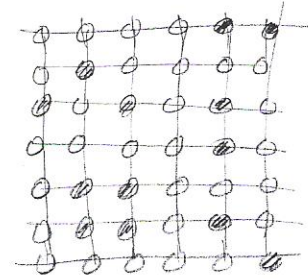
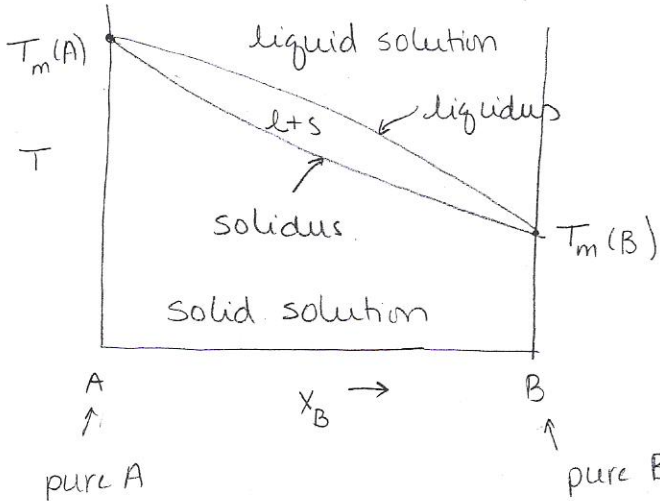


Phase diagrams

Last time: 1-component system, H_2O , $f(T, P)$

Now: 2 component systems, $f(T, x_B)$

2.1 Isomorphous: complete solubility, no change in "shape"
no change in structure with composition.



some A, some B
→ random.

same crystal structure.

(Hume Rothery rules for metals)

$$x_B = \frac{N_B}{N_A + N_B} = \text{mole fraction}$$

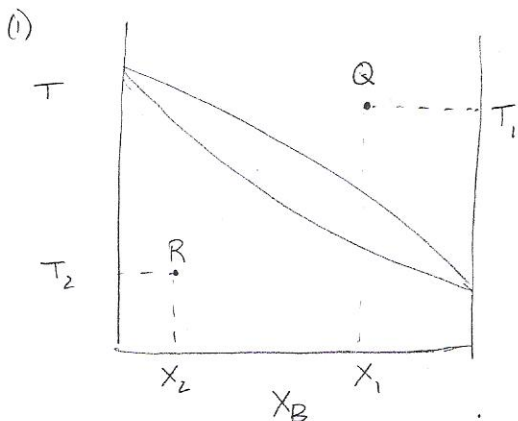
examples of isomorphous systems:

metals: Cu-Ni ; Ag-Au

oxides: NiO - MgO

semiconductors: Ge-Si

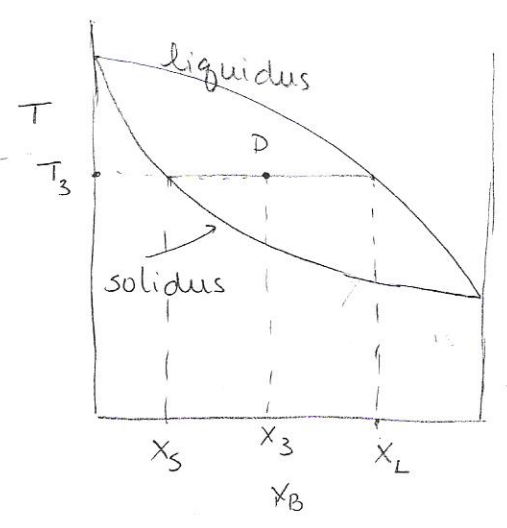
- 2 questions (1) how do we read this "map" ?
(2) how is it connected to chemical thermodynamics?



(a) at Q $T=T_1$, $x_B=x_1$
⇒ homogeneous liquid of composition x_1

(b) at R, $T=T_2$, $x_B=x_2$
⇒ homogeneous solid of composition x_2

Interesting part...



at D, $T=T_3$, $X_B = X_3$
 \Rightarrow map indicates S+L
 what are the compositions?
 how much of each?

