calculation of $\bar{M}_i$ from the *M*:

$$\boxed{\bar{M}_1 = M + x_2\frac{dM}{dx_1} \quad (11.15) \quad \text{and} \quad \bar{M}_2 = M - x_1\frac{dM}{dx_1} \quad (11.16)}$$

Determination of Partial Molar Properties of Binary Solutions

Determine M_1 and M_2, $\overline{M}_1$ and $\overline{M}_2$ from the plot of M ~ x_1 for a binary system (solution) at const T and P.



Solution:

The molar properties of the two pure species of 1 and 2: M_1 and M_2 is determined from the plot, based on

$$\lim_{x_i \to 1} M = M_i$$

To determine, $\overline{M}_1$ and $\overline{M}_2$ at x_1, draw a tangent line at the point, which intersects the edges (at x_1 = 1 and x_1 = 0) at points of I_1 and I_2.

The slope of the M~x_1 plot at the point of x_1 is:

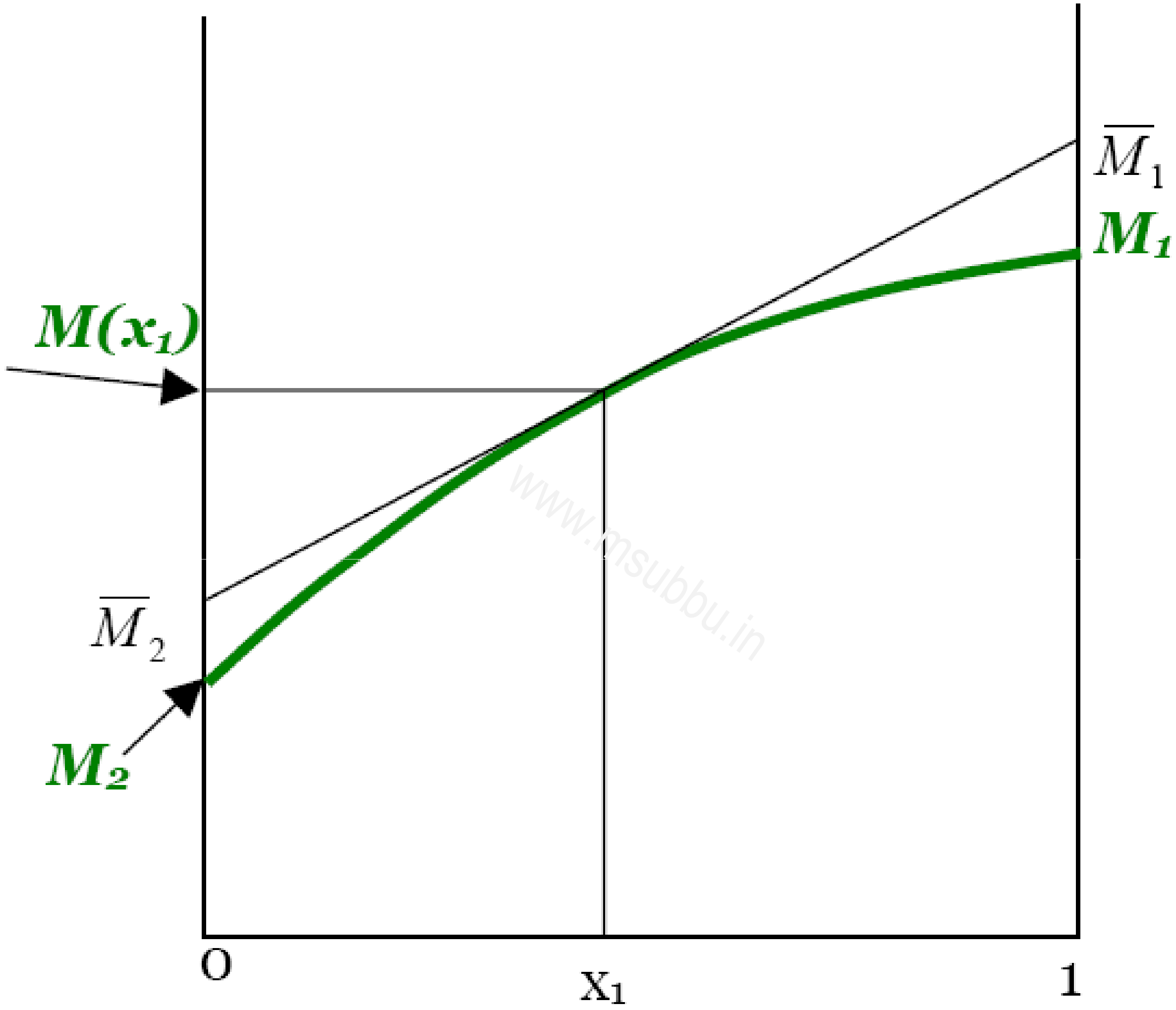
$$\text{Slope} = \frac{dM}{dx_1} = \frac{M - I_2}{x_1} \quad \longrightarrow \quad I_2 = M - x_1 \frac{dM}{dx_1}$$

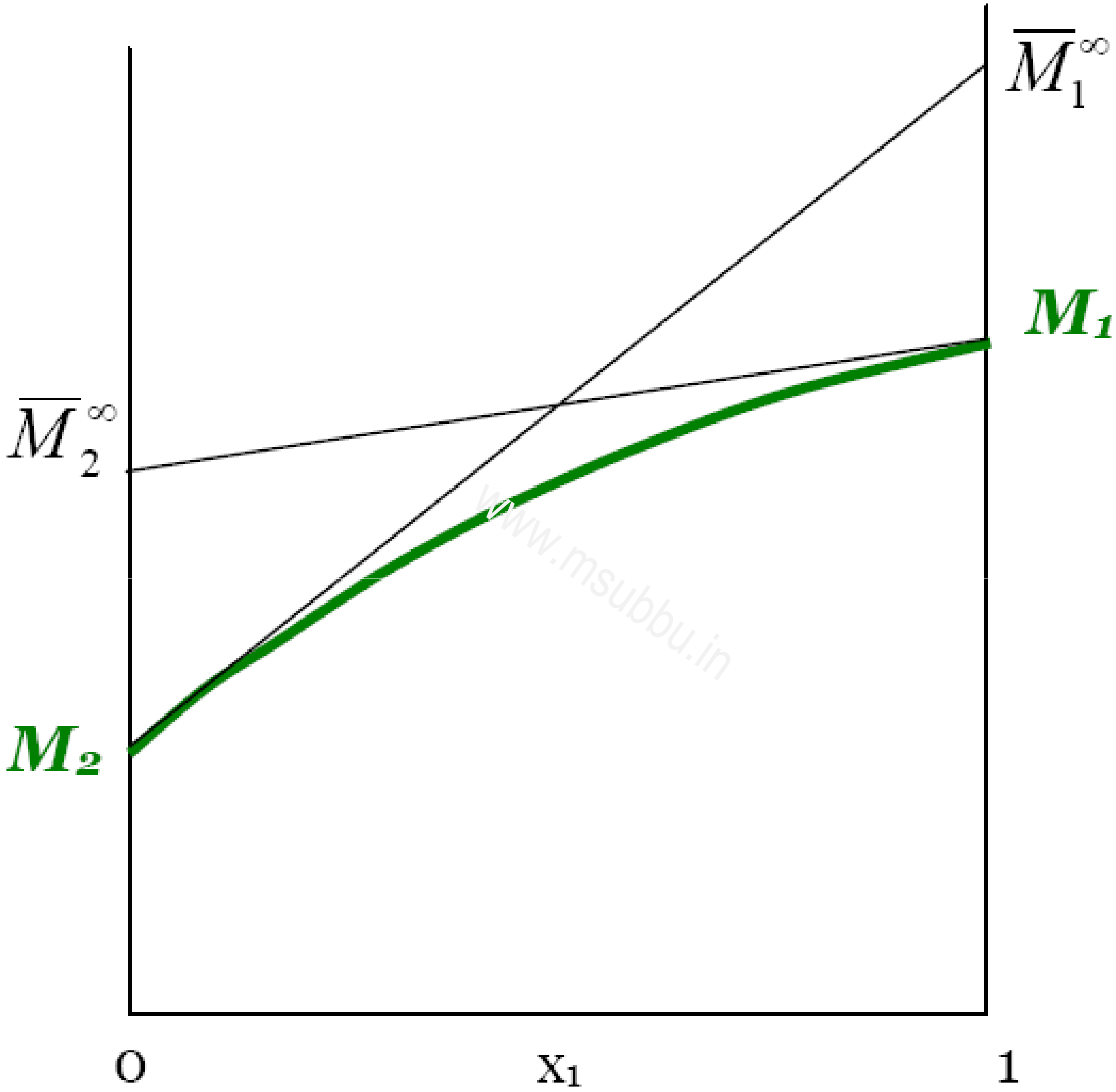
and

$$\text{Slope} = \frac{dM}{dx_1} = \frac{I_1 - M}{1 - x_1} = \frac{I_1 - M}{x_2} \quad \longrightarrow \quad I_1 = M + x_2 \frac{dM}{dx_1}$$

Comparing these expressions with Eqs. (11.15) and (11.16), we have

$$\overline{M}_1 = I_1 \quad \text{and} \quad \overline{M}_2 = I_2$$


$\overline{M}_1$
M_1
$M(x_1)$
$\overline{M}_2$
M_2
O
X_1
1


$\overline{M}_1^{\infty}$
M_1
$\overline{M}_2^{\infty}$
M_2
O
x_1
1

Partial molar properties in binary solution

- For binary system

$$\boxed{M = x_1\overline{M}_1 + x_2\overline{M}_2}$$

$$\boxed{dM = \cancel{x_1 d\overline{M}_1} + \overline{M}_1 dx_1 + \cancel{x_2 d\overline{M}_2} + \overline{M}_2 dx_2}$$

Const. P and T, using Gibbs/Duhem equation

$$\boxed{dM = \overline{M}_1 dx_1 + \overline{M}_2 dx_2}$$

$$\boxed{x_1 + x_2 = 1}$$

$$\boxed{\frac{dM}{dx_1} = \overline{M}_1 - \overline{M}_2}$$

$$\boxed{\overline{M}_1 = M + x_2\frac{dM}{dx_1}} \qquad \boxed{\overline{M}_2 = M - x_1\frac{dM}{dx_1}}$$

Partial Molar Quantities – Physical Interpretation

- The partial molar volume of component *i* in a system is equal to the infinitesimal increase or decrease in the volume, divided by the infinitesimal number of moles of the substance which is added, while maintaining T, P and quantities of all other components constant.

