Polymer free energy on stretch

\begin{align*}
\Delta A &= \Delta U - T \Delta S \\
\text{General expression for } \Delta A \\
\text{But } \Delta U &= 0 \text{ for polymer stretch (experimentally verified)} \\
\Delta A &= -T \Delta S \\
&= \text{reversible work of stretching (isothermal)}
\end{align*}

Consider a rubber band with a spring constant \( k = 10 \, \text{dyn/cm} \) \implies stretch it 10 cm (isothermally)

Work is done on the system \( (\text{the rubber}) \) \begin{align*}
W &= \int_0^{10} (10) \, dx \\
&= 10 \times \frac{10^2}{2} = 5 \times 10^5 \, \text{erg}
\end{align*}

Work is done on the system \implies free energy increases

Since \( \Delta A = -T \Delta S \) \implies makes sense that \( \Delta A > 0 \) because, for stretching, \( \Delta S < 0 \) and

\[-T \Delta S = +5 \, \text{erg} = Q_{\text{rev}}\]

\( T \Delta S \) represents the reversible heat exchanged with the environment during isothermal stretching.
Consider compressive resistance of cartilage

- charged polysaccharides
- entropic
- charge repulsion

Let's now consider some chemical properties
Start with macro model

STANDARD STATES REVISITED

For ideal solution we know
\[ M_A = M_A^0 + RT \ln x_A \]
Standard state: \( x_A = 1 \)

More convenient: \[ M_A = M_A^0 + RT \ln C_A \]
\[ C_A \left[ \text{mol} \right] \]

For example - 1mM EGF is a typical concentration
rarely use \( 10^{-11} = x_{EGF} \)

Consider a 2-component solution
\[ C_A = x_A C \]
\[ C = \text{total concn of species, \text{mol} / \text{vol}} \]
\[ C_B = x_B C \]
\[ C \] 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 \( C \)

\[ M_A = M_A^0 + RT \ln \frac{C_A}{C_0} = M_A^0 + RT \ln C_A \]
\[ M_B = M_B^0 + RT \ln \frac{C_B}{C_0} = M_B^0 + RT \ln C_B \]
Consider dilute solutions

\[ x_A < 1 \quad x_B < 1 \]

Thus \( C = \text{const} \approx c_B \)

Then chemical potentials become

\[ \mu_A = \mu_A^0 + RT \ln x_A \frac{C}{c_0} = \mu_A^0 + RT \ln x_A + RT \ln \frac{C}{c_0} \]
\[ \mu_B = \mu_B^0 + RT \ln x_B \frac{C}{c_0} = \mu_B^0 + RT \ln x_B + RT \ln \frac{C}{c_0} \]

Is it OK to redefine \( \mu \)?

Yes - if you are adding a constant \( \Delta \) are in one phase.

A little proof

Gibbs - Duhem

\[ \text{at const } T, P \]
\[ G = n_A \mu_A + n_B \mu_B \]
\[ dG = n_A d\mu_A + n_B d\mu_B + n_A d\mu_A + n_B d\mu_B \]

Fundamental eqn for \( G \)

\[ dG = V dP - S dT + E d\mu_i \]

\[ \text{const} T, P, 2 \text{ components} \]

\[ dG = n_A d\mu_A + n_B d\mu_B \]

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, mole version
Does new expression fit Gibbs-Duhem?

\[ M_A = M_A^0 + RT \ln x_A \quad (c_0) \]
\[ M_B = M_B^0 + RT \ln \left( \frac{X_A}{X_B} \right) \quad (c_0) \]

\[ \frac{dM_A}{dx_A} = \frac{RT}{x_A} \]
\[ \frac{dM_B}{dx_B} = \frac{-dM_B}{dx_A} = \frac{-RT}{x_B} \]

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

So on to using this in real dilute solutions.

Ionization of weak acids:

\[ H_A \rightarrow H^+ + A^- \]

Consider pure water:

\[ H_2O \rightarrow H^+ + OH^- \]

Unusual in that H_2O is also the solvent.

If pure water, \([H^+] = 10^{-7} \text{ M}\) so solution is ideal.

We can thus use:

\[ M_j = M_j^0 + RT \ln c_j \]

Dissociation rxn: \( \Delta G = \Delta G^0 \rightarrow \Delta G \)

\[ \Delta G = \Delta G^0 + RT \ln \left( \frac{[H^+][OH^-]}{[H_2O]} \right) \]

Since \([H_2O]\) is a constant set \([H_2O] = 1 \text{ M}\)

This gets absorbed into \( \Delta G^0 \)

For std \([H_2O] = 1 \text{ M}\)

\[ \Delta G^0 = -RT \ln K_w = -RT \ln \left( \frac{[OH^-]}{[H^+]} \right) \]
For pure H\textsubscript{2}O at 25\textdegree C \Rightarrow K\text{\textsubscript{w}} = 10^{-14} M

\[ \text{[OH}^-][\text{H}^+] = 10^{-14} \]

\[ [\text{H}^+] = 10^{-7} \]

\[ \text{pH} = -\log [\text{H}^+] = 7 \]

what is pH of pure water @ 37\textdegree C

\[ \Delta H^{\circ} \text{ (water) = 85.84 kJ/mol} \]

For \( T_2 = 37\textdegree C \) : 

\[ \ln \frac{K_{37}}{K_{25}} = -\frac{\Delta H^{\circ}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]

\[ \Delta H^{\circ} \text{ (water) = 85.84 kJ/mol} \]

\[ K_{37} = \frac{10^{-14} e^{87}}{8.314} (\frac{1}{310} - \frac{1}{298}) \]

\[ K_{37} = 1.4 \times 10^{-7} M \]

\[ [\text{H}^+] = 1.45 \times 10^{-7} M \]

\[ \text{pH} = 6.81 \]

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

\[ M_j = M_j^o + RT \ln \gamma_j C_j = M_j^o + RT \ln \gamma_j + RT \ln c_j \]

if \( \gamma_j \) is a const over conditions used, can include in \( M_j^o \), per Gibbs = Duhem

\[ M_j = M_j^o' + RT \ln c_j \]
So for example, one can show (see silksy text)

\[
\log \gamma_{H^+} = \frac{-A \frac{I}{12}}{1 + 1.6I^{1/2}}
\]

\(A = \) Debye constant
\(I = \) ionic strength
= \(\frac{Zm_i z^2}{2}\)
\(m_i = \) metal ion conc
\(z = \) charge

\[
\rightarrow pK_a = -\log \gamma_{H^+} \left[ H^+ \right] = -\log \left[ H^+ \right] + \frac{A \frac{I}{12}}{1 + 1.6I^{1/2}}
\]

what you measure with pH electrode

Easiest to define exps @ standard state
\(M_j = M_j^0 + RT \ln C_j\)
^ includes \(vCJ\)

\(\Delta G = RT \ln \left[ H^+ \right] \left[ OH^- \right] \)
\(pH_c = -\log \left[ H^+ \right]\)

\(pH_a - pH_c = \frac{A \frac{I}{12}}{1 + 1.6I^{1/2}} \quad 0.1 \text{ at } 0.1 M \)
\(> 25^\circ C\)