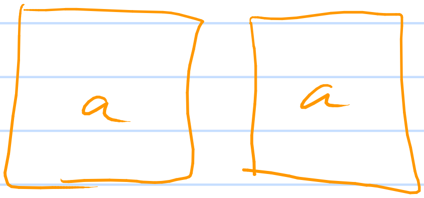
Chapter 5 Free energy and Chemical Thermodynamics

This chapter investigates properties of mixtures, reactions, phase transitions, energies released, ...

Must distinguish between extensive and intensive properties.

Double the system



Some properties double and some are unchanged

Intensive - quantities that don't double P, T, μ, density

Extensive - quantities that double U, V, N, S, mass, ...

extensive x intensive = extensive $V \cdot P$, $N \cdot T$, ...

extensive / intensive = " U/T, $(\partial U/\partial T)$, ...

extensive / extensive = intensive M/V, $(\partial S/\partial U)$, ...

extensive x extensive = nonsense

extensive + extensive OR intensive + intensive are OK

extensive + intensive = nonsense

Section 5.1 Free energy as available work

U - energy needed to bring isolated system at fixed V, N from ground state to to T (rarely of interest)

H (enthalpy) $= U_{ext} + P_{int} V_{ext}$ energy needed to create system and put in environment at const. P (accounts for work to move environment aside)

F (Helmholtz Free Energy) $= U_{ext} - T_{int} S_{ext}$ energy needed to create system minus heat you get (for free) from environment at const T

G (Gibbs Free Energy) $= U_{ext} + P_{int} V_{ext} - T_{int} S_{ext} = H - TS = F + PV$ accounts for both the work and heat from environment

U, H, F, G are thermodynamic potentials - related to energy needed to manipulate the system from one state to another taking into account simultaneous effect on the environment.

See pgs 404-405 for $\Delta G = \Delta H - S\Delta T - T\Delta S$

Prob 5.2 $N_2 + 3H_2 \rightarrow \overset{\text{ammonia}}{2NH_3}$

	ΔH	S	ΔG
N_2	0	191.61 J/K	0
H_2	0	130.68 J/K	0
NH_3	−46.11 kJ	192.43 J/K	−16.45 kJ

$\Delta G = \Delta H - T\Delta S$

$2(-16.45\,kJ) \overset{?}{=} 2(-46.11\,kJ) - 298\,K(2\cdot 192.45 - 3\cdot 130.68 - 191.61)\,J/K$

$-32.90\,kJ \overset{?}{=} -32.99\,kJ$

The changes in U, F, G, H are important $\Delta U = Q + W_{tot}$

Change system at const. T $\Delta F = \Delta U - \overset{0}{\cancel{\Delta T}} S - T\Delta S = \Delta U - T\Delta S$

For quasistatic $Q = T\Delta S$ (in general $Q < T\Delta S$)

$\Delta F = Q + W - T\Delta S \le W$ (W is all work done on system)

Change system at const T and P $\Delta G = \Delta U - \overset{0}{\cancel{\Delta T}} S - T\Delta S + P\Delta V + \overset{0}{\cancel{\Delta P}} V$

$\Delta G = Q + W - T\Delta S + P\Delta V$ $W = W_{env} + W_{you} = -P\Delta V + W_{you}$

$= Q - T\Delta S + W_{you} \le W_{you}$

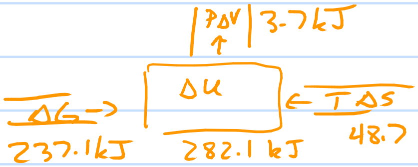
See book example $H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$ $\overset{\text{energy you put in}}{W_{you}} = ?$

	ΔH (kJ)	S (J/K)	ΔG (kJ)
$H_2O(l)$	−285.83	69.91	−237.13
$H_2(g)$	0	130.68	0
$O_2(g)$	0	205.14	0

$\Delta G = \Delta H - T\Delta S$

$W_{you} = 237.13\,kJ = 285.83\,kJ - 298\,K\,(130.68 + \frac{1}{2}205.14 - 69.91)\,J/K$

$= 237.15\,kJ$



You add 237.1 kJ and get

$\Delta U = 282.1\,kJ$

Prob 5.6 $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O(l)$

	ΔH (kJ)	S (J/K)	ΔG (kJ)
$C_6H_{12}O_6$	−1273	212	−910
O_2	0	205.1	0
CO_2	−393.5	213.7	−394.4
$H_2O(l)$	−285.8	69.9	−237.1

(a) $\Delta G = 6(-394.4\,kJ - 237.1\,kJ) - (-910\,kJ) = -2879\,kJ$

$\Delta H = 6(-393.5\,kJ - 285.8\,kJ) - (-1273\,kJ) = -2802.8\,kJ$

(b) $\max(W_{you}) = -\Delta G = 2879\,kJ$

(c) $Q = T\Delta S = 298\,K\,[6(213.7 + 69.9) - 212 - 6\cdot 205.1]$

$= 77.1\,kJ$ into $= \Delta H - \Delta G$

(d) entropy increased

(e) Q decreases, W_{you} decreases (Q might become negative - system gives off heat)

ΔG, ΔH unchanged even though not ideal

Thermodynamic Identities

Chap 3 $dU = TdS - PdV + \mu dN \Rightarrow \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}$ etc