- Another way to visualize this is to think of the change in volume on adding a small amount of component *i* to an infinite total volume of the system.

- Note: partial molar quantities can be positive or negative!

Example Problem

The enthalpy of a binary liquid system of species 1 and 2 at fixed T and P is given by the equation:

$$H = 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2)$$

Where H is in J mol^{-1}. Determine expressions for $\bar{H}_1$ and $\bar{H}_2$ as functions of x_1, and numerical values for the pure-species enthalpies H_1 and H_2.

<u>Solution:</u>

The given equation of H can be presented solely in terms of x_1 by substituting $x_2 = 1 - x_1$:

$$H = 600 - 180x_1 - 20x_1^3 \qquad \text{(A)}$$

Whence, $\dfrac{dH}{dx_1} = -180 - 60x_1^2$

By Eqs. (11.15) and (11.16),

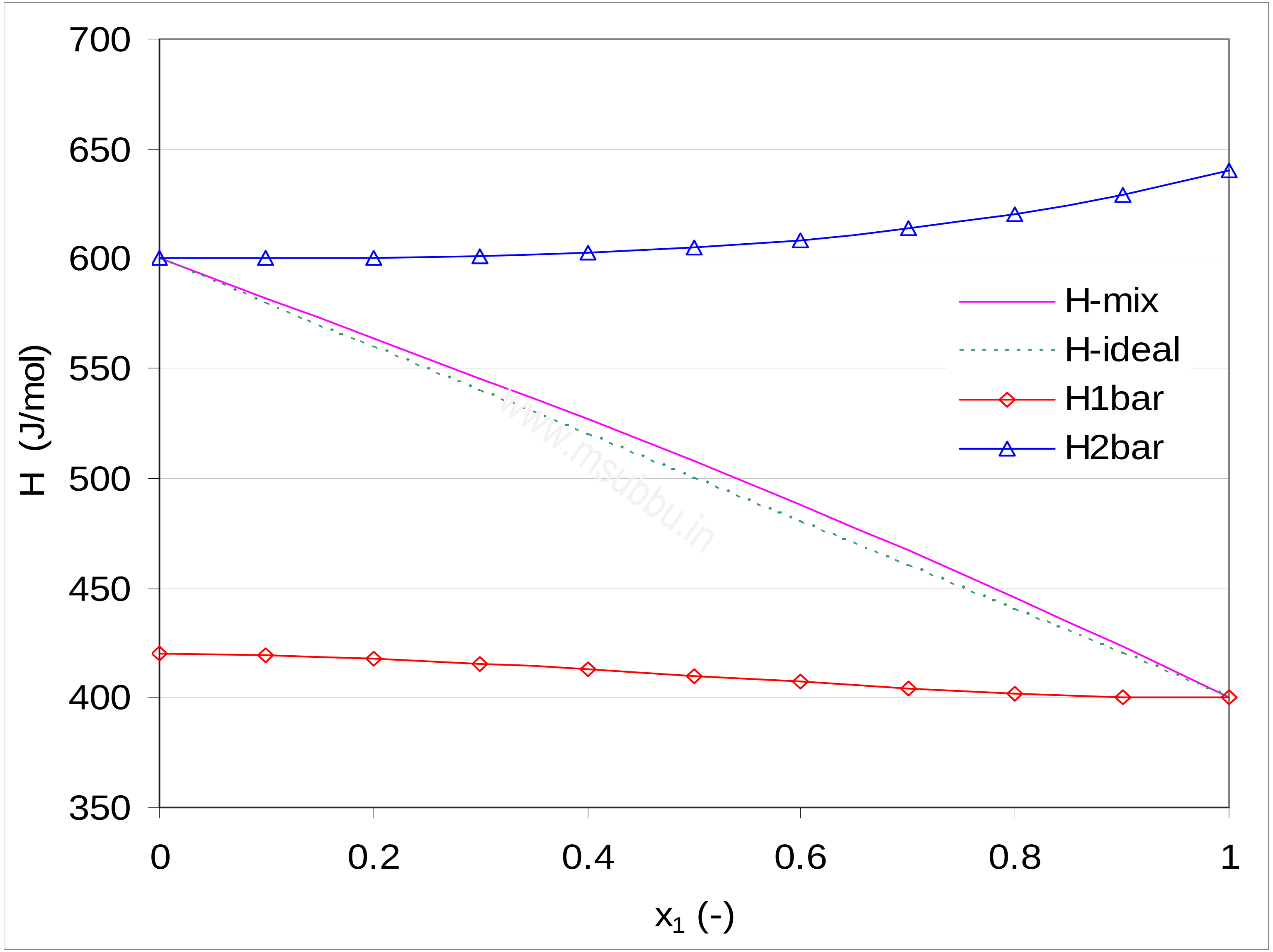
$$\bar{H}_1 = H + x_2\frac{dH}{dx_1} = 600 - 180x_1 - 20x_1^3 + x_2\left(-180 - 60x_1^2\right) = 420 - 60x_1^2 + 40x_1^3$$

$$\bar{H}_2 = H - x_1\frac{dH}{dx_1} = 600 - 180x_1 - 20x_1^3 - x_1\left(-180 - 60x_1^2\right) = 600 + 40x_1^3$$

The molar properties of the two pure species of 1 and 2: H_1 and H_2 is determined the Eq. (A), based on $\lim_{x_1 \to 1} H = H_1$ and $\lim_{x_2 \to 1 \text{ or } x_1 \to 0} H = H_2$

$$H_1 = \lim_{x_1 \to 1} H = 400 \text{ Jmol}^{-1} \text{ and } H_2 = \lim_{x_1 \to 0} H = 600 \text{ Jmol}^{-1}$$

x1	H (J/mol)	H-ideal (J/mol)	H1bar (J/mol)	H2bar (J/mol)
0	600	600	420	600
0.1	581.98	580	419.44	600.04
0.2	563.84	560	417.92	600.32
0.3	545.46	540	415.68	601.08
0.4	526.72	520	412.96	602.56
0.5	507.5	500	410	605
0.6	487.68	480	407.04	608.64
0.7	467.14	460	404.32	613.72
0.8	445.76	440	402.08	620.48
0.9	423.42	420	400.56	629.16
1	400	400	400	640


700
650
600
550
500
450
400
350
H (J/mol)
0
0.2
0.4
0.6
0.8
1
x_1 (-)
H-mix
H-ideal
H1bar
H2bar
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It is required to prepare 3 m^3 of a 60 mole% ethanol(1)-water(2) mixture. Determine the volumes of ethanol and water to be mixed in order to prepare the required solution. The partial molar volumes of ethanol and water in 60 mole% ethanol-water mixture are:

$$\bar{V}_1 = 57.5 \times 10^{-6} \ m^3/mol \qquad \bar{V}_2 = 16 \times 10^{-6} \ m^3/mol$$

The molar volumes of pure components are:
Ethanol $= 57.9 \times 10^{-6}$ m^3/mol; Water $= 18 \times 10^{-6}$ m^3/mol. *(Anna University, May-2006, 10 marks)*

Solution:

$$
\begin{aligned}
\text{Molar volume of mixture} &= \sum x_i \bar{V}_i = x_1 \bar{V}_1 + x_2 \bar{V}_2 \\
&= 0.6 \times 57.5 \times 10^{-6} + 0.4 \times 16 \times 10^{-6} \\
&= 40.9 \times 10^{-6} \text{ m}^3/\text{mol}
\end{aligned}
$$

$$
\begin{aligned}
\text{Number of moles in 3 m}^3 \text{ of mixture} &= \frac{3}{40.9 \times 10^{-6}} = 73,350 \text{ mol} \\
\text{Moles of ethanol in mixture} &= 0.6 \times 73350 = 44,010 \text{ mol} \\
\text{Volume of pure ethanol required} &= 44010 \times 57.9 \times 10^{-6} = \mathbf{2.548} \text{ m}^3 \\
\text{Moles of water in mixture} &= 0.4 \times 73350 = 29,340 \text{ mol} \\
\text{Volume of pure water required} &= 29340 \times 18 \times 10^{-6} = \mathbf{0.528} \text{ m}^3
\end{aligned}
$$

At constant T and P, the molar density of binary mixture is given by $\rho = 1 + x_2$, where x_2 is the mole fraction of component 2. The partial molar volume at infinite dilution for component 1, $\bar{V_1}^{\infty}$, is (GATE-2010-31)

(a) 0.75 (b) 1.0 (c) 2.0 (d) 4.0

Solution:

Given:

$$\text{Molar density } \rho = 1 + x_2$$

$$\text{Molar volume, } V = \frac{1}{\rho} = \frac{1}{1 + x_2}$$

$\bar{V}_1^{\infty} = ?$

Molar property M of a solution is related to partial molar properties of its constituents as,

$$M = \sum x_i \bar{M}_i$$

and

$$\bar{M}_1 = M + x_2 \frac{dM}{dx_1} \qquad \bar{M}_2 = M - x_1 \frac{dM}{dx_1}$$

$$\therefore \qquad \bar{V}_1 = V + x_2 \frac{dV}{dx_1} \tag{8.68}$$

$$V = \frac{1}{1+x_2} = \frac{1}{1+(1-x_1)} = \frac{1}{2-x_1} \tag{8.69}$$

$$\frac{dV}{dx_1} = \frac{(2-x_1)\times 0-(-1)}{(2-x_1)^2} = \frac{1}{(2-x_1)^2} \tag{8.70}$$

Using Eqn.(8.69) and (8.70) in Eqn.(8.68),

$$\bar{V}_1 = \frac{1}{2-x_1} + \frac{x_2}{(2-x_1)^2} = \frac{1}{2-x_1} + \frac{1-x_1}{(2-x_1)^2}$$

$$\bar{V}_1^{\infty} = \bar{V}_1\Big|_{x_1\to 0} = \frac{1}{2} + \frac{1}{2^2} = 0.75 \qquad \text{(a)} \checkmark$$

$\square$

If the partial volume of species 1 in a binary solution at constant T and P is given by

$$\bar{V_1} = V_1 + \alpha x_2^2$$

find the corresponding equation for $\bar{V_2}$. What equation for V is consistent with these equations for the partial volumes?

