



Thermodynamics II

Solution Thermodynamics: Theory

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Introduction

- In the chemical, petroleum, and pharmaceutical industries multicomponent gases or liquids commonly undergo composition changes as the result of mixing and separation processes, the transfer of species from one phase to another, or chemical reaction.
- The property of such systems depend strongly on composition as well as on temperature and pressure
- The purpose in this chapter is to develop the theoretical foundation for applications of thermodynamics to gas mixtures and liquid solutions.

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Fundamental property relation

- What is the most important property ?

.....G.....

- For pure component; $G = G(T, P)$
- For a homogeneous mixture e.g. containing i components mixture;

$$G = G(T, P, n_1, n_2, \dots, n_i)$$

- Also, for **closed system**: no mass transfer across boundary or in a single-phase fluid in a closed system wherein no chemical reactions occur

$$d(nG) = (nV)dP - (nS)dT$$

- *Since* n is the total number of moles of the system (= constant); $G = G(T, P)$

$$\rightarrow dG = VdP - SdT$$

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Fundamental property relation

$$\rightarrow \left[\frac{\partial \mathbf{G}}{\partial P} \right]_{T,n} = \mathbf{V} \quad \left[\frac{\partial \mathbf{G}}{\partial T} \right]_{P,n} = -\mathbf{S}$$

- Open system, single phase

$$\mathbf{G} = nG = g(P, T, n_1, n_2, \dots, n_i, \dots)$$

n_i is the number of moles of species i

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

all mole numbers held constant

all mole numbers except n_i held constant

- The fundamental property relation for single phase fluid systems of variable mass and composition

$$d(n\mathbf{G}) = (n\mathbf{V})dP - (n\mathbf{S})dT + \sum_i \mu_i dn_i$$

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Fundamental property relation

$$\mathbf{V} = \left[\frac{\partial \mathbf{G}}{\partial P} \right]_{T,n} \quad \mathbf{S} = - \left[\frac{\partial \mathbf{G}}{\partial T} \right]_{P,n}$$

- The chemical potential of species i

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

- This equation forms the basis for the definition of partial properties

- For pure species $n = n_i$

$$\mu_i = \left[\frac{\partial(n_i G)}{\partial n_i} \right]_{P,T} = G + n_i \frac{\partial G}{\partial n_i} = G + n_i \cdot 0$$

$$\rightarrow \mu_i = G \quad \text{molar Gibbs energy,}$$

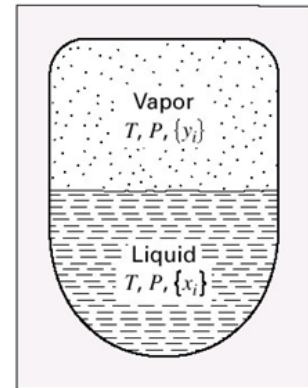
G is intensive property independent of the system size n_i

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The Chemical Potential and Phase Equilibria

- Consider the following:
 - A closed system and multicomponent
 - Containing two phases in equilibrium.
 - Mass transfer occurs if the equilibrium is disturbed
 - Each individual phase is an open system, free to transfer mass to the other



$$d(n\mathbf{G})^\alpha = (n\mathbf{V})^\alpha dP - (n\mathbf{S})^\alpha dT + \sum_i \mu_i^\alpha dn_i^\alpha$$

$$d(n\mathbf{G})^\beta = (n\mathbf{V})^\beta dP - (n\mathbf{S})^\beta dT + \sum_i \mu_i^\beta dn_i^\beta$$

- The total Gibbs energy of the two-phase system $n\mathbf{G} = (n\mathbf{G})^\alpha + (n\mathbf{G})^\beta$

$$d(n\mathbf{G}) = (n\mathbf{V})dP - (n\mathbf{S})dT + \sum_i \mu_i^\alpha dn_i^\alpha + \sum_i \mu_i^\beta dn_i^\beta$$

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The Chemical Potential and Phase Equilibria

