

The concept of Chemical work

- ☞ Work transfer is possible for any change in composition of a multi-component system
- ☞ Generalised coordinate associated with change in composition : No of moles, N_i
- ☞ Generalised force: Chemical Potential μ_i

$$dW_{chemical} = \sum_{i=1}^r \mu_i dN_i$$

Fundamental Relationships

$$U = U(S, V, N_1, N_2, \dots, N_r)$$

$$dU = \left(\frac{\partial U}{\partial S} \right)_{V, N} dS + \left(\frac{\partial U}{\partial V} \right)_{S, N} dV + \sum \left(\frac{\partial U}{\partial N_i} \right)_{S, V, N_{j \neq i}} dN_i$$

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

$$\mu_i = \left(\frac{\partial U}{\partial N_i} \right)_{S, V, N_{j \neq i}}$$

$$dU = TdS - PdV + \sum_{i=1}^r \mu_i dN_i$$

☞ We can also define other potentials

Fundamental Relationships

$$dU = TdS - PdV + \sum_{i=1}^{\gamma} \mu_i dN_i$$

Hence it follows

$$dH = d(U + PV) = TdS + VdP + \sum_{i=1}^{\gamma} \mu_i dN_i$$

$$dF = d(U - TS) = -SdT - PdV + \sum_i \mu_i dN_i$$

$$dG = d(H - TS) = -SdT + VdP + \sum_{i=1}^{\gamma} \mu_i dN_i$$

Fundamental Relationships

$$U = U(S, V, N_1, N_2, \dots, N_\gamma)$$

$$H = H(S, P, N_1, N_2, \dots, N_\gamma)$$

$$F = F(T, V, N_1, N_2, \dots, N_\gamma)$$

$$G = G(T, P, N_1, N_2, \dots, N_\gamma)$$

Fundamental Relationships

$$\begin{aligned}\mu_i &= \left(\frac{\partial U}{\partial N_i} \right)_{S,V,N_{j \neq i}} = \left(\frac{\partial H}{\partial N_i} \right)_{S,P,N_{j \neq i}} \\ &= \left(\frac{\partial F}{\partial N_i} \right)_{T,V,N_{j \neq i}} = \left(\frac{\partial G}{\partial N_i} \right)_{T,P,N_{j \neq i}}\end{aligned}$$

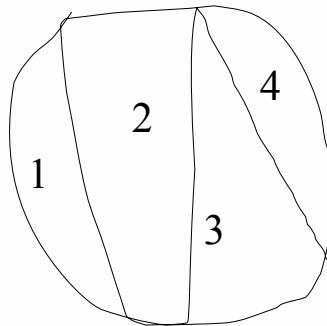
Physical Interpretation : change
in the values of the potentials
due to exchange of matter

Partial Molar Properties

Intuitive picture of a
multi component system

$$M = \sum_{i=1}^r m_i^0 N_i$$

In presence of
inter-molecular
interactions



$$M = \sum_{i=1}^r \bar{M}_i N_i$$

Partial Molar Properties

$$M = M(T, P, N_1, N_2, \dots, N_r)$$

if T, P are kept constant

$$dM = \sum_{i=1}^r \left(\frac{\partial M}{\partial N_i} \right)_{T, P, N_{j \neq i}} dN_i$$

If $dN_i = N_i d\lambda$ for each component

$$dM = M d\lambda$$

Substituting this in above equation

Lecture 5.2

General Relationships

Partial Molar Properties

$$M = \sum_{i=1}^r \left(\frac{\partial M}{\partial N_i} \right)_{T,P,N_{j \neq i}} N_i$$

Which gives on comparison with the equation defining partial molar property

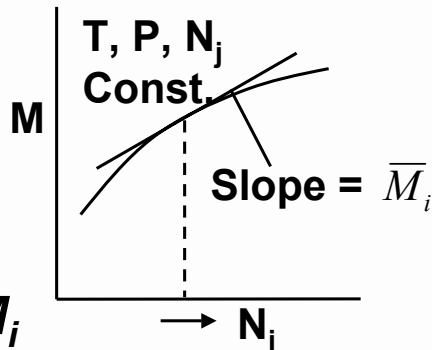
$$\bar{M}_i = \left(\frac{\partial M}{\partial N_i} \right)_{T,P,N_{j \neq i}}$$

PHYSICAL INTERPRETATION OF \bar{M}_i

The rate at which the property of the entire multicomponent substance changes with the no. of moles of component i in the substance when T, P & the extent of all other components remains fixed.

PHYSICAL INTERPRETATION OF \bar{M}_i

Experimental
determination of M_i
for a binary mixture



PHYSICAL INTERPRETATION OF \bar{M}_i

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

Partial Molar property = molar property of species i as it exists in the multi-component system

PHYSICAL INTERPRETATION OF \bar{M}_i

In reality, the constituents of a MCS are intimately intermixed & owing to intermolecular interactions can not have private properties of their own.

\bar{M}_i should \therefore be seen as assigned property values, in view of above eq.

EULER'S THEOREM ON HOMOGENEOUS FUNCTIONS

Def : A fn. $f(z_1, z_2, \dots, z_r)$ is said to be a

homogeneous fn. of degree m in z_i if

$$f(\lambda z_1, \lambda z_2, \dots, \lambda z_r) = \lambda^m f(z_1, z_2, \dots, z_r)$$

Where λ is a constant.

Euler's Theorem

A homogeneous fn. of degree m obeys the equation

$$m f(z_1, z_2, \dots, z_r) = \sum_{z_i \neq i} z_i \left(\frac{\partial f}{\partial z_i} \right)$$

Proof : Let

$$\gamma_1 = \lambda z_1; \gamma_2 = \lambda z_2; \dots \gamma_r = \lambda z_r$$

Euler's Theorem

$$\therefore f(\gamma_1, \gamma_2, \dots, \gamma_r) = \lambda^m f(z_1, z_2, \dots, z_r)$$

Differentiating w.r.t. λ at const. z_i gives

$$\sum_{\gamma_{ii \neq i}} \left(\frac{\partial f}{\partial \gamma_i} \right) (z_i) = m \lambda^{m-1} f(z_1, z_2, \dots, z_r)$$

This eq. is valid for all λ put $\lambda=1$ to get the THEOREM

Euler's Theorem

For any extensive property

$$M(T, P, \lambda N_1, \lambda N_2, \dots, \lambda N_\gamma) = \lambda M(T, P, N_1, N_2, \dots, N_\gamma)$$

**\Rightarrow M is a homogeneous fn.
of degree 1 in N_i 's.**

$$\therefore \text{Euler's Theorem} \Rightarrow M = \sum N_i \left(\frac{\partial M}{\partial N_i} \right)_{N_{i \neq i}}$$

Euler's Theorem

Applying this result to Gibbs fn. G:

$$G = \sum N_i \left(\frac{\partial G}{\partial N_i} \right)_{T, P, N_{j \neq i}}$$

**At constant T, P from the
fundamental we get relation**

$$\left(\frac{\partial G}{\partial N_i} \right)_{T, P, N_{j \neq i}} = \mu_i$$

Euler's Theorem

$$\therefore G = \sum_{i=1}^r N_i \mu_i$$

Corollary : for pure substance

$$G = \mu \cdot N \quad \text{or} \quad \mu = \frac{G}{N} = g \text{ the molar gibbs fn.}$$

GIBB'S – DUHEM EQ.

From above eq. Defining M_i

$$dM = \sum N_i d\bar{M}_i + \sum \bar{M}_i dN_i$$

Now $M = M(T, P, N_1, N_2, \dots, N_r)$

$$dM = \left(\frac{\partial M}{\partial P} \right)_{T,N} dP + \left(\frac{\partial M}{\partial T} \right)_{P,N} dT + \sum \overset{\uparrow}{\bar{M}_i} dN_i$$

$\left(\frac{\partial M}{\partial N_i} \right)_{T,P,N_j}$

PHYSICAL INTERPRETATION OF \bar{M}_i

from these two eqs. it follows :

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

This is called GIBBS – DUHEM EQ.