The following table gives the partial molar volumes at 298.15 K of ethyl acetate (1) and carbon tetra chloride (2) in solutions of the two.

(a) What is the volume of the solution when 3 moles of ethyl acetate are mixed with 7 moles of carbon tetra choloride?

(b) Calculate the change in volume when 0.6 moles of ethyle acetate are mixed with 0.4 moles of carbon tetrachloride.

x_1	$\bar{V}_1/(\mathrm{cm}^3.\mathrm{mol}^{-1})$	$\bar{V}_2/(\mathrm{cm}^3.\mathrm{mol}^{-1})$
1.0	97.81	96.74
0.9	97.81	96.68
0.8	97.82	96.63
0.7	97.83	96.59
0.6	97.87	96.52
0.5	97.87	96.52
0.4	97.91	96.49
0.3	97.96	96.47
0.2	98.03	96.45
0.1	98.13	96.44
0.0	98.25	96.43

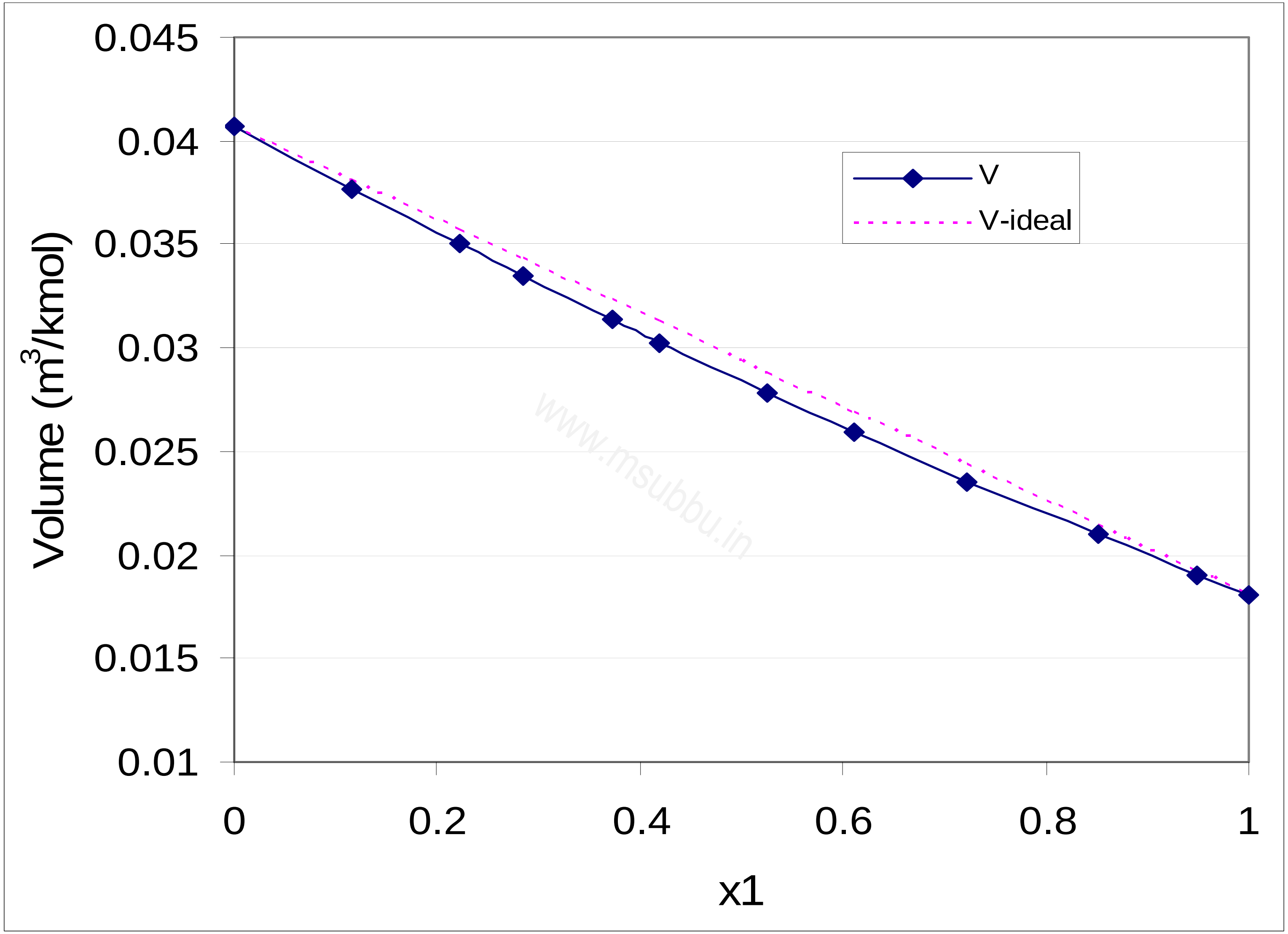
Partial Molar Properties from Experimental Data

- Partial molar volume:
  - Density data (ρ vs. x_1)

- Partial molar enthalpy:
  - Enthalpy data (H vs. x_1); can be directly used
  - Heat of mixing (also called as enthalpy change on mixing) data (ΔH_{mix} vs. x_1)
    - Obtained using differential scanning calorimetry
    - Reported normally as J/mol of solute; to be converted to J/mol of solution

Density data for Water (1) - Methanol (2) system at 298.15 K					
x_1	ρ (kg/m^3)	avgMW	V	V_{ideal}	ΔV_{mix}
			$m^3/kmol$	$m^3/kmol$	$m^3/kmol$
0	786.846	32.042	**0.040722**	0.040722	0.00000000
0.1162	806.655	30.41032	0.037699	0.038088	-0.00038867
0.2221	825.959	28.92327	0.035018	0.035687	-0.00066954
0.2841	837.504	28.05267	0.033496	0.034282	-0.00078631
0.3729	855.031	26.80574	0.031351	0.032269	-0.00091829
0.4186	864.245	26.16402	0.030274	0.031233	-0.00095908
0.5266	887.222	24.64748	0.027781	0.028785	-0.00100419
0.6119	905.376	23.4497	0.025901	0.026851	-0.00095055
0.722	929.537	21.90368	0.023564	0.024355	-0.00079116
0.8509	957.522	20.09366	0.020985	0.021433	-0.00044816
0.9489	981.906	18.71755	0.019062	0.019212	-0.00014922
1	997.047	18	**0.018053**	0.018053	0.00000000

$V_{ideal} = x_1V_1 + x_2V_2$ $\Delta V_{mix} = V - V_{ideal}$



0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
Volume (m^3/kmol)
0
0.2
0.4
0.6
0.8
1
x1
V
V-ideal
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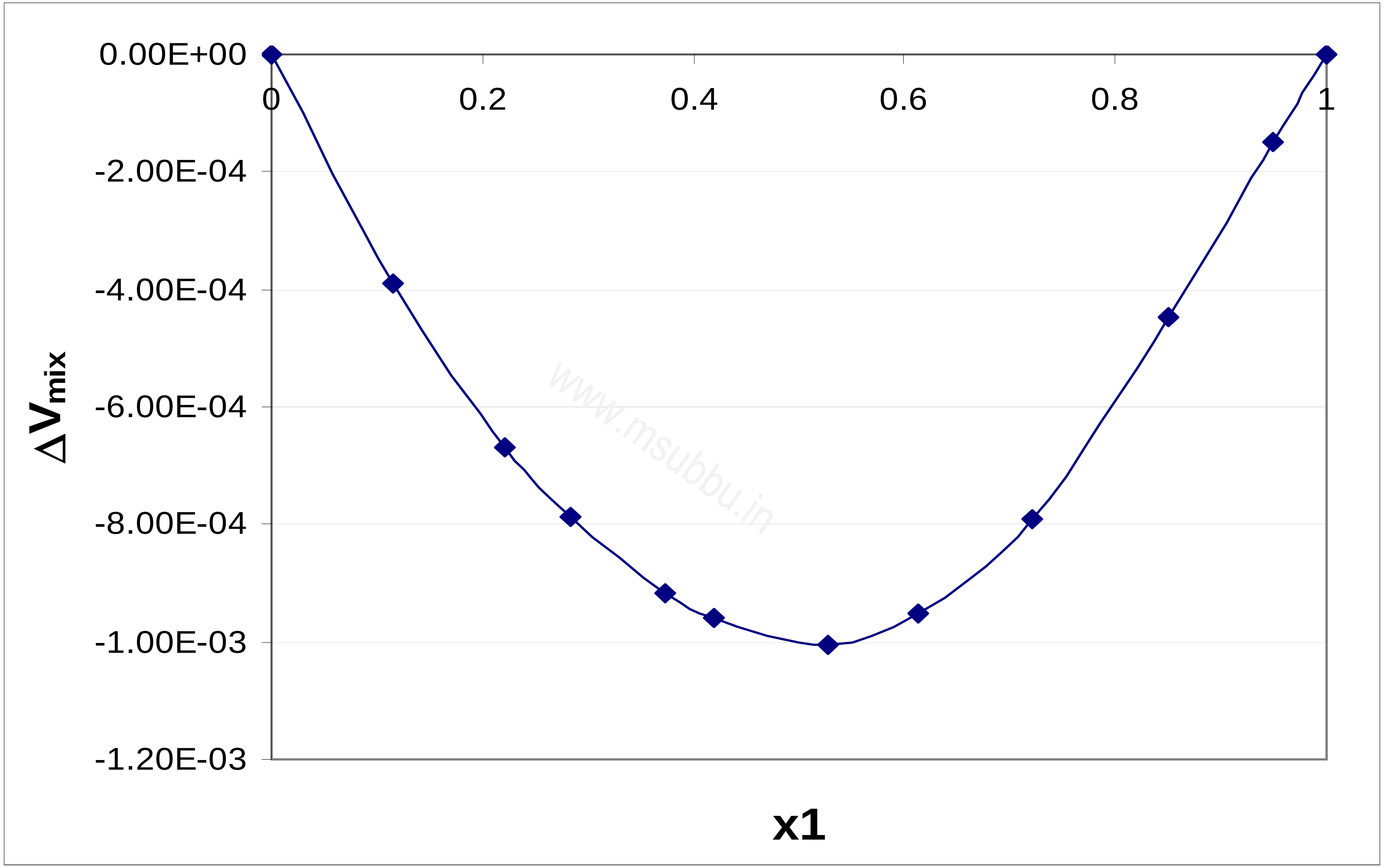