Construct new identities from G, F, H

Examples $dH = dU + PdV + VdP = TdS + VdP + \mu dN$

$dF = dU - TdS - SdT = -SdT - PdV + \mu dN$

$dG = dU + PdV + VdP - TdS - SdT = -SdT + VdP + \mu dN$

Relations $-S = \left(\frac{\partial F}{\partial T}\right)_{V,N}$ $-P = \left(\frac{\partial F}{\partial V}\right)_{T,N}$ $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$

$-S = \left(\frac{\partial G}{\partial T}\right)_{P,N}$ $V = \left(\frac{\partial G}{\partial P}\right)_{T,N}$ $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$

Note that the relations using G all involve derivatives with respect to intensive variables (except N)

Use these relations to extend data in the table pg 404-5

Prob 5.10 1 mole $H_2O(l)$ at $P = 1$ atm and $T = 25°C + 5°C = 303\,K$

$\Delta G(30°C) = \Delta G(25°C) - S\,\Delta T = -237.13\,kJ - 69.91\,\frac{J}{K}\,5K = -237.48\,kJ$

$V\,\Delta P - S\,\Delta T = 0 \Rightarrow V = 18g / 1000 kg/m^3 = 1.8 \times 10^{-5} m^3$

$\Delta P = 69.91 \cdot 5\,J / 1.8 \times 10^{-5} m^3 = 1.94 \times 10^{7} Pa \simeq 194$ atm.

Prob 5.12 Use $\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_{N,V}\right)_{S,N} = \left(\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_{S,N}\right)_{V,N} \Rightarrow \left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}$

$\left(\frac{\partial H}{\partial S}\right) = T$ $\left(\frac{\partial H}{\partial P}\right) = V$ $\Rightarrow \left(\frac{\partial T}{\partial P}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{V,N}$

$\left(\frac{\partial F}{\partial T}\right) = -S$ $\left(\frac{\partial F}{\partial V}\right) = -P$ $\Rightarrow \left(\frac{\partial S}{\partial V}\right)_{T,N} = -\left(\frac{\partial P}{\partial T}\right)_{V,N}$ measure

$\left(\frac{\partial G}{\partial T}\right) = -S$ $\left(\frac{\partial G}{\partial P}\right) = V$ $\Rightarrow -\left(\frac{\partial S}{\partial P}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{P,N}$

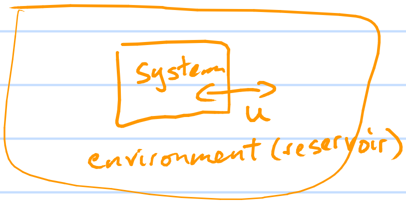
Section 5.2 Free energy as a force toward equilibrium

Environment – huge and acts as a reservoir of energy, pressure

Idea – Account for the environment without having to explicitly redo calculation of system + environment every time.

The relevant thermodynamic potential will depend on what you hold fixed and what is allowed to vary.

Example



Constant T, V, N
energy can go in and out of system
System and environment at same T

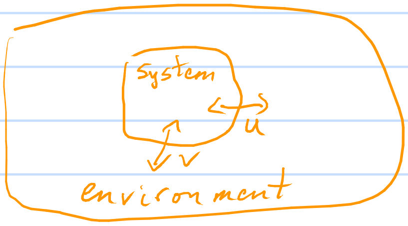
$$dS_{TOT} = \overbrace{dS}^{\text{system}} + \overbrace{dS_R}^{\text{reservoir}}$$

If only energy in/out $dS_R = \frac{dU_R}{T_R} = -\frac{dU}{T}$

$$\Rightarrow dS_{TOT} = dS - \frac{dU}{T} = -\frac{1}{T}(dU - TdS) = -\frac{dF_{\text{system}}}{T}$$

since $dF = dU - TdS - \cancel{SdT}^{\to 0}$

Fixed T, V, N of system $dS_{TOT} = -\frac{dF}{T}$ of system (doesn't depend on reservoir details). We know $dS_{TOT} \geq 0 \Rightarrow dF \leq 0$
⇒ The system goes to the state that minimizes F



Energy and volume of the system can change

For fixed T, P, N $dS_{TOT} = dS + dS_R$ $dS_R = \frac{dU_R}{T_R} + \frac{P_R}{T_R}dV_R = -\frac{1}{T}(dU + PdV)$

$$\Rightarrow dS_{TOT} = -\frac{1}{T}(dU + PdV - TdS) = -\frac{dG_{\text{system}}}{T}$$

since $dG = dU - TdS - \cancel{SdT}^{\to 0} + PdV + \cancel{VdP}^{\to 0}$

Fixed T, P, N of system $dS_{TOT} = -\frac{dG}{T}$ of system ⇒ $dG \leq 0$
⇒ The system goes to the state that minimizes G

Summary If you only look at the system
At constant U, V, N, the system evolves to maximize S
" " T, V, N " " " minimize F
" " T, P, N " " " " G

*Remember this is a shortcut for saying "the system plus environment evolves to maximize S_{TOT}"

Prob 5.18 Free energy KE+PE should evolve to minimum

An extremely important relationship between G and μ

$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} \Rightarrow G = N\mu$ because adding particles at const T, P does not change μ

explain why $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \not\Rightarrow F = N\mu$

or $\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V} \not\Rightarrow S = -N\frac{\mu}{T}$

Example Use $G = N\mu$ to derive form of μ for ideal gas

$$\frac{\partial \mu}{\partial P} = \frac{1}{N}\left(\frac{\partial G}{\partial P}\right)_{T,N} = \frac{V}{N} = \frac{kT}{P} \Rightarrow \mu(T,P) - \mu(T,P_0) = k_B T \ln(P/P_0)$$