PHYSICAL INTERPRETATION OF \bar{M}_i

SPL. CASES for $M \equiv G$

GIBBS – DUHEM EQ.

$$VdP - SdT - \sum_i N_i d\mu_i = 0$$

for const. T & P

$$\sum_i N_i d\bar{M}_i = 0$$

RELATIONSHIPS INVOLVING \bar{M}_i

=> There exist relations between \bar{M}_i analogous to those between parent extensive prop. (M)

e.g. $\Rightarrow G = H - T S$

$$\left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j} = \left(\frac{\partial H}{\partial N_i}\right)_{T,P,N_j} - T \left(\frac{\partial S}{\partial N_i}\right)_{T,P,N_j}$$

RELATIONSHIPS INVOLVING \bar{M}_i

or

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

Similarly

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

$$\bar{F}_i = \bar{U}_i - T \bar{S}_i$$

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End of Lecture

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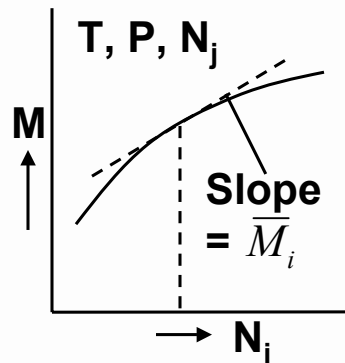
Lecture 5.3

Partial Molar properties

CALCULATION OF \bar{M}_i FROM EXPTL. DATA

Basic def.

$$\bar{M}_i = \left(\frac{\partial M}{\partial N_i} \right)_{T, P, N_j, j \neq i}$$

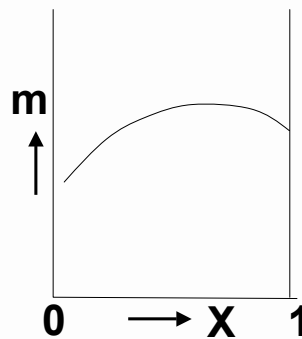


=> Limitations of this approach

DERIVATION OF \bar{M}_i FROM M vs X_i DATA FOR BINARY MIXTURES

$$x_i = \frac{N_i}{N} = \text{mole fraction}$$

$$m = \frac{M}{N} = \text{molar prop.}$$



DERIVATION OF \bar{M}_i FROM M vs X_i DATA FOR BINARY MIXTURES

From basic def. $M = \sum N_i \bar{M}_i$

dividing by N

$$m = \sum x_i \bar{M}_i = x_1 \bar{M}_1 + x_2 \bar{M}_2 \quad \left\{ \begin{array}{l} \text{For} \\ \text{binary} \\ \text{system} \end{array} \right\}$$

$$\therefore dm = x_1 d\bar{M}_1 + \bar{M}_1 dx_1 + x_2 d\bar{M}_2 + dx_2 \cdot \bar{M}_2$$

DERIVATION OF \bar{M}_i FROM M vs X_i DATA FOR BINARY MIXTURES

At Const T&P, Gibbs Duhem eq. gives

$$\sum N_i d\bar{M}_i = 0$$

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

since $x_1 + x_2 = 1$; $dx_2 = -dx_1$,

DERIVATION OF \bar{M}_i FROM M vs X_i DATA FOR BINARY MIXTURES

Combining the above two eqs. gives

$$dm = \bar{M}_1 dx_1 + \bar{M}_2 dx_2$$

$$= (\bar{M}_1 - \bar{M}_2) dx_1$$

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

DERIVATION OF \bar{M}_i FROM M vs X_i DATA FOR BINARY MIXTURES

$$\because m = \{x_1 \bar{M}_1 + (1 - x_1) \bar{M}_2\}$$

$$\bar{M}_2 = \frac{m - x_1 \bar{M}_1}{1 - x_1}$$

Substituting this in
earlier equation

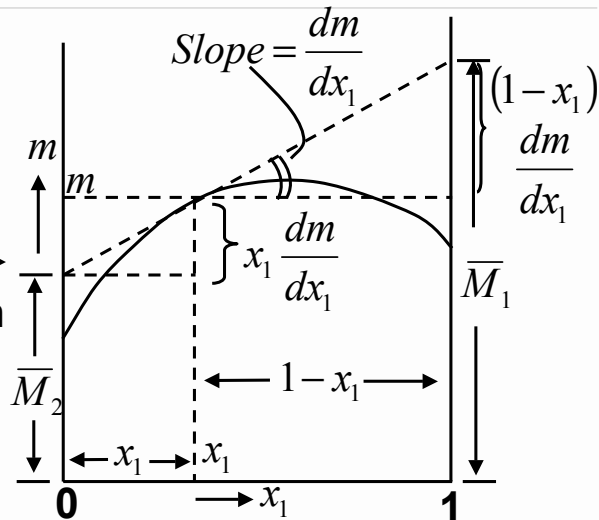
We get
$$\bar{M}_1 = m + (1 - x_1) \frac{dm}{dx_1}$$

Similarly, eliminating \bar{M}_1 gives sol. for \bar{M}_2

$$\bar{M}_2 = m - x_1 \frac{dm}{dx_1}$$

DERIVATION OF \bar{M}_i FROM m vs x_i DATA FOR BINARY MIXTURES

Graphical Interpretation →

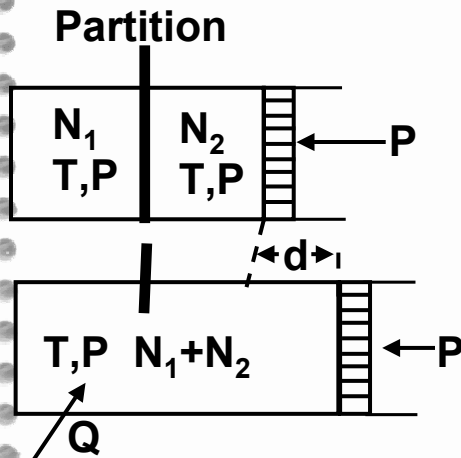


PROPERTY CHANGES OF MIXING

Importance : Changes in volume & enthalpy on mixing can be directly measured

These enable us evaluate the properties of mixtures from those of pure components

PROPERTY CHANGES OF MIXING



exptl. measurable

\Rightarrow Change in volume, ΔV

\Rightarrow Heat Input reqd. to maintain const. $T \Rightarrow Q$ or ΔH

{Heat of Mixing}

PROPERTY CHANGES OF MIXING

Clearly

$$\Delta V = (N_1 \bar{V}_1 + N_2 \bar{V}_2) - (N_1 v_1^0 + N_2 v_2^0)$$

$$Q = \Delta H = (N_1 \bar{H}_1 + N_2 \bar{H}_2) - (N_1 h_1^0 + N_2 h_2^0)$$

Where superscript 0 refers to pure substance properties

PROPERTY CHANGES OF MIXING

Per mole basis

$$\Delta v = \frac{\Delta V}{N_1 + N_2} = x_1(\bar{V}_1 - v_1^0) + x_2(\bar{V}_2 - v_2^0)$$

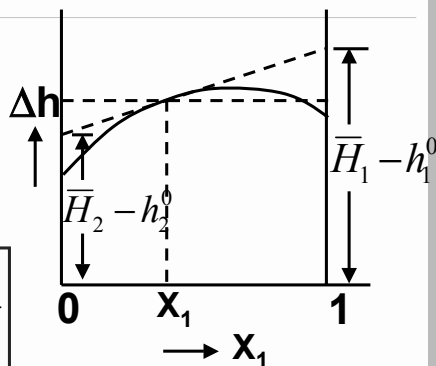
$$\Delta h = \frac{\Delta H}{N_1 + N_2} = x_1(\bar{H}_1 - h_1^0) + x_2(\bar{H}_2 - h_2^0)$$