0.00E+00
-2.00E-04
-4.00E-04
-6.00E-04
-8.00E-04
-1.00E-03
-1.20E-03
0
0.2
0.4
0.6
0.8
1
ΔV_{mix}
x1
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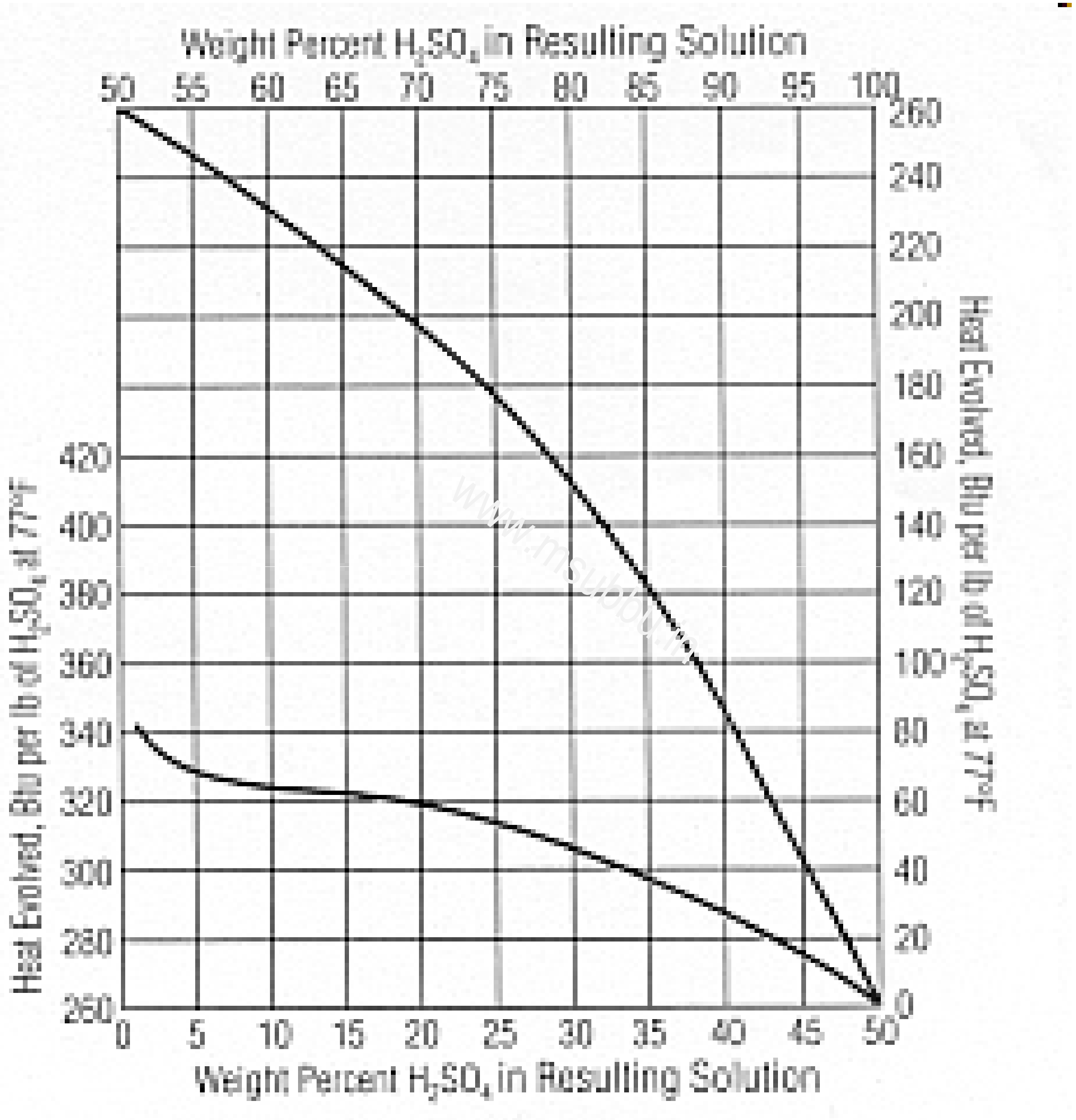
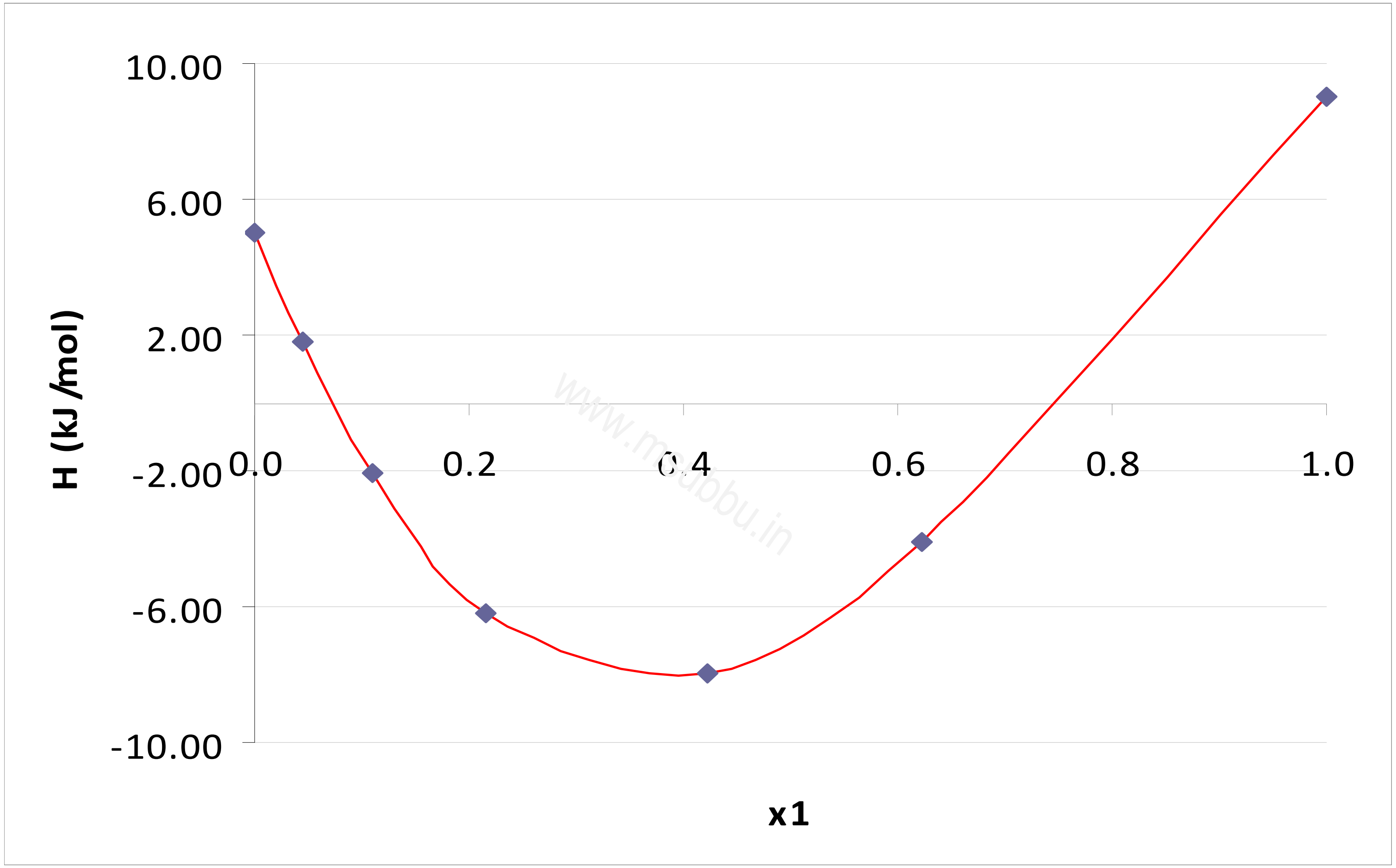

Weight Percent H_2SO_4 in Resulting Solution
50 55 60 65 70 75 80 85 90 95 100
260 240 220 200 180 160 140 120 100 80 60 40 20 0
Heat Evolved, Btu per lb of H_2SO_4 at 77°F
420 400 380 360 340 320 300 280 260
Heat Evolved, Btu per lb of H_2SO_4 at 77°F
0 5 10 15 20 25 30 35 40 45 50
Weight Percent H_2SO_4 in Resulting Solution

wt% H2SO4]	H (kJ/kg)	x1	avgMW	H (kJ/mol)	ΔH_{mix} (kJ/mol)	ΔH_{mix} Model (kJ/mol)
0	278	0.0000	18.00	5.00	0	0
20	85	0.0439	21.51	1.83	-3.3516	-3.3818
40	-78	0.1091	26.73	-2.08	-7.5264	-7.4880
60	-175	0.2160	35.28	-6.17	-12.0446	-12.0692
80	-153	0.4235	51.88	-7.94	-14.6412	-14.6637
90	-60	0.6231	67.85	-4.07	-11.5746	-11.5736
100	92	1.0000	98.00	9.02	0	0

