Biophysical Chemistry for Life Scientists

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Lectures 7 and 8

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Chemical Potentials: From ideal solutions to real systems

- **Ideal solutions**

(A) Gas mixtures

(1) $\mu_A(T) = \mu^\circ_A(T) + RT \ln (P_A/P^\circ), \quad P^\circ = 1$ atm

Standard state: pure A at 1 atm pressure and temperature T. That is, $\mu^\circ_A(T)$ is the molar free energy of pure A at 1 atm pressure and temperature T. The term RT ln (P_A/P°) is the extra free energy arising from the entropy of mixing of the component in the mixture.

(2) $\mu_A(T) = \mu^{\circ\prime}{}_A(T) + RT \ln x_A$

Standard state: pure A at pressure P atm and temperature T

(3) $\mu_A(T) = \mu^{\circ\prime\prime}{}_A(T) + RT \ln (c_A/c^\circ)$,

$c^\circ = 1$ mol/liter

Standard state: pure A at a concentration of 1 mol/liter and temperature T

(B) Liquid (and solid) solutions

$\mu_A(T) = \mu^\circ{}_A(T) + RT \ln x_A$

$\mu_B(T) = \mu^\circ{}_B(T) + RT \ln x_B$

Roault's Law applies: $P_A^{vapor} = P_A^* x_A$

$P_B^{vapor} = P_B^* x_B$

Standard state: pure liquid (or solid) A and B in equilibrium with their vapor pressures, but liquids are under total pressure of 1 atm at temperature T

- **Dilute solutions**

A $\equiv$ solvent; B $\equiv$ solute (low, or essentially no vapor pressure)

Solvent

$$\mu_A(T) = \mu^\circ_A(T) + RT \ln x_A$$

Roault's Law applies: $P_A^{vapor} = P_A^* \, x_A$

Standard state: pure liquid in equilibrium with its vapor pressure at temperature T, but under total pressure of 1 atm

Solute

(1) $$\mu_B(T) = \mu^\circ_B(T) + RT \ln x_B$$

Henry's Law applies: $P_B^{vapor} = k^H_B \, x_B$

k^H_B is Henry's Law constant; offers a measure of solute-solvent interactions, typically strong.

Standard state: hypothetical pure B with the same solute environment as an infinite dilution of B in A, at temperature T and 1 atm pressure.

(2) $\mu_B(T) = \mu^\circ{}_B{}'(T) + RT \ln (m_B/m^\circ{}_B)$

$m^\circ{}_B$ = 1 mole per 1000 gram of solvent

Standard state: hypothetical 1 m solution of B in A with same solute environment as an infinite dilution of B in A, at temperature T and 1 atm

(3) $\mu_B(T) = \mu^\circ{}_B{}''(T) + RT \ln (c_B/c^\circ{}_B)$, $c^\circ{}_B = 1$ M

Standard state: hypothetical 1 M solution of B in A, with same solute environment as an infinite dilution of B in A, at temperature T and 1 atm pressure

- **Colligative Properties of Solutions**

We now present three simple, yet important, examples of the effects of solute on the chemical potential of the solvent (A) in which the solute is dissolved.

(1) Boiling-point elevation

The solute decreases the vapor pressure in equilibrium with the solvent if the temperature T and the pressure P are otherwise unaltered.

$$P_A^{vap} = P_A^{*} X_A \qquad \textbf{(Roault's Law)}$$

where P_A^{*} is the equilibrium vapor pressure of pure solvent A at temperature T and x_A is the mole fraction of the solvent in the liquid. It follows then that at the normal boiling point of the pure solvent T_b^{*}, the equilibrium vapor pressure due to the solvent component in the solution will no longer be 1 atm. Accordingly, it is necessary to increase the temperature of the solution to bring the equilibrium vapor pressure of the solvent component back to 1 atm.

Now,

$$\mu_A^{vapor}(T, P_A) = \mu^{\circ}{}_A^{vapor}(T) + RT \ln P_A^{vapor}, \quad \text{and}$$

$\mu_A^{\text{liquid}}(T, P = 1\text{ atm}) = \mu^\circ{}_A^{\text{liquid}}(T, P = 1\text{ atm}) + RT \ln x_A$

For equilibrium at the boiling point T_b, the solvent molecules in the solution must be in equilibrium with the solvent molecules in the vapor phase, and $P_A^{\text{vapor}} =$ 1 atm. Therefore

$$\mu^\circ{}_A^{\text{vapor}}(T_b) = \mu^\circ{}_A^{\text{liquid}}(T_b, P = 1\text{ atm}) + RT_b \ln x_A$$