DETERMINATION OF PARTIAL MOLAR PROPERTIES FROM Δv & Δh

Following similar steps as above it can be easily shown that

$$\left(\bar{H}_1 - h_1^0\right) = \Delta h + (1 - x_1) \frac{d\Delta h}{dx_1}$$

&
$$\left(\bar{H}_2 - h_2^0\right) = \Delta h - x_1 \frac{d\Delta h}{dx_1}$$



DETERMINATION OF PARTIAL MOLAR PROPERTIES FROM Δv & Δh

$$(\bar{H}_1 - h_1^0), (\bar{H}_2 - h_2^0), (\bar{V}_1 - v_1^0), (\bar{V}_2 - v_2^0)$$

are sometimes referred to as Relative Partial Molar Properties

Practical importance of Δh , Δv

=> Mixture properties can be calculated from those of constituent pure substances

End of Lecture

Lecture 5.4

Problem Solving - Review

Problem on Multicomponent Systems

The partial molar volume of water (w) in its solution with methanol (m) at 25^o C and 1 bar pressure can be approximated by the equation

$$\bar{V}_w = 18.1 - 3.2x_m^2 \text{ litres/kmol}$$

....continued

Where X_m is the molefraction of methanol.

Find out an expression for partial molar volume of methanol at the same conditions. Given, the molar volume of pure methanol at 25°C and 1 bar pressure is 40.7 litres /kmol.

Solution.....

Gibbs-Duhem equation

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

$$x_w d\bar{V}_w + x_m d\bar{V}_m = 0$$

Here we are given \bar{V}_w

$$\bar{V}_w = 18.1 - 3.2 x_m^2$$

Solution

$$\therefore d\bar{V}_w = -6.4x_m dx_m$$

$$(1 - x_m)(-6.4x_m dx_m) = -x_m d\bar{V}_m$$

$$d\bar{V}_m = +6.4(1 - x_m)dx_m$$

which on integration gives.....

Solution

$$\bar{V}_m = 6.4\left(x_m - \frac{x_m^2}{2}\right) + C$$

To find the value of the constant C,
we note that

$$\bar{V}_m = v_m^0 \text{ for } x_m = 1$$

This gives :

$$40.7 = 6.4\left(1 - \frac{1}{2}\right) + C$$

Solution

$$\therefore c = 37.5$$

Therefore

$$\bar{V}_m = 37.5 + 6.4(x_m - x_m^2 / 2)$$

End of Lecture

Lecture 5.5

Equations of state for mixtures

IDEAL GAS MIXTURES

GIBBS – DALTON'S LAW

A mixture of ideal gases is also an ideal gas

$$\begin{array}{c} P \\ \uparrow \\ \text{mixt} \\ P \end{array} \begin{array}{c} V \\ \uparrow \\ \text{mixt} \\ V \end{array} = \begin{array}{c} N R T \\ \uparrow \\ \text{Total mols.} \end{array} \begin{array}{c} \nearrow \\ \text{Temp} \end{array}$$

IDEAL GAS MIXTURES

Each component of an ideal gas mixture behaves as an ideal gas at the temperature and volume of the mixture

$$P_i V = N_i R T$$

Dividing the two equations gives

$$\frac{P_i}{P} = \frac{N_i}{N} = x_i$$

IDEAL GAS MIXTURES

Since $\sum x_i = 1 \Rightarrow \sum P_i = P$

Total press. exerted by a mixt. is the sum of pressures exerted by the individual components if each were to occupy the whole vol. of the mixt. at the same temp.

IDEAL GAS MIXTURES

Gibbs Dalton Law

Any extensive prop.* of an ideal-gas mixture is the sum of the corresponding properties of individual components each evaluated at the mixture T and volume (or partial pr.)

*except volume

IDEAL GAS MIXTURES

Gibbs Dalton Law

$$\text{i.e } M^{ig}(T, P) = \sum_{\text{comp. } k} M_K^{ig}(T, P_K)$$

↑ partial pr. of comp. K.

$$= \sum N_K m_K^{ig}(T, P_k)$$

where $M \equiv H, S, U, F, \text{ or } G$

IDEAL GAS MIXTURES

Gibbs Dalton Law

Thus for enthalpy

$$H^{ig}(T, P) = \sum N_K h_k^{ig}(T, P_k)$$

Now, for ideal gases h is independent of pressure, i.e.

$$\begin{aligned} h_k^{ig}(T, P_k) &= h_k^{ig}(T, P) \\ &= h_k^{ig}(T) \end{aligned}$$

IDEAL GAS MIXTURES

$$\therefore H^{ig}(T, P) = \sum N_K h_k^{ig}(T);$$

or

$$h^{ig}(T, P) = \sum x_k h_k^{ig}(T)$$

where

$$h^{ig}(T, P) = \text{molar enth. of mixt.}$$

IDEAL GAS MIXTURES

From this eq. it follows

$$H^{ig}(T, P) - \sum N_K h_k^{ig}(T, P) = 0$$

i.e. Heat of mixing = 0, for ideal gas mixtures

=> Similar eq. for Internal energy since

$$U_k^{ig}(T, P_k) = U_k^{ig}(T, P) = U_k^{ig}(T)$$

IDEAL GAS MIXTURES

=> But this not true for entropy since

$$s_k^{ig}(T, p_k) \neq s_k^{ig}(T, P)$$

from basic eq. $ds = \frac{dh}{T} - \frac{v}{T} dP$

IDEAL GAS MIXTURES

we have for an ideal gas

$$s_k^{ig}(T, P) - s_k^{ig}(T, p_k) = \left(\int_{p_k}^P ds \right)_T$$
$$= -R \ln(P / p_k) = R \ln x_k$$

Using the
Gibbs Dalton's law

$$s^{ig}(T, P) = \sum x_k s_k^{ig}(T, P_k)$$

IDEAL GAS MIXTURES

$$= \sum x_k s_k^{ig}(T, P) - R \sum x_k \ln x_k$$

Rearranging, we get

$$s^{ig}(T, P) - \sum x_k s_k^{ig}(T, P) = -R \underbrace{\sum x_k \ln x_k}_{> 0}$$

$\because x_k < 1$

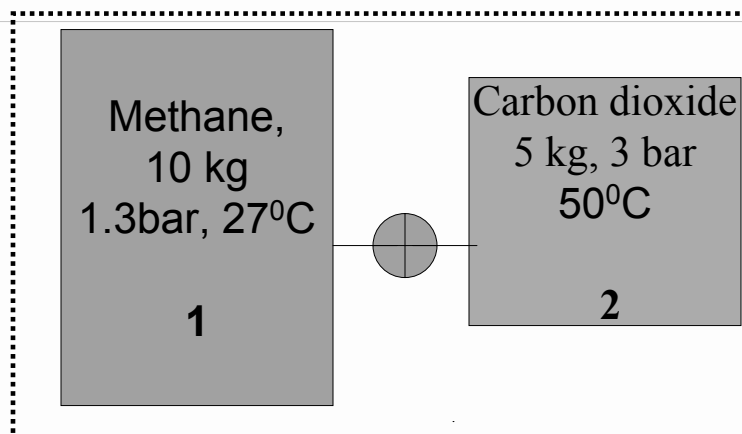
=> Mixing is inherently irreversible

Solving a Problem

A tank containing 10 kg methane at 1.3 bar and 27°C is connected to another tank containing 5 kg carbon dioxide at 3 bar and 50°C.

Determine the final temperature, pressure and irreversibility during the process of adiabatic mixing.

Solution...