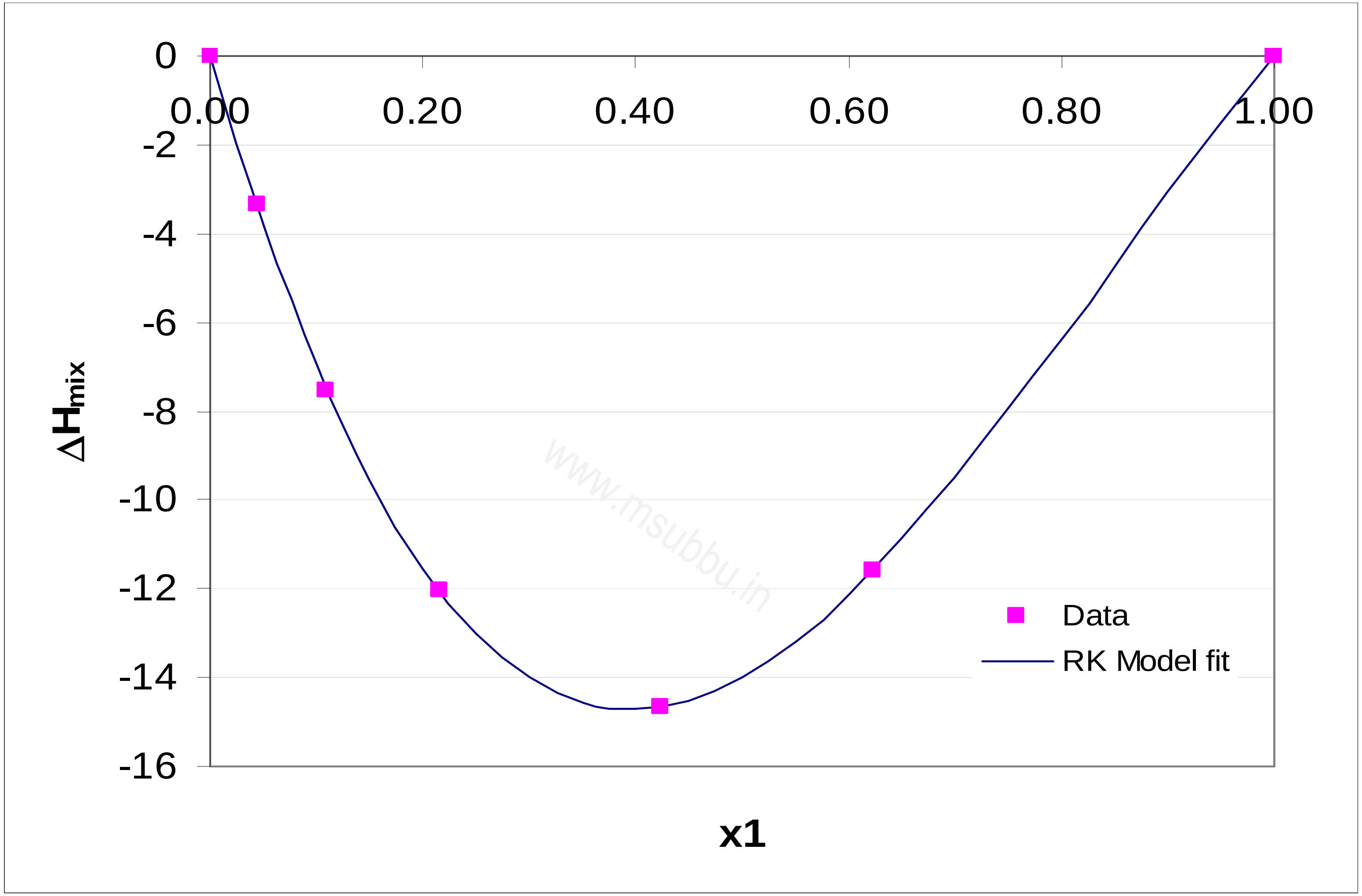
$H_{ideal} = x_1 H_1 + x_2 V_2$

$\Delta H_{mix} = H - H_{ideal}$


10.00
6.00
2.00
-2.00
-6.00
-10.00
H (kJ /mol)
0.0
0.2
0.4
0.6
0.8
1.0
x1

Redlich-Kister Model

- Also known as Guggenheim-Scatchard Equation
- Fits well the data of ΔM_{mix} vs. x_1

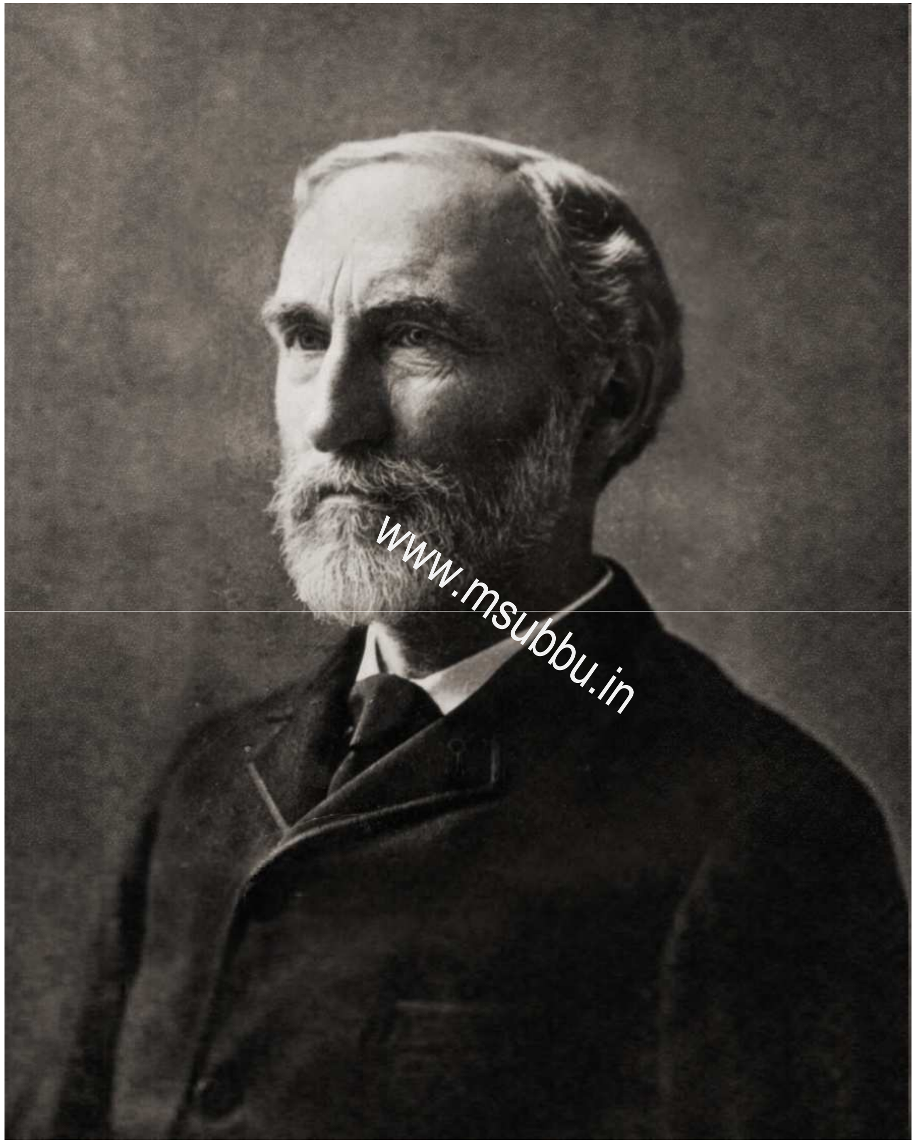


ao	-55.9287
a1	27.0094

Redlich-Kister model fits well the data of ΔM_{mix} vs. x_1

Weight % Ethanol	Density (g/mL) at 22 °C
0	0.99799
10	0.98061
20	0.96808
30	0.95155
40	0.93521
50	0.91778
60	0.89532
70	0.86838
80	0.84248
90	0.81570
100	0.78808

Calculate the partial molar volume of Ethanol and Water as a function of composition.



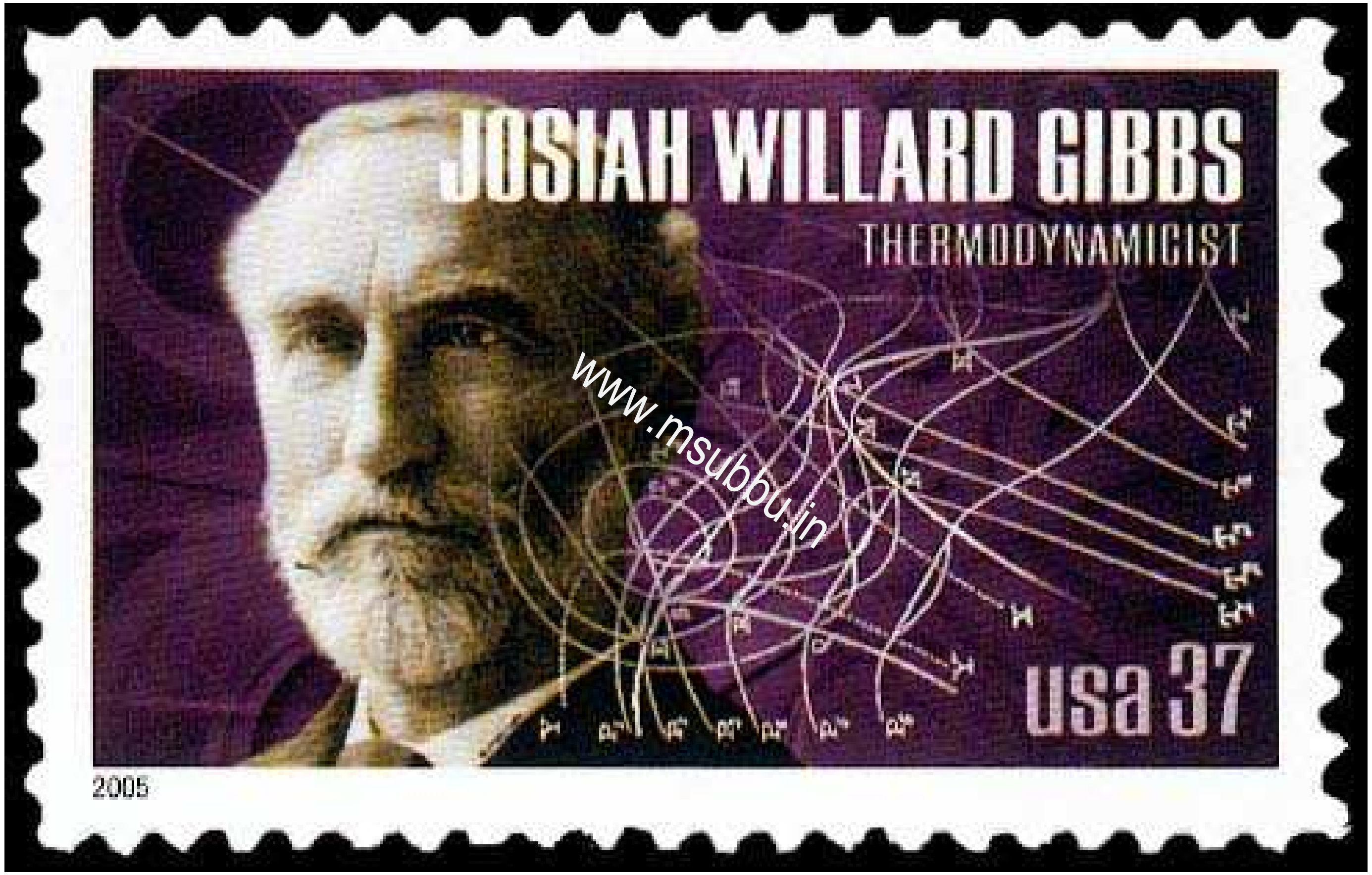
Gibbs

- Josiah Willard Gibbs (1839 – 1904)

- Gibbs greatly extended the field of thermodynamics, which originally comprised only the relations between heat and mechanical work. Gibbs was instrumental in broadening the field to embrace transformations of energy between all the forms in which it may be manifested, be they thermal, mechanical, electrical, chemical, or radiant.