- compare with $d(n\mathbf{G}) = (n\mathbf{V})dP - (n\mathbf{S})dT$ for the whole closed system

$$\longrightarrow \sum_i \mu_i^\alpha dn_i^\alpha + \sum_i \mu_i^\beta dn_i^\beta = 0$$

- Mass conservation requires

$$n_i^\alpha + n_i^\beta = \text{constant} \quad \longrightarrow \quad dn_i^\alpha + dn_i^\beta = 0$$

$$\longrightarrow \sum_i (\mu_i^\alpha - \mu_i^\beta) dn_i^\alpha = 0$$

- Quantities dn_i^α are independent and arbitrary (never be zero).

Hence

$$\mu_i^\alpha = \mu_i^\beta \quad (i = 1, 2, \dots, N)$$

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The Chemical Potential and Phase Equilibria

Chemical Potential (μ)

- Is an extensive property,
- Provides a measure of the work of a system is capable when a change in mole numbers occurs e.g. chemical reaction or a transfer of mass.
- For π phases at equilibrium, and N is the number of species, generalization to multiple phases in equilibrium

$$\mu_i^\alpha = \mu_i^\beta = \dots = \mu_i^\pi \quad (i = 1, 2, \dots, N) \quad N(\pi - 1) \text{ equations}$$

In addition to thermal and mechanical equilibrium criteria

$$T^\alpha = T^\beta = \dots = T^\pi \quad P^\alpha = P^\beta = \dots = P^\pi$$

Multiple phase at the same
T and P are in equilibrium
when the **chemical potential (μ_i)** of
each species is the **same** in
all phases

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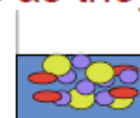
Partial (molar) properties

- Partial molar properties are defined as partial derivatives with respect to moles

$$\bar{M}_i \equiv \left[\frac{\partial \mathbf{M}}{\partial n_i} \right]_{P, T, n_j} \quad \mathbf{M} \text{ denotes for any extensive properties}$$

Where $M \equiv V, U, H, S, G$ etc.

This is a partial property of individual species **as they exist in a solution or mixture.**



This property **is different** from a pure species property primarily due to molecular interaction of **different** species in the solution or mixture

- It is a response function, i.e., a measure of the response of total property nM to the addition at constant T and P of a differential amount of species I to a finite amount of solution.

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Partial (molar) properties

Notations

- Solution properties M V, U, H, S, A, G
- Pure-species properties M_i $V_i, U_i, H_i, S_i, A_i, G_i$
- Partial molar properties \bar{M}_i $\bar{V}_i, \bar{U}_i, \bar{H}_i, \bar{S}_i, \bar{A}_i, \bar{G}_i$

- Re-call
$$\bar{G}_i \equiv \mu_i = \left(\frac{\partial \mathbf{G}}{\partial n_i} \right)_{P, T, n_j}$$

Hence, the **chemical potential of species i** (μ_i) is known also as **partial property of Gibbs energy for species i** .



Partial (molar) properties

- In general, for a homogenous mixture

$$nM = M(T, P, x_1, x_2, \dots, x_i)$$

- The total differential of M is

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

- Could also be written as

$$d(nM) = n \left[\frac{\partial(M)}{\partial P} \right]_{T, x} dP + n \left[\frac{\partial(M)}{\partial T} \right]_{P, x} dT + \sum \bar{M}_i dn_i \quad (11.9)$$

differentiation at constant composition



Partial (molar) properties

Since $n_i = x_i n$ $dn_i = x_i dn + n dx_i$

And $d(nM) = ndM + Mdn$

Substitute these terms to Eq. (11.9), and then rearrange:

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

Rearrange,

$$\underbrace{\left[dM - \left(\frac{\partial M}{\partial P} \right)_{T,x} dP - \left(\frac{\partial M}{\partial T} \right)_{P,x} dT - \sum_i \bar{M}_i dx_i \right]}_{=0.0} n + \underbrace{\left[M - \sum_i \bar{M}_i x_i \right]}_{=0.0} dn = 0$$



