MSE-204 Thermodynamics for Materials Science

L3.Part 2 | Molar & Partial Molar Quantities

Explicit Expressions for U, H, A, G | Gibbs-Duhem Equation | Partial Molar Quantities and Their Measurement

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EXPLICIT RELATIONSHIP FOR U

In view of the mathematical properties of extensive variables, we can now obtain explicit expressions for some of the extensive thermodynamic functions. We will start by calculating the **partial derivatives with respect to lamda**.

$$U(\lambda S, \lambda V, \lambda n_i) = \lambda U(S, V, n_i) \qquad U^* = \lambda U \qquad V^* = \lambda V \quad S^* = \lambda S \quad n_i^* = \lambda n_i$$

$$\frac{dU^*}{d\lambda} = \left(\frac{\partial U^*}{\partial S^*}\right)_{V^*, n_i^*} \cdot \underbrace{\left(\frac{\partial S^*}{\partial \lambda}\right)}_{=S} + \left(\frac{\partial U^*}{\partial V^*}\right)_{S^*, n_i^*} \cdot \underbrace{\left(\frac{\partial V^*}{\partial \lambda}\right)}_{=V} + \sum \left(\frac{\partial U^*}{\partial n_i^*}\right)_{S^*, V^*, n_{j \neq i}^*} \underbrace{\left(\frac{\partial n_i^*}{\partial \lambda}\right)}_{=n_i}$$

$$\frac{dU^*}{d\lambda} = \underbrace{\left(\frac{\partial U}{\partial S}\right)_{V, n_i}}_{=T} \cdot S + \underbrace{\left(\frac{\partial U}{\partial V}\right)_{S, n_i}}_{=-p} \cdot V + \sum_i \underbrace{\left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_{j \neq i}}}_{=\mu} \cdot n_i$$

$$\frac{dU^*}{d\lambda} = \frac{d(\lambda U)}{d\lambda} = U = TS - pV + \sum_i \mu_i n_i \quad \text{explicit relation of } U$$

Explicit Relationships for U, H, A, and G

$$U = TS - pV + \sum_i \mu_i n_i$$

$$H = TS + \sum_i \mu_i n_i$$

$$A = -pV + \sum_i \mu_i n_i$$

$$\boxed{G = \sum_i \mu_i n_i}$$

All of these derivations are significant because they really allow us to understand the meaning of U, H, A, and G.

For any material

- At vacuum ($p=0$ atm) & at absolute 0, 0 K

  $U = H = A = G$

- At 0 K

  $U = A$, $H = G$

- At $p = 0$ atm

  $U = H$, $A = G$

GIBBS-DUHEM EQUATION

If we now look at the two possible differential forms of G we get:

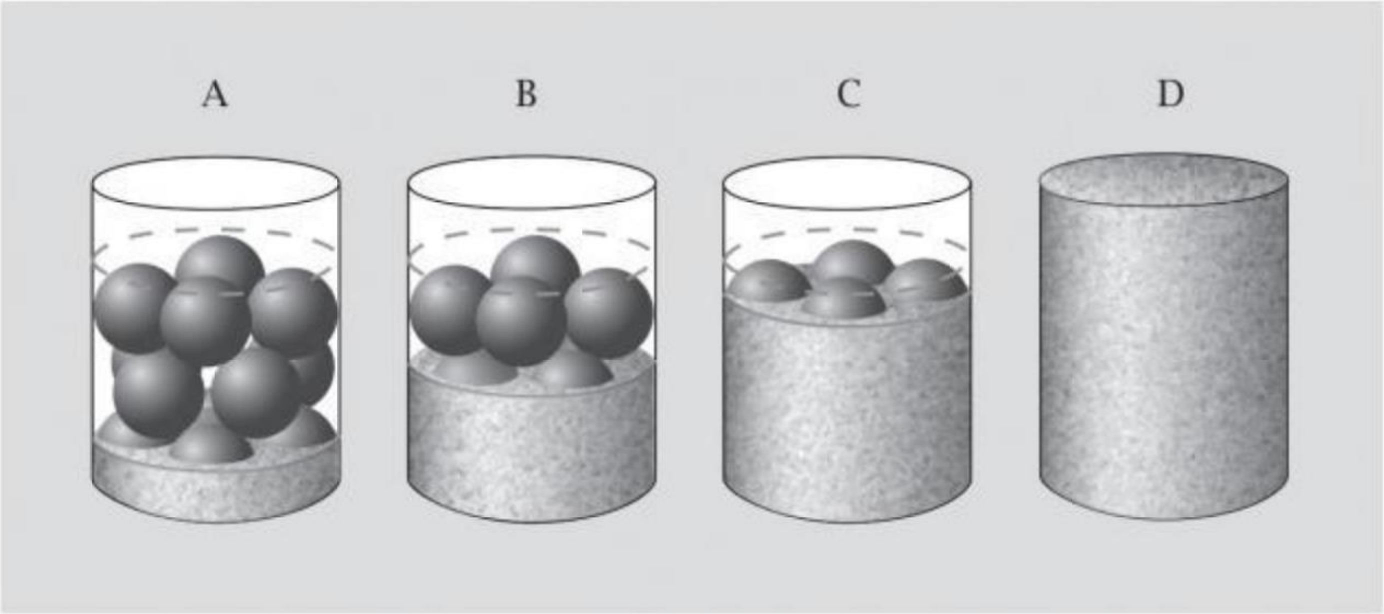
$$dG = -SdT + Vdp + \sum_i \mu_i dn_i$$

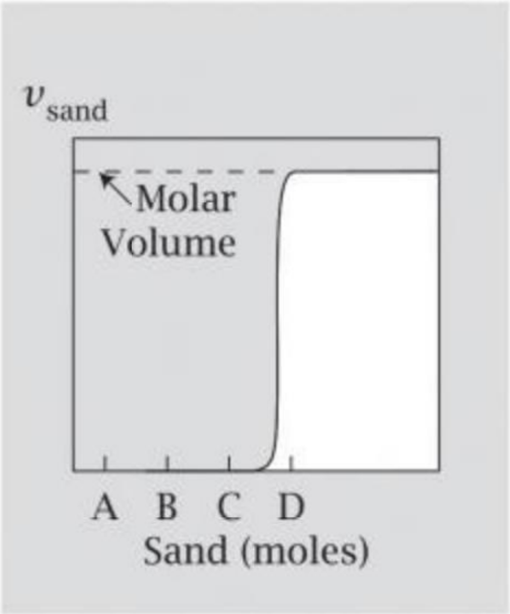
$$dG = d\left(\sum_i \mu_i dn_i\right) = \sum_i d\mu_i n_i + \sum_i dn_i \mu_i$$

$$\Rightarrow \boxed{SdT - Vdp + \sum_i n_i d\mu_i = 0}$$

teaches us how the intensive properties vary with each other

MULTICOMPONENT SYSTEMS HAVE PARTIAL MOLAR QUANTITIES





Adding sand to a barrel of bowling balls indicates the idea of partial molar quantities. At first, the sand is at low "concentration", adding sand just fills in the holes between the bowling balls and does not increase the barrel volume that is needed to contain the bowling balls and sand. However, when all the space between the bowling balls is filled, adding sand does add volume. At the point D, the partial molar volume of the sand equals the molar volume.

PARTIAL MOLAR QUANTITIES

It is of particular interest to consider extensive variables as functions of temperature and pressure, since then the only extensive variable needed to define the state of the system are the number of moles of the various components. We will consider X to be an extensive variable and take the derivative with respect to lamda:

$$X(T, p, \lambda n_i) = \lambda X(T, p, n_i)$$

generic X extensive variable

$$X^* = \lambda X$$

$$X = \frac{dX^*}{d\lambda} = \sum_i \left(\frac{\partial X^*}{\partial n_i^*}\right)_{T,p,n_j^* \neq i} \frac{\partial n_i^*}{\partial \lambda} = \sum_i \left(\frac{\partial X}{\partial n_i}\right)_{T,p,n_j \neq i} \cdot n_i$$

