Reminder From Last Week

from observations all extensive TD state functions are homogeneous functions of order 1 $\rightarrow$ intensive functions are homogeneous functions of order 0

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

$X(T, P, n_i)$

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

partial molar quantities $\bar{X}_i = \left(\frac{\partial X}{\partial n_i}\right)_{T, P, n_{j \neq i}}$

generalized Gibbs-Duhem equation

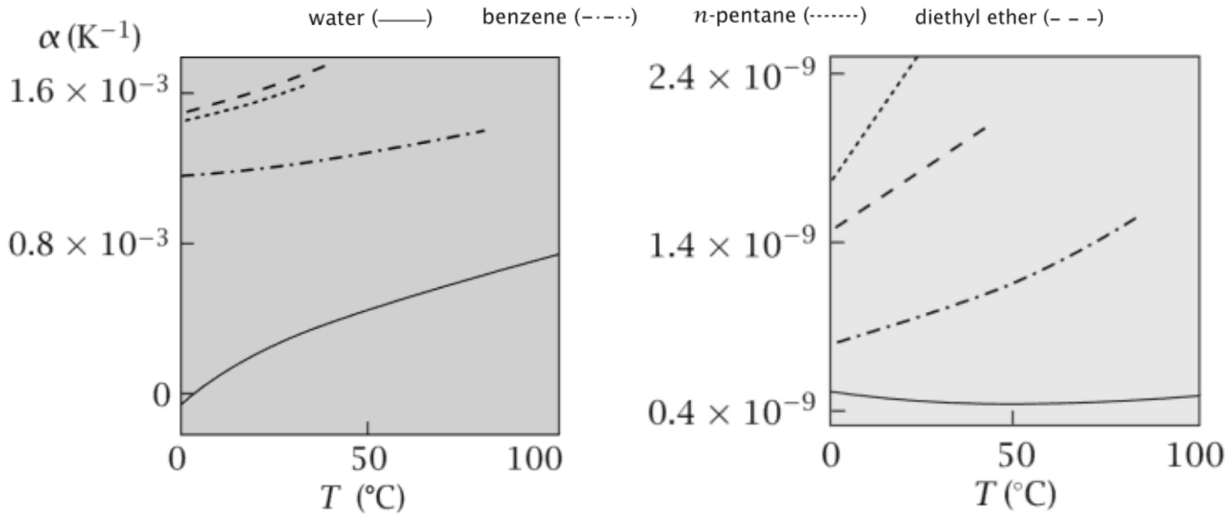
$$\left(\frac{\partial X}{\partial T}\right)_{P, n_i} dT + \left(\frac{\partial X}{\partial P}\right)_{T, n_i} dP + \sum_i n_i \, d\bar{X}_i = 0$$

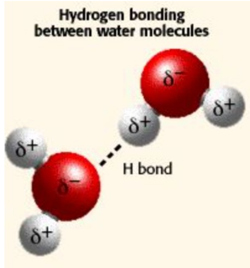
for $dP = 0$ $dT = 0$ $\quad \sum_i n_i \, d\bar{X}_i = 0 \rightarrow$ if X is G

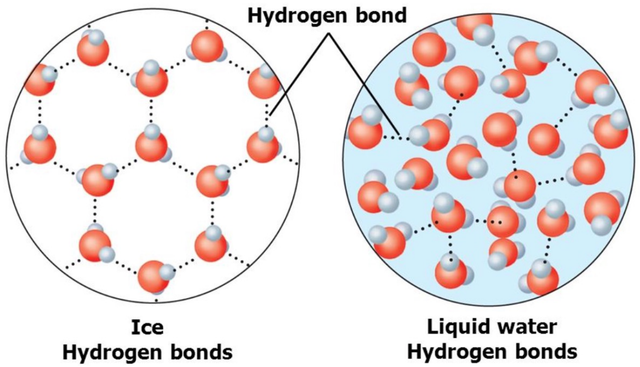
$$\sum_i n_i \, d\mu_i = 0$$

WATER DIFFERS FROM SIMPLE LIQUIDS: ENTROPY, VOLUME, & STRUCTURE

The thermal expansion coefficient and the isothermal compressibility are small for water, which is hydrogen bonded, than for simpler liquids like benzene which are not.







