

Chemistry 163B, Winter 2013

Lecture 16 Multicomponent Systems and Partial Molar Quantities

Chemistry 163B

Introduction to Multicomponent Systems and Partial Molar Quantities

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the problem of partial molar quantities

mix: 10 moles ethanol C₂H₅OH (580 mL)
with
1 mole water H₂O (18 mL)
get (580+18) = ~~598 mL~~ of solution?
no only 594 mL

for pure H₂O $\left(\frac{\partial V}{\partial n_{H_2O}}\right)_{T=298, P=1 \text{ bar}, n_{EtOH}=0} = \bar{V}_{H_2O} = 18 \text{ mL}$

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

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partial molar quantities (systems of variable composition)

system of n₁ moles substance 1, n₂ moles substance 2, ...
Ω some extensive property of system (volume, free energy, etc)

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

"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.unl.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 any 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.

$$V = f(p, T, n_A, n_B, \dots)$$

At constant T and p


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

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

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PARTIAL MOLAR VOLUME

Add n_A of A to mixture



Very Large Mixture of A and B

Composition remains essentially unchanged. **In this case:**

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

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

The total change in volume is n_AV_A + n_BV_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_AV_A + n_BV_B. Because V is a state function:

$$V = V_A n_A + V_B n_B + \dots$$

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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?

$$\text{The change in volume is } 18\text{cm}^3 \quad V_{\text{H}_2\text{O}} = \left(\frac{\partial V}{\partial n_{\text{H}_2\text{O}}} \right)_{P,T} = 18\text{cm}^3$$

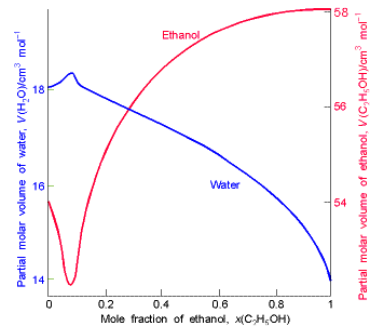
A different answer is obtained if we add 1 mol of water to a large volume of ethanol.

$$\text{The change in volume is } 14\text{cm}^3 \quad V_{\text{H}_2\text{O}} = \left(\frac{\partial V}{\partial n_{\text{H}_2\text{O}}} \right)_{P,T,n(\text{CH}_3\text{CH}_2\text{OH})} = 14\text{cm}^3$$

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PARTIAL MOLAR QUANTITIES

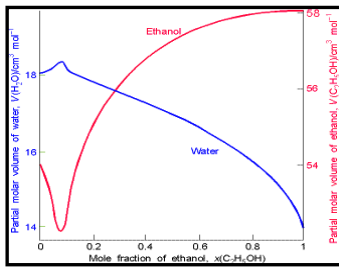
V_A is not generally a constant; it is a function of composition



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Gibbs-Duhem (later)

$$X_{\text{EtOH}} \left(\frac{\partial \bar{V}_{\text{EtOH}}}{\partial n_{\text{EtOH}}} \right)_{T,P,n_{\text{H}_2\text{O}}} = -X_{\text{H}_2\text{O}} \left(\frac{\partial \bar{V}_{\text{H}_2\text{O}}}{\partial n_{\text{H}_2\text{O}}} \right)_{T,P,n_{\text{EtOH}}}$$



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

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partial molar quantities in biology

Proc. Natl. Acad. Sci. USA
Vol. 84, pp. 7938-7942, November 1987
Biophysics

The partial molar volume of water in biological membranes

(phospholipid/intermolecular forces/van der Waals/repulsive forces)
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Communicated by Bryce Crawford, Jr., July 26, 1987

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 interpenetration 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_2 and L_3 phases of dimyristoyl phosphatidylcholine and the L_2 phase of egg phosphatidylcholine. The partial molar volume of water depends critically on the degree of lipid hydration and the presence of tails between the head groups of adjacent lipids. The calculated head-group spacings at minimum hydration are consistent with those obtained from osmotic deflection and indicate that the methyl groups of the choline are absent in contact with interpenetrating groups in the spanning 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:

$$d = d_l + d_w \quad (1)$$

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

$$\phi = 1 + (\epsilon - \epsilon_0)(v_0/v)^{-1} \quad (2)$$

where ϵ is the weight fraction of lipid, ϵ_0 and v_0 are the partial specific volumes of lipid and water (8). It is commonly assumed that ϵ_0 and v_0 are both 1 cm³/g. White and King (7) have questioned the last assumption by pointing out that it leads to a value of d for egg phosphatidylcholine (E-PPC) in the L_2 phase that changes by 1 Å over its full hydration range. However, the distance between phosphate groups across the bilayer, d_w , obtained by their analysis of x-ray data of Torbet and Willens (8), does not change by more than 4 Å. Schieber, Jentsch et al. (9) have shown that in the L_2 phase of dimyristoyl phosphatidylcholine (DMPC) d_w is

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partial molar factoids #1 total differentials

- state function differentials for systems of variable composition (still $\sigma_{\text{wotho}}=0$)

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

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

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

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

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partial molar factoids #2 the chemical potential

- 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):

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

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

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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

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

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

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

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 :

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

or

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

[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 + H₂O

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

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

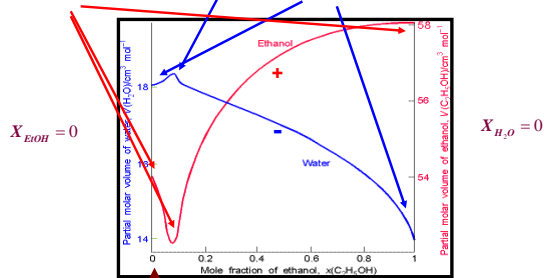
[note : the variation is with respect to one of the components
(∂n_{EtOH} in both denominators)]

[derivation done in class]

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

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



$X_{EtOH} = 0$

$X_{H_2O} = 0$

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

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End of Lecture

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