Partial (molar) properties

$$dM - \left(\frac{\partial M}{\partial P} \right)_{T,x} dP - \left(\frac{\partial M}{\partial T} \right)_{P,x} dT - \sum_i \bar{M}_i dx_i = 0$$

$$dM = \left(\frac{\partial M}{\partial P} \right)_{T,x} dP + \left(\frac{\partial M}{\partial T} \right)_{P,x} dT + \sum_i \bar{M}_i dx_i \quad (11.10)$$

$$M - \sum_i x_i \bar{M}_i = 0$$

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

$$nM = \sum_i n_i \bar{M}_i \quad (11.12)$$

Eqns 11.11 and 11.12 show that the calculation of mixture properties of constituent species from **partial properties** is by a simple summability relation!



Partial (molar) properties

Differentiating Eq 11.11
$$dM = \sum_i x_i d\bar{M}_i + \sum_i \bar{M}_i dx_i$$

- Comparison of this equation with Eq. (11.10) (**Subtraction gives**) yields

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

This eqn shows that the partial properties of species making up a solution are dependent on one another.

- This equation must be satisfied for all changes in P, T, and the M_i caused by changes of state in a homogeneous phase

- **As a special case at constant T and P:**
$$\sum_i x_i d\bar{M}_i = 0$$

Gibbs-Duhem equation at constant T and P

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Partial Properties in Binary Solutions

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

- For a binary solution

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

$$dM = x_1 d\bar{M}_1 + \bar{M}_1 dx_1 + x_2 d\bar{M}_2 + \bar{M}_2 dx_2 \quad \text{B}$$

- Gibbs-Duhem equation is
$$\sum_i x_i d\bar{M}_i = 0$$

- For a binary solution
$$x_1 d\bar{M}_1 + x_2 d\bar{M}_2 = 0 \quad \text{C}$$

Dividing by dx_1 , we have the Gibbs-Duhem equation in derivative forms

$$x_1 \frac{d\bar{M}_1}{dx_1} + x_2 \frac{d\bar{M}_2}{dx_1} = 0$$

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Partial Properties in Binary Solutions

Since

$$\begin{aligned} x_1 + x_2 &= 1 \\ dx_1 &= -dx_2 \end{aligned}$$

Eq. B becomes


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

D

➤ From Eq A and D

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

These equations can be used to obtain partial molar properties from solution property.

➤ As a solution becomes pure in species i , both properties approach pure species property

$$\lim_{x_i \rightarrow 1} M = \lim_{x_i \rightarrow 1} \bar{M}_i = M_i$$

➤ In the limit of infinite dilution $\lim_{x_i \rightarrow 0} \bar{M}_i = \bar{M}_i^\infty \neq M_i$