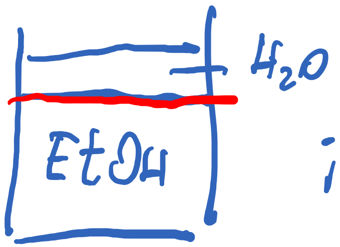
$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \qquad -\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial S}{\partial p}\right)_T$$

Maxwell relations

EXAMPLE | MIXTURE OF WATER & ETHANOL

Calculate the total volume before and after mixing of 1 mol of water with 100 mol of ethanol.

Data: molar volumes of pure water and ethanol are 18.00 and 58.00 cm^3/mol, respectively; the partial molar volume of water in a dilute solution of water in ethanol is 14.00 cm^3/mol.



initial

$$V_I = V_e + V_w = n_e \bar{V}_e + n_w \bar{V}_w =$$

$$100\ mol \cdot 58 \frac{cm^3}{mol} + 1\ mol \cdot 18 \frac{cm^3}{mol} =$$

$$5818\ cm^3$$

$$\bar{V}_e \simeq V_e$$

remove the membrane

final

$$V_F = n_e \bar{V}_e + n_w \bar{V}_w = 100\ mol\ 58 \frac{cm^3}{mol} + 1 \cdot 14 \frac{cm^3}{mol}$$

$$= 5814\ cm^3$$

$$\Delta V^{mix} = -4\ cm^3$$

We mix two substance 1 and 2 $\quad V = \sum_i n_i \bar{v}_i$

EXAMPLE | GRAPHICAL EXTRACTION OF PARTIAL MOLAR QUANTITIES

We will now determine the partial molar volumes in a water-ethanol mixture at 20°C and at a pressure of 1 atm.

prior to mixing $\quad V_I = n_1 v_1 + n_2 v_2$

after mixing $\quad V_F = n_1 \bar{v}_1 + n_2 \bar{v}_2$

v_i is the molar volume

$\bar{v}_1$ is the partial molar volume

$\bar{v}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}} \quad V(T,P,n_i)$

$$\underbrace{\frac{\Delta V^{mix}}{\sum_i n_i}}_{y} = \frac{V_F - V_I}{n} = \frac{n_1(\bar{v}_1 - v_1) + n_2(\bar{v}_2 - v_2)}{n_1 + n_2}$$

mole fraction $\quad x_i = \frac{n_i}{\sum_i n_i} \rightarrow x_1 = \frac{n_1}{n_1+n_2} \; ; \; x_2 = \frac{n_2}{n_1+n_2} \quad x_2 = 1 - x_1$

$$y = x_1(\bar{v}_1 - v_1) + (1 - x_1)(\bar{v}_2 - v_2)$$

Example | Graphical Extraction of Partial Molar Quantities

$e = 1 \quad w = 2$

$$\frac{\Delta_{mix}V}{\sum n} = (1-x_e)(\bar{V}_w - v_w) + x_e(\bar{V}_e - v_e) = (1-x)(\bar{V}_2 - V_2) + x(\bar{V}_1 - V_1)$$

