

Chapter 5 - ΔG and Equilibria

Didn't we just do that?

↳ Yes, this chapter presents a lot of concrete examples. Applications

Will use concepts from Chapters 2-4 specifically → chemical potential (new, from Chapt 4)

Phases: oil-water
water-membrane
water-membrane-water (a cell)!

If chemical A has different chemical potentials in two phases, then it ~~"must"~~ "can" ← why "can"?
move spontaneously towards equalizing the potentials (i.e. to reach equilibrium).

Phase Equilibria

Evaporation of liquid water (water molecule being transported from the liquid phase to the gas phase).

Similarly we talked about experiments transferring some solute (small molecule) from hexane to water.

Phase Separations — Ask for examples

Oil and water (vinegar)

Detergent micelles and water

Lipid membrane bilayers

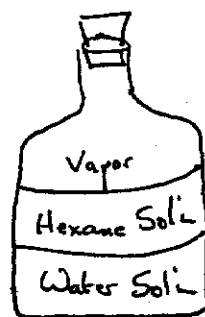
Protein folding

DNA folding

Simple/ideal system for example:

Why "hexane solution"?

Because water and hexane are
not completely immiscible



$$X_{\text{hexane in water}} = 2.1 \times 10^{-6}$$

$$[\text{hexane}] \text{ in water} = 3.8 \times 10^{-8} \text{ M} \quad (\text{compare w/ } \underline{55\text{M}} \text{ water})$$

Similarly, water has limited miscibility with hexane...

How many phases?

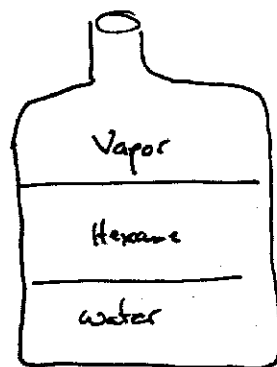
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Equilibria with vapor phase too.

At 25°, $P_{H_2O} = 25.76 \text{ Torr}$

$P_{\text{hexane}} = 150.8 \text{ Torr}$

At equilibrium, each component must have the same chemical potential in each/all 3 phases



e.g.

$$\bar{G}_{\text{Hexane}}(\text{hexane sol'n}) = \bar{G}_{\text{Hexane}}(\text{water sol'n}) = \bar{G}_{\text{Hexane}}(\text{gas})$$

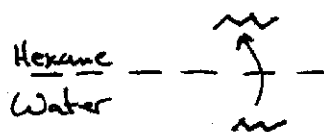
Why?

Remember $\bar{G}_A = \left(\frac{\partial G}{\partial n_A} \right)_{T,P,n_j \neq n_A}$

Partial molar free energy

If $\bar{G}_{\text{Hexane}}(\text{hexane sol'n}) = 10 \text{ kJ/mol}$

and $\bar{G}_{\text{Hexane}}(\text{water sol'n}) = 5 \text{ kJ/mol}$



unbalanced
phony $\Rightarrow$

then we could transfer a mole of hexane from water sol'n to hexane sol'n

We'd pay 5 kJ to remove water from water sol'n but we'd gain 10 kJ to place water ~~into~~ into the hexane solution $\rightarrow$ net gain of 5 kJ/mole.

There would be a driving force

Overall system could reach a lower energy
by appropriate transfer
(ie. to reach equilibrium)

So ~~the~~ for equilibrium, the chemical potential
of each species must be the same
in the two (or more) phases.

Remember: $\mu_A = \mu_A^\circ + RT \ln a_A$

If we use the same reference μ_A° for both,
then

$$\mu_A(\text{phase 1}) = \mu_A^\circ + RT \ln a_A(\text{phase 1}) = \mu_A(\text{phase 2}) = \mu_A^\circ + RT \ln a_A(\text{phase 2})$$

which simplifies to: $a_A(\text{phase 1}) = a_A(\text{phase 2})$

$\Rightarrow$ the activities must be equal.

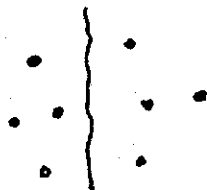
If γ_A is the same on both sides (Not true
above), then $\gamma_A C_A(\text{phase 1}) = \gamma_A C_A(\text{phase 2})$

$$\Rightarrow C_A(\text{phase 1}) = C_A(\text{phase 2})$$

BUT READ IT.