<u>Pure solvent:</u>

For pure solvent, $x_A = 1$, $T_b = T_b^* =$ <u>normal</u> boiling point of pure A

$$\mu_A^{\text{vapor}}(T_b, P_A = 1\text{ atm}) \quad = \mu_A^{\text{liquid}}(T_b, P = 1\text{ atm})$$

<u>Solution:</u>

But for $x_A < 1$, we must adjust T_b so that

$$\mu^\circ{}_A^{\text{vapor}}(T_b) = \mu^\circ{}_A^{\text{liquid}}(T_b, P = 1\text{ atm}) + RT_b \ln x_A$$

or $$(1/T_b)[\mu^\circ{}_A^{\text{vapor}}(T_b) - \mu^\circ{}_A^{\text{liquid}}(T_b, P = 1\text{ atm})]$$

$$= R \ln x_A = R \ln (1 - x_B)$$

Recalling that $\mu^\circ{}_A^{\text{vapor}}(T_b) - \mu^\circ{}_A^{\text{liquid}}(T_b, P = 1\text{ atm})$

$$= \Delta\overline{G}^\circ{}_{A,\text{vap}}(T_b, 1\text{ atm})$$

$$= \Delta\overline{H}^\circ{}_{A,\text{vap}}(T_b, 1\text{atm}) - T_b\, \Delta\overline{S}^\circ{}_{A,\text{vap}}(T_b, 1\text{ atm})$$

we obtain the following result for the boiling point

elevation.

$$T_b - T_b^* \equiv \text{boiling point elevation}$$

$$= \left(RT_b^{*2}/\Delta\overline{H}^\circ_{vap,A}\right) x_B$$

For dilute solutions,

$$x_B = (\underline{m}_B M_A)/(1000 + \underline{m}_B M_A) \quad \approx \underline{m}_B M_A/\,1000$$

$$T_b - T_b^* \quad = \quad \left(RT_b^{*2}\, M_A/\,1000 \bullet \Delta\overline{H}^\circ_{vap,A}\right) \bullet \underline{m}_B$$

$$= \quad k_b \bullet \underline{m}_B \quad \text{where } \underline{m}_B \text{ is the molality of solute}$$

Since T_b, M_A, and $\Delta\overline{H}^\circ_{vap,A}$ are known for most solvents, k_b is readily obtained and have been tabulated for a range of solvents. A few examples are:

	k_b
Water	0.514
Benzene	2.67
Acetone	1.67

For water, k_b is quite small due to its low molecular weight and high $\Delta\overline{H}^\circ_{vap,A}$.

Finally, note that the boiling point elevation may be used to infer the molecular weight of a solute. From $T_b - T_b^*$, one obtains the m_B of the solute in the solution, and from the mass of the solute to give m_B, one can infer M_B, the molecular weight of the solute.

(2) Freezing point depression

Similarly, the chemical potential of the solvent is lowered if a solute is added to a pure liquid, and the solution will no longer be in equilibrium with the solid phase, if the solute is not equally soluble in the crystalline phase, at the normal freezing point. To attain new equilibrium, we must lower the temperature such that the chemical potential of the solvent in the pure solid becomes equal to that of the solvent in the liquid solution. The physics is the same as for boiling point elevation. At equilibrium, we require

$$\mu^\circ{}_A^{\text{solid}}(T_f, P = 1\text{ atm}) = \mu^\circ{}_A^{\text{liquid}}(T_f, P = 1\text{ atm}) + RT_f \ln x_A$$

if the solute is soluble in the liquid only.

The result:

$$T_f - T_f^* = -(RT_f^{*2} M_A / 1000 \cdot \overline{\Delta H}^\circ_{fusion,A}) \cdot \underline{m}_B$$

$$= k_f \ \underline{m}_B$$

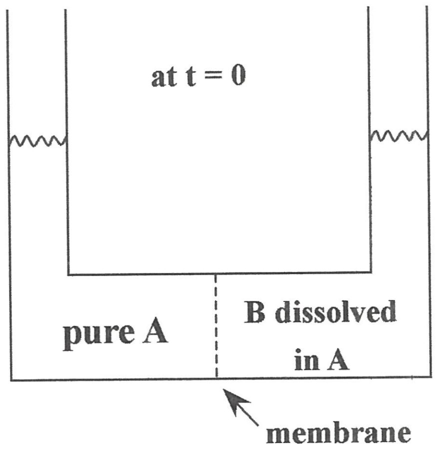
where T_f^* is the normal freezing point of the solvent (A), and $\Delta H^\circ_{fusion,A}$ is the heat of fusion of the solid > 0.