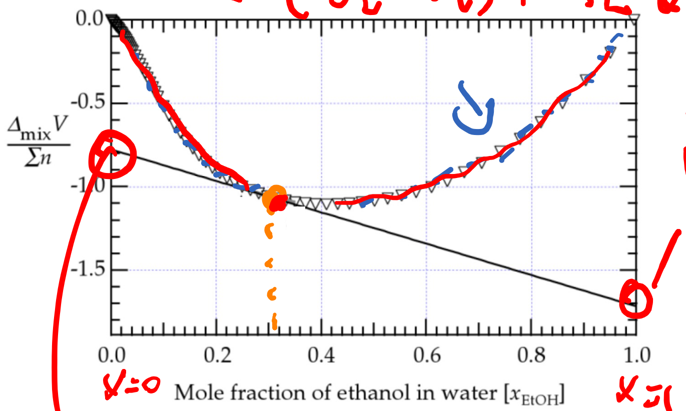
$$\rightarrow = (\bar{V}_2 - V_2) + x_1\left[(\bar{V}_1 - V_1) - (\bar{V}_2 - V_2)\right]$$

$$\frac{dy}{dx} = -(\bar{V}_2 - V_2) + (1-x)\,d\bar{V}_2 + (\bar{V}_1 - V_1) + x\,d\bar{V}_1$$

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

G. D. equation

@ $dp=0$ @ $dT=0$



$\bar{V}_1 - V_1$

$\bar{V}_2 - V_2 \qquad \underline{x_0}$

$$\frac{dy}{dx} = a(x) = -(\bar{V}_2 - V_2) + (\bar{V}_1 - V_1)$$

calculate the tangent @ x_0 to $y\left(\frac{\Delta_{mix}V}{n}\right)$

$\rightarrow y = mx + n$

$n = \bar{V}_2 - V_2 \qquad y = ax + (\bar{V}_2 - V_2)$

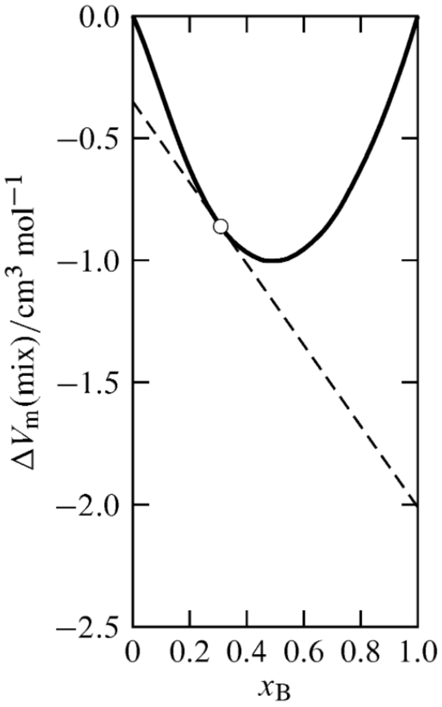
$m = a(x_0) \qquad y = ax + n$

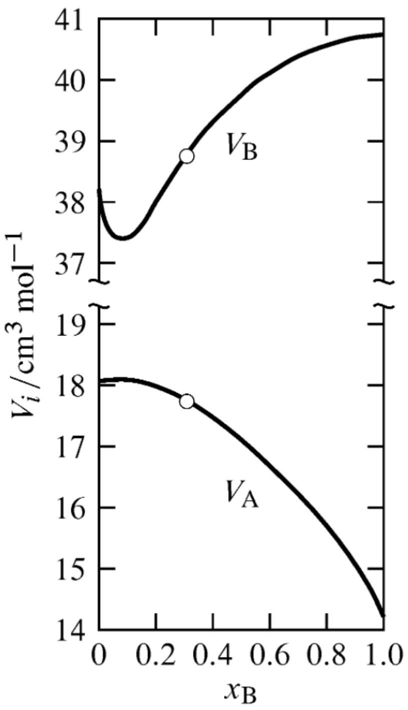
where does the tangent intercept the y axis @

$x = 0 \rightarrow \bar{V}_2 - V_2$

$x = 1 \rightarrow \bar{V}_1 - V_1$

EXAMPLE | GRAPHICAL EXTRACTION OF PARTIAL MOLAR QUANTITIES





EXAMPLE | ADDING SOLUTE IN DILUTE SOLUTIONS

Calculate the total volume of a beaker of liquid water when it is increased by 1 mol of water, at 298 K and 1 atm.