P_0 is reference pressure

$$\mu(T,P) = \mu(T,P_0) + k_B T \ln(P/P_0) = \mu_0(T) + kT\ln(P/P_0)$$

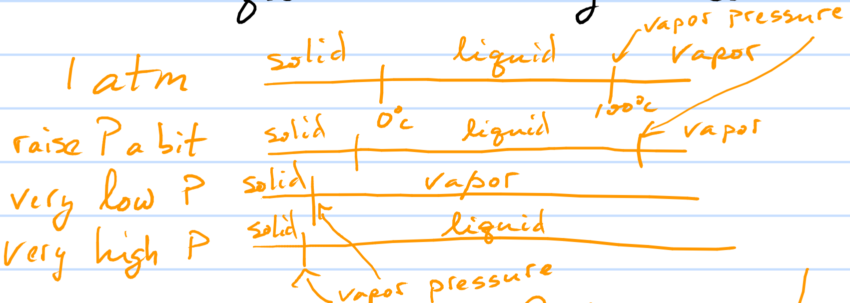
Example Find ΔG for 1 mole H_2 at 298 K and 3 atm

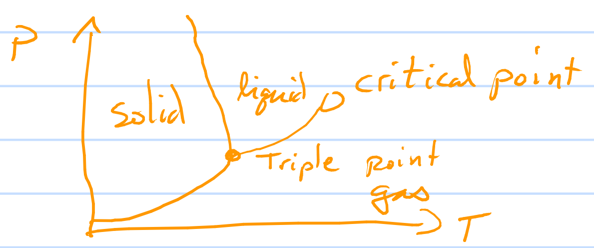
$$\mu(298\text{ K}, 3\text{atm}) = \mu_0(298\text{ K}) + kT\ln(3)$$

$$\Delta G(298\text{ K}, 3\text{atm}) = \Delta G_{table} + 8.31\tfrac{\text{J}}{\text{K}}\,298\text{ K}\ln 3 = \overset{0\text{ kJ}}{\Delta G_{table}} + \underline{2.72\text{ kJ}}$$

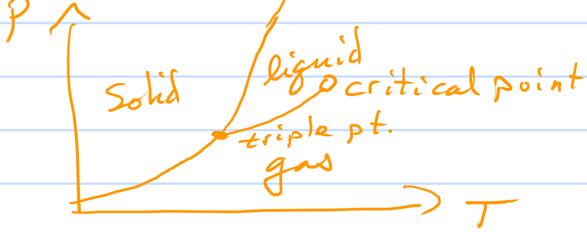
Section 5.3 Phase Transformations of Pure Substances

Start w/ H_2O although peculiar because solid is less dense than liquid ⇒ raising P lowers T of solid/liquid phase transition





More typical



Triple point - solid/liquid/gas coexist
Critical point - liquid/gas transition goes away
Vapor pressure - pressure where gas and liquid (or solid) coexist

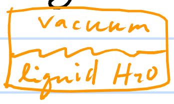
All sorts of phase transitions: superfluid, superconducting, lattice type changes, magnetizations (ferro, para, antiferro ...), ...

First order phase transition (solid-liquid, gas-liquid, ...) have S and V discontinuous at transition (first derivatives of G)

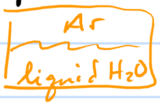
Continuous phase transition (superconductivity, ...) higher derivatives of G are discontinuous

Just because a phase of a material has smaller G than another phase does not mean material will be in that phase.
Examples supercooled water, graphite/diamond

Why does water evaporate at room temp? What happens if you have



or



Prob 5.24 Graphite $\Delta H = 0$, $\Delta G = 0$, $S = 5.74\ J/K$, $V = 5.30\ cm^3$
diamond $\Delta H = 1.895\ kJ$, $\Delta G = 2.900\ kJ$, $S = 2.38\ J/K$, $V = 3.42\ cm^3$

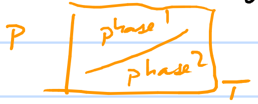
$\Delta G_{diam} > \Delta G_{grap}$ why doesn't diamond convert to graphite

At what P are the ΔG the same? $\left(\frac{\partial G}{\partial P}\right)_{T,N} = V$

$$2.900 \times 10^3\ J + 3.42 \times 10^{-6}\ m^3\ \Delta P = 0 + 5.30 \times 10^{-6}\ m^3\ \Delta P$$

$$\Delta P = 2900\ J / 1.88 \times 10^{-6}\ m^3 = 1.54 \times 10^9\ Pa \Rightarrow P \sim 15\ kbar$$

The slope of the line on the phase diagram can be found from the latent heat and other properties



Clausius-Clapeyron relation

At boundary $G_1 = G_2$ because material equally stable in form 1 or 2

on bdry

$$dG_1 = dG_2 \Rightarrow -S_1\,dT + V_1\,dP + \cancelto{0}{\mu_1\,dN_1} = -S_2\,dT + V_2\,dP + \cancelto{0}{\mu_2\,dN_2}$$

$$\Rightarrow \text{slope } \frac{dP}{dT} = \frac{S_1 - S_2}{V_1 - V_2} = \frac{L}{T\Delta V}$$