For water, $k_f = -1.86$.

(3) Osmotic pressure

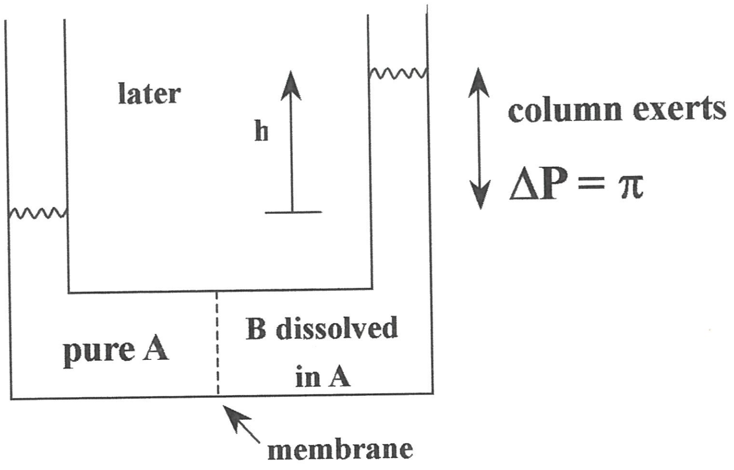
Another way to increase the chemical potential or activity (see later) of the solvent molecules in a solution without adjusting the temperature would be to increase the hydrostatic pressure on the liquid. The incremental pressure needed to increase the chemical potential of the solvent molecules in the solution so that it becomes equal to that of the pure solvent is called the osmotic pressure. Since the concept of osmotic pressure is extremely important in biology, we shall consider this issue in some detail here.

Consider the following experiment (shown in the figure below). Into the base of a U-tube is placed a semi-permeable membrane of a type that will only pass solvent molecules, labeled A. To the right of the membrane is a solution of B in that solute. To the left is pure A.



At time t = 0, let equal heights of the pure solvent and the solution be on the two sides of the membrane. We notice that the solution level on the right rises until the level eventually stabilizes at a certain h above the level of the pure solvent on the left. While the pressure at the top of the pure solvent on the left is 1 atm, that on the bulk solution at the same level is (1 atm + ΔP), where ΔP is the hydrostatic pressure of the solution column of height h. This pressure ΔP =

π, necessary to establish equilibrium between the solvent molecules on both sides of the membrane, is called the osmotic pressure of the solution.



Now, at equilibrium we require

$$\mu_A^{left} = \mu_A^{right}$$

or $\mu_A^{left}(T, 1\ \text{atm, pure A}) = \mu_A^{right}(T, 1\ \text{atm} + \pi, \text{solution})$

where π is the added pressure of the column, as mentioned. Expanding both sides in terms of the same standard state, and assuming ideal solutions, we have

$$\mu^\circ_A(T, 1\ \text{atm}) + RT \ln x_A^{left} = \mu^\circ_A(T, 1\ \text{atm}) + RT \ln x_A^{right}$$

$$+ \int_{1atm}^{1atm+\pi} \overline{V}_A dP$$

where the last term corresponds to $\displaystyle\int_{1atm}^{1atm+\pi} \left(\frac{\partial \mu_A}{\partial P}\right)_T dP$,

$\overline{V}_A$ is the partial molar volume of the solvent at x_A,

and $x_A^{left} = 1$ (pure solvent).

We may assume that $\overline{V}_A^{solution}$ (dilute) $= (\overline{V}_A)_{pure\ solvent}$

$= \text{constant}$

Then $\quad RT \ln x_A^{right} = -\overline{V}_A \bullet \pi$

So for sufficiently dilute solutions,

$$\begin{aligned} \pi &= -(RT/\overline{V}_A) \ln x_A^{right} \\ &= -(RT/\overline{V}_A) \ln(1 - x_B^{right}) \\ &\approx (RT/\overline{V}_A)\, x_B^{right} \end{aligned}$$

and since $x_B = n_B/(n_A + n_B) \approx n_B/n_A \quad (n_B \leq n_A)$

$$\pi \approx (RT/\overline{V}_A)\, n_B/n_A = RT \bullet m'$$

where $m' = n_B/(n_A \overline{V}_A)$ is the "volume molarity" of B in A, i.e., the concentration of B in moles per ml of solvent. Recall π is the incremental pressure on the solution required to increase the chemical potential or

activity of the solvent molecules to be equal to that of the pure solvent at 1 atm at the same temperature.

