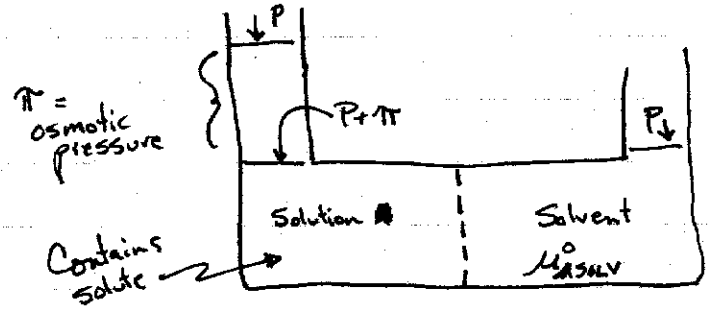
11/3/99

Mutaz → dropped 11/3

Classic Picture



Start w/ picture balanced

$$\mu_{SOLVENT}(P+\pi) = \mu_{SOLVENT}(P)$$

The presence of the solute lowers the activity of the solvent by Z

$$\Delta\mu_{OSM} = \mu_A(\text{sol'n}, P) - \mu_A^{\circ}(\text{pure}, P) = RT \ln a_{A,S}$$

But for equilib, total μ must be the same on both side

Answer: apply pressure to increase solvent activity

From before

$$\Delta\mu = \bar{G}_2 - \bar{G}_1 = \int_{P_1}^{P_2} \bar{V}\, dP = \bar{V}(P_2 - P_1)$$

$$\therefore \quad \Delta\mu_{OSM} = RT \ln a_{A,SOLV} = \int_{1}^{1+\pi} \bar{V}_{A,SOLV}\, dP = -\bar{V}_{A,SOLV}\,\pi$$

$$\therefore \quad \ln a_{A,SOLV} = \frac{-\pi \bar{V}_{SOLV}}{RT}$$

For dilute sol'ns, $a_{SOLV} \approx 1$

$$\ln a_{SOLV} = \ln X_{SOLV} = \ln(1 - X_{SOLUTE}) \approx -X_B \quad (X_{SOLUTE} \approx 0)$$

$$\ln a_{SOLV} \approx -X_B = -\frac{n_B}{n_A + n_B} \approx -\frac{n_B}{n_A}$$

$$\therefore \quad -\frac{n_B}{n_A} \approx -\frac{\pi \bar{V}_{SOLV}}{RT}$$

OR

$$\pi = \frac{RT}{n_{SOLV} \bar{V}_{SOLV}} n_B \qquad \text{but } n_{SOLV} \bar{V}_{SOLV} \approx V_{TOTAL}$$

$$\therefore \quad \pi \approx RT \frac{n_B}{V}$$

$$= \underset{(\text{MOLAR})}{C} RT$$

Example

if $C = 0.5\,M$ at $37^\circ C$

then $\pi \approx 13$ atm

Post-Lecture Note:

Remember that the activity of a pure solvent at standard temp and pressure is 1.

Therefore $RT \ln a_{SOLV}^{PURE} = 0$!

Why? $\Delta\mu_{SOLN} = \mu_{SOLV}(\text{sol'n, 1 atm}) - \mu^{\circ}_{SOLV}(\text{solv}$

$= RT \ln a_A$

$RT \ln a_{SOLV}^{SOLN} - RT \ln a_{SOLV}^{PURE}$

$= 1$!

Chapter 6 — Why?

Remember that thermo describes the overall/average behaviour of a large collection of molecules.

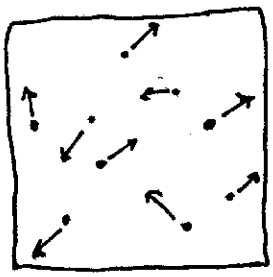
Thermo, in the end, really deals with the overall energetics of different states represented above.

KINETICS is both the other half of the story and the underlying basis for thermo.

Now we'll look at how individual molecules are constantly moving. (We'll still deal with average behaviors).

KINETIC THEORY — Easiest example? Gases

IDEAL GAS → No interactions between molecules
↳ dilute and infinitely small
Collisions with container considered



Gases

Maxwell-Boltzmann Theory - probability, molecular velocities, Kinetic energy } average

Pressure ≡ Collisions

Translational Kinetic Energy ⇒ $U = \frac{1}{2} m u^2$ ($K.E. = \frac{1}{2}mv^2$)

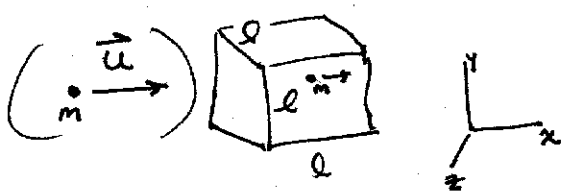
m: mass, u: velocity

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{f}{A}$$

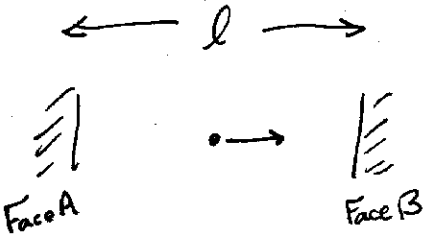
Newton's Law ⇒ $f = ma = \frac{d(mu)}{dt}$ (momentum)

(Remember that above f, u, and a are vectors $\vec{f}$ $\vec{u}$ and $\vec{a}$)

Perspective of one atom/molecule



Look x-component of velocity vector, u_x.



Atom collides with face B

$\frac{u_x}{2l}$ ≡ collisions/sec

Momentum component ≡ mu_x

Change in momentum per collision = $2mu_x$

Then f_x = (momentum change/collision) × (# collisions/sec) $\equiv \frac{dp}{dt}$

$$= (2mu_x) \times \left(\frac{u_x}{2l}\right)$$

$$= \frac{mu_x^2}{l}$$

Pressure $\Rightarrow$ $P_x = f_x/A = \frac{f_x}{l^2} = \frac{mu_x^2}{l^3}$ (per molecule)