$S_1 - S_2 = \frac{L}{T}$ ← latent heat of transition

$\Delta V = V_1 - V_2$ volume change

Prob 5.35 $\frac{dP}{dT} = \frac{L}{T\Delta V} \simeq \frac{L}{TV}$ $V = \frac{NkT}{P}$

$\Rightarrow \frac{dP}{dT} = \frac{L}{Nk_BT^2}P$ if L is for 1 mole $\frac{dP}{P} = \frac{L}{RT^2}dT \Rightarrow \ln P = -\frac{L}{RT} + \text{const}$

$P = \text{const}\, e^{-L/RT}$

only true for: small changes, $L \simeq$ const, go to gas, ideal gas law

Prob 5.42 $P = P_0 e^{-L/RT}$ From Fig 5.11 at 25°C $L = 43.99 \frac{kJ}{mol}$ $\frac{L}{R} = 5294K$

$0.0317\text{ bar} = P_0 e^{-\frac{5294 K}{298 K}} \Rightarrow P_0 = 1.64 \times 10^6$ bar

a)

T (K)	P (bar)
273	0.006
283	0.012
293	0.023
303	0.042

b) $0.9 \times 0.042 = 0.038 = P_0 e^{-L/RT} \Rightarrow e^{-L/RT} = 2.32 \times 10^{-8}$

$-L/RT = -17.6 \Rightarrow T = 301\text{ K} = 28°C$

$0.4 \times 0.042 = 0.0168 = P_0 e^{-L/kT} \Rightarrow e^{-L/RL} = 1.02 \times 10^{-8}$

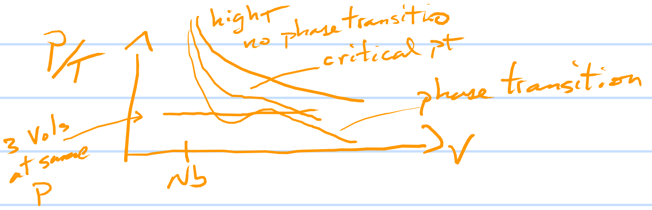
$-L/RT = -18.4 \Rightarrow T = 288\text{ K} = 15°C$

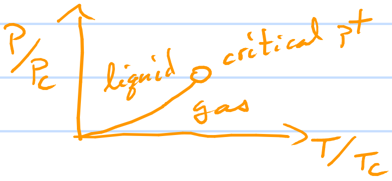
The van der Waals model - a simple extension of the ideal gas law gives phase transition

Equation of state $(P + \frac{aN^2}{V^2})(V - Nb) = Nk_BT$

from interactions ↖ excluded volume

$\Rightarrow P = \frac{NkT}{V-Nb} - \frac{aN^2}{V^2}$ Typical $b \sim 10^{-28}\,m^3$ $a \sim 10^{-21}\,J\ 10^{-28}\,m^3$





Prob 5.48 The critical pt has $\frac{dP}{dV} = 0$ and $\frac{d^2P}{dV^2} = 0$

$\Rightarrow -\frac{NkT}{(V-Nb)^2} + \frac{2aN^2}{V^3} = 0 \Rightarrow 2aN^2(V-Nb)^2 = NkTV^3$

$\frac{2NkT}{(V-Nb)^3} - \frac{6aN^2}{V^4} = 0 \Rightarrow 6aN^2(V-Nb)^3 = 2NkTV^4$

ratio $\Rightarrow 3(V-Nb) = 2V$

$\boxed{V_c = 3Nb}$

$$NkT = 2aN^2(V-Nb)^2/V^3 = \frac{2aN^2 4}{27Nb} = \frac{8aN}{27b} \Rightarrow \boxed{kT_c = \frac{8a}{27b}}$$

$$P_c = \frac{NkT_c}{V_c - Nb} - \frac{N^2 a}{V_c^2} = \frac{N\, 8a/27b}{2Nb} - \frac{N^2 a}{9N^2 b^2} = \boxed{\frac{1}{27}\frac{a}{b^2} = P_c}$$

if $b = 10^{-28}\,m^3$, $a = 10^{-21}\,J\;10^{-28}\,m^3$ $\qquad kT_c = \frac{8}{27}10^{-21}\,J \Rightarrow T_c \sim 21\,K$

To find out how the system behaves when in contact, need to know G

$$dG = -S\,dT + V\,dP + \mu\,dN \Rightarrow \left(\frac{\partial G}{\partial V}\right)_{N,T} = V\left(\frac{\partial P}{\partial V}\right)_{NT}$$

$$\left(\frac{\partial G}{\partial V}\right)_{N,T} = -V\frac{NkT}{(V-Nb)^2} + \frac{2aN^2}{V^2} = -\frac{NkT}{V-Nb} - \frac{N^2kTb}{(V-Nb)^2} + \frac{2aN^2}{V^2}$$

$$\Rightarrow G = -NkT\ln(V-Nb) + \frac{N^2kTb}{V-Nb} - \frac{2aN^2}{V} + C(N,T)$$

$$G = -NkT\left\{\ln\left(\frac{V}{Nb}-1\right) - \frac{1}{\frac{V}{Nb}-1}\right\} - \frac{2aN^2}{V} + \tilde{C}(N,T)$$

$$= \frac{NkT}{\frac{V}{Nb}-1}\left[1 - \left(\frac{V}{Nb}-1\right)\ln\left(\frac{V}{Nb}-1\right)\right] - \frac{2aN^2}{V} + \tilde{C}(N,T)$$