For low concentrations of solute, 1000 m′ → c, the molarity, i.e., moles of solutes/1000 ml of solution, and

$$\pi \approx (RT/1000) \bullet c \qquad \text{(van't Hoff equation)}$$

Order of magnitude: **In biological systems, the concentration of solutes usually does not exceed 0.4 m in water. For such a solution, vapor pressure of solvent will decrease by 0.27 Torr, very small!**

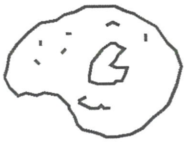
$$P_{water}^{vapor}(38°C) \bullet x_A = 49.69 \text{ Torr x } [55.5/(55/5 + 0.4)]$$

$$= 49.69 \text{ x } 0.9928 \text{ Torr}$$

In contrast, osmotic pressure ≈10 atm!

Osmotic pressure is important in biology!

Red blood cell



osmotic pressure
≅8 atm.
if external medium is
pure H_2O

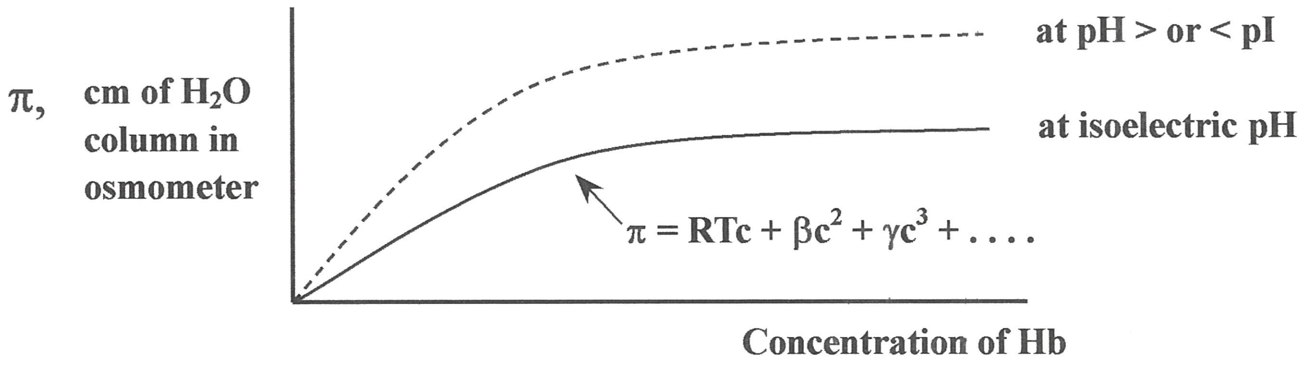
The red blood cell above is said to be in a “hypotonic”

medium. Water will flow into the cell, and pressure will build up to try to reach osmotic equilibrium. Ultimately, the red cell membrane will rupture. The red blood cell actually ruptures before osmotic equilibrium is reached. Only cells with walls to reinforce the membrane are able to withstand such pressures.

"Isotonic" medium	~0.31M sucrose at 37°
"Hypertonic" medium	shrinkage of the cell

Osmotic concentration

So far, we have used the stoichiometric solute concentration in calculating the chemical potential. That is, we have assumed that we are dealing with non-dissociating or non-aggregating solutes. In general, we need to replace m' or c by the osmotic volume molarity $\overline{m}'$, or c by the osmotic molarity $\overline{c}$. An example of a dissociating solute would be an electrolyte such as NaCl, and an example of an aggregating solute would be planar heterocycles or porphyrin molecules. A protein exhibits both behaviors depending on condition. For example, for a solution of hemoglobin (Hb),



At the isoelectric pH, the protein is neutral. At pH's greater than or less than the isoelectric pH, Hb is charged and additional ions are needed to compensated for the charge on the protein. Therefore, $\overline{m}'_{solute} > m'_{Hb}$.

Determination of molecular weights from osmostic pressure

Before we can make a plot of π *vs* m′ plot, we need to know the molecular weight of the solute. If the molecular weight of the solute is not known, one plots π against the concentration of the solute expressed in gram/liter.

Now, $m' =$

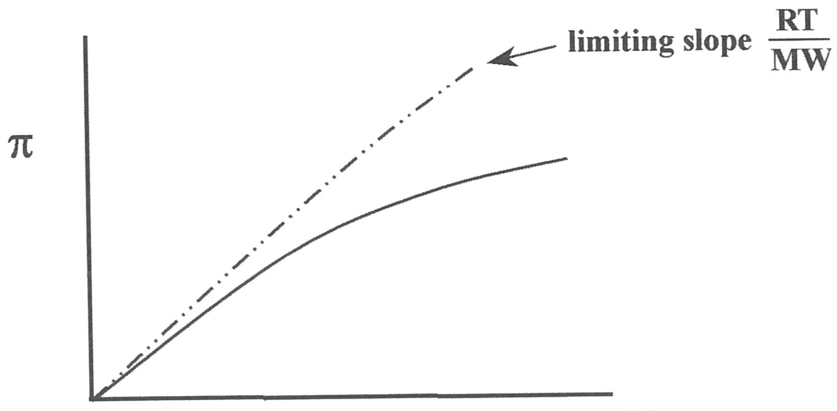
$$\frac{\text{Solute concentration in gram/liter solvent}}{\text{Molecular weight in gram/mole}}$$

