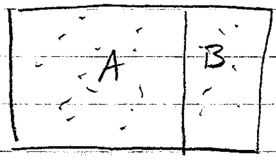
5.4 Phase Transformations of Mixture



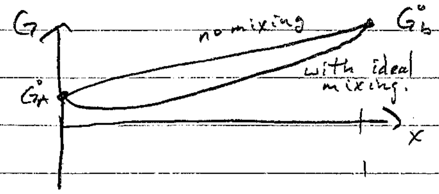
Suppose there are n total moles
$x \equiv n_B/n$ $\quad V_A = V\frac{n_A}{n}$ $\quad V_B = \frac{n_B}{n}V$
$\Rightarrow G = (1-x)G_A^\circ + x\,G_B^\circ$

where G_A° = free energy if all type A
" G_B° = " " " B

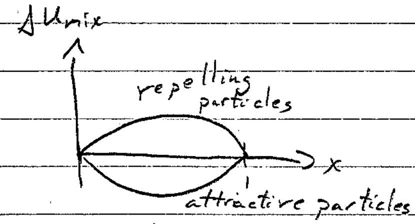
If you allow particles to mix and presence of A in B is not large perturbation, G increases due to entropy of mixing.

From prob 2.38 $\Delta S_{mix} = -nR\,[x\ln x + (1-x)\ln(1-x)]$

Ideal mixing $\quad G = U + PV - TS = (1-x)G_A^\circ + x\,G_B^\circ + nRT[x\ln x + (1-x)\ln(1-x)]$



Non ideal mixing: U changes due to mixing



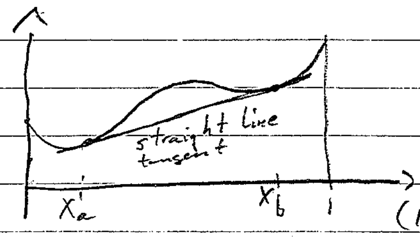
The competition between ΔU_{mix} and $T\Delta S_{mix}$ determines whether two materials mix or not

$$\Delta G_{mix} = G - [(1-x)G_A^\circ + x\,G_B^\circ] = \overbrace{nRT[x\ln x + (1-x)\ln(1-x)]}^{\text{negative}} + \overbrace{\Delta U_{mix}}^{\text{positive or negative}}$$

How to tell whether two materials mix? If $\Delta U_{mix} < 0$ then always mix because of both entropy and energy considerations.

If $\Delta U_{mix} > 0$, then can have a single-homogenous 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 $(1-x_a)A + x_a B$ and $(1-x_b)A + x_b B$
Get lower G if don't mix because line always lower than G

For $x < x_a$ or $x > x_b$ have a single mixed system. Between x_a and x_b have fraction $* x_a$ plus $(1-\text{fraction}) * x_b$

Prob 5.58 $\frac{d}{dx}\Delta S_{mix} = -nR\frac{d}{dx}[x\ln x + (1-x)\ln(1-x)]$

$= -nR[\ln x + 1 - \ln(1-x) - 1]$

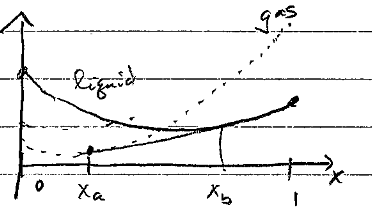
$= -nR\ln[x/(1-x)]$ infinite at $x=0$ and 1

Phase change for an ideal mixture (book does liquefication of N_2 and O_2 mixture)

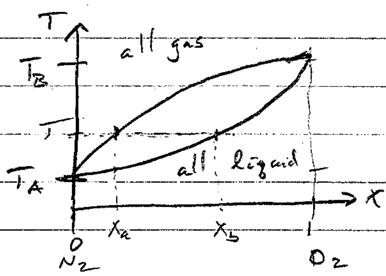
T_A = temp of phase change of A
T_B = " " " " B
$T_A < T_B$

If $T > T_B$ have mixed gas $\Rightarrow G_{gas} < G_{liquid}$ all x
If $T < T_A$ have mixed liquid $\Rightarrow G_{gas} > G_{liquid}$ all x

For $T_A < T < T_B$ $G_{gas} > G_{liquid}$ some x only
Why? If all B you know all liquid but if all A you know it is all gas



For $T_A < T < T_B$ have liquid fraction $* x_b$ and gas $(1-\text{fraction}) * x_a$



between x_a and x_b $f \cdot x_a + (1-f)x_b = x \Rightarrow f = \frac{x_b - x}{x_b - x_a}$

you have $\frac{x_b - x}{x_b - x_a}$ gas and $\frac{x - x_a}{x_b - x_a}$ liquid

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

the liquid is mixture x_b of type B and $1-x_b$ type A

Prob 5.61 Start at $x = 0.21$ at low enough T so all is liquid. Slowly raise T and pump off gas that evaporate. The gas will be N_2 rich

Prob 5.62 $f = \frac{x_b - x}{x_b - x_a}$ = fraction gas $1-f = \frac{x - x_a}{x_b - x_a}$ = fraction liquid

liquid / gas $= \frac{x - x_a}{x_b - x}$