this is known as “linearization”

Fact:

\[
a = \exp \left( \frac{\Pi \bar{V}_A}{RT} \right) = \exp (y) = 1 + y + \frac{y^2}{2!} + \ldots + \frac{y^n}{n!}
\]

Ignore if \( y << 1 \)

\[
\alpha = y_A X_A \approx X_A = 1 - X_B \quad \text{solute}
\]

\[
1 - X_B = 1 - \frac{\Pi \bar{V}_A}{RT} + \text{smaller stuff}
\]

\[
X_B = \frac{\Pi \bar{V}_A}{RT} = \frac{n_B}{n_A + n_B} \approx \frac{n_B}{n_A}
\]

\( n_B << n_A \) (dilute solution)

\[
\frac{\Pi \bar{V}_A}{RT} = \frac{n_B}{n_A}
\]

\[
\Pi V_A n_A = n_B RT
\]

\[
\Pi V_{\text{solution}} = n_B RT
\]
\[ \Pi V_{\text{solution}} = \Pi B \cdot RT \]

or

\[ \Pi \neq \frac{\text{MB} \cdot RT}{V_{\text{solution}}} \]

\[ y_B [B] = 1 \text{ M at } 298 \quad RT = 0.082 \text{ Latm} \times 298 \frac{\text{Latm}}{\text{molK}} \]

\[ \Pi = 25 \text{ atm} \times \frac{2.5 \text{ f} + \text{Hg}}{\text{atm}} \times 13.6 \frac{\text{f} + \text{H}_2\text{O}}{\text{f} + \text{Hg}} = 850 \text{ ft} + \text{Hg} \]
Molecular Wt of Polymer B
from Osmotic Pressure.

\[ \Pi = \frac{n_B \text{ mol B}}{L_{\text{solution}}} \times RT \]

\[ = \frac{K_g B}{L_{\text{sol.}}} \times \frac{\text{mol B}}{K_g B} \times RT \]

\[ \Pi = \left( \frac{K_g}{L} \right) \times \frac{1}{M\left( \frac{K_g}{\text{mol}} \right)} \times RT \]

\[ M\left( \frac{K_g}{\text{mol}} \right) = \left( \frac{K_g}{L} \right) \frac{1}{\Pi} \times RT \]

\[ R = \frac{0.082 \text{ L atm}}{\text{mol K}} \times \frac{760 \text{ mm Hg}}{\text{atm}} \times \frac{13.6 \text{ mm Hg}}{\text{mm Hg}} \]

\[ = 8.48 \text{ mm Hg L mm Hg}^{-1} \text{ mol K} \]

Example

\[ 0.001 \text{ kg L}^{-1} \times \Pi = 8.48 \text{ mm Hg} \]

\[ M = 0.001 \times 8.48 \times 298 = 29.8 \text{ Kg mol}^{-1} \]

\[ = \frac{29800 \text{ g mol}^{-1}}{8.48} \]
Derive \( \Delta T_{\text{freeze}} = -K_{\text{freez}} \frac{m_B}{m.p.} \) for H2O

\[
\ln a = -\frac{\Delta H_{\text{fus}}^0}{R} \left( \frac{1}{T_{\text{mp}}} - \frac{1}{273} \right)
\]

\[
\ln(1-x_B) = -\frac{\Delta H_{\text{fus}}^0}{R} \left( \frac{273 - T_m}{T_{\text{mp}} \cdot 273} \right)
\]

\[
-x_B = \frac{\Delta H_{\text{fus}}^0}{R} \left( \frac{273 - T_m}{T_{\text{mp}} \cdot 273} \right)
\]

\[
\frac{n_B}{n_A + n_B} \left( \frac{n_B}{n_A} \right) \approx \frac{\Delta H_{\text{fus}}^0}{R} \left( -\frac{\Delta T_{\text{mp}}}{273^2} \right)
\]

\( n_B \ll n_A \)