$$= g / MW_{solute}$$

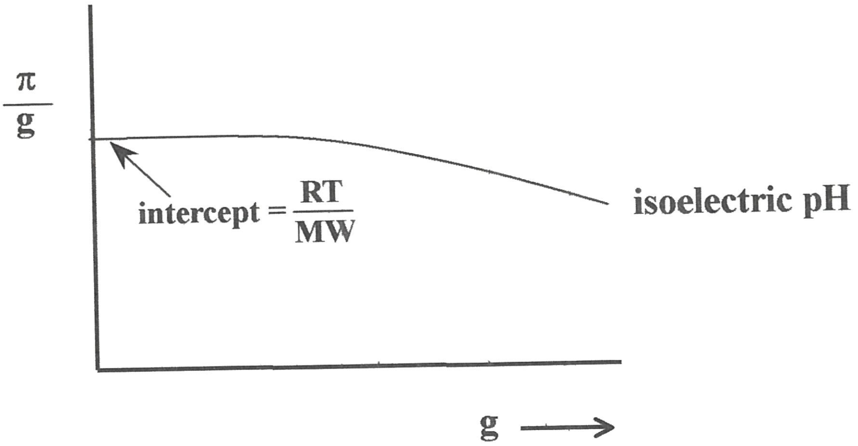
so that

$$\pi = RT\,(g/MW_{solute}) + \text{higher order terms in } (g/MW_{solute})$$

Accordingly, in a plot of π *vs* g , the limiting slope of the curve near g = 0 would be (RT/MW_{solute}).



Usually, because of curvature in the curve, it is more convenient to plot π/g *vs* g.



For Hb. the molecular weight measured by this method was 68,000 Daltons. From the amino acid sequence of the α and β subunits that make up the protein, each with "molecular weight" of 17,000, Hb must be a tetramer of these subunits. It turns out to be $\alpha_2\beta_2$.

Real Systems

We now discuss real systems wherein intermolecular interactions are significant as in a high pressure gas, or in liquid (or solid) solutions where solute-solute interactions are significant, and where solute-solvent interactions might disrupt the solvent structure.

(1) Real gases

Introduce the quantity fugacity such that

$$\mu_A(T) = \mu^\circ_A(T) + RT \ln (f_A/P^\circ)$$

where $f_A \equiv$ fugacity of A

We may of course write $f_A = \gamma_A P_A$, where γ_A is the fugacity coefficient. Clearly, $\lim_{P \to 0} f_A/P_A \to 1$

The fugacity coefficient γ_A provides a measure of the intermolecular interactions experienced by the A molecules in the mixture. The extra free energy arising from these interactions is just $RT \ln \gamma_A$. Thus, γ_A or $RT \ln \gamma_A$ is a function of P_T and the composition of the gas.

(2) Real Solutions

Introduce the quantity activity a and the activity coefficent γ for both the solvent and solute:

Solvent

$$\mu_A(T) = \mu^\circ_A(T) + RT \ln a_A$$

$$a_A = \gamma_A x_A$$

γ_A is the activity coefficient for the solvent. RT ln γ_A is the extra free energy arising from interactions of the solvent molecules with the solute, including disruption of solvent structure. Clearly $\gamma_A \to 1$ as $x_B \to 0$ (pure solvent).

Solute

$$\mu_B(T) = \mu^\circ_B(T) + RT \ln a_B$$

where $a_B \equiv$ activity of the solute B.

Depending on the standard state used, we may introduce three activity coefficients for the solute:

(i) $a_B = \gamma_B\, x_B$

(ii) $a_B = \gamma_B^m\, (m_B/m^\circ_B)$ **or** $\gamma_B^m\, m_B$

(iii) $a_B = \gamma_B^c\, (c_B/c^\circ_B)$ **or** $\gamma_B^c\, c_B$

Clearly,

$$\gamma_B \to 1 \quad \text{as } x_B \to 0,$$

$$\gamma_B^m \to 1 \quad \text{as } m_B \to 0,$$

$$\gamma_B^c \to 1 \quad \text{as } c_B \to 0,$$

that is, as one approaches infinite dilution.