Final U = Sum of initial U's

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End of Lecture

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Lecture 5.6

Mixtures of Gases and
Vapour

MIXTURES OF GASES & VAPOUR

Simplifying Assumptions

- ⇒ **Gases don't dissolve in liquid phase**
- ⇒ **Gaseous Phase \equiv mixture of ideal gases**

MIXTURES OF GASES & VAPOURS

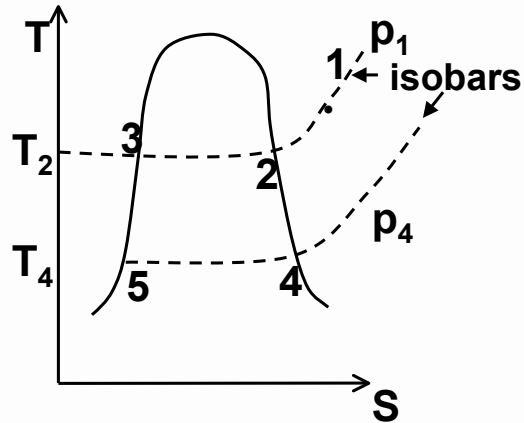
- ⇒ **Eqlbm. between the condensed phase & its vapour not influenced by the presence of other components**

i.e. at eqlbm. partial pr. of saturated vapour = sat. press. at the mixt. T

MIXTURES OF GASES & VAPOURS

Its implications

Cooling gas + vap. mixt at constant press. from st.1, p.p. of vap remains constant till it reaches saturation state 2



MIXTURES OF GASES & VAPOURS

$T_2 \Rightarrow$ Dew point temp

Below this temp. its p.p. falls & is governed by sat. press - temp relationship e.g. at T_4 , its partial pressure is p_4

Some measures of moisture content

Specific humidity

$$w = \frac{m_{w.v.}}{m_a} \left(\frac{\text{kg } wv}{\text{kg dry air}} \right)$$

$$= \frac{V \cdot P_{w.v.} / R_w T}{V P_a / R_a T} = \frac{P_{w.v.}}{P_a} \cdot \frac{R_a}{R_w}$$

MIXTURES OF GASES & VAPOURS

For moist air

$$w = .622 \frac{P_{wv}}{P - P_{wv}}$$

Relative humidity

$$\phi = \frac{m_{w.v.}}{(m_{w.v.})_{sat}} = \frac{P_{wv} V / R_w T}{P_{sat} V / R_w T} = \frac{P_{wv}}{P_{sat}}$$

(at same T)

MIXTURES OF GASES & VAPOURS

Enthalpy of Moist Air

$$H = H_a + H_{wv} = m_a h_a + m_{wv} h_{wv}$$

Dividing by $\underline{m_a}$

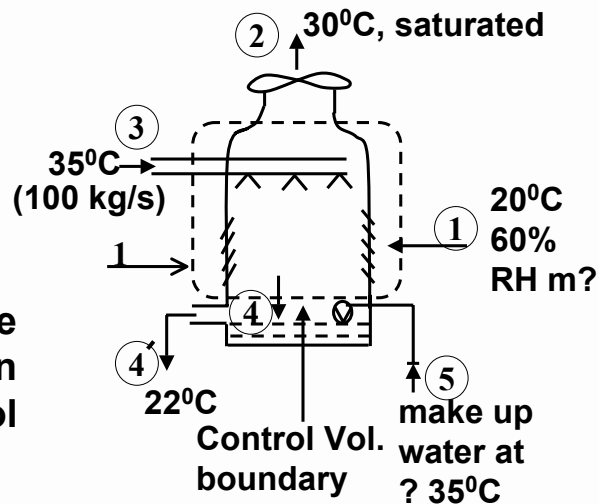
$$h = \frac{H}{m_a} = h_a + w h_{w.v.} \quad (\text{kJ / kg dry air})$$

further
$$h_{w.v.} \approx (h_{sat,v.})_T$$

MIXTURES OF GASES & VAPOURS

Example (modified form of C&B p 690)

Assuming
steady state
op. within
the control
volume



MIXTURES OF GASES & VAPOURS

Dry air balance :

$$\dot{m}a_1 = \dot{m}a_2 = \dot{m}a$$

Water balance :

$$\dot{m}_3 + \dot{m}_a \cdot w_1 = \dot{m}_4 + \dot{m}_a w_2$$

or

$$\dot{m}_3 - \dot{m}_4 = \dot{m}_a (w_2 - w_1)$$

MIXTURES OF GASES & VAPOURS

Energy balance :

$$\dot{m}_3 h_3 + \dot{m}_a h_1 = \dot{m}_4 h_4 + \dot{m}_a h_2$$

Mass balance of sump :

$$\dot{m}_5 + \dot{m}_4 = \dot{m}'_4 = \dot{m}_3$$

$$\begin{aligned} \therefore \dot{m}_5 &= \text{make up} &= \dot{m}_3 - \dot{m}_4 \\ &\text{water flow} \\ &\text{rate} &= \dot{m}_a (w_2 - w_1) \end{aligned}$$

MIXTURES OF GASES & VAPOURS

from energy balance :

$$\begin{aligned}\dot{m}_a &= (-\dot{m}_4 h_4 + \dot{m}_3 h_3) / (h_2 - h_1) \\ &= [\dot{m}_3 h_3 - (\dot{m}_3 - \dot{m}_a (w_2 - w_1) h_4)] / (h_2 - h_1)\end{aligned}$$

Solving

$$\dot{m}_a = \dot{m}_3 (h_3 - h_4) / [(h_2 - h_1) - (w_2 - w_1) h_4]$$

MIXTURES OF GASES & VAPOURS

Now $h_3 - h_4 =$ Diff in water enth. at 35°C & 22°C

$$\approx c_{p_w} (35 - 22) = 4.186 \times 13 = 54.41 \text{ kJ/kg}$$

$$h_4 = \text{enth. at } 22^\circ\text{C} \approx 4.186 \times (22 - 0) = 92.1 \text{ kJ/kg}$$

$$h_2 - h_1 = h_{a_2} + w_2 h_{w_2} - (h_{a_1} + w_1 h_{w_1})$$

MIXTURES OF GASES & VAPOURS

at 1 $T = 20^{\circ}\text{C}$

$$P_{Sat} = 2.339\text{kPa} : P_{wv} = RH * P_{Sat} = 2.339 \times .6 \\ = 1.403\text{kPa}$$

$$\therefore w_1 = .622 \frac{1.403}{100 - 1.403} = 8.853 \times 10^{-3} \text{ kg / kg da}$$

$$h_{wv_1} = h_{sat} \text{ at } 20^{\circ}\text{C} = 2538.1\text{ kJ / kg}$$

MIXTURES OF GASES & VAPOURS

$$\therefore h_1 = ha_1 + w_1 h_{wv_1} = 1.005 \times 20 \\ + 8.853 \times 10^{-3} \times 2538.1 \\ = 42.57\text{ kJ / kg da}$$

at 2 sat air at 30°C

$$P_{wv} = 4.246\text{kPa}$$

$$\therefore w_2 = .622 \frac{4.246}{100 - 4.246} = .02758\text{ kg w / kg da}$$

$$h_{wv_2} = 2556.3\text{ kJ / kg}$$

MIXTURES OF GASES & VAPOURS

$$\begin{aligned}\therefore h_2 &= ha_2 + w_2 h_{wv_2} = 1.005 \times 30 \\ &+ .02758 \times 2556.3 = 100.65 \text{ kJ / kg}\end{aligned}$$

Substituting values

$$\begin{aligned}\dot{m}_a &= 100 (54.41) / [100.65 - 42.57 \\ &- (.02758 - .00885) \times 92.1] \\ &= 96.55 \text{ kg / s}\end{aligned}$$

MIXTURES OF GASES & VAPOURS

$$\begin{aligned}\text{Make up water} &= \dot{m}_5 = \dot{m}_a (w_2 - w_1) \\ &= 96.55 (.02758 - .008853) \\ &= 1.808 \text{ kg / s}\end{aligned}$$