We define

$$\overline{X}_i = \left(\frac{\partial X}{\partial n_i}\right)_{T,p,n_j \neq i}$$

$\Rightarrow$ Partial molar generic quantity of extensive variable X

$\Downarrow$

intensive property

$$X = \sum_i n_i \overline{X}_i$$

Partial Molar Quantities – Examples

$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j \neq i}$

$$U = \sum_i n_i \overline{U_i}$$

$U = \sum_i n_i \left(\frac{\partial U}{\partial n_i}\right)_{T,p,n_j \neq i}$

$$V = \sum_i n_i \overline{V_i}$$

$$S = \sum_i n_i \overline{S_i}$$

$$H = \sum_i n_i \overline{H_i}$$

$$A = \sum_i n_i \overline{A_i}$$

$$G = \sum_i n_i \overline{G_i}$$

$G = \sum_i n_i \underline{\left(\frac{\partial G}{\partial n_i}\right)}_{T,p,n_j \neq i} = \sum_i n_i \cdot \underline{\mu_i}$

$\mu_i = \overline{G_i}$

$$C_p = \sum_i n_i \overline{C_{p,i}}$$

Relationship Between Partial Molar Quantities

The differentials of partial molar quantities are exact differentials. We will now write two expressions for the differential of X:

$$X = X(T, p, n_i) \Rightarrow dX = \left(\frac{\partial X}{\partial T}\right)_{p,n_i} dT + \left(\frac{\partial X}{\partial p}\right)_{T,n_i} dp + \sum_i \underbrace{\left(\frac{\partial X}{\partial n_i}\right)_{T,p,n_{j\neq i}}}_{=\bar{X}_i} dn_i$$

$$X = \sum_i n_i \bar{X}_i \Rightarrow dX = \sum_i n_i \, d\bar{X}_i + \sum_i \bar{X}_i \, dn_i$$

$$\Rightarrow -\left(\frac{\partial X}{\partial T}\right)_{p,n_i} dT - \left(\frac{\partial X}{\partial p}\right)_{T,n_i} dp + \sum_i n_i \, d\bar{X}_i = 0$$

Generalized Gibbs-Duhem equation

X is a generic extensive variable

We can see that if G is selected as X, this gives us the Gibbs-Duhem equation. Importantly, for isothermal and isobaric conditions, we get:

$dT = 0$

$dp = 0$

$$\Rightarrow \sum_i n_i \, d\bar{X}_i = 0$$

EXAMPLE | ADDING SOLUTE IN DILUTE SOLUTIONS

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

Data: molar volume of pure water is18.00 cm^3/mol

ONE SUBSTANCE: $\bar{V}_w = \left(\frac{\partial V}{\partial n}\right)_{T,P} = \boxed{V_w} = \frac{V}{n} = \frac{m/d}{n} = \frac{M}{d}$

partial molar volume of water

molar volume of water

molar mass

Prior to mixing: $V_I = (n_w V_w)_{beaker} + (n_w \cdot V_w)_{1\,mol} = (n_w V_w)_{beaker} + 18\ (cm^3)$

After mixing: $V_F = (n_w \bar{V}_w)_{beaker} + (n_w + \bar{V}_w)_{1\,mol} = (n_w V_w)_{beaker} + (18\ cm^3)$

$\Delta_m V = V_F - V_I = 0$

EXAMPLE | MIXTURE OF WATER & ETHANOL

excess in ethanol

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

Data: molar volumes of pure water and ethanol are 18.00 and 58.00 cm³/mol, respectively; the partial molar volume of water in a dilute solution of water in ethanol is 14.00 cm³/mol.