The γ_B 's provide a measure of the solute-solute interactions, as well as the effects of solute disruption of the solvent structure on the solute-solute interactions.

Gibbs-Duhem Equation

Even at constant temperature and pressure (T and P), the activity of the solvent in a solution is a useful quantity, as it can be used to determine the activity of the solute. It turns out, μ_A and μ_B at constant T and P are related and cannot be varied arbitrarily as the solute concentration is varied. Since in biology, the solute molecules are the molecules of interest, we can from measuring the activity of the solvent, derive some information about the way the biological molecules interact among themselves and with the solvent.

Consider a multicomponent system (gas mixture or solution mixture).

In general, we may write

$$G_{system} = \sum_{\substack{i \\ all\ components}} \mu_i n_i$$

and

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

Previously we wrote

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,\ composition} dT + \left(\frac{\partial G}{\partial P}\right)_{T,\ composition} dP$$

$$+ \sum_i \mu_i dn_i$$

$$= -S_{system} dT + V_{system} dP + \sum_i \mu_i dn_i$$

Clearly, $\sum_i n_i d\mu_i = -\underbrace{S dT + V}_{\text{system}} dP$

Now at constant T and P, right-hand side = 0

$$\therefore \left(\sum_i n_i d\mu_i \right)_{T,P} = 0 \qquad \underline{\text{Gibbs - Duhem equation}}$$

Thus, not <u>all</u> of chemical potentials can be independently varied.

Let's be more specific. Take a two component one-phase system.

Recall $f = c - p + 2 = 2 - 1 + 2 = 3$

f = # of degrees of freedom

Thus if T & P fixed, only 1 other property can be varied. If μ_B is chosen, then μ_A is fixed, i.e., cannot be independently varied. That's what the Gibbs-Duhem equation says. For a 2-component mixture:

$$\boxed{n_A d\mu_A + n_B d\mu_B = 0} \quad \text{at constant T \& P.}$$

<u>Develop this further</u>

Divide by $n_A + n_B$: $\left(\frac{n_A}{n_A + n_B}\right)d\mu_A + \left(\frac{n_B}{n_A + n_B}\right)d\mu_B = 0$

or $X_A d\mu_A + X_B d\mu_B = 0$

Divide by dX_A : $X_A \frac{d\mu_A}{dX_A} + X_B \frac{d\mu_B}{dX_A} = 0$

or $\frac{d\mu_A}{dX_A} \Big/ \frac{d\mu_B}{dX_A} = -\frac{X_B}{X_A}$

so derivatives of μ_A, μ_B with respect to X_A **related simply by** $-\frac{X_B}{X_A}$**.**

This result is completely general, irrespective of whether solution is ideal or non-ideal.

Suppose that $\mu_A(T) = \mu_A{}^{\circ}(T) + RT\,ln X_A$ **(solvent)**

then $\frac{d\mu_A}{dX_A} = \frac{RT}{X_A}$.

Applying Gibbs-Duhem equation:

$$\frac{d\mu_B}{dX_A} = -\frac{X_A}{X_B}\frac{d\mu_A}{dX_A}$$

$$\frac{d\mu_B}{dX_A} = -\frac{d\mu_B}{dX_B} = -\frac{X_A}{X_B} \cdot \frac{RT}{X_A}$$

or $$\frac{d\mu_B}{dX_B} = \frac{RT}{X_B}$$

Integrating: $\mu_B(T) = \text{constant} + RT \ln X_B$

Both Raoult's and Henry's Law satisfy this! But Gibbs-Duhem equation is much more general!

Importance of Gibbs-Duhem equation

The Gibbs-Duhem equation gives a way to determine μ_B of nonvolatile solute from measurements of μ_A, chemical potential of the solvent, which can be obtained from vapor pressure measurements or measurements of osmotic pressure. This is not a big issue for ideal solutions, since μ 's of both the solvent and solute are related to X_B, X_A in a known manner. But this is not the case for a real solution. Let's illustrate this by way of an example.

Example

$$X_B d\mu_B = -X_A d\mu_A$$

$$d\mu_B = \frac{-X_A}{1-X_A} d\mu_A$$

Integrate from infinite dilution to concentration desired.

$$\int_{\substack{infinite\\dilution}}^{concentrated} d\mu_B \quad = \int_{dilute}^{concentrated} -\frac{X_A}{1-X_A}\, d\mu_A$$

For ideal solution, $d\mu_A = \frac{RT}{X_A} dX_A$

So RHS

$$= \int_{dilute}^{concentrated} -\frac{X_A}{1-X_A} \cdot \frac{RT}{X_A} dX_A \;=\; \int_{dilute}^{concentrated} \frac{RT}{X_B} dX_B$$

and we get the trivial solution.

