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**.

Explicit Relationships for U, H, A, and G

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

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

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

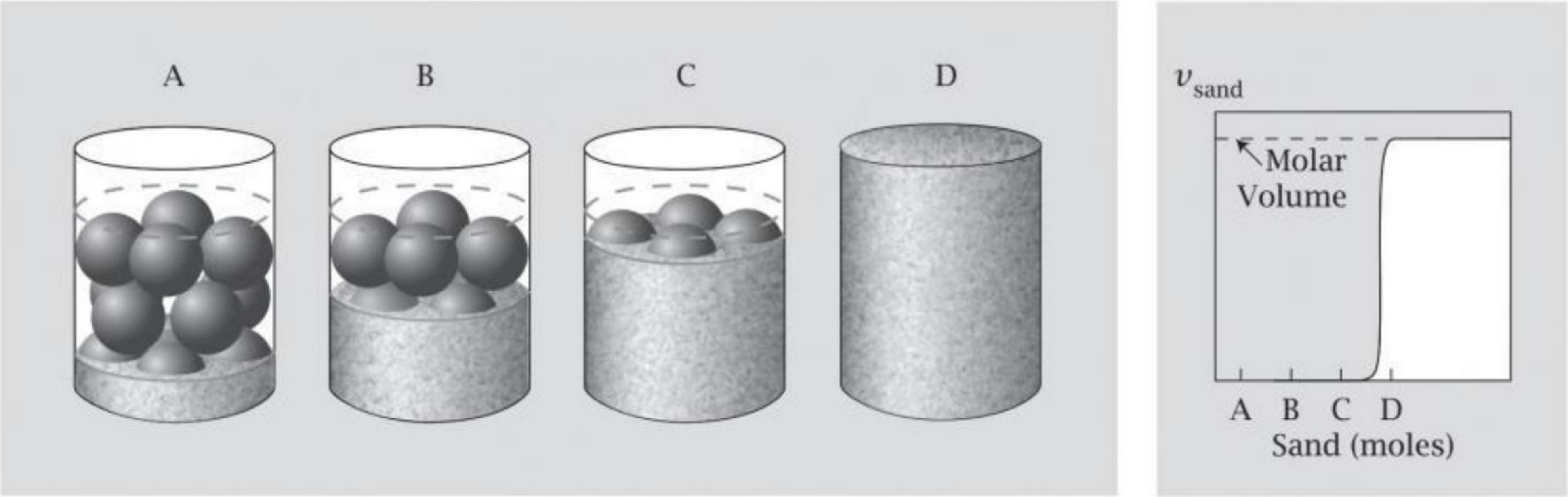
$$G = \sum_i \mu_i n_i$$

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

Gibbs-Duhem Equation

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

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:

Partial Molar Quantities – Examples

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

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

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

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

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

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

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

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:

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:

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

EXAMPLE | MIXTURE OF WATER & 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.

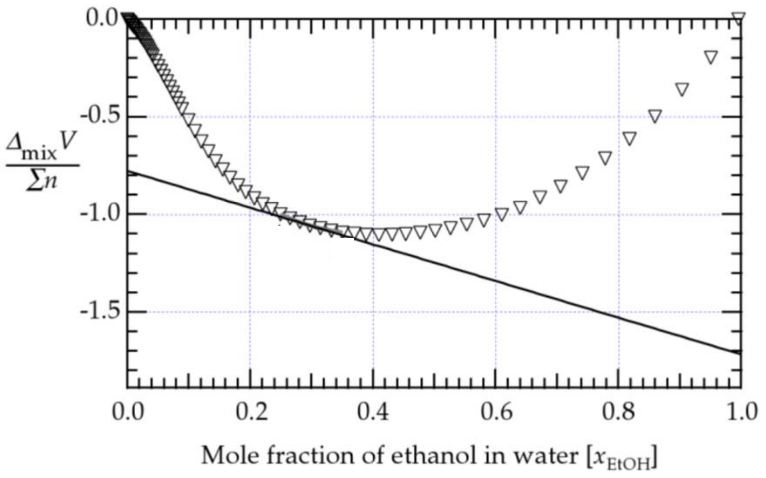
Data: molar volumes of pure water and ethanol are 18.00 and 58.00 cm^3/mol, respectively; the partial molar volume of water in a dilute solution of water in ethanol is 14.00 cm^3/mol.

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.

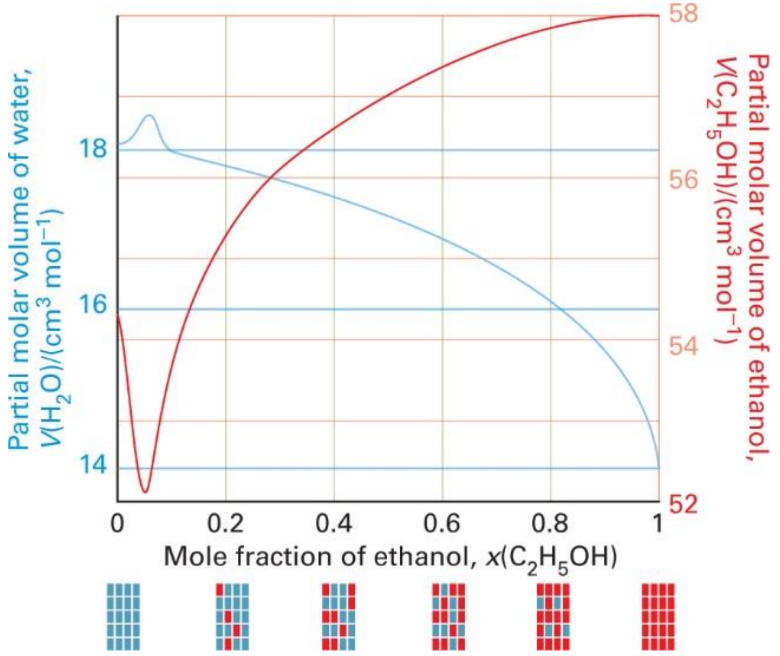
EXAMPLE | GRAPHICAL EXTRACTION OF PARTIAL MOLAR QUANTITIES

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



EXAMPLE | WATER AND ETHANOL MIXTURE

What is the total volume of a mixture of 50 g of ethanol and 50 g of water at 25ºC and 1 atm? The molar masses of ethanol and water are 46.07 g mol-1 and 18.02 g mol-1.



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.