Partial Properties in Binary Solutions

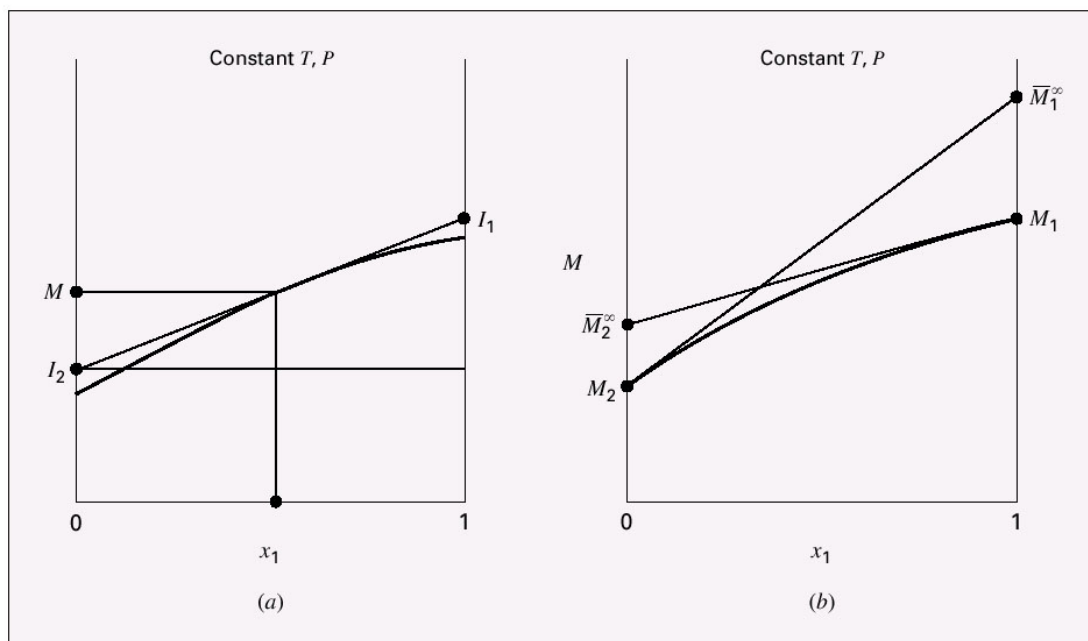


Figure 11.1: (a) Graphical construction of Example 11.2. (b) Infinite-dilution values of partial properties.



Partial Properties in Binary Solutions

➤ For a binary (For two components) solution

$$dH = TdS + VdP + (\mu_1)_{S,P}dn_1 + (\mu_2)_{S,P}dn_2$$

$$dU = TdS - PdV + (\mu_1)_{V,S}dn_1 + (\mu_2)_{V,S}dn_2$$

$$dG = VdP - SdT + (\mu_1)_{T,P}dn_1 + (\mu_2)_{T,P}dn_2$$

$$dA = -PdV - SdT + (\mu_1)_{T,V}dn_1 + (\mu_2)_{T,V}dn_2$$

$$\mu_1 = \left(\frac{\partial H}{\partial n_1} \right)_{S,P,n_2} = \left(\frac{\partial U}{\partial n_1} \right)_{V,S,n_2} = \left(\frac{\partial G}{\partial n_1} \right)_{T,P,n_2} = \left(\frac{\partial A}{\partial n_1} \right)_{T,V,n_2}$$

➤ Also,

$$\begin{aligned} \bar{H}_i &= \bar{U}_i + P\bar{V}_i \\ d\bar{G}_i &= \bar{V}_i dP - \bar{S}_i dT \end{aligned}$$

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Example

The need arise in a laboratory for 2000 cm³ of an antifreeze solution consisting of 30 mol % methanol in water. What volumes of pure methanol and of pure water at 25 °C must be mixed to form the of antifreeze, also at 25 °C ? Partial molar volumes for methanol and water in a 30 mol % methanol solution and their pure-species molar volume, both at 25 °C , are:

Methanol (1) and water (2):

$$\bar{V}_1 = 38.632 \text{ cm}^3 \text{ mol}^{-1} \quad V_1 = 40.727 \text{ cm}^3 \text{ mol}^{-1}$$

$$\bar{V}_2 = 17.765 \text{ cm}^3 \text{ mol}^{-1} \quad V_2 = 18.068 \text{ cm}^3 \text{ mol}^{-1}$$

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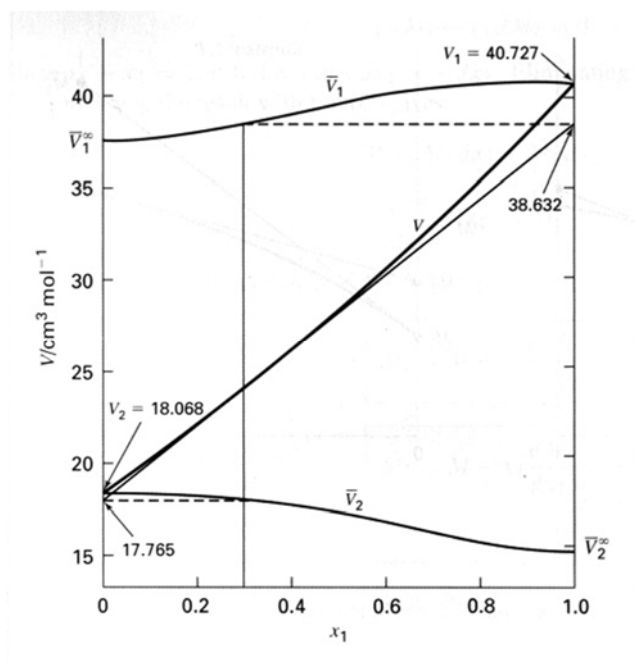