But for real solution

$$d\mu_A = RTd\ln a_A = RTd\ln \gamma_A + RTd\ln X_A$$

Actual problem reduces to one of relating γ_B to a_A's. Take a concrete example: a solution of sucrose in water at molal concentration m_B.

Gibbs-Duhem equation:

$$-n_{solvent}\, d\mu_{solvent} = n_{solute}\, d\mu_{solute}$$

$$n_{solvent} = 1000\ gram / 18 = 55.51\ mols$$
$$if\ n_{solute} = m_B$$

so $$55.51\, d\mu_A = -m_B\, d\mu_B$$

Now $$d\mu_A = RT d \ln a_A$$

$$d\mu_B = RT \overset{d}{\wedge} \ln a_B = RT d \ln \gamma_B + RT d \ln m_B$$

Substituting,

$$-55.51\, d \ln a_A = m_B d \ln m_B + m_B d \ln \gamma_B$$

Need to integrate, but nontrivial because of singularities as $m_B \to 0$.

We get around this by introducing molal osmotic coefficient (ϕ). The molal osmotic coefficient was first introduced in 1918 by Bjerrum:

$$\boxed{\phi = -\frac{X_A}{X_B} \ln a_A} \qquad (\text{A} \equiv \text{solvent})$$

In aqueous solution

$$\frac{X_A}{X_B} = \frac{n_A \text{ in 1000 grams of solvent}}{m_B}$$

$$= \frac{1000/18}{m_B} \qquad \textbf{in } \mathbf{H_2O}$$

$$= \frac{55.51}{m_B} \qquad \textbf{in } \mathbf{H_2O}$$

$$\therefore \boxed{\phi = -\frac{55.51}{m_B} \ln a_A}$$

Since $d(m_B\phi) = \phi dm_B + m_B d\phi = -55.51\ d\ln a_A$

$$\phi dm_B + m_B d\phi = m_B d\ln m_B + m_B d\ln\gamma_B$$

Dividing by m_B **and rearranging**

$$d\ln\gamma_B = (\phi - 1) d\ln m_B + d\phi$$

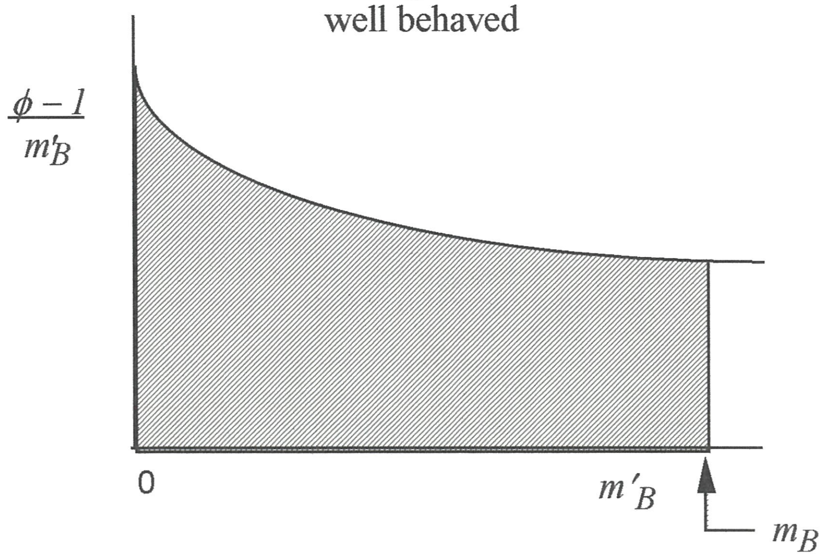
Integrating

$$\int_{\underset{\text{infinite dilution}}{\uparrow\ 1}}^{\gamma_B} d\ln \underset{\substack{\uparrow \\ \text{dummy variable}}}{\gamma'_B} = \int_0^{m_B} (\phi - 1)\, d\ln m'_B + \int_1^{\phi} d\phi'$$

lower limit: infinite dilution $m_B \to 0,\ \gamma_B \to 1$

$$\phi \to \frac{-55.51\ \ln X_A}{m_B} = +\frac{55.51\, X_B}{m_B} = \frac{55.51}{m_B}\ \frac{m_B}{m_B + 55.51} \cong 1$$

$$\int_1^{\gamma_B} d\ln \gamma'_B = \int_0^{m_B} \underset{\text{integrand well behaved}}{\frac{(\phi - 1)}{m_{B'}}} dm'_B + (\phi - 1)$$



Now **ϕ or a_A** can be deduced from vapor pressure of the solvent.

