Chemistry 163B Introduction to Multicomponent Systems and Partial Molar Quantities

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the problem of partial mmolar quantities

mix: 10 moles ethanol C_2H_5OH (580 mL)
with
1 mole water H_2O (18 mL)

get ~~(580+18)=598 mL of solution?~~

no only 594 ml

for pure H_2O $$\left(\frac{\partial V}{\partial n_{H_2O}}\right)_{T=298,P=1bar,n_{EtOH}=0} = \bar{V}_{H_2O} = 18\ mL$$

but
in 10 mol EtOH $$\left(\frac{\partial V}{\partial n_{H_2O}}\right)_{T=298,P=1bar,n_{EtOH}=10} = 14\ mL$$

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partial molar quantities (systems of variable composition)

system of n_1 moles substance 1, n_2 moles substance 2, …
Ω some extensive property of system (volume, free energy, etc)

$$\bar{\Omega}_i = \left(\frac{\partial \Omega_{total}}{\partial n_i}\right)_{\underline{T,P},n_j \neq n_i}$$

"partial molar Ω" for component *i*
contribution of substance *i* to property Ω at T, P
when other components present at concentrations n_j
"molar Ω" in presence of other species

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slides 4-7 are taken from:
http://www.chem.unt.edu/faculty/cooke/3510/3510_chap7.ppt
apparently no longer available

A site from: Stephen A. Cooke, Ph.D.
Department of Chemistry
University of North Texas

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PARTIAL MOLAR QUANTITIES

In a system that contains at least two substances, the total value of <u>any</u> extensive property of the system is the sum of the contribution of each substance to that property.

The contribution of one mole of a substance to the volume of a mixture is called the **partial molar volume** of that component.

$$V = f\left(p, T, n_A, n_B \ldots\right)$$

$$\boxed{V_A = \left(\frac{\partial V}{\partial n_A}\right)_{p,T,n\neq A}}$$

At constant T and p

$$dV = \left(\frac{\partial V}{\partial n_A}\right) dn_A + \left(\frac{\partial V}{\partial n_B}\right) dn_B + \ldots$$

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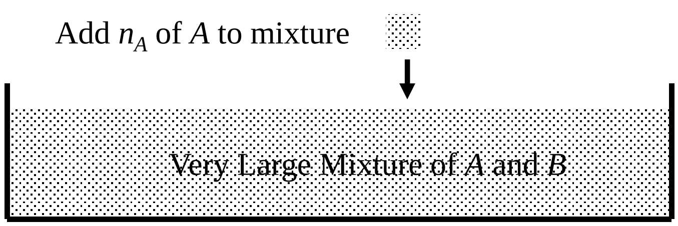
PARTIAL MOLAR VOLUME

Add n_A of A to mixture



Composition remains essentially unchanged. <u>In this case</u>:

$$V_A = \left(\frac{\partial V}{\partial n_A}\right)_{p,T,n\neq A}$$

can be considered constant and the volume change of the mixture is $n_A V_A$. Likewise for addition of B.

The total change in volume is $n_A V_A + n_B V_B$. (Composition is essentially unchanged).

Scoop out of the reservoir a sample containing n_A of A and n_B of B its volume is $n_A V_A + n_B V_B$. Because V is a state function:

$$\boxed{V = V_A n_A + V_B n_B + \ldots}$$

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PARTIAL MOLAR VOLUME

Illustration:

What is the change in volume of adding 1 mol of water to a large volume of water?

The change in volume is $18 cm^3$

$$V_{H_2O} = \left(\frac{\partial V}{\partial n_{H_2O}}\right)_{p,T} = 18 cm^3$$

A different answer is obtained if we add 1 mol of water to a large volume of ethanol.

The change in volume is $14 cm^3$

$$V_{H_2O} = \left(\frac{\partial V}{\partial n_{H_2O}}\right)_{p,T,n(CH_3CH_2OH)} = 14 cm^3$$

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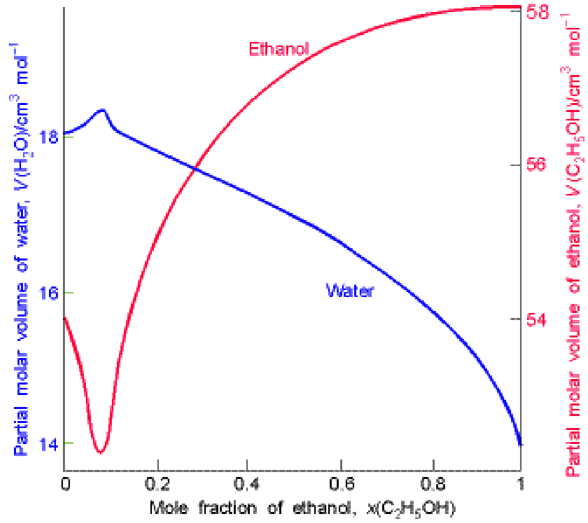
PARTIAL MOLAR QUANTITIES