Example Cont.

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Example Cont.



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Relations among Partial Properties

We show now how partial properties are related to one another. By Eq. (11.8), $\mu_i \equiv \bar{G}_i$, and Eq. (11.20) may be written:

$$d(nG) = (nV)dP - (nS)dT + \sum \bar{G}_i dn_i \quad (11.17)$$

Application of the criterion of exactness, Eq. (6.12), yields the Maxwell relation,

$$\left(\frac{\partial V}{\partial T} \right)_{P,n} = - \left(\frac{\partial S}{\partial P} \right)_{T,n} \quad (6.16)$$

$$\left(\frac{\partial \bar{G}_i}{\partial T} \right)_{P,n} = - \left(\frac{\partial (nS)}{\partial n_i} \right)_{P,T,n_j} \quad \text{and} \quad \left(\frac{\partial \bar{G}_i}{\partial P} \right)_{T,n} = \left(\frac{\partial (nV)}{\partial n_i} \right)_{P,T,n_j}$$



Relations among Partial Properties

- One can write the RHS in the form of partial molar, and change the composition from n to x .

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

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

- Every equation that provides a linear relation among thermodynamic properties of a constant-composition solution has as its counterpart an equation connecting the corresponding partial properties of each species in the solution.



Relations among Partial Properties

$$H = U + PV$$

For n moles , $nH = nU + P(nV)$

$$\left[\frac{\partial(nH)}{\partial n_i} \right]_{P,T,n_j} = \left[\frac{\partial(nU)}{\partial n_i} \right]_{P,T,n_j} + P \left[\frac{\partial(nV)}{\partial n_i} \right]_{P,T,n_j}$$

$$\overline{H}_i = \overline{U}_i + P \overline{V}_i$$

$$d\overline{G}_i = \left(\frac{\partial \overline{G}_i}{\partial P} \right)_{T,x} dP + \left(\frac{\partial \overline{G}_i}{\partial T} \right)_{P,x} dT$$

$$d\overline{G}_i = \overline{V}_i dP - \overline{S}_i dT$$

- This may be compared with Eq. (6.10). These examples illustrate the parallelism that exists between equations for a constant composition solution and the corresponding equations for the partial properties of the species in solution. We can therefore write simply by analogy many equations that related partial properties.



Example



The Ideal-Gas Mixture Model

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The Ideal-Gas Mixture Model

➤ Dalton Law: Every gas has the same V and T .

$$P_i = y_i P_t \quad \text{where } y_i = \frac{n_i}{n_t}$$

$$P_t = \sum_i P_i$$

System A contain species 1 at T, P

System B contain species 2 at T, P

System C contain mixture 1 and 2 at T, P

$$(V^{ig})_A = \frac{RT}{P} = V_1^{ig}$$

$$(V^{ig})_C = \frac{RT}{P} = V^{ig}$$

$$(V^{ig})_B = \frac{RT}{P} = V_2^{ig}$$

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Molar Volume and Partial Molar Volume

- Application of partial properties to molar volume

$$\bar{V}_i^{ig} = \left[\frac{\partial(nV_i^{ig})}{\partial n_i} \right]_{P,T,n_j} = \left[\frac{\partial(nRT)/P}{\partial n_i} \right]_{P,T,n_j} = \frac{RT}{P} \left(\frac{\partial n}{\partial n_i} \right)_{n_j}$$

$$n = n_i + \sum_j n_j$$

$$\rightarrow \bar{V}_i^{ig} = V_i^{ig} = V^{ig} = \frac{RT}{P}$$

- **partial molar volume = pure species molar volume = mixture molar volume**

$$V^{ig}(T, P) = V_i^{ig}(T, P) = \bar{V}_i^{ig}(T, P)$$

- Note: Partial pressure of species i (It is not partial molar property)



Partial molar properties

- Properties of each component species are independent of the presence of other species.