- He is considered to be the **founder of chemical thermodynamics**.

- He is an American theoretical physicist, chemist, and mathematician. He devised much of the theoretical foundation for chemical thermodynamics as well as physical chemistry.


JOSIAH WILLARD GIBBS
THERMODYNAMICIST
usa 37
2005

Fundamental Equation for Closed System

- The basic relation connecting the Gibbs energy to the temperature and pressure in any closed system:

$$\boxed{d(nG) = (nV)dP - (nS)dT}$$

  - applied to a single-phase fluid in a closed system wherein no chemical reactions occur.

$$\boxed{\left[\frac{\partial(nG)}{\partial P}\right]_{T,n} = nV \qquad \text{and} \qquad \left[\frac{\partial(nG)}{\partial T}\right]_{P,n} = -nS}$$

Fundamental Equation for Open System

- Consider a single-phase, open system: $nG = \mathcal{G}(P, T.n_1, n_2, n_3, \ldots)$

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

- Definition of chemical potential:

$$\mu_i \equiv \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j}$$

(The partial derivative of G with respect to the mole number n_i at constant T and P and mole numbers $n_j \neq n_j$)

- The fundamental property relation for single-phase fluid systems of constant or variable composition:

$$d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i dn_i$$

When n = 1,

$$\boxed{dG = VdP - SdT + \sum_i \mu_i dx_i} \longrightarrow \boxed{G = G(P, T, x_1, x_2, \ldots, x_i, \ldots)}$$

$$\boxed{V = \left(\frac{\partial G}{\partial P}\right)_{T,x}} \qquad \boxed{S = \left(\frac{\partial G}{\partial T}\right)_{P,x}}$$

The Gibbs energy is expressed as a function of its canonical variables.

Solution properties, M
Partial properties, $\bar{M}_i$
Pure-species properties, M_i

$$\boxed{\mu_i \equiv \bar{G}_i}$$

For a system of constant composition,

$$d(nG) = (nV)dP - (nS)dT \tag{13}$$

For a open system, composition of the components varies, and total Gibbs free energy of the system depends on:

$$nG = \mathcal{G}(P, T.n_1, n_2, n_3, \ldots)$$

Taking derivative,

$$d(nG) = \left[\frac{\partial(nG)}{\partial P}\right]_{T,n} dP + \left[\frac{\partial(nG)}{\partial T}\right]_{P,n} dT + \sum_i \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j} dn_i \tag{14}$$

Using Eqn.(13) in Eqn.(14), we get

$$d(nG) = (nV)dP - (nS)dT + \sum \bar{G}_i dn_i \tag{15}$$

$$\mu_i = \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j \neq i} = \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j} = \bar{G}_i$$

Chemical potential and phase equilibria

- Consider a closed system consisting of two phases in equilibrium:

$$\boxed{d(nG)^{\alpha} = (nV)^{\alpha}dP - (nS)^{\alpha}dT + \sum_i \mu_i^{\alpha} dn_i^{\alpha}}$$

$$\boxed{d(nG)^{\beta} = (nV)^{\beta}dP - (nS)^{\beta}dT + \sum_i \mu_i^{\beta} dn_i^{\beta}}$$

$$\boxed{nM = (nM)^{\alpha} + (nM)^{\beta}}$$

$$\boxed{d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i^{\alpha} dn_i^{\alpha} + \sum_i \mu_i^{\beta} dn_i^{\beta}}$$

Since the two-phase system is closed,

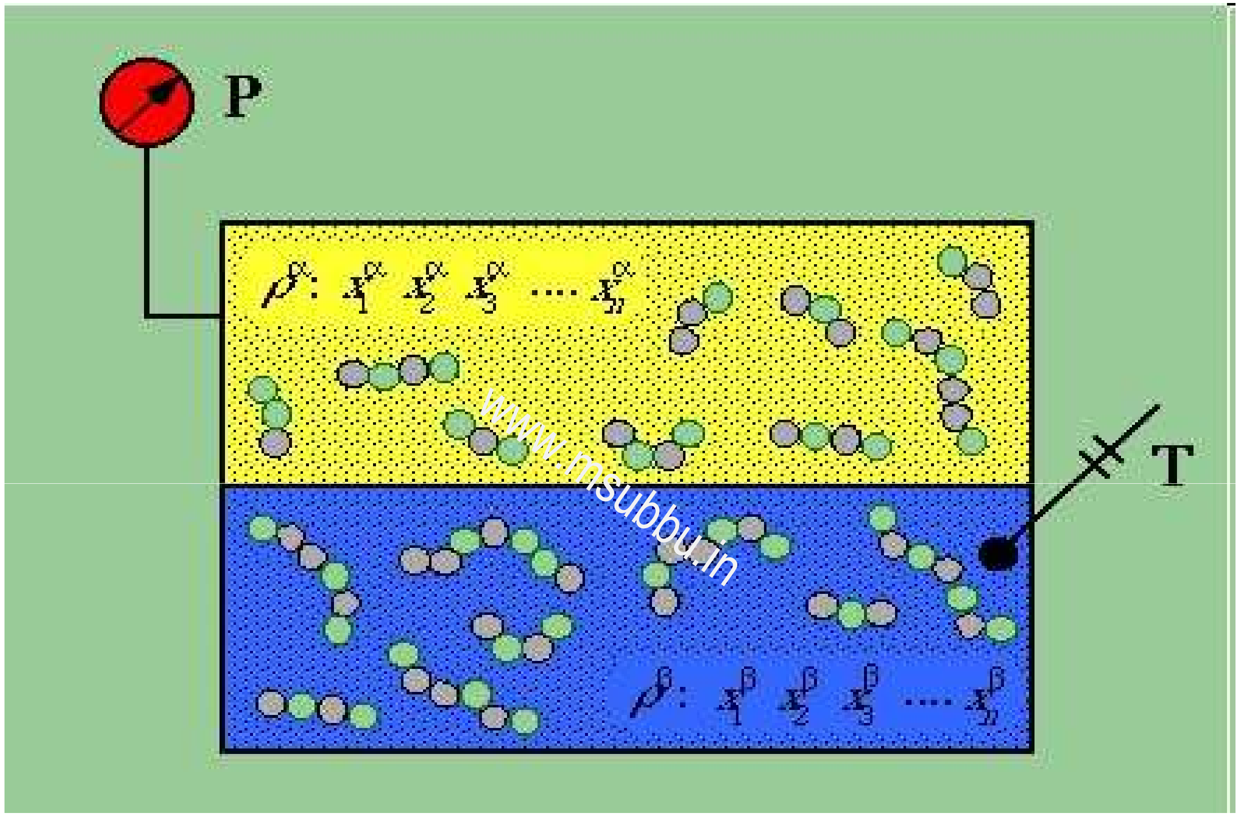
$$\boxed{d(nG) = (nV)dP - (nS)dT}$$

Mass balance:

$$\boxed{dn_i^{\alpha} = -dn_i^{\beta}}$$

$$\boxed{\mu_i^{\alpha} = \mu_i^{\beta}}$$

Multiple phases at the same T and P are in equilibrium when chemical potential of each species is the same in all phases.


P
T

Partial Molar Energy Properties and Chemical Potentials

The partial molar Gibbs free energy is chemical potential; however, the other partial molar energy properties such as that of internal energy, enthalpy, and Helmholtz free energy are not chemical potentials: because chemical potentials are derivatives with respect to the mole numbers with the natural independent variables held constant.

$$\mu_i = \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_{j\neq i}} = \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j}$$

$$nA = \mathcal{A}(V, T.n_1, n_2, n_3, \ldots)$$

$$\mu_i = \left[\frac{\partial(nA)}{\partial n_i}\right]_{V,T,n_j}$$

$$nU = \mathcal{U}(V, S.n_1, n_2, n_3, \ldots)$$

$$\mu_i = \left[\frac{\partial(nU)}{\partial n_i}\right]_{V,S,n_j}$$

$$nH = \mathcal{H}(P, S.n_1, n_2, n_3, \ldots)$$

$$\mu_i = \left[\frac{\partial(nH)}{\partial n_i}\right]_{P,S,n_j}$$

$$\begin{aligned} dU &= TdS - PdV \\ dH &= VdP + TdS \\ dG &= -SdT + VdP \\ dA &= -PdV - SdT \end{aligned}$$

Variation of μ with T and P

- Variation of μ with P: **partial molar volume**

- Variation of μ with T: partial molar entropy, can be expressed in terms of **partial molar enthalpy**

$$d(nG) = (nV)dP - (nS)dT + \sum \bar{G}_i dn_i \tag{19}$$

If $F = F(x, y, z)$ then

$$dF = Mdx + Ndy + Pdz$$

Exactness Criteria:

$$\left(\frac{\partial M}{\partial y}\right)_{x,z} = \left(\frac{\partial N}{\partial x}\right)_{y,z}$$
$$\left(\frac{\partial M}{\partial z}\right)_{x,y} = \left(\frac{\partial P}{\partial x}\right)_{y,z}$$
$$\left(\frac{\partial N}{\partial z}\right)_{x,y} = \left(\frac{\partial P}{\partial y}\right)_{x,z}$$