Let $V = \tilde{V}V_c$, $T = \tilde{T}T_c$, $P = \tilde{P}P_c$

$$G = \frac{N\tilde{T}\frac{8a}{27b}}{3\tilde{V}-1}\left[1 - (3\tilde{V}-1)\ln(3\tilde{V}-1)\right] - \frac{2aN}{3b\tilde{V}} + \tilde{C}$$

$$= \frac{2aN}{3\;b}\left\{\frac{\frac{4}{9}\tilde{T}}{3\tilde{V}-1}\left[1-(3\tilde{V}-1)\ln(3\tilde{V}-1)\right] - \frac{1}{\tilde{V}}\right\} + \tilde{C}(N,T)$$

Recast the original equation of state $P = \frac{NkT}{V-Nb} - \frac{aN^2}{V}$

$$\tilde{P}\frac{1}{27}\frac{a}{b^2} = \frac{N\tilde{T}\frac{8}{27}\frac{a}{b}}{Nb(3\tilde{V}-1)} - \frac{aN^2}{\tilde{V}^2 9N^2b^2} \Rightarrow \tilde{P} = \frac{8\tilde{T}}{3\tilde{V}-1} - \frac{3}{\tilde{V}^2}$$

Section 5.4 Phase Transformations of Mixtures

Properties of a mixture as a function of the fraction of one type

The entropy of mixing will play a huge role.

Suppose there are n total moles $\quad X = \frac{n_B}{n} \quad 1-X = \frac{n_A}{n}$

$V_A = \frac{n_A}{n}V \qquad V_B = \frac{n_B}{n}V \qquad$ ideal gas

$$G = X\,G_B^\circ + (1-X)\,G_A^\circ$$

G_A° = free energy if all type A

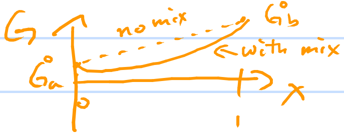
G_B° = " " " " B

If you allow particles to mix and the presence of A in B is not a large perturbation, G increases due to the entropy of mixing. If there's no wall, each position could be either particle

$$\Delta S_{mix} = k\ln\left(\frac{N!}{N_A!\,N_B!}\right) \doteq k\ln\left(\frac{(N/e)^N}{(N_A/e)^{N_A}(N_B/e)^{N_B}}\right) = k\ln\left(\left(\frac{N}{N_A}\right)^{N_A}\left(\frac{N}{N_B}\right)^{N_B}\right)$$

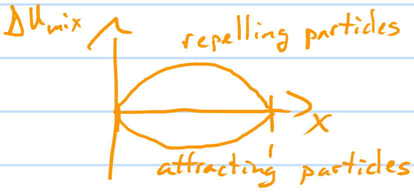
$$= -kN\left[\frac{N_A}{N}\ln\left(\frac{N_A}{N}\right) + \left(\frac{N_B}{N}\right)\ln\left(\frac{N_B}{N}\right)\right] = -nR\left[x\ln x + (1-x)\ln(1-x)\right]$$

For ideal mixing $G = U + PV - \overset{\text{add to}}{TS} = (1-x)G_A^\circ + xG_B^\circ + nRT\left[x\ln x + (1-x)\ln(1-x)\right]$



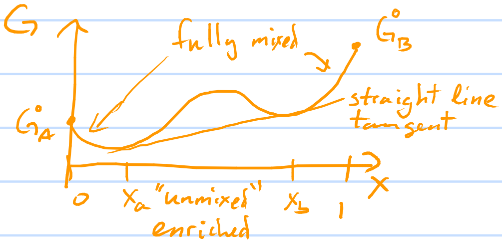
$x = 0$ all A
$x = 1$ all B

For nonideal mixing
U changes due to mixing



The competition between ΔU_{mix} and ΔS_{mix} determines whether two materials mix or not. If $\Delta U_{mix} \leq 0$, the substances will always mix because both entropy and energy considerations give lower G. If $\Delta U_{mix} > 0$, then can have a single homogeneous mixture or an A rich part and a B rich part. Depends on T!

Neat trick described in book



Think of mixture between x_a and x_b as trying to mix two new substances $(1-x_a)A + x_aB$ and $(1-x_b)A + x_bB$. Get lower G if don't mix these because straight line is lower than G

For $x < x_a$ or $x > x_b$ have a single mixed system

Between x_a and x_b have two regions unmixed fraction $\bar{A}$ + (1-fraction) $\bar{B}$

$\bar{n}_{\bar{A}} = (1-x_a)\,n_A + x_a\,n_B$ $\qquad$ $\bar{n}_{\bar{B}} = (1-x_b)\,n_A + x_b\,n_B$

fraction $= (x_b - x)/(x_b - x_a)$ $\qquad$ 1 - fraction $= (x - x_a)/(x_b - x_a)$

$$\text{fraction}\,\bar{A} + (1-\text{fraction})\,\bar{B} = \left[\frac{x_b - x}{x_b - x_a}(1-x_a) + \frac{x - x_a}{x_b - x_a}(1-x_b)\right]n_A + \left[\frac{x_b - x}{x_b - x_a}x_a + \frac{x - x_a}{x_b - x_a}x_b\right]n_B$$

$$= (1-x)\,n_A + x\,n_B \quad \checkmark$$

Prob 5.56 $\frac{d}{dx}\Delta S_{mix} = -nR\frac{d}{dx}[x\ln x + (1-x)\ln(1-x)] = -nR[1+\ln x - 1 - \ln(1-x)]$