MIXTURES OF GASES & VAPOURS

Using these results we can now improve upon the appx. that $T_4 = T_4' = 22^\circ\text{C}$. In reality as the make up water is at a higher temp., $T_4 < T_4'$. This temp can be estimated from sump energy balance as

$$m_4 T_4 + m_5 T_5 = m_4' T_4'$$

$$98.192 T_4 + 1.808 \times 35 = 100 \times 22$$

$$\rightarrow T_4 = 21.76^\circ\text{C}$$

MIXTURES OF GASES & VAPOURS

Using this in the CV energy balance,

$$h_4 = 91.09$$

$$h_3 - h_4 = 55.42$$

$$\begin{aligned} \therefore \dot{m}_a &= \frac{100 \times 55.42}{[100.65 - 42.57 - (.02758 - .00885) \times 91.09]} \\ &= 98.3 \text{ kg/s} \end{aligned}$$

Make up water $\dot{m}_5 = 1.84 \text{ kg/s}$

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End of Lecture

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Lecture 5.7

Equations of state for real
gas mixtures

EQ. OF STATE FOR REAL-GAS MIXT.

→ Dalton's Law type approach

$$i.e. \quad P = \sum P_i$$

Where P_i are calculated at mixt T,V using real gas eq. of state

or

Amagat's Law type approach

$$i.e. \quad V = \sum V_i$$

EQ. OF STATE FOR REAL-GAS MIXT.

where $V_i = f(T, P)$ from a real gas eq. of state

→ Obtaining Mixture EOS from component pure substance EOS.

Obtain the constants of the eq. of state for a mixture from those of its constituent pure substances by using suitable mixing rules, e.g.

EQ. OF STATE FOR REAL-GAS MIXT.

Linear combination : $\kappa = \sum x_i \kappa_i$

Linear sq. root : $\kappa = \left(\sum x_i \kappa_i^{1/2} \right)^2$

Lorentz combination :

$$\kappa = \frac{1}{4} \sum x_i \kappa_i + \frac{3}{4} \left(\sum x_i \kappa_i^{1/3} \right) * \left(\sum x_i \kappa_i^{2/3} \right)$$

EQ. OF STATE FOR REAL-GAS MIXT.

→ Use of Generalized Compressibility Chart

approach I

Determine Z_i at T,V of mixture
{or T,P of mixture}

& Find $Z = \sum x_i Z_i$

or any other combining rule

EQ. OF STATE FOR REAL-GAS MIXT.

approach II

Define pseudo critical properties of the mixture, as (e.g.Kay's rule)

$$P'_c = \sum x_i P_{ci} \quad T'_c = \sum x_i T_{ci}$$

& use Generalised Charts with these as 'critical' properties for the mixture.

Solving a few problems

Problem 1

Derive an expression for \bar{V}_i using R-K eq. of state with its constants for mixture determined from those of constituents by using following “mixing-rules”.

$$a_m = \left[\sum x_i \sqrt{a_i} \right]^2 \quad b_m = \sum x_i b_i$$

Problem 1

Solution

$$\bar{V}_i = \left(\frac{\partial V}{\partial N_i} \right)_{T, P, N_{j \neq i}}$$

R-K eq. of state

$$P = \frac{RT}{v - b_m} - \frac{a_m}{\sqrt{T}v(v + b_m)}$$

$$P = \frac{NRT}{V - Nb_m} - \frac{N^2 a_m}{\sqrt{TV}(V + Nb_m)}$$

Problem 1

Since this is explicit in P, with V, T, N₁,----- as independent variables, the definition of \bar{V}_i is better written as

$$\bar{V}_i = \left(\frac{\partial V}{\partial N_i} \right)_{T,P,N_j} = - \frac{(\partial P / \partial N_i)_{T,V,N_j}}{(\partial P / \partial V)_{T,N}}$$

The denominator is easily found from R-K eq. as

Problem 1

$$\left(\frac{\partial P}{\partial V} \right)_{T,N} = \frac{NRT}{(V-Nb_m)^2} + \frac{N^2 a_m}{\sqrt{T}} \cdot \frac{(2V+Nb_m)}{V^2(V+Nb_m)^2} \dots\dots I$$

To calculate the value of numerator, we need to substitute for a_m & b_m using mixing rules. The two derivatives needed are

Problem 1

$$\left\{ \frac{\partial}{\partial N_i} (N^2 a_m) \right\}_{T,v,N_j} = \frac{\partial}{\partial N_i} \left[\left(\sum_{\kappa=1}^N N_{\kappa} a_{\kappa}^{1/2} \right)^2 \right]_{T,v,N_j}$$

$$= 2 \left(\sum_{\kappa=1}^n N_{\kappa} a_{\kappa}^{1/2} \right) a_i^{1/2} = 2 N a_m^{1/2} a_i^{1/2}$$

$$\frac{\partial}{\partial N_i} (N b_m)_{T,v,N_j} = \frac{\partial}{\partial N_i} \left[\sum_{\kappa=1}^n N_{\kappa} b_{\kappa} \right]_{T,v,N_j} = b_i$$

Problem 1

This gives

$$\left(\frac{\partial P}{\partial N_i} \right)_{T,v,N_j} = RT \left[\frac{1}{V - N b_m} + \frac{N b_i}{(V - N b_m)^2} \right]$$

$$- \frac{1}{\sqrt{T} V} \left[\frac{2 N a_m^{1/2} a_i^{1/2}}{V + N b_m} - \frac{N^2 a_m b_i}{(V + N b_m)^2} \right] \text{-----II}$$

Combining I & II, an expression for \bar{V}_i for real gas mixture can be obtained.

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End of Lecture

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Lecture 5.8

Equations of state for real
gas mixtures.....contd

Solving a few problems

PROBLEM

A CNG cylinder of volume 0.1m^3 contains a mixture of methane (90% by mols), ethane (5%) and CO_2 (5%) at a pressure of 200 bar at 30°C .

Estimate the total mass of CNG in the cylinder by using

📄 Ideal gas equation of state

PROBLEM

- (b) Compressibility chart with Dalton's model
- (c) Compressibility chart with Amagat's model
- (d) Kay's pseudocritical method

SOLUTION

Let us consider the various alternatives in sequence

(a) Ideal Gas Equation of State

Here we can directly use equation (8.59) to get, the total number of moles as

$$N = \frac{PV}{RT} = \frac{(200 \times 10^5)(0.1)}{8314.3 \times 303}$$
$$= 0.7939 \text{ kmoles}$$

SOLUTION

The molecular weight for the mixture is

$$M = \sum x_i M_i = .9 \times 16 + .05 \times 30 + .05 \times 44 \\ = 14.4 + 1.5 + 2.2 = 18.1$$

Hence total mass of CNG =

$$.7939 \times 18.1 = 14.37 \text{ kg}$$

SOLUTION

(b) To use compressibility charts, we note the critical properties of the constituent gases from property data. These are

	P_c (bar)	T_c (K)
Methane	46.4	191
Ethane	48.8	305
Carbondioxide	73.9	304

SOLUTION

Using Comp Charts + Dalton's Model

Let us assume that total number of moles in cylinder is 0.8 k mol, thus component moles are

$$CH_4 = .8 \times .9 = .72$$

$$C_2H_6 = .05 \times .8 = .04$$

$$CO_2 = .05 \times .8 = .04$$

SOLUTION

We tabulate the calculations as :

Component	\bar{v} ($m^3/kmol$)	\bar{RT}_C/P_C	v'_R	T_R	Z_i	$Z_i x_i$
CH ₄	$\frac{.1}{.72}$	$\frac{8314.3 \times 191}{46.4 \times 10^5}$.406	$\frac{303}{191} = 1.59$.85	.765
C ₂ H ₆	$\frac{.1}{.04}$	$\frac{8314.3 \times 305}{48.8 \times 10^5}$	4.81	$\frac{303}{305} = .993$.93	.0465
CO ₂	$\frac{.1}{.04}$	$\frac{8314.3 \times 304}{46.4 \times 10^5}$	4.59	$\frac{303}{304} = .997$.92	.046

SOLUTION

This gives $Z = .8575$

which yields the following expression for total number of moles of the mixture

$$N = \frac{V}{\bar{v}} \quad \text{where}$$
$$\bar{v} = \frac{ZRT}{P} = \frac{.8575 \times 8314.3 \times 303}{(200 \times 10^5)} \frac{m^3}{k \text{ mol}}$$
$$= 0.108 m^3 / k \text{ mol}$$

SOLUTION

$$\therefore N = \frac{.1}{.108} = .926 \text{ k mol}$$

Since this is different from our assumed value of $N (= .8 \text{ km})$ we need to do another iteration.