Using the above exactness criteria relations, for Eqn.(19) we get,

$$\left(\frac{\partial \bar{G}_i}{\partial P}\right)_{T,n} = \left[\frac{\partial (nV)}{\partial n_i}\right]_{P,T,n_j} = \bar{V}_i \tag{20}$$

and

$$\left(\frac{\partial \bar{G}_i}{\partial T}\right)_{P,n} = -\left[\frac{\partial (nS)}{\partial n_i}\right]_{P,T,n_j} = -\bar{S}_i \tag{21}$$

From the definition of G,

$$G = H - TS$$

i.e.,

$$nG = nH - T(nS)$$

Differentiation with respect to n_i at constant P, T, and n_j yields

$$\left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j} = \left[\frac{\partial(nH)}{\partial n_i}\right]_{P,T,n_j} - T\left[\frac{\partial(nS)}{\partial n_i}\right]_{P,T,n_j}$$

By applying the definition of partial molar property in the above equation, we get

$$\bar{G}_i = \bar{H}_i - T\bar{S}_i \tag{22}$$

Rearrangin Eqn.(22), we get

$$T\bar{S}_i + \bar{G}_i = \bar{H}_i \tag{23}$$

Since $\bar{G}_i = \mu_i$, we can write Eqns.(20) and (21) as

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n} = \bar{V}_i \tag{24}$$

and,

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n} = -\bar{S}_i \tag{25}$$

Variation of μ_i with T is $\bar{S}_i$. However, experimental data are available in terms of $\bar{V}_i$ and $\bar{H}_i$.

Whereas,

$$\frac{\partial(\mu_i/T)}{\partial T} = \frac{T(\partial\mu_i/\partial T) - \mu_i}{T^2}$$

Using Eqn.(25) in the above equation, we get,

$$\frac{\partial(\mu_i/T)}{\partial T} = \frac{-T\bar{S}_i - \mu_i}{T^2}$$

Using Eqn.(23) in the above equation, we get,

$$\frac{\partial(\mu_i/T)}{\partial T} = \frac{-\bar{H}_i}{T^2} \tag{26}$$

Partial molar volume ($\bar{V}_i$) and partial molar enthalpy ($\bar{H}_i$) are useful properties as they represent the variation of chemical potential with pressure and temperature

Entropy Change

The second law of thermodynamics

For an isolated system

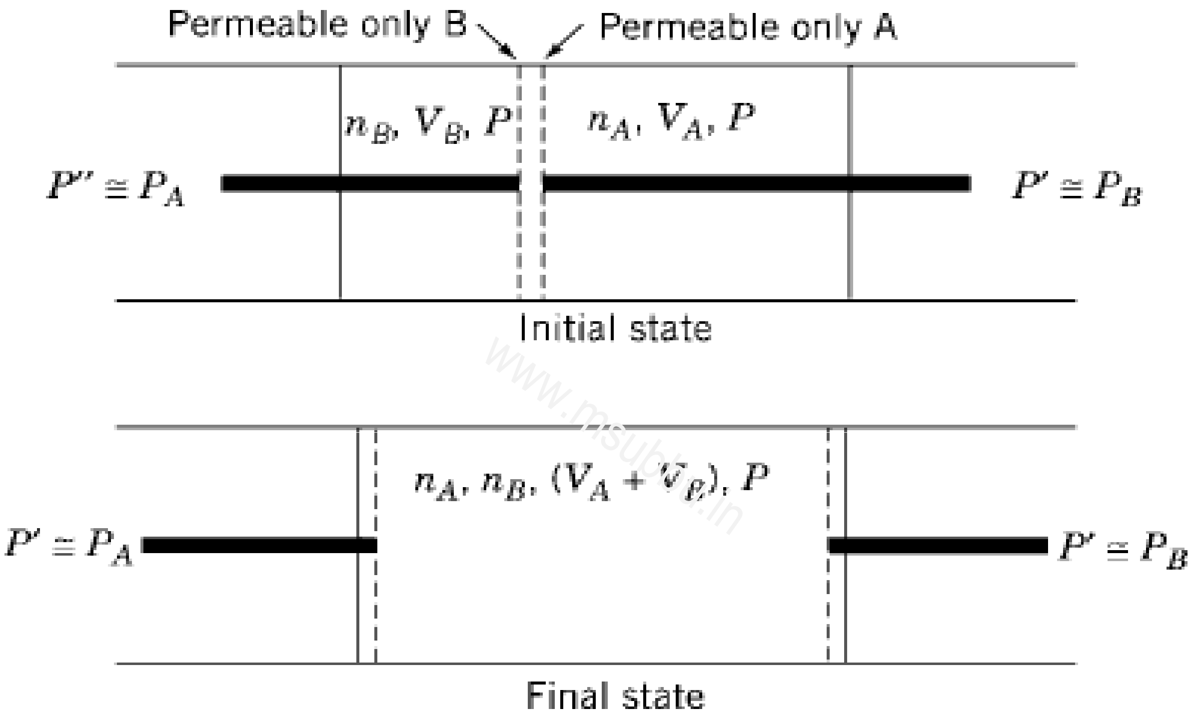
$$\Delta S \geq 0$$

in which the equality refers to a system undergoing a reversible change and the inequality refers to a system undergoing an irreversible change.

For systems that are not isolated it will be convenient to use the criteria of reversibility and irreversibility such as in the following equation:

$$dS \geq \frac{dQ}{T}$$

Mixing at Constant T and P



To carry out the mixing process in a reversible manner, the external pressure P' on the right piston is kept infinitesimally less than the pressure of B in the mixture; and the external pressure P'' on the left piston is kept infinitesimally less than the pressure of A in the mixture.

$$W_{\text{rev}} = W_A + W_B$$

$$= -\int_{V_A}^{V_A+V_B} P dV - \int_{V_B}^{V_A+V_B} P dV$$

$$= -\int_{V_A}^{V_A+V_B} n_A RT \frac{dV}{V} - \int_{V_B}^{V_A+V_B} n_B RT \frac{dV}{V}$$

$$= -n_A RT \ln \frac{V_A + V_B}{V_A} - n_B RT \ln \frac{V_A + V_B}{V_B}$$

$$W_{\text{rev}} = -n_A RT \ln \frac{n_A + n_B}{n_A} - n_B RT \ln \frac{n_A + n_B}{n_B}$$

$$= n_A RT \ln \frac{n_A}{n_A + n_B} + n_B RT \ln \frac{n_B}{n_A + n_B}$$

$$= n_A RT \ln X_A + n_B RT \ln X_B$$

As the mixing process is isothermal, and the mixture is an ideal gas,

$$\Delta U = 0$$

$$Q_{\text{rev}} = -W_{\text{rev}} = -n_A RT \ln X_A - n_B RT \ln X_B$$

$$\Delta S_{\text{mixing}} = \frac{Q_{\text{rev}}}{T} = -n_A R \ln X_A - n_B R \ln X_B$$

Entropy Change of Mixing

- Consider the process, where n_A moles of ideal gas A are confined in a bulb of volume V_A at a pressure P and temperature T. This bulb is separated by a valve or stopcock from bulb B of volume V_B that contains n_B moles of ideal gas B at the same pressure P and temperature T. When the stopcock is opened, the gas molecules mix spontaneously and irreversibly, and an increase in entropy ΔS_{mix} occurs.

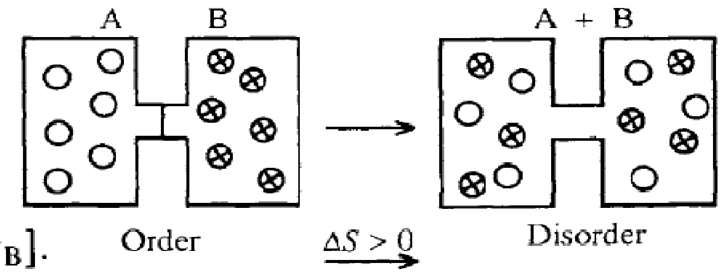
- The entropy change can be calculated by recognizing that the gas molecules do not interact, since the gases are ideal. ΔS_{mix} is then simply the sum of ΔS_A, the entropy change for the expansion of gas A from V_A to $(V_A + V_B)$ and ΔS_B, the entropy change for the expansion of gas B from V_B to $(V_A + V_B)$. That is,

$$\Delta S_A = n_A R \ln \frac{V_A + V_B}{V_A}$$

$$\Delta S_{mix} = \Delta S_A + \Delta S_B$$

$$\Delta S_B = n_B R \ln \frac{V_A + V_B}{V_B}.$$

$$\Delta_{mix} S_m = -R[x_A \ln x_A + x_B \ln x_B].$$



For the isothermal process involving ideal gases, ΔH is zero.
Therefore,

$$\Delta G_{\text{mixing}} = -T\Delta S_{\text{mixing}}$$

$$\Delta G_{\text{mixing}} = n_A\, RT\, \ln X_A + n_B\, RT\, \ln X_B$$

$$\Delta H^{\text{ig}}_{\text{mix}} = 0$$
$$\Delta V^{\text{ig}}_{\text{mix}} = 0$$

Partial Molar Entropy of Component i in an ideal gas mixture

$$\begin{aligned}\text{Property change of mixing} &= \text{Property of the mixture after mixing}\\ &\quad -\text{Property of the mixture before mixing}\end{aligned}$$

For the entropy change of mixing of an ideal gas mixture

$$\Delta S^{\text{ig}}_{\text{mix}} = S^{\text{ig}} - \sum y_i S_i^{\text{ig}}$$

We know that for the mixture $S^{\text{ig}} = \sum y_i \bar{S}_i^{\ \text{ig}}$. Therefore, the above equation becomes

$$\Delta S^{\text{ig}}_{\text{mix}} = \sum y_i \bar{S}_i^{\ \text{ig}} - \sum y_i S_i^{\text{ig}}$$