$= nR[\ln(1-x) - \ln x]$ diverges $x \to 0$ and $x \to 1$

Example Phase change for an ideal mixture

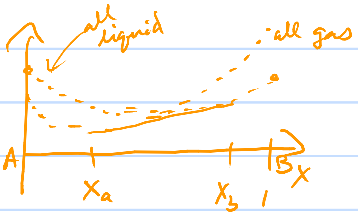
Book: Liquefication of N_2 and O_2 mixture

Boiling points $T_{N_2} \simeq 77\,K$ $T_{O_2} \simeq 90\,K$ $T_A < T_B$

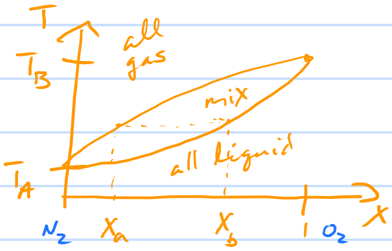
Easy cases first: $T > T_B$ have mixed gas $G_{gas} < G_{liquid}$ all x

$T < T_a$ have mixed liquid $G_{liq} < G_{gas}$ all x

$T_A < T < T_B$



Straight line below all gas and all liquid



For $T_A < T < T_B$ have gas fraction $\cdot\, x_a$ and liquid (1-fraction) x_b

f = fraction that is gas $= (x_b - x)/(x_b - x_a)$

There is f gas and $1-f$ liquid

The gas is mixture: x_a of type B and $1-x_a$ of type A

" liquid " " x_b " " " $1-x_b$ " " A

Check

$f\cdot[x_a n_B + (1-x_a)n_A] + (1-f)\cdot[x_b n_B + (1-x_b)n_A]$

$= \frac{x_b - x}{x_b - x_a}(1-x_a)n_A + \frac{x - x_a}{x_b - x_a}(1-x_b)n_A + \frac{x_b - x}{x_b - x_a}x_a n_B + \frac{x - x_a}{x_b - x_a}x_b n_B = (1-x)n_A + x n_B$ ✓

Prob 5.61 How to get 95% O_2?

Start at $x = 0.21$ at low enough T so all is liquid. Slowly raise T and pump off gas that evaporates. The gas will be N_2 rich.

Prob 5.62 What is the ratio of liquid to gas?

$$\left.\begin{aligned} f &= (x_b - x)/(x_b - x_a) = \text{fraction gas} \\ 1-f &= (x - x_a)/(x_b - x_a) = \text{〃 liquid} \end{aligned}\right\}\ \text{ratio} = \frac{x - x_a}{x_b - x}$$

Section 5.5 Dilute Solutions

Solution - one component of the mixture (solvent) is primary and the other component(s) (solutes) is secondary
Mainly, solutes don't interact with each other, only interacts with solvent.

As usual, need to get G

$$\left.\begin{array}{l} N_a = \#\text{ of solvent atoms or molecules} \\ N_b = \text{'' '' solute '' ''} \end{array}\right] N_a >> N_b$$

Pure solvent $G = N_a \mu_0(T,P)$

Solvent + solute $G = U - TS + PV = N_a \mu_0(T,P) + G_{add}$

Mixing increase

$$-TS = -kT\{(N_a+N_b)\ln(N_a+N_b) - N_a \ln N_a - N_b \ln N_b]$$

$$= -kT[(N_a+N_b)[\ln(N_a) + \tfrac{N_b}{N_a}\} - N_a \ln N_a - N_b \ln N_b]$$

$$= -kT\{N_b \ln N_a + N_b - N_b \ln N_b\}$$

Because 2 b's almost never meet $(U+PV)_{add} = N_b f(T,P)$

Put together $G = N_a \mu_0(T,P) + N_b f(T,P) - N_b kT \ln N_a + N_b kT \ln N_b - N_b kT$

Get the two chemical potentials

$$\mu_a = \left(\frac{\partial G}{\partial N_a}\right)_{T,P,N_b} = \mu_0(T,P) - \frac{N_b}{N_a} kT$$

$$\mu_b = \left(\frac{\partial G}{\partial N_b}\right)_{T,P,N_a} = f(T,P) + kT \ln(N_b/N_a)$$

Prob 5.74 Check $G = N_a \mu_a + N_b \mu_b$

$$G \overset{?}{=} N_a \mu_0 - N_b kT + N_b f + N_b kT \ln(N_b/N_a) \quad ✓$$

Technical detail

$$G = N_a \mu_0(T,P) + N_b f(T,P) + N_b kT \ln(N_b/N_a) - N_b kT$$

$$= N_a \mu_0(T,P) + N_b \tilde{f}(T,P) + N_b kT \ln(m_b) - N_b kT$$

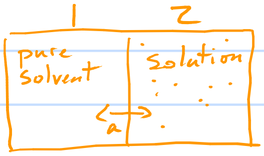
$$m_b = \text{molality} = \frac{\text{moles solute}}{\text{kgs solvent}} = \frac{N_b/N_A}{M_a/1\text{kg}} = \frac{N_b \, 1\text{kg}}{N_a N_A M_{1,a}}$$

Another way to write μ_b is in terms of the chemical potential at $m=1$

$$\mu_b = \mu_{0,b}(T,P) + kT \ln(m)$$

This allows you to relate the chemical potential at any molality to a "standard" value that can be measured/tabulated.