SINGLE COMPONENT IDEAL GAS

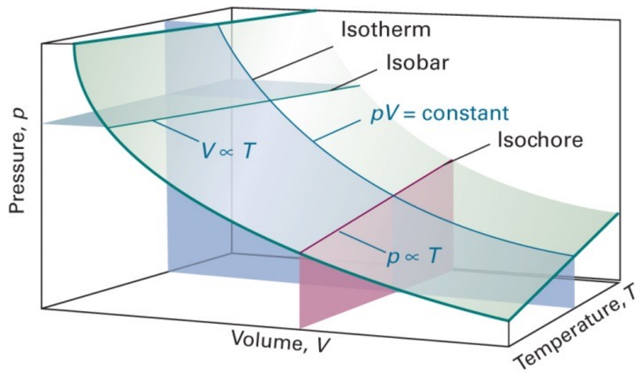
We have introduced all of the key thermodynamics' variables. It is now time to try applying the concepts we have found to understand materials' behavior. We will start with gases as they are the simplest form of material to study in thermodynamics and slowly move to liquids and solids. The key property that renders gases easier to study is the fact that we can define an ideal state. Let's recall that an ideal gas is formed of identical molecules of negligible size in ceaseless random motion that interact only through brief elastic collisions. As a consequence, an ideal gas is a gas at 0K and infinite pressure. Obviously, this cannot be true for any material.

Yet the ideal gas law is a key stepping stone to understand the whole thermodynamics of materials. The first property of ideal gases is that they obey the ideal gas law:

$$pV = nRT$$

if $p=\infty$ $V=0$

if $T=0$ $Vp=0$



GIBBS FREE ENERGY AND CHEMICAL POTENTIAL OF THE IDEAL GAS

The Gibbs free energy of a single component ideal gas is:

$$dG = -S\,dT + V\,dp + \sum_i \mu_i\,dn_i = -S\,dT + V\,dp + \mu\,dn$$

We need now to calculate the chemical potential. To do so we will use one of Maxwell relations: $\left(\frac{\partial \mu}{\partial p}\right)_{T,n}$

$$\left(\frac{\partial}{\partial p}\left(\frac{\partial G}{\partial n}\right)_{T,p}\right)_{T,n} = \left(\frac{\partial}{\partial n}\left(\frac{\partial G}{\partial p}\right)_{T,n}\right)_{T,p}$$

$$\left(\frac{\partial \mu}{\partial p}\right)_{T,n} = \left(\frac{\partial V}{\partial n}\right)_{T,p} \qquad V = n\frac{RT}{p}$$

$$\left(\frac{\partial \mu}{\partial p}\right)_{T,n} = \frac{RT}{p} \Rightarrow d\mu = \frac{RT}{p}dp \Rightarrow \int_{\mu^\theta}^{\mu} d\mu = \int_{p_0}^{p}\frac{RT}{p}dp \Rightarrow \mu = \mu^\theta + RT\ln\frac{p}{p_0}$$

$$\Rightarrow \mu = \mu^\theta(T) + RT\ln p$$

ENTHALPY AND INTERNAL ENERGY OF THE IDEAL GAS

$G = \sum_i n_i \mu_i$

$G = n\mu$

We know that: $\left(\frac{\partial G}{\partial T}\right)_{p,n} = -S$

$\left(\frac{d\mu}{dT}\right)_{p,n} = -s$ molar entropy $\mu = \frac{G}{n}$

$G = H - TS \rightarrow g = h - Ts \rightarrow h = g + Ts$ $\quad g = \mu = \mu^{\theta} + RT\ln p$