Solvent: $\mu_A(T) = \mu_A{}^{\circ}(T) + RT\, ln\, a_A$

Vapor in equilibrium:

$$\mu_A(T,\ gas) = \mu_A{}^{\circ}(gas,\ T) + RT\, ln\, f_A$$

At equilibrium,

$$\mu_A{}^{solvent}(T) = \mu_A(T,\ gas)$$

or $\underline{\mu_A{}^{\circ}(T)} + RT\, ln\, a_A = \underline{\mu_A{}^{\circ}(gas,\ T)} + RT\, ln\, f_A$

pure solvent: $a_A = 1$ and $\mu_A{}^{\circ}(T) = \mu_A{}^{\circ}(gas,\ T) + RT\, ln\, f_A{}^*$

So $a_A = \dfrac{f_A}{f_A{}^*} \cong \dfrac{P_A}{P_A{}^*}$

Physical meaning of the molal osmotic coefficient (ϕ)

We now show that the molal osmotic coefficient ϕ could be related to the ratio of the true molality of the solution to the stoichiometric molality.

Now for a sufficiently dilute solution,

$$a_A = \gamma_A x_A \approx x_A \quad \text{and}$$

$$-\ \ln a_A \approx -\ln x_A = -\ln(1 - \overline{x_B})$$

where $\overline{x_B} \equiv$ the "true" osmotic mole fraction.

In general, $\overline{x_B}$ can be significantly different from x_B, The stoichiometric mole fraction x_B, if, for example, the solute molecule associate or dissociate.

Therefore,

$$\phi = - (x_A / x_B) \ln x_A = - (x_A / x_B) \ln (1 - \overline{x_B})$$

or $\phi \approx + \overline{x_B} / x_B$ for $x_A \rightarrow 1$ and $\ln(1 - \overline{x_B}) \approx - \overline{x_B}$

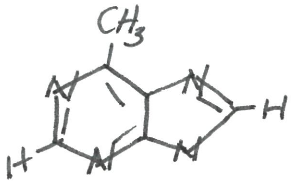
<u>or</u> $\phi \approx \overline{m_B} / m_B$

= true molality of solution/ stoichiometric molality

So, molal osmotic coefficient has a physical meaning!

<u>An interesting example</u>

Nucleic acid bases, nucleosides and nucleotides aggregate in aqueous solution. It turns out they stack. The equilibrium constants of association between these molecules are of interest, as is the average number of molecules in a "stack". Chan and Ts'o measured ϕ as a function of m_B for a number of these nucleic acid bases, nucleosides, and nucleotides. Reference: Chan and Ts'o, J. Am. Chem. Soc. 86, 4176 (1964).



Data for 6-methylpurine

m_B	ϕ
0.0517	0.785
0.116	0.665
0.302	0.515
0.702	0.400

Chan and Ts'o postulated the following multiple equilibrium to account for the observations:

$$M_1 \quad + \quad M_1 \quad \leftrightarrow \quad M_2 \qquad K_2$$

monomer dimmer

$$M_2 \quad + \quad M_1 \quad \leftrightarrow \quad M_3 \qquad K_3$$

$$M_3 \quad + \quad M_1 \quad \leftrightarrow \quad M_4 \qquad K_4$$

$$\vdots$$

$$M_{n-1} \quad + \quad M_1 \quad \leftrightarrow \quad M_n \qquad K_n$$

According to this model,

$$\overline{m} = m_1 + m_2 + m_3 + m_4 + \ldots m_n$$

$$m = m_1 + 2m_2 + 3m_3 + 4m_4 + \ldots nm_n$$

Also, $\gamma_B{}^m = m_1 / m$!

If assume $K_2 = K_3 = K_4 = \ldots . = K_n = K$,

Chan and Ts'o obtained $K = 6.7\ \underline{m}^{-1}$ and $5 < N < \infty$

for 6-methylpurine.

Other compounds

Compounds	K, $\underline{m}^{-1}$	N
purine	2.1	$5 < N < \infty$
6-methylpurine	6.7	$5 < N < \infty$
adenosine	4.5	$5 < N < \infty$
uridine	0.61	$5 < N < \infty$
cytidine	0.87	$5 < N < \infty$
5-bromouridine	$K_1 = 1.0$ $\overline{K} = 2.9$	$N = 4$
urea	0.041	—

From these results, Chan and Ts'o concluded that "stacking" interactions are stronger for purine than for pyrimidine bases!