We assume $N = .93 \text{ kmol}$, which gives moles of various constituents as

$$\text{CH}_4 = .837, \text{C}_2\text{H}_6 = .0465, \text{CO}_2 = .0465$$

SOLUTION

We repeat the above calculations as follows

Component	\bar{v}	v'_R	T_R	Z_i	$Z_i x_i$
CH_4	$\frac{.1}{.837}$.399	1.59	.850	.765
C_2H_6	$\frac{.1}{.0465}$	4.14	.993	.920	.046
CO_2	$\frac{.1}{.0465}$	3.95	.997	.915	.04575

$\therefore Z = .8568$ which is appx equal to the earlier value.

SOLUTION

Thus, we get the solution as $N = .93$ k mol, and the corresponding mass = $.93 \times 18.1 = 16.83$ kg

(C) To use generalised charts along with Amagat's model, we need to find component Z_i at mixture pressure and temperature.

SOLUTION

Component	X_i	T_c	T'_R	P_c	P'_R	Z_i	$Z_i X_i$
CH_4	.9	191	1.59	46.4	4.31	.851	.766
C_2H_6	.05	305	.993	48.8	4.098	.57	.0285
CO_2	.05	304	.997	73.9	2.706	.41	.0205

$$\therefore Z = .815$$

SOLUTION

From which we get

$$\bar{v} = \frac{ZRT}{P} \frac{.815 \times 8314.3 \times 303}{200 \times 10^5}$$
$$= .10266 \text{ m}^3/\text{kmol}$$

$$\text{and } N = \frac{.1}{.10266} = .9741 \text{ kmol}$$

This gives the mass of CNG as $= .974 \times 181 = 17.6 \text{ kg}$

SOLUTION

(d) To use Kay's pseudo critical method, we first calculate the pseudo critical properties

This gives

$$P'_c = \sum x_i P_{c_i} = .9 \times 464 + .05 \times 488 + .05 \times 739 \\ = 47.9 \text{ bar}$$

SOLUTION

$$T'_c = \sum x_i T_{c_i} = .9 \times 191 + .05 \times 305 + .05 \times 304 \\ = 202.35 \text{ K}$$

Using these pseudo critical properties, we get for the mixture,

$$P'_R = \frac{200}{47.9} = 4.175$$

$$T'_R = \frac{303}{202.35} = 1.498$$

SOLUTION

For these values of P_R' and T_R' , we get the compressibility factor from charts as **$Z = .805$**

This gives $\bar{v} = \frac{.805 \times 83143 \times 303}{200 \times 10^5} = .1014 \frac{m^3}{kmol}$

$$\therefore N = \frac{.1}{.1014} = .9862 \text{ kmol}$$

and $\therefore \text{Mass} = .9862 \times 18.1 = 17.85 \text{ kg}$

Comparison of methods

Method of Calculation	Estimated Mass
Ideal Gas	14.37 kg
Dalton +Comp Chart	16.83 kg
Amagat+Comp Chart	17.6 kg
Kays Method	17.85 kg

SOLUTION

The exergy loss is clearly,

$$\begin{aligned}e_{x_1} - e_{x_2} &= (h_1 - T_0 s_1) - (h_2 - T_0 s_2) \\ &= h_1 - h_2 - T_0 (s_1 - s_2) \\ &= 0 - 300(2.05 - 2.4) = 105 \text{ kJ/kg}\end{aligned}$$

Total exergy loss, per unit time

$$\frac{105 \times .1}{60} \text{ kW} = .175 \text{ kW}$$

SOLUTION

Work output of the turbine

$$W = \frac{0.1}{60} (570 - 480) \text{ kW} = .15 \text{ kW}$$

Exergy drop of propane

$$\begin{aligned}E_{x_1} - E_{x_3} &= \frac{0.1}{60} (e_{x_1} - e_{x_3}) \\ &= \frac{0.1}{60} (h_1 - h_3 - T_0 (s_1 - s_3)) \\ &= \frac{.1}{60} (h_1 - h_3) = .15 \text{ kW} \quad \left\{ \text{since } (s_1 = s_3) \right\}\end{aligned}$$

Exergy loss = 0.0

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End of Lecture

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Lecture 5.9

Chemical Potential and
Fugacity

RELATIONSHIP INVOLVING μ_i

Basic eq.

$$dG = -SdT + VdP + \sum \mu_i dN_i$$

at const $T, N_j \Rightarrow dG = VdP + \mu_i dN_i$

**Reciprocity
relation**

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

RELATIONSHIP INVOLVING μ_i

Similarly at const P, N_j

$$dG = -SdT + \mu_i dN_i$$

reciprocity relation

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

Further, from $\bar{G}_i = \bar{H}_i - TS_i;$

since $\bar{G}_i = \mu_i$

RELATIONSHIP INVOLVING μ_i

$$\mu_i = \bar{H}_i + T \left(\frac{\partial \mu_i}{\partial T} \right)_{P,N}$$

or

$$\frac{1}{T} \left(\frac{\partial \mu_i}{\partial T} \right)_{P,N} - \frac{\mu_i}{T^2} = \frac{-\bar{H}_i}{T^2}$$

or

$$\left[\frac{\partial(\mu_i/T)}{\partial T} \right]_{P,N} = \frac{-\bar{H}_i}{T^2}$$

RELATIONSHIP INVOLVING μ_j

Similarly at const T, P, N_j $j \neq i, k$

$$dG = \mu_i dN_i + \mu_k dN_k$$

Reciprocity
rel. $\left(\frac{\partial \mu_i}{\partial N_k} \right)_{T,P,N_j, j \neq k} = \left(\frac{\partial \mu_k}{\partial N_i} \right)_{T,P,N_j, j \neq i}$

**OTHER SIMILAR RELATIONS FROM
EXACTNESS OF dU, dF, dH etc.**

RELATIONSHIP INVOLVING μ_i

=> Since $\mu_i = \mu_i(T, P, N_1, N_2, \dots, N_r)$

$$d\mu_i = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} dT + \left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} dP + \sum_{\substack{K=1 \\ j \neq i}}^r \left(\frac{\partial \mu_i}{\partial N_K}\right)_{T,P,N_j} dN_K$$

which can be simplified using above results for gradients of μ_i

$$d\mu_i = -\bar{S}_i dT + \bar{V}_i dP + \sum_{\substack{K=1 \\ j \neq i}}^r \left(\frac{\partial \mu_i}{\partial N_K}\right)_{T,P,N_j} dN_K$$

RELATIONSHIP INVOLVING μ_i

Thus knowing μ_i as a function of T, P, N_i we can obtain all other properties of a mixture

$$\mu_i = \mu_i(T, P, N_1, N_2, \dots, N_r)$$

is thus a fundamental equation for multi-component systems

How to obtain it ?