Example: Osmosis



Solvent can go through wall but solute can not

Equil $\Rightarrow$ $\mu_{a,1} = \mu_{a,2} = \mu_0(T,P_2) - \frac{N_b}{N_a} kT = \mu_0(T,P_1)$ $\qquad \frac{N_b}{N_a}$ in solution

The pressures must be different otherwise there would be a flow of a from 1 into 2.

For "small" pressure change $\mu_0(T,P_2) = \mu_0(T,P_1) + (P_2 - P_1)\left(\frac{\partial \mu_0}{\partial P}\right)_T$

For a pure substance $\left(\frac{\partial \mu_0}{\partial P}\right)\Big|_T = \frac{1}{N_a}\left(\frac{\partial G}{\partial P}\right)_{N_a,T} = V/N_a$

Put together $\underbrace{(P_2 - P_1)}_{\text{osmotic pressure}} = \frac{N_b}{V} kT = \frac{n_b}{V} RT$ $\qquad \frac{n_b}{V}$ = # of moles per volume of solute

(why does it look like the ideal gas law?)

Prob 5.77 Do crude estimate from osmotic pressure

$\Delta P = \rho\, g\, \Delta h = 1000\,\mathrm{kg/m^3}\ 9.8\,\mathrm{m/s^2}\ \Delta h$

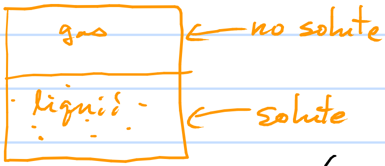
$n_b/V = (M_{tot}/M_{1b})/V \quad \Rightarrow \quad M_{1b} = \frac{M_{TOT}}{V} RT/\Delta P = \dfrac{\frac{5.6\times10^{-3}\,\mathrm{kg}}{10^{-3}\,\mathrm{m^3}}\ 8.31\frac{\mathrm{J}}{\mathrm{mol\,K}}\ 276\,\mathrm{K}}{1000\frac{\mathrm{kg}}{\mathrm{m^3}}\ 9.8\,\mathrm{m/s^2}\ 2\times10^{-2}\,\mathrm{m}}$

$M_{1b} = 66\,\mathrm{kg/mol} = 66000\,\mathrm{g/mol}$

Example Impurity shift of boiling/freezing point

Having impurity in liquid shifts the vaporization pressure at a given T see book for derivation.

The shift of the PT boundary between different phases occurs because there's a different concentration of solute in different phases.



At fixed P, how does T of boiling change?

No solute $\mu_{a,liq}(T_0,P) = \mu_{a,gas}(T_0,P)$ $\qquad T_0$ = phase trans. at P

(equal because no cost for solvent gas $\leftrightarrow$ liquid)

With solute $\mu_{a,liq}(T,P) - \frac{N_b}{N_a} kT = \mu_{a,gas}(T,P)$ $\qquad$ write $T = T_0 + \overbrace{T - T_0}^{\text{small}}$

$$\cancel{\mu_{a,liq}(T_0,P)} + (T - T_0)\left(\frac{\partial \mu_{a,liq}}{\partial T}\right)_P - \frac{N_b}{N_a} kT_0 = \cancel{\mu_{a,gas}(T_0,P)} + (T - T_0)\left(\frac{\partial \mu_{a,gas}}{\partial T}\right)_P$$

Get expression $\left(\frac{\partial \mu_{a,liq}}{\partial T}\right)_P - \left(\frac{\partial \mu_{a,gas}}{\partial T}\right)_P = \frac{1}{N_{liq}}\left(\frac{\partial G_{liq}}{\partial T}\right)_P - \frac{1}{N_{gas}}\left(\frac{\partial G_{gas}}{\partial T}\right)_P = \frac{S_{gas}}{N_{gas}} - \frac{S_{liq}}{N_{liq}}$

The difference in entropy per particle between gas and liquid is

$L m_a/T$ L = latent heat, m_a = mass of 1 solvent particle, T = temperature

Put together

$$T - T_0 = \frac{N_b k T_0}{N_a (L m_a/T_0)} = \frac{n_b R T_0^2}{M_a L} = \overset{\text{molality}}{m} \, R T_0^2/L$$

Prob 5.79 Add 1 tsp salt to pot of water, $\Delta T = ?$

1 tsp ≈ 6 g

avg mass NaCl ≈ 29 g/mol ⇒ $n_b = \frac{6\text{g}}{29\text{ g/mol}} \approx 0.2$ mol

If pot holds 1 liter $M = 1$ kg

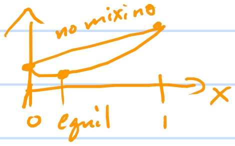
$L = 2.26 \times 10^6$ J/kg $T_0 = 373$ K

$$\Delta T = 0.2\text{ mol } 8.31 \frac{\text{J}}{\text{mol K}} (373\text{ K})^2 / (1\text{ kg } 2.26 \times 10^6 \frac{\text{J}}{\text{kg}}) \approx 0.1\text{ K}$$

Section 5.6 Chemical Equilibrium

You have a closed system where reaction can take place $AB \Leftrightarrow A + B$

Why don't you see all AB or all $A + B$



x = frac AB

Suppose you have a system at fixed P, T but number of constituents can change

Equilibrium ⇒ $dG = 0 = \mu_1 dN_1 + \mu_2 dN_2 + \ldots$

<u>Important</u> $dN_1, dN_2 \ldots$ are <u>not</u> independent

Example $N_2 + 3H_2 \rightarrow \overset{\text{ammonia}}{2NH_3}$ $dN_{N_2} = -1$ $dN_{H_2} = -3$ $dN_{NH_3} = 2$

