

11/21

Polymer free energy on stretching
interconversion of heat \rightleftharpoons work

$$\Delta A = \Delta U - T \Delta S \quad \text{General expression for } \Delta A$$

But $\Delta U = 0$ for polymer stretch (experimentally verified)

$$\Delta A = -T \Delta S$$

= reversible work of stretching (isothermal)

Consider a rubber band with a spring constant

$$k = 10 \text{ dyne/cm} \Rightarrow \text{stretch it } 10 \text{ cm (isothermally)}$$

Work is done on the system (the rubber)

vis:

$$w = \int_0^{10} (10) dx = 10 \frac{10^2}{2} = 5 \times 10^5 \text{ erg}$$

work is done on the system \Rightarrow free energy increases

Since $\Delta A = -T \Delta S \Rightarrow$ makes sense that ΔA is \oplus

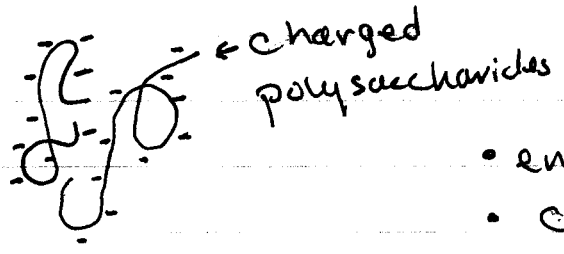
because, for stretching, ΔS is \ominus and

$$-T \Delta S = +5 \text{ erg} = Q_{\text{rev}}$$

$T \Delta S$ represents the reversible heat exchanged with the environment during isothermal stretching

11/21

Consider compressive resistance of cartilage



- entropic
- charge repulsion

lets now consider some chemical properties
start w/ macro model

STANDARD STATES REVISITED

For ideal solution we know

$$\mu_A = \mu_A^\circ + RT \ln x_A$$

standard state: $x_A = 1$

More convenient: $\mu_A = \mu_A^\circ + RT \ln C_A$ $C_A [] \frac{\text{moles}}{\text{vol}}$

For example - 1 ~~n~~ M EGF is a typical concentration
rarely use $10^{-11} = x_{EGF}$

Consider a 2-component solution

$$C_A = x_A C \quad C = \text{total conc}^n \text{ of species, } \frac{\text{moles}}{\text{vol}}$$

$C_B = x_B C$ C is NOT constant over wide range
of x_A (unless A & B have identical molar volumes)

Now, with standard state of C_0 defined as "1"
in the units of C

$$\mu_A = \mu_A^\circ + RT \ln \frac{C_A}{C_0} = \mu_A^\circ + RT \ln C_A$$

$$\mu_B = \mu_B^\circ + RT \ln \frac{C_B}{C_0} = \mu_B^\circ + RT \ln C_B$$

Consider dilute solutions

$$x_A \ll 1 \quad x_B \approx 1$$

Thus $c \approx \text{const} \approx c_B$

Then chemical potentials become

$$\begin{aligned} \mu_A &= \mu_A^\circ + RT \ln x_A \frac{c}{c_0} = \mu_A^\circ + RT \ln x_A + RT \ln \frac{c}{c_0} \\ \mu_B &= \mu_B^\circ + RT \ln x_B \frac{c}{c_0} = \mu_B^\circ + RT \ln x_B + RT \ln \frac{c}{c_0} \end{aligned}$$

constant
for dilute

is it ok to redefine μ ?

Yes - if you are adding a constant μ are in one phase.

a little proof

Gibbs-Duhem

at const T, P

$$G = n_A \mu_A + n_B \mu_B$$

$$dG = n_A d\mu_A + \mu_A dn_A + n_B d\mu_B + \mu_B dn_B$$

Fundamental eqⁿ for G

$$dG = VdP - SdT + \sum \mu_i dn_i$$

const T, P, 2 components

$$dG = \mu_A dn_A + \mu_B dn_B$$

Comparing equations; we see

$$n_A d\mu_A + n_B d\mu_B = 0$$

Gibbs Duhem

Also
divide
by n

$$x_A d\mu_A + x_B d\mu_B = 0$$

Gibbs-Duhem, note version

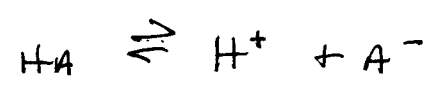
Does new expression fit Gibbs Duhem?