Prior to mixing $V_I = n_e V_e + n_w V_w = 100 \cdot 58 + 1 \cdot 18 = 5818 \text{ cm}^3$

After mixing $V_F = n_e \bar{V}_e + n_w \bar{V}_w$ because ethanol is in excess, I assume $\bar{V}_e = V_e$ & also solution is homogeneous

$V_F = n_e V_e + n_w \bar{V}_w = 5814 \text{ cm}^3$

$\Delta_m V = -4 \text{ cm}^3$

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: $V_I = n_e v_e + n_w v_w$

After mixing: $V_F = n_e \bar{V}_e + n_w \bar{V}_w$

$$\frac{\Delta_m V}{\Sigma n} = \frac{V_F - V_I}{\Sigma n} = \frac{n_e(\bar{V}_e - v_e) + n_w(\bar{V}_w - v_w)}{n_e + n_w} \quad (A)$$

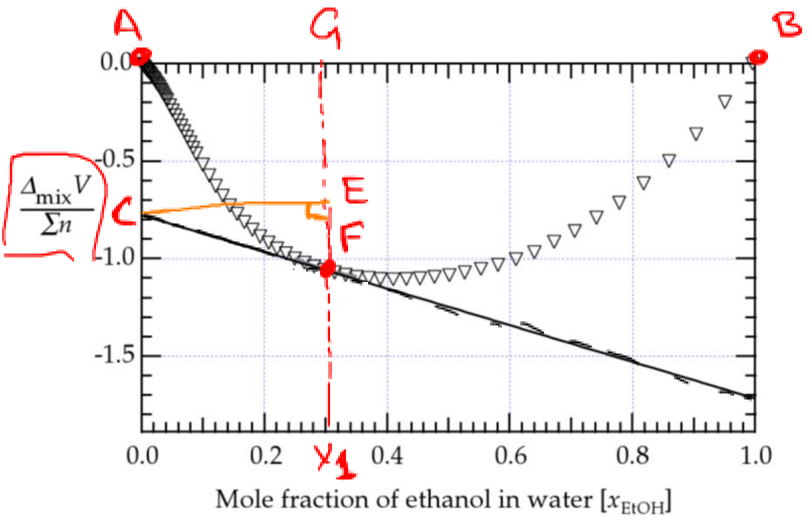
mole fractions $x_i = \dfrac{n_i}{\sum_i n_i}$

$x_e = \dfrac{n_e}{n_e + n_w}$ (1), $x_w = \dfrac{n_w}{n_e + n_w}$ (2), $x_e + x_w = 1$ (3)

$$Y = \frac{\Delta_m V}{\Sigma n} = x_e(\bar{V}_e - v_e) + (1 - x_e)(\bar{V}_w - v_w)$$

EXAMPLE | GRAPHICAL EXTRACTION OF PARTIAL MOLAR QUANTITIES

$$y = \frac{\Delta_{mix}V}{\sum n} = (1 - x_e)(\bar{V}_w - v_w) + x_e(\bar{V}_e - v_e)$$



$$\frac{dy}{dx_e} = d\left[(1-x_e)(\bar{V}_w - v_w)\right] + d\left[x_e(\bar{V}_e - v_e)\right]$$

$$= -(\bar{V}_w - v_w) + \boxed{(1-x_e)\,d\bar{V}_w} + (\bar{V}_e - v_e) + \boxed{x_e\,d\bar{V}_e}$$

because $dp=0$, $dT=0$, $\sum_i n_i\,d\bar{V}_i = 0$ or $\sum_i x_i\,d\bar{V}_i = 0$

$$\frac{dy}{dx_e} = -(\bar{V}_w - v_w) + (\bar{V}_e - v_e)$$

at $x_e = x_1$

$$\left.\frac{dy}{dx_e}\right|_{x_e=x_1} = -(\bar{V}_{w,x_1} - v_w) + (\bar{V}_{e,x_1} - v_e)$$

&

$$y\Big|_{x_e=x_1} = (1-x_1)(\bar{V}_{w,x_1} - v_w) + x_1(\bar{V}_{e,x_1} - v_e)$$

Eliminate the term $\bar{V}_{e,x_1} - v_e$

Solve for $\bar{V}_{w,x_1} - v_w$

at $x_e = x_1$

$$\Rightarrow \bar{V}_{w,x_1} - v_w = y\Big|_{x_e=x_1} - x_1 \left.\frac{dy}{dx_e}\right|_{x_e=x_1} = FG - \cancel{AG}\cdot\frac{EF}{\cancel{CE}} = FG - EF = GE = AC$$