→ (p. 200-201)
 Skip section — tells us about saturated solutions and how free energies of transfer are measured...

Transfer between
Same Solvents



Math tells us:

$$\Delta \bar{G} = \mu_A(\text{phase 2}) - \mu_A(\text{phase 1})$$

$$= RT \ln \frac{a_A(\text{phase 2})}{a_A(\text{phase 1})}$$

Intuition/statistics tells us:

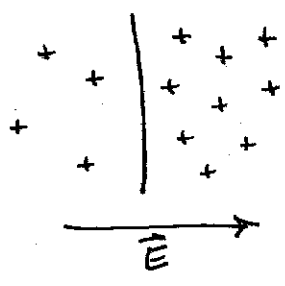


When a molecule randomly crosses the (solid line) interface, it can cross from one side to the other.

It will be statistically much more likely to observe "right to left" crossing than "left to right" simply because there are more on the right (higher activity).

That was with free, unbiased diffusion.

Additional factor:
the applied voltage
biases the diffusion
(i.e. alters the overall
energetics).



$$\Delta \bar{G} = \mu_A(\text{phase 2}) - \mu_A(\text{phase 1}) + FZV$$

difference in
electrical
potential

↑ ↑
 Faraday
Constant charge
96,485 C/V on
 species

$$= RT \ln \frac{a_A(\text{phase 2})}{a_A(\text{phase 1})} + FZV$$

If we talk about the electrical potential on each side (remember, it's only the difference that we're really interested in):

$$V = \phi_2 - \phi_1$$

then

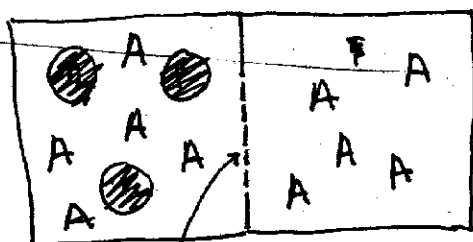
$$\Delta \bar{G} = \overset{\mu_A^\circ}{\underset{\sim}{RT \ln a_A(\text{phase 2})}} - \overset{\mu_A^\circ}{\underset{\sim}{RT \ln a_A(\text{phase 1})}} + FZ\phi_2 - FZ\phi_1$$

$$= \underbrace{(\mu_A + ZF\phi)}_{\mu_A^{\text{TOTAL}}}(\text{phase 2}) - \underbrace{(\mu_A + ZF\phi)}_{\mu_A^{\text{TOTAL}}}(\text{phase 1})$$

$$\mu_A^{\text{TOTAL}}(\text{phase 2}) - \mu_A^{\text{TOTAL}}(\text{phase 1})$$

Very important in many membrane transport phenomena:
(H^+ , metabolites⁺ or ⁻, DNA, proteins w/ net charge, ...)

Equilibrium Dialysis ← the "right" way to do binding measurements



(dialysis)
Semi-permeable membrane:
permeable to small solutes
(impermeable to large proteins)

At equilibrium:

$$\mu_A(\text{left}) = \mu_A(\text{right})$$

If we use same μ_A° then

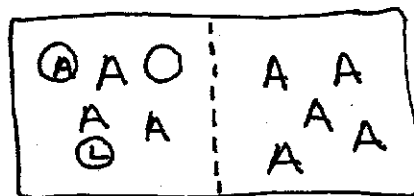
$$a_A(\text{left}) = a_A(\text{right})$$

If ~~same~~ no interactions on either side:

$$C_A(\text{left}) = C_A(\text{right})$$

But what if there are interactions?

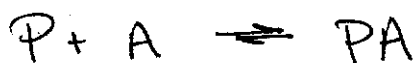
e.g. P binding to a protein-



So L will flow from right to left until

$$a(\text{left}) = a(\text{right})$$

New free concentration (activity) is higher on right than on left



$$K = \frac{a_{PA}}{a_P a_A} = \frac{C_{PA}}{C_P C_A}$$

↑
"free conc"