$$\mu_A = \mu_A^\circ + RT \ln x_A c/c_0 \qquad \mu_B = \mu_B^\circ + RT \ln (1-x_A) c/c_0$$

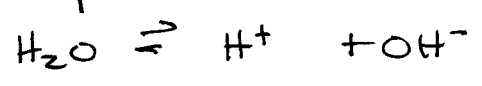
$$\frac{d\mu_A}{dx_A} = \frac{RT}{x_A} \qquad \frac{d\mu_B}{dx_B} = \frac{-d\mu_B}{dx_A} = -\frac{RT}{x_B}$$

Plug in to G-D: $x_A \left(\frac{RT}{x_A} dx_A \right) + x_B \left(-\frac{RT}{x_B} dx_A \right) = 0 \quad \checkmark$

So on to using this in real dilute solutions
 Ionization of weak acids



Consider pure water.



unusual in that H_2O is also the solvent

if pure water, $[H^+] \approx 10^{-7} M$ so solution is ideal ^{dilute}

We can thus use

$$\mu_j = \mu_j^\circ + RT \ln c_j$$

Dissociation rxn: $\Delta G = \mu_{H^+} + \mu_{OH^-} - \mu_w$

$$= \underbrace{[\mu_{H^+}^\circ + \mu_{OH^-}^\circ - \mu_w^\circ]}_{\Delta G^\circ} + RT \ln \underbrace{\frac{[H^+][OH^-]}{[H_2O]}}_{K_w}$$

Since $[H_2O]$ is a const \Rightarrow set $[H_2O] = 1M$

This gets absorbed into def of μ_w°

For std $[H_2O] = 1M$

$$\Delta G^\circ = -RT \ln K_w = -RT \ln [OH^-][H^+]$$

For pure H_2O at $25^\circ C \Rightarrow K_w = 10^{-14} M$
 $[OH^-][H^+] = 10^{-14}$
 $[H^+] = 10^{-7}$
 $pH = -\log [H^+] = 7$

what is pH of pure water @ $37^\circ C$
 Van't Hoff equation

$$\left. \frac{d \ln K}{dT} \right|_P = -\frac{\Delta H^\circ}{R} \quad \text{for } \Delta H^\circ \approx \text{const wrt } T$$

$$\ln \frac{K_{T_2}}{K_{T_1}} = -\frac{\Delta H}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$\Delta H_{H_2O}^\circ (25^\circ C) = 55.84 \text{ kJ/mol}$$

For $T_2 = 37^\circ C$:

$$\ln \frac{K_{37}}{10^{-14}} = \frac{-55,840}{8.314} \left(\frac{1}{310} - \frac{1}{298} \right)$$

$$K_{37} = 10^{-14} e^{0.87} = 2.4 \times 10^{-14} = [H^+]^2$$

$$[H^+] = 1.5 \times 10^{-7} M$$

$$pH = 6.81$$

in fact, you never have pure water
 mostly care about water with other solutes
 then

$$\mu_j = \mu_j^\circ + RT \ln \gamma_j C_j = \mu_j^\circ + RT \ln \gamma_j + RT \ln C_j$$

if γ_j is ~ const over conditions used, can include
 in μ_j° , per Gibbs - Duhem

$$\mu_j = \mu_j^{\circ'} + RT \ln C_j$$

so for example, one can show (see silkey text)

$$\log \gamma_{H^+} = \frac{-A I^{1/2}}{1 + 1.6 I^{1/2}}$$

- A = Debye const
- I = ionic strength
 $= \frac{1}{2} \sum m_i z_i^2$
- m_i = molal concⁿ
- z_i = charge

$$\begin{aligned} \rightarrow \text{pH}_a &= -\log \gamma_{H^+} [H^+] \\ &= -\log [H^+] + \frac{A I^{1/2}}{1 + 1.6 I^{1/2}} \end{aligned}$$

what you measure w/ pH electrode

Easiest to define expts @ standard state

$$\mu_j = \mu_j^\circ + RT \ln c_j$$

↑
includes $\gamma [I]$

$$\Delta G^\circ = RT \ln [H^+][OH^-]$$

$$\text{pH}_c = -\log [H^+]$$

$$\text{pH}_a - \text{pH}_c = \frac{A I^{1/2}}{1 + 1.6 I^{1/2}} \approx 0.1 @ 0.1M \text{ \& } 25C$$