

PROPERTIES OF SOLUTIONS

Dr. Sumitra Maurya
Chemistry Department
Brahmanand P. G. College, Kanpur

Ideal solutions

An ideal mixture is one, for which there is **no change in volume due to mixing**. In other words for an ideal solution, **partial molar volume** of each component will be **equal to its pure component volume** at same temperature and pressure.

--- Raoult's law

$$\bar{V}_i = V_i$$

$$V = \sum \bar{V}_i x_i = \sum x_i V_i$$

Ideal solutions are formed when similar components or adjacent groups of group are mixed

$$\bar{V}_i = V_i$$

Eg: Benzene-Toluene, Methanol- Ethanol, Hexane- Heptane

Solution undergo change in volume due to mixing are known as non ideal solutions

$$\bar{V}_i \neq V_i$$

Eg: Methanol-Water, Ethanol-water.

Ideal solutions formed when the intermolecular force between like molecules and unlike molecules are of the same magnitude.

Non-ideal solutions are formed when intermolecular forces between like molecules and unlike molecules of different magnitude.

For ideal solutions

$$V^t = \sum n_i V_i \text{-----(1)}$$

V_i is the molar volume of pure component i

$$\bar{V}_i = \left[\frac{\partial V^t}{\partial n_i} \right]_{T,P,n_j} = V_i$$

The residual volume for the pure component is

$$\alpha = V_i - \frac{RT}{p}$$

Therefore we know from reduced properties

$$\ln \frac{f_i}{P} = \frac{1}{RT} \int_0^P \left(V_i - \frac{RT}{P} \right) dP \quad \text{----(3)}$$

For component i in terms of partial molar properties

$$\ln \frac{\bar{f}_i}{P_i} = \frac{1}{RT} \int_0^P \left(\bar{V}_i - \frac{RT}{P} \right) dP \quad \text{----(4)}$$

Subtracting equation (3) from (4)

$$\ln \frac{\bar{f}_i P}{f_i P_i} = \frac{1}{RT} \int_0^P (\bar{V}_i - V_i) dP \quad \text{----(5)}$$

we know that $\bar{P}_i = y_i P$

equation (5) reduces to

$$\ln \frac{\bar{f}_i}{f_i y_i} = \frac{1}{RT} \int_0^P (\bar{V}_i - V_i) dP$$

comparing equation (2)

$$\frac{\bar{f}_i}{f_i y_i} = 1 \qquad \bar{f}_i = f_i y_i$$

--Lewis Randal rule

Lewis Randal rule is applicable for evaluating fugacity of components in gas mixture.

Lewis Randal rule is valid for

1. At low pressure when gas behaves ideally.
2. When Physical properties are nearly same.
3. At any pressure if component present in excess.

Henry's Law

This law is applicable for small concentration ranges. For ideal solution Henry's law is given as

$$\bar{f}_i = x_i k_i$$

$$\bar{P}_i = x_i k_i$$

k_i - Henry's Constant, \bar{f}_i - Partial molar fugacity,

\bar{P}_i - Partial pressure of component i.

Non Ideal solutions

For ideal solutions $\bar{f}_i = x_i k_i$ -----(a)

For non ideal solutions $\bar{f}_i = \gamma_i x_i k_i$ -----(b)

γ_i - is an activity coefficient of component i

Comparing equation (a) and (b)
$$\gamma_i = \frac{\bar{f}_i(\text{nonideal})}{f_i(\text{ideal})}$$

For both ideal and Non ideal solutions the fugacity of solution is given by equation

$$\ln f = \sum x_i \ln \frac{\bar{f}_i}{x_i}$$

$$\ln \phi = \sum x_i \ln \bar{\phi}_i$$

Activity in Solutions:

The activity of a component in a solution is defined as the ratio of fugacity of a component in the solution to the fugacity of that component in the standard state.