Gibb's Theorem,

- A partial molar property (other than volume) of a constituent species in an ideal-gas mixture is equal to the corresponding molar property of the species as a pure ideal gas at the mixture temperature but at a pressure equal to its partial pressure in the mixture.

$$\bar{M}_i^{ig}(T, P) = M_i^{ig}(T, p_i)$$



Partial molar properties

$$\bar{H}_i^{ig}(T, P) = H_i^{ig}(T, p_i) = H_i^{ig}(T, P)$$

$$\bar{H}_i^{ig} = H_i^{ig}$$

Since H^{ig} is independent of pressure

Similarly,

$$\bar{U}_i^{ig} = U_i^{ig} \quad \bar{C}_{p,i}^{ig} = C_{p,i}^{ig} \quad \bar{C}_{v,i}^{ig} = C_{v,i}^{ig}$$

U^{ig} , C_p^{ig} and C_v^{ig} are also independent of pressure

So for ideal-gas mixture,

$$H^{ig} = \sum y_i H_i^{ig} \quad U^{ig} = \sum y_i U_i^{ig} \quad C_P^{ig} = \sum y_i C_{P,i}^{ig} \quad \text{etc}$$



Partial molar entropy

S^{ig} is dependent of pressure,
$$dS_i^{ig} = C_{p,i}^{ig} \frac{dT}{T} - R \frac{dP}{P} \quad (6.24)$$

For isothermal mixing,
$$dS_i^{ig} = -R \frac{dP}{P}$$

Integrate from p_i to P ,

$$S_i^{ig}(T, P) - S_i^{ig}(T, p_i) = -R \ln \frac{P}{p_i} = -R \ln \frac{1}{y_i}$$

$$S_i^{ig}(T, p_i) = S_i^{ig}(T, P) - R \ln y_i$$

From Gibbs Theorem,

$$\bar{S}_i^{ig}(T, P) = S_i^{ig}(T, p_i) = S_i^{ig}(T, P) - R \ln y_i$$



Partial molar Gibbs energy

By parallel relation, $G^{ig} = H^{ig} - TS^{ig}$

$$\bar{G}_i^{ig} = \bar{H}_i^{ig} - T\bar{S}_i^{ig}$$

So,

$$\bar{G}_i^{ig} = \bar{H}_i^{ig} - T(S_i^{ig} - R \ln y_i) = H_i^{ig} - T(S_i^{ig} - R \ln y_i) = G_i^{ig} + RT \ln y_i$$

So for ideal-gas mixture,

$$G^{ig} = \sum y_i \bar{G}_i^{ig}$$

$$G^{ig} = \sum y_i G_i^{ig} + RT \sum y_i \ln y_i$$



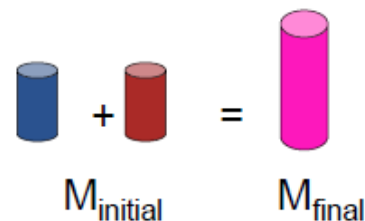
Property Change of Mixing

$$\Delta M_{mix}^{ig} = M_{final} - M_{initial} = M^{ig} - \sum y_i M_i^{ig}$$

$$\text{but } M^{ig} = \sum y_i M_i^{ig}$$

so

$$\Delta M_{mix}^{ig} = 0 \quad \text{for } M = H, U$$



Note: Both initial and final conditions (T,P) are the same.

