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Simple Mixtures, TD description of ↑ → (Atkins chapter 7)

Partial molar quantities (PWA pp. 161 - 166)

Regard the binary mixture water (\underline{W} , H_2O) with ethanol (\underline{E} , $\text{CH}_3\text{CH}_2\text{OH}$), e.g. n_E moles ethanol and n_W moles water

The "mole fractions" are defined as

$$X_E \equiv \frac{n_E}{n_E + n_W} \quad (1)$$

$$X_W \equiv \frac{n_W}{n_E + n_W}$$

→ generalization for C components

$$X_k = \frac{n_k}{n} \quad n = \sum_{k=1}^C n_k$$

$$\sum_{k=1}^C X_k = 1$$

We have $X_E + X_W = 1$

The volume of the mixture is an extensive quantity of the mole numbers n_1, n_2 (at $p, T = \text{const}$)

$$\underline{V}(n_1, n_2)$$

(UPAC recommends to underline extensive quantities)

and for extensive quantities the Euler theorem for homogeneous functions is valid

$$\underline{V}(\alpha n_1, \alpha n_2) = \alpha \underline{V}(n_1, n_2) \quad (\text{cf. 3rd lecture!})$$

differentiate with respect to scaling factor α

$$n_1 \left(\frac{\partial \underline{V}(\alpha n_1, \alpha n_2)}{\partial n_1} \right)_{n_2} + n_2 \left(\frac{\partial \underline{V}(\alpha n_1, \alpha n_2)}{\partial n_2} \right)_{n_1} = \underline{V}(n_1, n_2)$$

and set $\alpha = 1$. We obtain

$$n_1 \bar{V}_1 + n_2 \bar{V}_2 = \underline{V} \quad (2)$$

with $\bar{V}_1 \equiv \left(\frac{\partial \underline{V}(n_1, n_2)}{\partial n_1} \right)_{n_2}$

$$\bar{V}_2 \equiv \left(\frac{\partial \underline{V}(n_1, n_2)}{\partial n_2} \right)_{n_1} \quad (3)$$

② The quantities \bar{V}_1, \bar{V}_2 are the partial molar volumes of species 1 and 2 in the mixture, and they depend only on the mole fractions x_1, x_2 , i.e.

\bar{V}_1 and \bar{V}_2 are intensive quantities (argue why?)

(IUPAC recommends to denote partial molar quantities by a superscribed bar \bar{V})

Example

→ Mixture of water and ethanol

Molar mass of pure substances $\overset{15.9994}{M_W} = M(H_2O) \approx (2 \cdot 1007 + 1 \cdot 16) \frac{g}{mol} = 18 \frac{g}{mol}$ (18.0153) molar mass W

$\overset{15.9994}{M_E} = M(CH_3CH_2OH) \approx (2 \cdot 12.011 + 6 \cdot 1.0079 + 1 \cdot 16) \frac{g}{mol} = 46 \frac{g}{mol}$ (46.07) molar mass E

→ Molar volume of pure substances

$$V^{\circ} = \frac{M}{\rho_0}$$

ρ_0 density of pure species at given T and p
 25°C 1 atm
 298.15 K 10¹³258

$$\left\{ \begin{aligned} \rho_W &= 0.99707 \frac{g}{cm^3} \approx 1 \frac{g}{cm^3} \\ \rho_E &= 0.791 \frac{g}{cm^3} \approx 0.8 \frac{g}{cm^3} \end{aligned} \right.$$

$$\left\{ \begin{aligned} V_W^{\circ} &= \frac{M_W}{\rho_W} \approx \frac{18 \frac{g}{mol}}{1 \frac{g}{cm^3}} = 18 \frac{cm^3}{mol} \quad (18.07) \\ V_E^{\circ} &= \frac{M_E}{\rho_E} \approx \frac{46 \frac{g}{mol}}{0.8 \frac{g}{cm^3}} = 58 \frac{cm^3}{mol} \quad (58.24) \end{aligned} \right.$$

→ Molar mass of mixture W, E

$$M(x_1, x_2) = x_W M_W + x_E M_E$$

molar fractions $x_W = \frac{n_W}{n}$
 $n \equiv n_W + n_E$ $x_E = \frac{n_E}{n}$

→ Molar volume of mixture in case of "ideal mixing"

$$V(x_1, x_2) = x_W V_W^{\circ} + x_E V_E^{\circ} = V_W^{\circ} + (V_E^{\circ} - V_W^{\circ}) x_E$$