CHEMICAL POTENTIAL OF IDEAL GAS MIXTURES

We start from the equation for Gibbs function

$$\begin{aligned} G &= Ng = N(h - Ts) = \\ N &\left(\sum x_k h_k - T \sum x_k s_k + RT \sum x_k \ln x_k \right) \\ &= \sum_{i=1}^r N_i g_i + RT \sum N_i \ln x_i \end{aligned}$$

IDEAL GAS MIXTURES

$$\begin{aligned} G &= N_i g_i + \sum_{j \neq i} N_j g_j^{ig} + RT N_i (\ln N_i - \ln N) \\ &\quad + RT \sum_{j \neq i} N_j (\ln N_j - \ln N) \\ &= N_i g_i + \sum_{j \neq i} N_j g_j + RT N_i \ln N_i \\ &\quad + RT \sum N_j \ln N_j - RT N \ln N \end{aligned}$$

IDEAL GAS MIXTURES

$$\begin{aligned} \therefore \mu_i &= \left(\frac{\partial G}{\partial N_i} \right)_{T,P,N_j} = g_i + RT \left[N_i \left(\frac{\partial \ln N_i}{\partial N_i} \right)_{N_j} + \ln N_i \right] \\ &\quad - RT \left[N \left(\frac{\partial \ln N}{\partial N_i} \right) + \ln N \left(\frac{\partial N}{\partial N_i} \right)_{N_j} \right] \end{aligned}$$

since $N = N_i + \sum_{j \neq i} N_j$ $\frac{\partial N}{\partial N_i} = 1$

IDEAL GAS MIXTURES

$$\begin{aligned} \therefore \mu_i &= g_i + RT \left[1 + \ln N_i - (1 + \ln N) \right] \\ &= g_i + RT \ln(N_i/N) \end{aligned}$$

for an ideal
gas mixture

$$\mu_i = g_i + RT \ln x_i$$

Clearly as $x_i \rightarrow 0$, $\mu_i \rightarrow -\infty$
Similar difficulty w r t P

IDEAL GAS MIXTURES

To relate μ_i to P
differentiate at const T $\mu_i = g_i + RT \ln x_i$

$$d\mu_i = dg_i + RT d(\ln x_i)$$

From basic eq. $dg = -sdT + VdP$

$$(dg_i)_T = v_i dP = \frac{RT}{P} dP = RT d(\ln P)$$

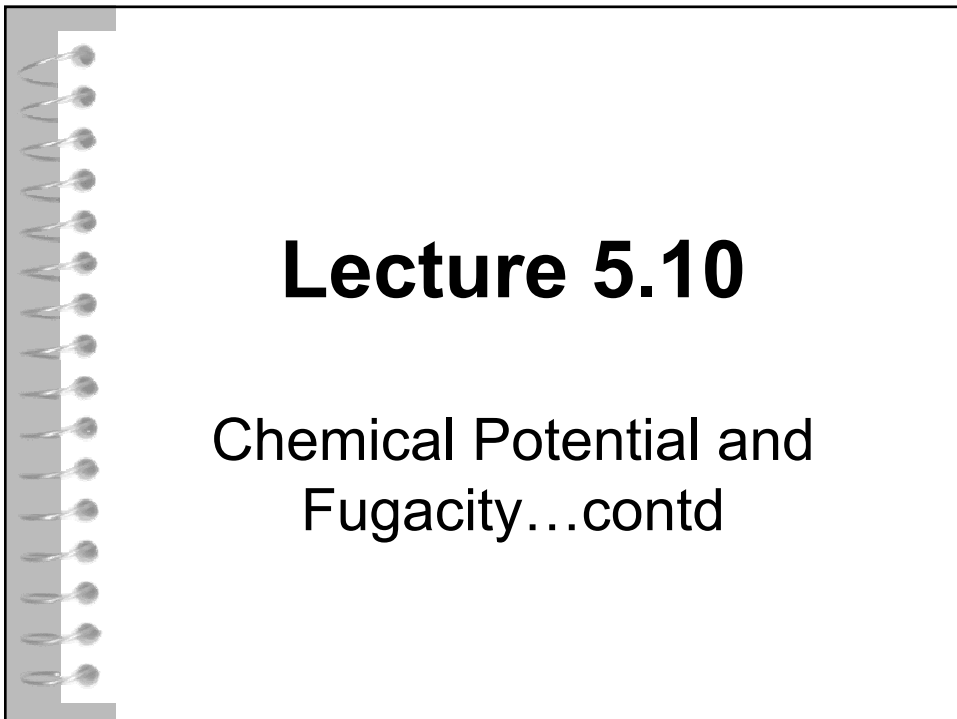
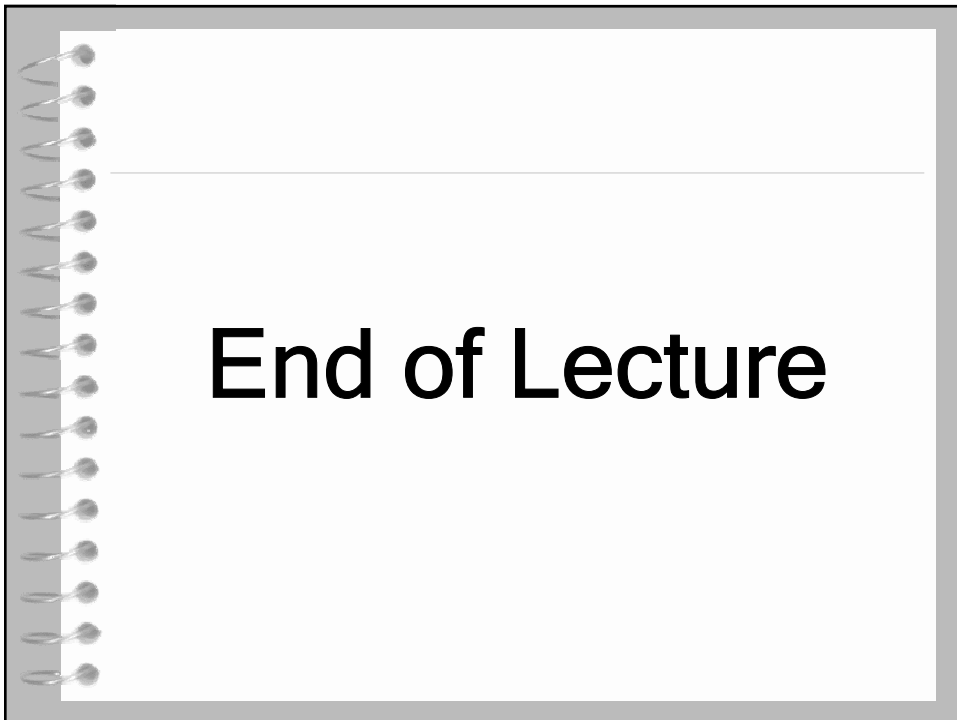
IDEAL GAS MIXTURES

$$\therefore d\mu_i = RT d(\ln P) + RT d(\ln x_i)$$

or
$$d\mu_i = RT d \ln (x_i P)$$

$$\Rightarrow \text{As } P \rightarrow 0 \quad ; \quad \mu_i \rightarrow -\infty$$

=> relates μ_i to measurable quantities like P & x_i



IDEAL GAS MIXTURES

At const T

$$d\mu_i = RT d \ln(x_i P)$$

=>relates μ_i to measurable quantities like P & x_i

CONCEPT OF FUGACITY

Extending above eq to all multicomponent system we define a new property f_i such that

$$(d\mu_i)_T = (d\bar{G}_i)_T = RT d(\ln f_i)_T$$

$$\lim_{P \rightarrow 0} \left(\frac{f_i}{x_i P} \right) = 1$$

CONCEPT OF FUGACITY

Since all gases tend to show ideal gas behaviour, as $P \rightarrow 0$, the limiting condition ensures that the above eq. is consistent with the result for ideal gas mixtures

Clearly, for an ideal gas mixture

$$f_i = Px_i$$

fugacity \equiv pseudo - pressure

CONCEPT OF FUGACITY

Fugacity is a property which can be intuitively comprehended and is a mathematically well behaved function of other properties.