\( T_{\text{mp}} \approx 273 \)

\[
\frac{n_B}{n_A} = K_{\text{fus}}(n_A) = m_B(\text{Molecular weight of species}) = \frac{\Delta H_{f}^0}{R} \left( -\frac{\Delta T_{\text{mp}}}{273^2} \right)
\]

\[
m_B \left[ \frac{M_A R T_{\text{mp}}^2}{\Delta H_{f}^0} \right] = -\Delta T_{\text{mp}}.
\]

\[
= m_B \left( 0.018 \right) \left( 8.314 \right) \frac{273^2}{6007} = -m_B(1.86) = +\Delta T_{\text{mp}}.
\]
NaDNA = Sodium salt of DNA which is a very polyprotic acid.

Donnen Membrane Potential

Initially: Charge balanced $\phi_{in} = \phi_{out}$

$Na^+$ is at equilibrium

$\mu^{Na^+}_{in} = \mu^{Na^+}_{out}$

but $Cl^-$ is NOT at equilibrium

$Cl^-_{out} \rightarrow Cl^-_{in}$ very spontaneous

$\Delta \mu_{Cl^-} = \Delta \mu_{Cl^-}^0 + 5.7 \log \frac{[Cl^-]_{in}}{[Cl^-]_{out}} + (-1) f \Delta \phi_{in-out}$

Equil: $0 = 0 + 5.7 \log \frac{x}{1} - f \Delta \phi$

$x = (Cl^-)_{in}$ negative inside
Equilibrium is reached when negative $\Delta G$ from $\frac{RT \ln [Cl_{in}]}{[Cl_{out}]}$ balances positive $\Delta G$ from $(-1)F\left(\psi_{in} - \psi_{out}\right)$.

Similarly for $Na^+$:

$Na^+$ follows $Cl^-$ in

At equilibrium:

\[ [Na^+]_{eq} = 0.1 \]
\[ [Cl^-]_{eq} = 0.1 \]

\[ Na^+ : 5.7 \log \frac{0.1 + x}{0.1} + (-1)F\Delta \phi = 0 \]

\[ Cl^- : 5.7 \log \left(\frac{x}{0.1}\right) + (-1)F\Delta \phi = 0 \]

Solved by $x = 0.0618 M$

$\Delta \phi = \frac{-5.7}{F} \log \left(\frac{0.1618}{0.1}\right) = -0.0592 \log(1.62) = -0.012 \text{ Volts}$

Charge is nominally balanced $\sim 0.14$ mol more $Cl^-$ than $Na^+$ creates the voltage difference.
Equilibrium:

\[ [\text{Na}^+] = 0.1 \]
\[ [\text{Cl}^-] = 0.1 \]

\[ [\text{Na}^+] = 0.1 + x \]
\[ [\text{Cl}^-] = x \]

\[ \Delta \phi = 0 \]
\[ \text{Solved by } x = 0.0618 \text{ M} \]
\[ \Delta \phi = -5.7 \log(0.0618) = -0.0592 \text{ log(0.62)} \]
\[ -12 \text{ mV} \]

\[ \frac{0.1 + x}{0.1} = \frac{0.1}{x} \]
\[ x^2 + 0.1x = 0.01 \]

**Quadratic equation:** \( x^2 + 0.1x - 0.01 = 0 \)

\[ x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.1 \pm \sqrt{0.01 + 0.04}}{2} = 0.0618 \text{ or } -0.1618 \]
Surface Tension

\[ \gamma = \frac{\text{Change in free energy}}{\text{Change in surface area}} \]

\[ \gamma = \left( \frac{\Delta G}{\Delta A} \right)_{T, P} \]

Examples:
- Hg: 487 mJ/m²
- H₂O: 72
- Hexane: 18

\[ \Delta H_{\text{vap}} \text{ (kJ/mol)} \]
- G1: 44

Problem: Subdivide particle of radius \( r_1 \) into \( n \) particles (spheres). What is \( \Delta G \) for process?