⇒ $\mu_{N_2} + 3\mu_{H_2} = 2\mu_{NH_3}$

In general, if $\nu_1 X_1 + \nu_2 X_2 + \ldots \Leftrightarrow \nu_3 X_3 + \nu_4 X_4 \ldots$

$\nu_1 \mu_1 + \nu_2 \mu_2 + \ldots = \nu_3 \mu_3 + \nu_4 \mu_4 \ldots$

Example for all gases Eq 5.39 $\mu(T,P) = \mu(T,P_0) + kT\ln\left(\frac{P}{P_0}\right)$

Example $N_2 + 3H_2 \longleftrightarrow 2NH_3$

$$\mu_{0,N_2} + kT\ln\left(P_{N_2}/P_0\right) + 3\mu_{0,H_2} + 3kT\ln\left(\frac{P_{H_2}}{P_0}\right) = 2\mu_{0,NH_3} + 2kT\ln\left(\frac{P_{NH_3}}{P_0}\right)$$

$$\Rightarrow \ln\left(\frac{P_{N_2}P_{H_2}^3}{P_{NH_3}^2 P_0^2}\right) = \frac{2\mu^\circ_{NH_3} - 3\mu_{0,H_2} - \mu_{0N_2}}{kT} = \frac{\Delta G_0}{RT}$$

$\Delta G^\circ_{H_2} = \Delta G^\circ_{N_2} = 0 \qquad \Delta G^\circ_{NH_3} = -16.45kJ$

$R \cdot 298 = 2.48\ kJ$

$$\frac{P_{NH_3}^2 P_0^2}{P_{N_2}P_{H_2}^3} = e^{-\Delta G_0/RT} \equiv K$$ Law of mass action

Example 5.85 Show $\frac{d\ln K}{dT} = \frac{\Delta H^\circ}{RT^2}$

$$\frac{d\ln K}{dT} = \frac{d}{dT}\left(-\frac{\Delta G_0}{RT}\right) = \frac{\Delta G_0}{RT^2} - \frac{1}{RT}\frac{d\Delta G_0}{dT} = \frac{\Delta G_0}{RT^2} + \frac{ST}{RT^2} = \frac{\Delta H_0}{RT^2}$$

If ΔH_0 has little T dependence $\ln K(T_2) - \ln K(T_1) = \frac{\Delta H_0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$\Rightarrow K(T)e^{\frac{\Delta H_0}{kT}} = \text{const}$

Example Dissociation of solvent

Even a pure molecular substance is not "pure". The molecules can dissociate to give "solvent" particles.

$H_2O \longleftrightarrow H^+ + OH^- \Rightarrow \mu_{H_2O} = \mu_{H^+} + \mu_{OH^-} \qquad N_{H^+} = N_{OH^-}$

Assume dilute

$$\left[\begin{array}{ll} \text{Eq 5.69} & \mu_{H_2O} = \mu_{0,H_2O} - \frac{2N_{H^+}}{N_{H_2O}}kT \\ \text{Eq 5.72} & \mu_{H^+,0} + \mu_{OH^-} = \mu_{0,H^+} + kT\ln(m_{H^+}) + \mu_{0,OH^-} + kT\ln(m_{OH^-}) \end{array}\right.$$

If really dilute $\frac{N_{H^+}}{N_{H_2O}} \ll 1 \Rightarrow \mu_{0,H_2O} = \mu_{0,H^+} + \mu_{0,OH^-} + kT\ln(m_{H^+}m_{OH^-})$

For 1 mole $RT\ln(m_{H^+}m_{OH^-}) = -N_A(\mu_{0,H^+} + \mu_{0,OH^-} - \mu_{0,H_2O}) = -\Delta G_0$

$m_{H^+}m_{OH^-} = e^{\frac{-\Delta G_0}{RT}} \equiv K \qquad \Delta G_0 = 0 - 157.24kJ + 237.13\ kJ = 79{,}900J$

$$m_{H^+}m_{OH^-} = e^{\frac{-79{,}900}{8.31\cdot 298}} = e^{-32.3} = 1.0\times10^{-14} \Rightarrow m_{H^+} = m_{OH^-} = 1.0\times10^{-7}\left.\right] \frac{10^{-7}\,\text{mol } H^+}{kg\ H_2O}$$

$pH = ?$

The previous problem let's us look at the T dependence

$K(T_2) = K(T_1)\, e^{\frac{\Delta H}{RT_1} - \frac{\Delta H}{RT_2}}$ $\Delta H_0 = 0 - 229.99\,kJ + 285.83\,kJ = 55{,}800\,J$

$T = 35°C = 308\,K$ $K(35°C) = 1.0 \times 10^{-14}\, e^{\frac{55800}{8.31}\left(\frac{1}{248} - \frac{1}{308}\right)} = 1.0 \times 10^{-14} e^{0.73} = 2.1 \times 10^{-14}$

$\Rightarrow \sim 1.4X$ more H^+

$T = 45°C = 318\,K$ $K(45°C) = 1.0 \times 10^{-14} e^{1.42} = 4.1 \times 10^{-14}$ $\Rightarrow \sim 2X$ more H^+

See book about O_2 dissolving into H_2O and ionizing H atoms