$g = \frac{G}{n} = \mu$

$$h = \mu^{\theta}(T) + RT\ln p + T\left(-\left(\frac{d\mu}{dT}\right)_p\right) = \mu^{\theta} + RT\ln p - T\left[\left(\frac{d\mu^{\theta}}{dT}\right)_p + \frac{d(RT\ln p)}{dT}\right]$$

$$= \mu^{\theta} + RT\cancel{\ln p} - T\left(\frac{d\mu_0}{dT}\right) - RT\cancel{\ln p} = \boxed{\mu^{\theta}(T) - T\left(\frac{d\mu^{\theta}}{dT}\right)_p}$$

$$h = -T^2 \frac{d\left(\frac{\mu^{\theta}}{T}\right)}{dT}$$

$h = u + pV$ $\quad n=1$ $\quad pV = RT$

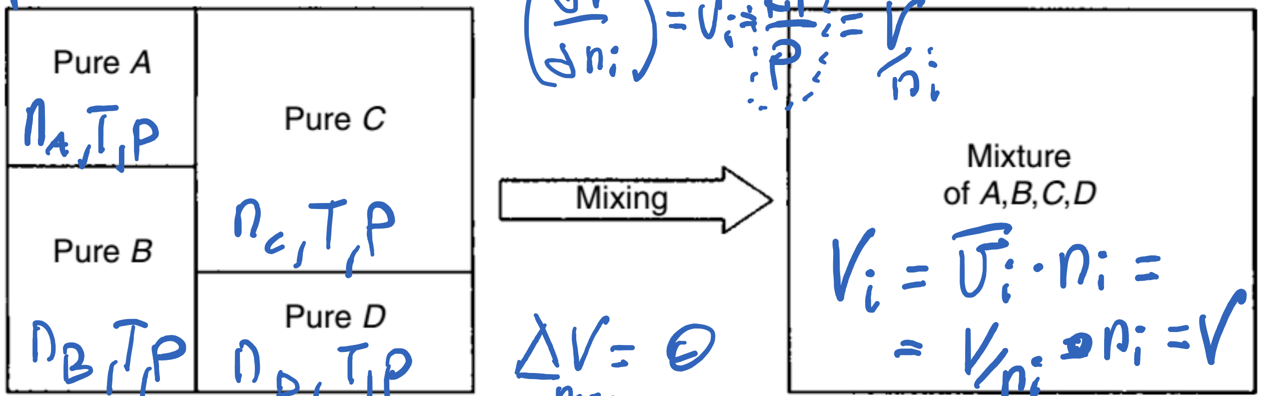
$$u = -T^2 \frac{d\left(\frac{\mu^{\theta}}{T}\right)_p}{dT} - RT$$

Volume and Pressure in Mixtures of Ideal Gases

$V_i = V$

partial volume $V_i = n_i \frac{RT}{P}$ $\quad \frac{RT}{P} = \frac{V_1}{n_1} = \frac{V_2}{n_2} = \dots \frac{V_i}{n_i} = \frac{V}{n}$ $\quad P_i V_i = n_i RT$

partial molar volume $\left(\frac{\partial V}{\partial n_i}\right) = \bar{V}_i = \frac{RT}{P} = \frac{V}{n_i}$



$\Delta V_{mix} = 0$

for ideal mixtures of ideal gases

$U = \sum_i U_i \quad H = \sum_i H_i$

$H = \sum_i H_i = \sum_i (U_i + p_i V_i) =$

$= \sum_i U_i + \sum_i p_i V_i = U + \sum n_i RT =$

$= U + nRT$

$p_i \rightarrow$ partial pressure

$p_i V = n_i RT$

$p = \sum_i p_i$

$\frac{p_i}{n_i} = \frac{RT}{V} = \frac{p_1}{n_1} = \frac{p_2}{n_2} = \frac{p_3}{n_3} = \dots \frac{p_i}{n_i} = \frac{p}{n}$

$\frac{p_i}{n_i} = \frac{p}{n} \Rightarrow p_i = p \frac{n_i}{n} = p x_i$

$x_i = \frac{n_i}{n} = \frac{n_i}{\sum_i n_i}$

$\mu_i = \mu_i^{\theta}(T) + RT \ln p_i =$

$= \mu_i^{\theta}(T) + RT \ln p + RT \ln x_i$