V_A is not generally a constant; it is a function of composition



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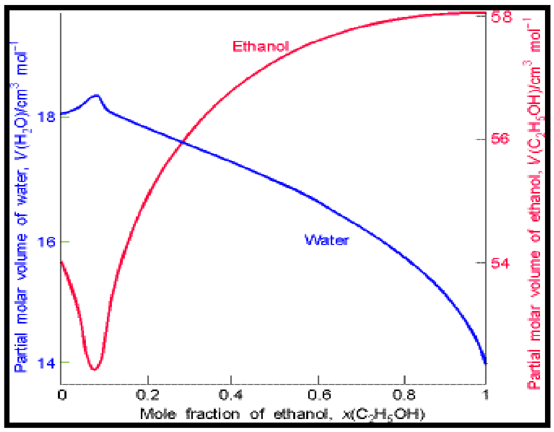
Gibbs-Duhem (later)

$$X_{EtOH}\left(\frac{\partial \overline{V}_{EtOH}}{\partial n_{EtOH}}\right)_{T,P,n_{H_2O}} = -X_{H_2O}\left(\frac{\partial \overline{V}_{H_2O}}{\partial n_{EtOH}}\right)_{T,P,n_{H_2O}}$$



http://www.chem.unt.edu/faculty/cooke/3510/3510_chap7.ppt

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partial molar quantities in biology

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Biophysics

The partial molar volume of water in biological membranes

(phospholipids/intermolecular forces/x-ray diffraction/neutron diffraction)

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ABSTRACT **A new algorithm is presented for interpreting the hydration dependence of x-ray diffraction measurements. The method assumes that the volume of the hydrocarbon phase of the lipid bilayer is not affected by hydration and that the volume expansion between bilayers at maximum hydration is caused by incorporation of water molecules whose partial molar volume is that of pure bulk water. These simple assumptions lead to a determination of the area expansion (and hence change in hydrocarbon-phase thickness) as a function of hydration. An analysis is made of x-ray data of the L_α and $L_{\beta'}$ phases of dimyristoyl phosphatidylcholine and the L_α phase of egg phosphatidylcholine. The partial molar volume of water depends critically on the degree of lipid hydration and the presence of voids between the head groups of adjacent lipids. The calculated head-group spacings at minimum hydration are consistent with those obtained from neutron diffraction and indicate that the methyl groups of the choline are almost in contact with corresponding groups in the opposing bilayer. This calls into question the origin of the repulsive forces observed in dehydration experiments.**

across the lipid part of the bilayer, and d_w, the distance across the aqueous region between bilayers:

$$d = d_l + d_w. \qquad [1]$$

d_l is usually obtained from d and the volume fraction, ϕ: $d_l = \phi d$.

$$\phi = [1 + (1-c)\overline{v}_w / c\overline{v}_l]^{-1}, \qquad [2]$$

where c is the weight fraction of lipid, and $\overline{v}_l$ and $\overline{v}_w$ are the partial specific volumes of lipid and water (6). It is commonly assumed that $\overline{v}_l$ and $\overline{v}_w$ are both 1 cm^3/g. White and King (7) have questioned the last assumption by pointing out that it leads to a value of d_l for egg phosphatidylcholine (E-PtdCho) in the L_α phase that changes by 14 Å over its full hydration range. However, the distance between phosphate groups across the bilayer, d_{pp}, obtained by their analysis of x-ray data of Torbet and Wilkins (8), does not change by more than 4 Å. Similarly, Janiak *et al.* (9) have shown that in the L_α phase of dimyristoyl phosphatidylcholine (Myr_2-PtdCho) at

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partial molar factoids #1 total differentials

1. state function differentials for systems of variable composition
(still $đw_{other}=0$)

$$U(S,V,n_1,....,n_N) \qquad dU = TdS - PdV + \sum_{i=1}^{N}\left(\frac{\partial U}{\partial n_i}\right)_{\underline{S,V,n_j\neq n_i}} dn_i$$

$$H(S,P,n_1,....,n_N) \qquad dH = TdS + VdP + \sum_{i=1}^{N}\left(\frac{\partial H}{\partial n_i}\right)_{\underline{S,P,n_j\neq n_i}} dn_i$$

$$A(T,V,n_1,....,n_N) \qquad dA = -SdT - PdV + \sum_{i=1}^{N}\left(\frac{\partial A}{\partial n_i}\right)_{\underline{T,V,n_j\neq n_i}} dn_i$$

$$G(T,P,n_1,....,n_N) \qquad dG = -SdT + VdP + \sum_{i=1}^{N}\left(\frac{\partial G}{\partial n_i}\right)_{\underline{T,P,n_j\neq n_i}} dn_i$$