Therefore its usefulness is analysis of multicomponent systems

RELATING FUGACITY TO OTHER PROPERTIES

Integrating above eq. gives (T const.)

$$\mu_i - \mu_i^* = RT \ln (f_i / f_i^*)$$

* => very low pressure p^* where ideal gas behaviour can be assumed

Now, $\mu_i - \mu_i^* = \bar{G}_i - \bar{G}_i^* =$ Diff. in values of partial molar Gibbs fn. of the same mixture, at const Temp., and two different pressures P and P^* .

RELATING FUGACITY TO OTHER PROPERTIES

From basic eq., at const. composition

$$d\bar{G}_i = -S_i dT + \bar{V}_i dP$$

& further, const T

$$d\bar{G}_i = \bar{V}_i dP$$

$$\therefore \mu_i - \mu_i^* = \left[\int_{P^*}^P \bar{V}_i dP \right]_T$$

RELATING FUGACITY TO OTHER PROPERTIES

$$\therefore \ln f_i = \ln f_i^* + \left[\int_{P^*}^P \frac{\bar{V}_i}{RT} dP \right]_T$$

Subtracting from it the identity

$$\ln P = \ln P^* + \int_{P^*}^P \frac{dP}{P}$$

RELATING FUGACITY TO OTHER PROPERTIES

gives

$$\ln(f_i/P) = \ln(f_i^*/P^*) + \int_{P^*}^P \left[\frac{\bar{V}_i}{RT} - \frac{1}{P} \right] dP$$

At low pressures, where ideal gas behaviour is valid,

$$f_i^* = x_i P^*$$

$$\therefore \ln f_i = \ln(Px_i) + \int_{P^* \rightarrow 0}^P \left\{ \frac{\bar{V}_i}{RT} - \frac{1}{P} \right\} dP$$

RELATING FUGACITY TO OTHER PROPERTIES

This eq. enable us to compute f_i if \bar{V}_i are known. The other properties can then be found using following equations

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

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

RELATING FUGACITY TO OTHER PROPERTIES

$$\bar{G}_i = \bar{G}_i^* + RT \ln(f_i / f_i^*)$$

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

$$\bar{U}_i = \bar{H}_i - P\bar{V}_i$$

$$\bar{F}_i = \bar{G}_i - P\bar{V}_i$$

Other properties related to fugacity

Activity = fugacity of component i in the mixture / fugacity in some standard ref state, which is usually taken as the corresponding pure substance at P, T of the mixture :

$$a_i = f_i / f^\circ$$

Activity coefficient $\gamma_i = a_i / x_i$

Relating Activity to other properties

$$\mu_i - \mu_0 = RT \ln(f_i / f_i^0) = RT \ln(a_i)$$

$$\left(\frac{\partial \ln a_i}{\partial P} \right)_{T,N} = \frac{\bar{V}_i - v_i^0}{RT}$$

$$\left(\frac{\partial \ln a_i}{\partial T} \right)_{P,N} = \frac{\bar{H}_i - h_i^0}{RT^2}$$

Ideal Solution Model

Definition :

$$f_i = f_i^0 x_i \text{ or activity } a_i = x_i$$

It therefore follows that

$$\bar{V}_i = v_i^0 \text{ and } \bar{H}_i = h_i^0$$

$$\therefore v^{id} = \sum x_i v_i^0$$

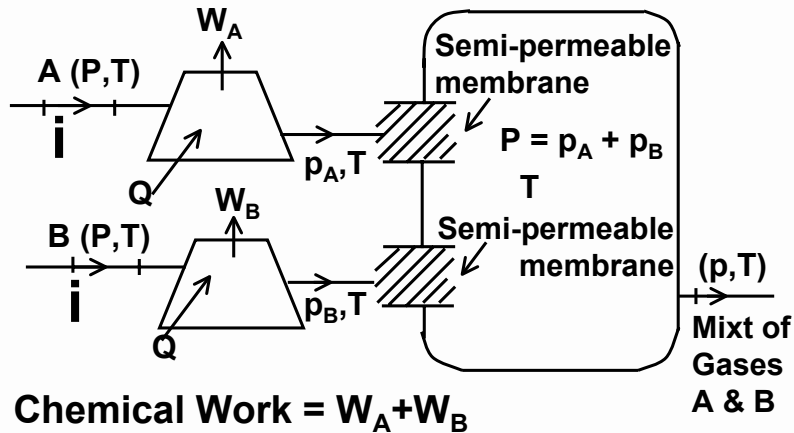
$$h^{id} = \sum x_i h_i^0$$

Ideal Solution Model

Similarly it can be shown that equations governing ideal solution properties are similar to those for ideal gases, the only difference being that properties of pure components are not obtained from ideal gas assumption.

UNDERSTANDING CHEMICAL WORK

Reversible Mixing of two gases at P, T to form a mixture at P, T

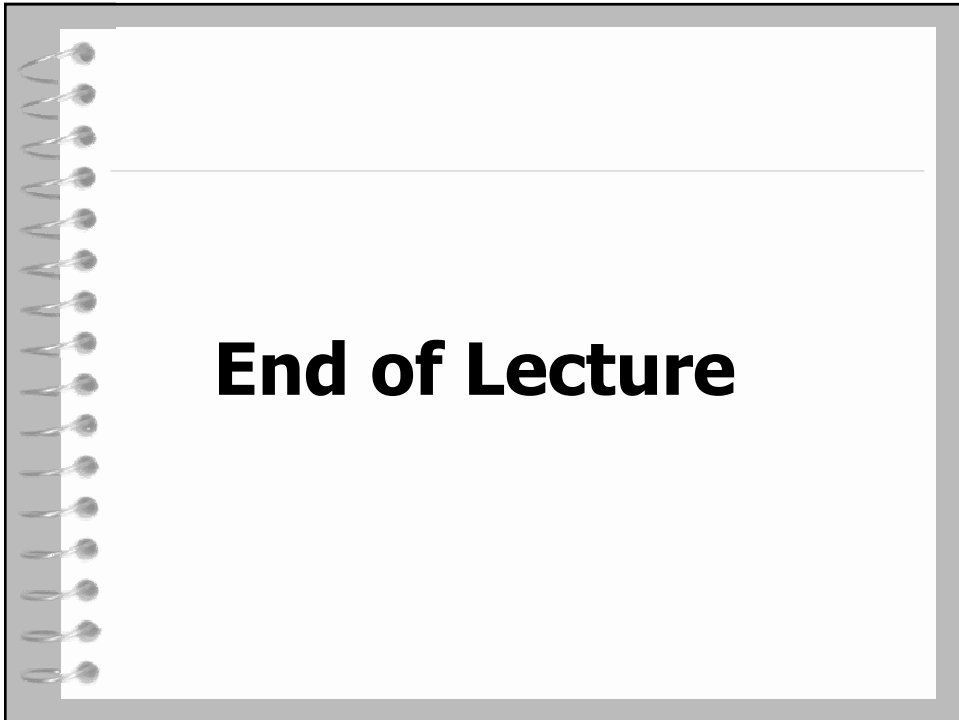


UNDERSTANDING CHEMICAL WORK....contd

Show that Chemical work = $W_A + W_B$

$$\begin{aligned}
 &= (\mu_{ai}^0 - \mu_a) N_a + (\mu_{bi}^0 - \mu_b) N_b \\
 &= -RT(N_a \ln x_a + N_b \ln x_b)
 \end{aligned}$$

Since the process can be reversed this is also the amount of work needed for separation of the constituents of a mixture of ideal gases.



End of Lecture