For example,

Enthalpy change of mixing for ideal gas mixture,

$$\Delta H_{mix}^{ig} = 0$$



Property Change of Mixing

$$\Delta V_{mix}^{ig} = V_{final} - V_{initial} = V^{ig} - \sum y_i V_i^{ig} = V^{ig} - V_i^{ig} \sum y_i$$

note : $V^{ig} = V_i^{ig} = V_j^{ig}$

so

$$\Delta V_{mix}^{ig} = 0$$

Note: Both initial and final conditions (T,P) are the same.



Property Change of Mixing

for ideal-gas mixture,

$$S^{ig}(T, P) = \sum y_i S_i^{ig}(T, p_i) = \sum_k y_i \left(S_i^{ig}(T, P) - R \ln y_i \right)$$

$$S^{ig}(T, P) = \sum y_i S_i^{ig} - R \sum y_i \ln y_i \quad (11.26)$$

So *entropy* change of mixing for ideal gas mixture,

$$\begin{aligned} \Delta S_{mix}^{ig} &= S^{ig}(T, P) - \sum y_i S_i^{ig} \\ &= -R \sum y_i \ln y_i \\ &= R \sum y_i \ln \frac{1}{y_i} \end{aligned}$$



Property Change of Mixing

$$\begin{aligned}\Delta G_{\text{mix}}^{\text{ig}} &= G^{\text{ig}} - \sum y_i G_i^{\text{ig}} \\ &= RT \sum y_i \ln y_i\end{aligned}$$

In terms of variables (T, P) for Gibbs Energy ,

$$dG_i^{\text{ig}} = V_i^{\text{ig}} dP - S_i^{\text{ig}} dT \xrightarrow{\text{for constant T}} \frac{RT}{P} dP = RT d \ln P \quad (\text{for constant T})$$

Integrate

$$G_i^{\text{ig}} = \Gamma_i(T) + RT \ln P \quad (11.28)$$

↙ Integration constant at constant T



The Ideal-Gas Mixture Model

so

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

$$\bar{G}_i^{\text{ig}} = \Gamma_i(T) + RT \ln y_i P \quad (11.29)$$

Hence for ideal-gas mixture,

$$G^{\text{ig}} = \sum y_i \bar{G}_i^{\text{ig}} = \sum y_i \Gamma_i(T) + RT \sum y_i \ln(y_i P) \quad (11.30)$$



Summary

$$\overline{M}_i^{ig}(T,P) = M_i^{ig}(T,p_i) \quad (11.21)$$

$$H^{ig} = \sum_i y_i H_i^{ig} \quad (11.23)$$

$$U^{ig} = \sum_i y_i U_i^{ig} \quad (11.23)$$

$$H^{ig} - \sum_i y_i H_i^{ig} = 0$$

$$S^{ig} = \sum_i y_i S_i^{ig} - R \sum_i y_i \ln y_i \quad (\text{where } y_i = p_i/P) \quad (11.25)$$

S_i^{ig} is the pure - species value at the mixture T and P.

The entropy change of an ideal gas mixing is

$$S^{ig} - \sum_i y_i S_i^{ig} = R \sum_i y_i \ln \frac{1}{y_i}$$



Summary

$$\mu_i^{ig} = \overline{G}_i^{ig} = G_i^{ig} + RT \ln y_i \quad (11.26)$$

$$\text{From } dG_i^{ig} = V_i^{ig} dP = \frac{RT}{P} dP = RT d \ln P$$

$$G_i^{ig} = \Gamma_i(T) + RT \ln P \quad (11.27)$$

$\Gamma_i(T)$ is the integration constant

$$\mu_i^{ig} = \Gamma_i(T) + RT \ln y_i P \quad (11.28)$$

$$G^{ig} = \sum_i y_i \Gamma_i(T) + RT \sum_i y_i \ln y_i P \quad (11.29)$$



Example

What is the change in entropy when 0.7 m³ of CO₂ and 0.3 m³ of N₂ each at 1 bar and 25 °C blend to form a gas mixture at the same condition? Assume ideal gases.