$$a_i = \frac{\bar{f}_i}{f_i^o}$$

The fugacities are related to chemical potential as

$$\mu_i = RT \ln \bar{f}_i + C \quad \text{--(1)}$$

at standard state

$$\mu_i^o = RT \ln f_i^o + C \quad \text{-----(2)}$$

Subtracting equation 2 from 1

$$\Delta\mu_i = RT \ln \frac{\overline{f}_i}{f_i} = RT \ln a_i$$

$$\Delta\mu_i = \mu_i - \mu_i^o$$

Is the increase in chemical potential of species *i* when it is brought into solution from its standard state

For ideal solutions $\overline{f}_i = x_i f_i$

$$a_i = \frac{f_i}{f_i^o}$$

$$a_i = x_i \quad (\text{for ideal solutions})$$

Activity coefficients:

The calculation of fugacity of a component in a real solution should take into account of the degree of the departure from ideal behavior

For real solutions the partial molar fugacities is given by the relation $\bar{f}_i = \gamma_i x_i f_i^o$

for ideal solutions $\bar{f}_i = x_i f_i^o \quad \gamma_i = 1$

Here we have observed two types of ideal behavior

$f_i^o = f_i$ --- Lewis Randall rule or Raoult's law

$f_i^o = K_i$ ----- Henry's law

In case of Lewis Randall rule or Raoult's law

$$\bar{f}_i = \gamma_i x_i f_i^o$$

$$\gamma_i = \frac{\bar{f}_i}{x_i f_i^o} = \frac{a_i}{x_i} \quad a_i = \gamma_i x_i$$

For Henry's Law

$$\bar{f}_i = \gamma_i x_i K_i \quad \bar{P}_i = \gamma_i x_i K_i$$

Effect Pressure on Activity Coefficients

Effect of pressure on fugacity

$$\left(\frac{\partial \ln f_i}{\partial P} \right)_T = \frac{V_i}{RT} \quad \text{-----(A)}$$

In terms of Partial molar properties

$$\left(\frac{\partial \ln \bar{f}_i}{\partial P} \right)_T = \frac{\bar{V}_i}{RT} \quad \text{-----(B)}$$

Equation B-A

$$\left(\frac{\partial \ln(\bar{f}_i / f_i)}{\partial P} \right)_T = \frac{\bar{V}_i - V_i}{RT} \quad \frac{\bar{f}_i}{f_i} = \gamma_i x_i$$

$$\left(\frac{\partial \ln \gamma_i x_i}{\partial P} \right)_T = \frac{\bar{V}_i - V_i}{RT}$$

Mole fraction is independent of pressure $\left[\frac{\partial \ln x_i}{\partial P} \right] = 0$

$$\left(\frac{\partial \ln \gamma_i}{\partial P} \right)_T = \frac{\bar{V}_i - V_i}{RT}$$

\bar{V}_i - Partial molar volume

V_i - Pure component volume

Effect of Temperature on activity Coefficients

The effect of temperature on fugacity of a pure substance was given by the equation

$$\left(\frac{\partial \ln \bar{f}_i}{\partial T} \right)_P = \frac{H_i^o - H_i}{RT^2} \quad \text{-----(C)}$$

Similarly for the substance in the solution (Partial molar properties)

$$\left(\frac{\partial \ln \bar{f}_i}{\partial T} \right)_P = \frac{H_i^o - \bar{H}_i}{RT^2} \text{ -----(D)}$$

Equation D-C

$$\left(\frac{\partial \ln \gamma_i}{\partial T} \right)_P = \frac{H_i - \bar{H}_i}{RT^2}$$

$(\bar{H}_i - H_i)$ - **Partial heat of mixing of component i** from its pure state of given composition both in the same state of aggregation and pressure.