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partial molar factoids #2 the chemical potential

2. The partial molar Gibbs free energy, **the chemical potential**, plays a central role

$$\bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j\neq n_i} \equiv \mu_i$$

thus

$$dG = -SdT + VdP + \sum_{i=1}^{N}\mu_i dn_i$$

and a very cute derivation give (see handout):

$$\mu_i \equiv \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j\neq n_i} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j\neq n} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j\neq n} = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j\neq n}$$

*note: for A,H,U these are **NOT** partial molar quantities* $\bar{A}_i$, $\bar{H}_i$, and $\bar{U}_i$

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factoid #3: properties of a system are sum of partial molar properties

3. An extensive property of a multi-component system is the sum of partial molar contributions from each of the components

$$V_{total} = \sum_i^N n_i \bar{V}_i = n_1 \bar{V}_1 + n_2 \bar{V}_2 + \cdots$$

$$G = \sum_i^N n_i \bar{G}_i$$

$$H = \sum_i^N n_i \bar{H}_i \quad note: \bar{H}_i = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_j \neq n_i} \neq \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j \neq n_i} = \mu_i$$

etc.

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factoid #4: relationships among partial molar quantities

4. Relationships among thermodynamic quantities derived for one-component systems often hold for partial molar quantities

examples:

$$G \equiv H - TS \quad \Rightarrow \quad \bar{G}_i = \bar{H}_i - T\bar{S}_i$$

or

$$H \equiv U + PV \quad \Rightarrow \quad \bar{H}_i = \bar{U}_i + P\bar{V}_i$$

[proof in class for G; students do similar proof for H]

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factoid #5: Gibbs Duhem

5. The Gibbs-Duhem relationship shows that partial molar quantities for substances in a mixture can not **vary** independently

example: $\bar{V}_i$ for a two component mixture e.g. EtOH + H_2O

$$X_A\left(\frac{\partial \bar{V}_A}{\partial n_B}\right)_{T,P,n_A} = -X_B\left(\frac{\partial \bar{V}_B}{\partial n_B}\right)_{T,P,n_A}$$

$$X_{H_2O}\left(\frac{\partial \bar{V}_{H_2O}}{\partial n_{EtOH}}\right)_{T,P,n_{H_2O}} = -X_{EtOH}\left(\frac{\partial \bar{V}_{EtOH}}{\partial n_{EtOH}}\right)_{T,P,n_{H_2O}}$$

[note : the variation is with respect to one of the components (∂n_{EtOH} in both denominators)]

[derivation done in class]

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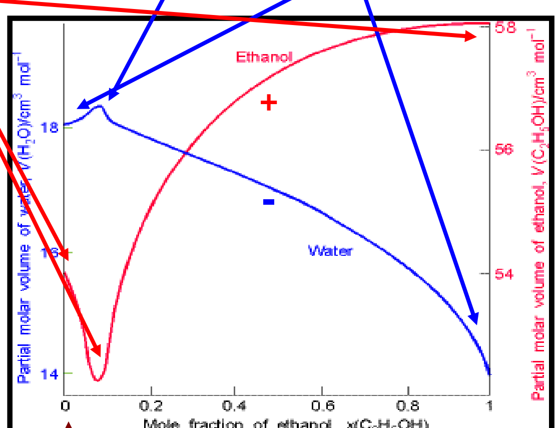
Gibbs-Duhem (slope of partial molar volume vs mole fraction)

$$\left(\frac{\partial \bar{V}_{EtOH}}{\partial n_{EtOH}}\right)_{T,P,n_{H_2O}} = -\frac{\boxed{X_{H_2O}}}{\boxed{X_{EtOH}}}\left(\frac{\partial \bar{V}_{H_2O}}{\partial n_{EtOH}}\right)_{T,P,n_{H_2O}} \qquad \left(\frac{\partial \bar{V}_{H_2O}}{\partial n_{EtOH}}\right)_{T,P,n_{H_2O}} = -\frac{\boxed{X_{EtOH}}}{\boxed{X_{H_2O}}}\left(\frac{\partial \bar{V}_{EtOH}}{\partial n_{EtOH}}\right)_{T,P,n_{H_2O}}$$

$X_{EtOH} = 0$



$X_{H_2O} = 0$

http://www.chem.unt.edu/faculty/cooke/3510/3510_chap7.ppt

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End of Lecture

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