Substituting for $\Delta S^{\text{ig}}_{\text{mix}}$ from Eqn.(37), in the above equation, we get

$$-\sum y_i R \ln y_i = \sum y_i \bar{S}_i^{\ \text{ig}} - \sum y_i S_i^{\text{ig}}$$

Rearranging the above,

$$\sum y_i \bar{S}_i^{\ \text{ig}} = \sum y_i S_i^{\text{ig}} - \sum y_i R \ln y_i$$

From this, we can write

$$\boxed{\bar{S}_i^{\ \text{ig}} = S_i^{\text{ig}} - R \ln y_i} \qquad (38)$$

Gibbs free energy change of mixing

By definition, $G = H - TS$. Therefore

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

For an ideal gas mixture,

$$\Delta G^{ig}_{mix} = \Delta H^{ig}_{mix} - T\Delta S^{ig}_{mix} - S^{ig}\Delta T$$

For the changes at constant temperature, $\Delta T = 0$, and enthalpy change of mixing is zero for ideal gas mixture. Therefore, the above equation reduces to

$$\Delta G^{ig}_{mix} = -T\Delta S^{ig}_{mix} \tag{39}$$

Using Eqn.(37) in (39), we get

$$\Delta G^{ig}_{mix} = \sum y_i RT \ln y_i \tag{40}$$

From this we can get

$$\boxed{\bar{G}_i^{\ ig} = G_i^{ig} + RT \ln y_i} \tag{41}$$

Chemical potential of component i in an ideal gas mixture

From the fundamental property relation,

$$dG = VdP - SdT$$

At constant T and for an ideal gas i, the above equation reduces to

$$dG_i^{\mathrm{ig}} = V_i^{\mathrm{ig}} dP$$

Since $V_i^{\mathrm{ig}} = RT/P$, the above equation becomes

$$dG_i^{\mathrm{ig}} = RT\, d\ln P \tag{42}$$

Integrating the above equation, we get

$$G_i^{\mathrm{ig}} = RT \ln P + \Gamma_i(T) \tag{43}$$

Substituting this in Eqn.(41), we get

$$\bar{G}_i^{\mathrm{ig}} = RT \ln P + \Gamma_i(T) + RT \ln y_i$$

Rearranging the above, we get

$$\boxed{\bar{G}_i^{\mathrm{ig}} = RT \ln(y_i P) + \Gamma_i(T)} \tag{44}$$

This equation gives the chemical potential of component i in an ideal gas mixture, in terms of measurable quantities (T, P, and y_i). We need a similar expression for chemical potential of component i in a real gas mixture and any solution. To this need, we will define a property what is called as *r*esidual property.

$$\boxed{\mu_i^{ig} \equiv \overline{G}_i^{ig} = G_i^{ig} + RT \ln y_i}$$

$$\boxed{G_i^{ig} = \Gamma_i(T) + RT \ln P}$$

$$\boxed{\mu_i^{ig} = \Gamma_i(T) + RT \ln y_i P}$$

Residual Property

For any extensive thermodynamic property, the molar value of residual property M^{R} is defined as

$$M^{\mathrm{R}} = M - M^{\mathrm{ig}}$$

For pure component i,

$$M_i^{\mathrm{R}} = M_i - M_i^{\mathrm{ig}}$$

For the component i in a solution,

$$\bar{M}_i{}^{\mathrm{R}} = \bar{M}_i - \bar{M}_i{}^{\mathrm{ig}}$$

For Gibbs free energy, of pure component i

$$G_i{}^{\mathrm{R}} = G_i - G_i{}^{\mathrm{ig}} \tag{45}$$

For Gibbs free energy, of component i in a solution

$$\bar{G}_i{}^{\mathrm{R}} = \bar{G}_i - \bar{G}_i{}^{\mathrm{ig}} \tag{46}$$

Fugacity of a component i

For a component i at any P, T condition, Eqn.(42) can be written conveniently as

$$dG_i = RT\,d\ln f_i \tag{47}$$

where f_i is called as the fugacity of component i. This fugacity is a measure of deviation from ideal gas state. This conceptual property f, which is having the unit of pressure, is helpful to get simple relations for Gibbs free energy change.

Integrating Eqn.(47), we get

$$G_i = RT\ln f_i + \Gamma_i(T) \tag{48}$$

Using Eqns.(43) and (48), in Eqn.(45), we get

$$G_i^{\mathrm{R}} = RT\ln f_i - RT\ln P$$

i.e.,

$$G_i^{\mathrm{R}} = RT\ln\frac{f_i}{P} = RT\ln\phi_i \tag{49}$$

where $\phi_i = f_i/P =$ fugacity coefficient of component i.

Chemical potential of component i in a solution in terms of fugacity

Partial molar Gibbs free energy of component i in a solution ($\bar{G}_i$ or μ_i) can be written in terms of residual Gibbs free energy ($\bar{G}_i^{\mathrm{R}}$) and ideal gas value ($\bar{G}_i^{\mathrm{ig}}$) as

$$\mu_i = \bar{G}_i = \bar{G}_i^{\mathrm{ig}} + \bar{G}_i^{\mathrm{R}} \tag{50}$$

For a component i in a solution, Eqns.(48) and (49) are written as

$$\bar{G}_i = RT \ln \hat{f}_i + \Gamma_i(T) \tag{51}$$

and

$$\bar{G}_i^{\mathrm{R}} = RT \ln \hat{\phi}_i \tag{52}$$

where $\hat{f}_i$ is the fugacity of component i in solution, and $\hat{\phi}_i$ is the fugacity coefficient of i in solution. Using the above equations and Eqn.(44), in Eqn.(50), we get

$$RT \ln \hat{f}_i + \Gamma_i(T) = RT \ln(y_i P) + \Gamma_i(T) + RT \ln \hat{\phi}_i$$

i.e.,

$$RT \ln \hat{f}_i - RT \ln(y_i P) = RT \ln \hat{\phi}_i$$

$\Longrightarrow$

$$\hat{\phi}_i = \frac{\hat{f}_i}{y_i P}$$

i.e.,

$$\boxed{\hat{f}_i = \hat{\phi}_i y_i P} \tag{53}$$

This equation for fugacity coefficient is applicable for a component at any state (gas, liquid, or solid). However, this expression is normally used for gaseous solution.

Fugacity and fugacity coefficient: species in solution

- For species *i* in a mixture of real gases or in a solution of liquids:

$$\boxed{\mu_i \equiv \Gamma_i(T) + RT \ln \hat{f}_i}$$

Fugacity of species *i* in solution (replacing the particle pressure)

- Multiple phases at the same T and P are in equilibrium when the fugacity of each constituent species is the same in all phases:

$$\boxed{\hat{f}_i^{\alpha} = \hat{f}_i^{\beta} = \ldots = \hat{f}_i^{\pi}}$$

The residual property: $$M^R = M - M^{ig}$$

The partial residual property: $$\bar{M}_i^R = \bar{M}_i - \bar{M}_i^{ig}$$

$$\bar{G}_i^R = \bar{G}_i - \bar{G}_i^{ig}$$

$$\mu_i \equiv \Gamma_i(T) + RT \ln \hat{f}_i$$

$$\mu_i^{ig} = \Gamma_i(T) + RT \ln y_i P$$

$$\mu_i - \mu_i^{ig} = RT \ln \frac{\hat{f}_i}{y_i P}$$

$$\mu_i \equiv \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j} = \bar{G}_i$$

$$\bar{G}_i^R = RT \ln \hat{\phi}_i$$

$$\hat{\phi}_i \equiv \frac{\hat{f}_i}{y_i P}$$

The fugacity coefficient of species *i* in solution

For ideal gas,

$$\bar{G}_i^R = 0$$

$$\hat{\phi}_i = \frac{\hat{f}_i}{y_i P} = 1$$

$$\hat{f}_i = y_i P$$

The excess Gibbs energy and the activity coefficient

- The excess Gibbs energy is of particular interest:

$$\boxed{G^E \equiv G - G^{id}}$$

$$\boxed{\overline{G}_i = \Gamma_i(T) + RT \ln \hat{f}_i}$$

$$\boxed{\overline{G}_i^{id} = \Gamma_i(T) + RT \ln x_i f_i}$$

$$\boxed{\overline{G}_i^E = RT \ln \frac{\hat{f}_i}{x_i f_i}}$$

$$\boxed{\gamma_i \equiv \frac{\hat{f}_i}{x_i f_i}}$$

The activity coefficient of species *i* in solution.
A factor introduced into Raoult's law to account for liquid-phase non-idealities.
For ideal solution, $\boxed{\overline{G}_i^E = 0, \quad \gamma_i = 1}$

$$\boxed{\overline{G}_i^E = RT \ln \gamma_i}$$

c.f. $\boxed{\overline{G}_i^R = RT \ln \hat{\phi}_i}$

$$\boxed{\hat{\phi}_i y_i P = \gamma_i x_i f_i}$$

$$\boxed{\hat{\phi}_i = \frac{\hat{f}_i}{y_i P} = 1} \longrightarrow \boxed{\hat{f}_i = y_i P}$$

$$\boxed{\gamma_i \equiv \frac{\hat{f}_i}{x_i f_i}}$$

$$\boxed{\overline{G}_i^{\,E} = RT \ln \gamma_i}$$

$$\boxed{\overline{G}_i^{\,R} = 0}$$

For ideal solution,

$$\boxed{\overline{G}_i^{\,E} = 0, \quad \gamma_i = 1}$$

Fugacity of a pure liquid

- The fugacity of pure species *i* as a compressed liquid:

$$G_i - G_i^{sat} = RT \ln \frac{f_i}{f_i^{sat}}$$

$$G_i - G_i^{sat} = \int_{P_i^{sat}}^{P} V_i dP \quad (isothermal \quad process)$$

$$\ln \frac{f_i}{f_i^{sat}} = \frac{1}{RT} \int_{P_i^{sat}}^{P} V_i dP$$

Since V_i is a weak function of P

$$\ln \frac{f_i}{f_i^{sat}} = \frac{V_i^l (P - P_i^{sat})}{RT}$$

$$f_i^{sat} = \phi_i^{sat} P_i^{sat}$$

$$f_i = \phi_i^{sat} P_i^{sat} \exp \frac{V_i^l (P - P_i^{sat})}{RT}$$

Infinite dilution of girls in boys