PROBLEM

The fugacity of component 1 in binary liquid mixture of component 1 and 2 at 298K and 20bar is given by

$$\overline{f}_1 = 50 x_1 - 80 x_1^2 + 40 x_1^3$$

Where f is in bar and x_1 is the mole fraction of component 1
Determine

- (a) The fugacity f_1 of pure component 1 ϕ_1
- (b) The fugacity coefficient γ_1
- (c) The Henrys law constant K_1
- (d) The activity coefficient

Gibbs Duhem Equation

Consider a multi component solution having n_i moles of component i , let the property of solution be M in terms of partial molar properties

$$M^t = nM = \sum n_i \bar{M}_i \quad \text{-----(1).}$$

Where n is the total no of moles of solution

Differentiating eq (1) we get

$$d(nM) = \sum n_i d\bar{M}_i + \sum M_i dn_i \quad \text{-----(2)}$$

We know that

$$nM = f[T, P, n_1, n_2, \dots]$$

$$\begin{aligned} \partial(nM) = & \left[\frac{\partial(nM)}{\partial T} \right]_{P, n_1, n_2, \dots} dT + \left[\frac{\partial(nM)}{\partial P} \right]_{T, n_1, n_2, \dots} dP + \left[\frac{\partial(nM)}{\partial n_1} \right]_{T, P, n_2, n_3, \dots} dn_1 \\ & + \left[\frac{\partial(nM)}{\partial n_2} \right]_{T, P, n_1, n_3, \dots} dn_2 + \dots \end{aligned}$$

$$\partial(nM) = \left[\frac{n \partial(M)}{\partial T} \right]_{P, n_1, n_2, \dots} dT + \left[\frac{n \partial(M)}{\partial P} \right]_{T, n_1, n_2, \dots} dP + \sum \left[\frac{\partial(nM)}{\partial n_i} \right]_{T, P, n_j} dn_i$$

From the definition of partial molar properties

$$\partial(nM) = \left[\frac{n\partial(M)}{\partial T} \right]_{P, n_1, n_2} dT + \left[\frac{n\partial(M)}{\partial P} \right]_{T, n_1, n_2} dP + \sum \bar{M}_i dn_i \quad \text{---(3)}$$

Subtracting equation (2) from equation (3)

$$\left[\frac{n\partial(M)}{\partial T} \right]_{P, n_1, n_2} dT + \left[\frac{n\partial(M)}{\partial P} \right]_{T, n_1, n_2} dP - \sum n_i d\bar{M}_i = 0 \quad \text{-----(4)}$$

Equation (4) is the fundamental form of Gibbs Duhem equation

Special Case

At constant temperature and pressure, dT and dP are equal to zero. The equation becomes

$$\sum x_i d\overline{M}_i = 0$$

For binary solution at constant temperature and pressure the equation becomes

$$x_1 d\overline{M}_1 + x_2 d\overline{M}_2 = 0$$

$$x_1 d\overline{M}_1 + (1 - x_1) d\overline{M}_2 = 0 \text{ -----(5)}$$

dividing equation(5) by dx_1

$$x_1 \frac{d\overline{M}_1}{dx_1} + (1 - x_1) \frac{d\overline{M}_2}{dx_1} = 0$$

The above equation is Gibbs Duhem equation for binary solution at constant temperature and pressure in terms of Partial molar properties.

Any Data or equation on Partial molar properties must satisfy Gibbs Duhem equation.

Problem:

Find whether the equation given below is thermodynamically consistent

$$G = 100x_1 + 150x_2 + x_1x_2(10x_1 + x_2)$$

$$\overline{G}_1 = G + (1 - x_1) \frac{\partial G}{\partial x_1} \quad \overline{G}_1 = 18x_1^3 + 35x_1^2 + 16x_1 + 101$$

$$\overline{G}_2 = G - x_1 \frac{\partial G}{\partial x_1} \quad \overline{G}_2 = 18x_1^3 - 8x_1^2 + 150$$

$$\frac{d\overline{G}_1}{dx_1} = 54x_1^2 - 70x_1 + 16$$

$$\frac{d\overline{G}_2}{dx_1} = 54x_1^2 - 16x_1$$

GD equation

$$x_1 \frac{d\overline{M}_1}{dx_1} + (1 - x_1) \frac{d\overline{M}_2}{dx_1} = 0$$

$$x_1(54x_1^2 - 70x_1 + 16) + (1 - x_1)(54x_1^2 - 16x_1) = 0$$

It satisfies the GD equation, the above equation is consistent.