- ① draw tie-line
- ② solid has composition X_S (tie-line & solidus intersection)
- ③ liquid has composition X_L (tie-line & liquidus intersection)

quantities:

$$f_S = \frac{X_3 - X_L}{X_S - X_L}$$

$$f_L = \frac{X_3 - X_S}{X_L - X_S}$$

} lever rule

the closer X_3 is to solidus \Rightarrow the larger f_S
 close X_3 is to liquidus \Rightarrow the larger f_L

\Rightarrow useful mnemonic for the lever rule.

How is phase diagram connected to G?

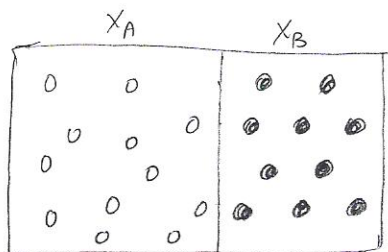
recall: $G = \sum_i \mu_i X_i$

what we see on the "map" corresponds to minimum G at given $T \in X_B$.

Evaluate $G(T, P, \{X_i\})$ in a two component system at $P = \text{const.}$

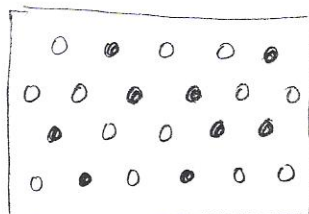
$\rightarrow G(T, X_B)$ $X_A = 1 - X_B \iff$ only 1 composition variable

For a given X_B ($\in T$) compare two states



unmixed.

$G^{(1)} = \mu_A^\circ X_A + \mu_B^\circ X_B$
fixed $\neq f(X_B)$

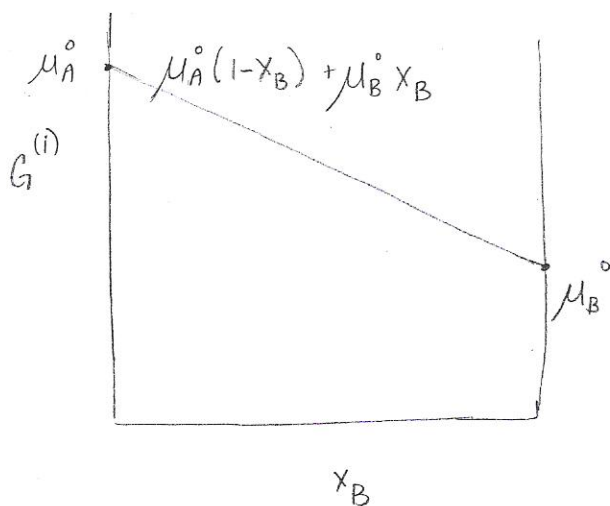


mixed.

$G^{(2)} = \mu_A X_A + \mu_B X_B$

unknown $n = f(X_B)$

now vary X_B from 0 to 1 (X_A from 1 to 0)



what is change in G due to mixing?

consider mixed to be final state

$\Delta G = G^{(2)} - G^{(1)} = \Delta G^{mix} = (\mu_A - \mu_A^\circ) X_A + (\mu_B - \mu_B^\circ) X_B$

but also: $\Delta G^{mix} = \underbrace{\Delta H^{mix}}_{\text{chem bonding}} - T \underbrace{\Delta S^{mix}}_{\text{change in randomness}}$

We already know how to evaluate S.

$$S = k_b \ln \Omega$$

↖ # of distinguishable, equal energy ways of arranging atoms in the solution.

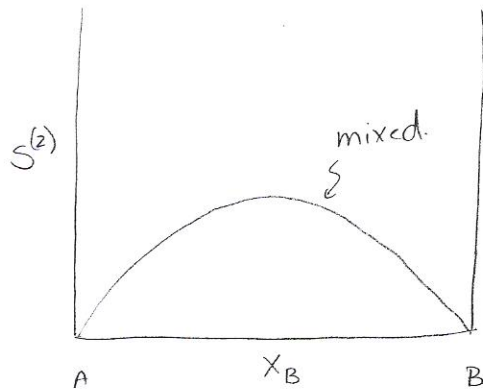
$$\Delta S^{mix} = S^{(2)} - S^{(1)}$$

state (1): $\Omega^{(1)} = 1 \Rightarrow S^{(1)} = 0$

state (2) already showed for n_v vacancies on N_0 sites:

$$\Omega = \frac{N_0!}{(N_0 - n_v)! n_v!}$$

here: $\Omega^{(2)} = \frac{N_0!}{N_B! N_A!}$



Stirling's approximation

$$\ln N! \approx N \ln N - N \quad \text{for large } N$$

can show this } $\Rightarrow S^{(2)} = -R X_A \ln X_A - R X_B \ln X_B$
plus $R = k_b \cdot N_0$

$$\Delta S^{mix} = S^{(2)} - S^{(1)} \rightarrow 0 = S^{(2)}$$

$$\Delta G^{mix} = \Delta H^{mix} - T \Delta S^{mix}$$

$$= \Delta H^{mix} + RT(X_A \ln X_A + X_B \ln X_B)$$

Categorize solutions on the basis of ΔH^{mix}

2.1 Binary, amorphous phase diagram corresponds to an ideal solution, $\Delta H^{mix} = 0$

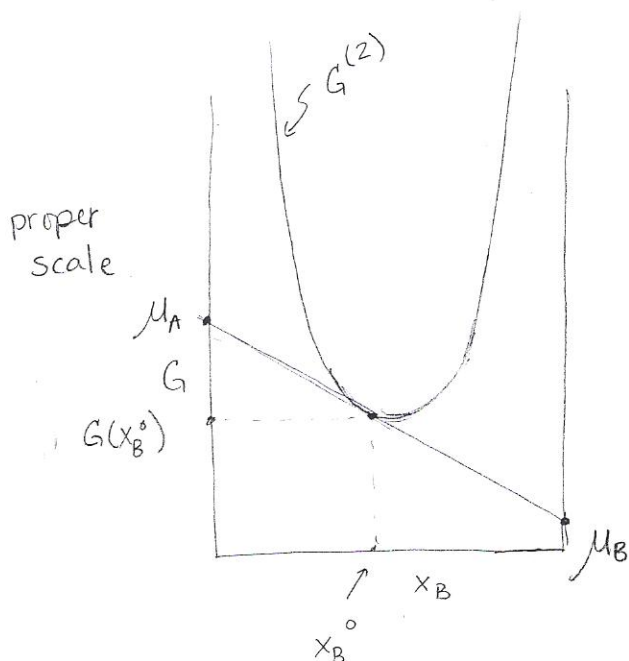
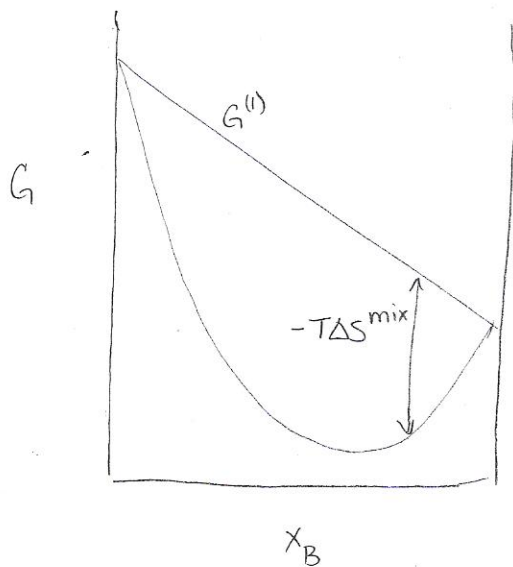
Ideal: A & B don't care if neighbors are A or B.

\Rightarrow G minimization dominated by entropy maximization

$$\Delta G^{mix} = RT(X_A \ln X_B + X_B \ln X_A) < 0.$$

$$G^{(2)} \equiv G^{mixed} = G^{(1)} + \Delta G^{mix}$$

↑
unmixed



consider composition X_B^0

at any X_B we have $G = \mu_A X_A + \mu_B X_B$ where $X_A = 1 - X_B$

$$\text{at } X_B^0 \quad G = \mu_A (1 - X_B^0) + \mu_B (X_B^0)$$

↑ ↑
evaluated at $X_B = X_B^0$

this is the equation of a line that passes through $G(X_B^0), X_B^0$

can show this line is tangent to $G(X_B)$ at $X_B = X_B^0$

\Rightarrow tangent rule, extrapolate to $X_B = 0, 1 \Rightarrow \mu_A, \mu_B$.