Volume is constant so \( V_2 = V_1 \)

\[ \frac{V_2}{V_1} = \frac{\frac{4}{3} \pi r_2^3}{\frac{4}{3} \pi r_1^3} = \left( \frac{r_2}{r_1} \right)^3 \]

\[ \frac{V_2}{V_1} = \frac{1}{n} \]

New area = \( \frac{4}{3} \pi n r_2^2 = \frac{4}{3} \pi \left( \frac{r_1}{n} \right)^{2/3} \)

\[ = \frac{1}{n^{2/3}} \times \text{old area} \]

1 mol H₂O → 2 μ dm³:

\[ A = 54 m^2 \]

\[ \Delta G_{\text{surface}} = 54 m^2 \times 72 \times 10^{-3} \]

\[ = 3.9 J \]

Ana Yang: Bubble show!

https://www.youtube-nocookie.com/embed/KMrvR836TFI?rel=0
I was going home to dinner, past a shallow pool, which was green with springing grass, . . . when it occurred to me that I heard the dream of the toad. It rang through and filled all the air, though I had not heard it once. And I turned my companion’s attention to it, but he did not appear to perceive it as a new sound in the air. Loud and prevailing as it is, most men do not notice it at all. It is to them, perchance, a sort of simmering or seething of all nature. That afternoon the dream of the toads rang through the elms by Little River and affected the thoughts of men, though they were not conscious that they heard it. How watchful we must be to keep the crystal well that we are made, clear!

THOREAU
Henry Bent

In human thermodynamics education, Henry Albert Bent (c.1927-) was an American physical chemist noted for his 1965 book The Second Law, for his 1971 article “Haste Makes Waste: Pollution and Entropy”, in which he attempts at a connection between the maintenance of the environment and entropy, and for his thermodynamics workshops, where he attempted to educate students on how to live ethically according to the laws of thermodynamics. [1]

Specifically, instead of a national energy policy, Bent states:

"What we need is a personal entropy ethic."
Chapters 2-4, 6, 7: Thermodynamics (equilibrium states)  
All about what is possible or not  
(never whether or how how fast)

Chapters 8-10: Study rate at which physical and chemical processes that are NOT AT EQUILIBRIUM proceed to equilibrium

Chapter 9: Kinetics: rates of chemical reactions

Chapter 8: About processes that depend on how fast molecules move:  
Diffusion  
Sedimentation  
Electrophoresis  
first we examine velocities of molecules
Maxwell-Boltzmann Distribution (of velocities), \( u \)

\[ N(u_x) = \text{number of molecules with velocity, } u_x, \text{ between } u_x \text{ and } u_x + du_x \]

i.e., a frequency distribution

\[ N(u_x) \propto e^{-\frac{E}{K_B T}} = e^{-\frac{1}{2}mu_x^2/KT} \]

A histogram

Speed Distribution

\[ N(u) = e^{-\frac{E}{KT}} = \frac{u^2}{e^{\frac{1}{2}mu_x^2/KT}} \]
Maxwell-Boltzmann Speed Distribution

\[ N(\mathbf{u}) = e^{-\frac{E}{kT}} \cdot \left( u^2 \frac{e^{-\frac{1}{2}m\mathbf{u}^2}}{kT} \right) \]

Speed: \[ u = |\mathbf{u}| \]

\[ \text{degeneracy} \]
\[ \text{Prob}(u) \propto \text{Probability to observe } u \]
\[ \text{between } u \pm \Delta u \]

\[ \langle u \rangle = \text{Average } u \]
\[ \langle u^2 \rangle^{1/2} = u_{\text{rms}} \]

\[ u_{\text{rms}} = \sqrt{\frac{3RT}{M}} \text{ for } N_2 \]

\[ \langle u \rangle = \sqrt{\frac{8}{\pi} \frac{RT}{M}} = \sqrt{2.546 RT} \]

\[ u_{\text{most prob.}} = \sqrt{2 \frac{RT}{M}} \]

\[ = 1200 \text{ K} \]