Property Changes of Mixing:

For ideal solution

For any thermodynamic property

$$V = \sum x_i V_i \quad M = \sum x_i M_i$$

For non ideal solutions, we apply a correction term ΔM known as property change of mixing.

For non ideal solutions

$$M = \sum x_i M_i + \Delta M$$

ΔM is the **difference in the property of the solution M** and sum of the properties of the pure components that make it up thus

$$\Delta M = M - \sum x_i M_i$$

in terms of volume

$$V = \sum x_i V_i + \Delta V$$

For ideal solutions $\Delta V = 0$

More general definition of ΔM $\Delta M = M - \sum x_i M_i^o$

Properties change in terms Partial molar $\Delta M = \sum x_i (\overline{M}_i - M_i^o)$

$\overline{M}_i - M_i^o$ - **change in property of component i** when one mole of pure i in its in its standard state is brought to the solution of given composition at same T and P.

In terms of Volume

$$\Delta V = \sum x_i (\overline{V}_i - V_i^o)$$

$$\Delta G = \sum x_i (\overline{G}_i - G_i^o)$$

Activity and property change of mixing

Free energy change of mixing (ΔG): Using the definition of fugacity the change of free energy of substance when it is brought from the standard state to the solution, it can be written as

$$\bar{G}_i - G_i^o = RT \ln \frac{\bar{f}_i}{f_i^o} = RT \ln a_i$$

We know that

$$\Delta G = \sum x_i (\bar{G}_i - G_i^o)$$

$$\frac{\Delta G}{RT} = \sum x_i \ln a_i$$

Volume change of Mixing ΔV :

The partial molar free energy(chemical potential) varies with pressure as

$$\left(\frac{\partial \bar{G}_i}{\partial P} \right)_{T,x} = \bar{V}_i$$

Similarly for pure substance, we have

$$\left(\frac{\partial G_i^o}{\partial P} \right)_{T,x} = V_i^o \quad \Delta V = \sum x_i \left[\frac{\partial(\bar{G}_i - G_i^o)}{\partial P} \right]_{T,x}$$

$$\Delta V = \sum x_i (\bar{V}_i - V_i^o)$$
$$\Delta V = \sum x_i \left[\frac{\partial(\bar{G}_i - G_i^o)}{\partial P} \right]_{T,x}$$

Result of the above equation

$$\Delta V = RT \sum x_i \left[\frac{d \ln a_i}{\partial P} \right]_{T,x}$$

The above equation can be rewritten in the form

$$\frac{P\Delta V}{RT} = \sum x_i \left[\frac{d \ln a_i}{d \ln P} \right]_{T,x}$$

Enthalpy change of mixing ΔH :

The Gibbs Helmholtz equation is given as

$$\left[\frac{\partial(G_i / T)}{\partial T} \right]_P = -\frac{H_i^o}{T^2}$$

in terms of partial molar properties

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

The enthalpy of mixing $\Delta H = \sum x_i (\bar{H}_i - H_i^o)$

Using the above equations

$$\Delta H = -T^2 \sum x_i \left[\frac{\partial}{\partial T} \left(\frac{\bar{G}_i - G_i^o}{T} \right) \right]_{P,x}$$

$$\Delta H = -T^2 R \sum x_i \left[\frac{\partial}{\partial T} \ln a_i \right]_{P,x}$$

$$\frac{\Delta H}{RT} = - \sum x_i \left[\frac{\partial \ln a_i}{\partial \ln T} \right]_{P,x}$$



THANK YOU