Chapter 7 → Reactions a necessary evil?

Problem 7.1 → optional

Lecture 12/2024

1) $g(\underbrace{g_0, s_0}_{1^{\circ} \text{ props}}, \overset{V_0,}{\underbrace{C_p, K_T, \alpha_p}_{2^{\circ} \text{ props}}})$ → g_0 → calorimetry
1st principles
phase equilibria

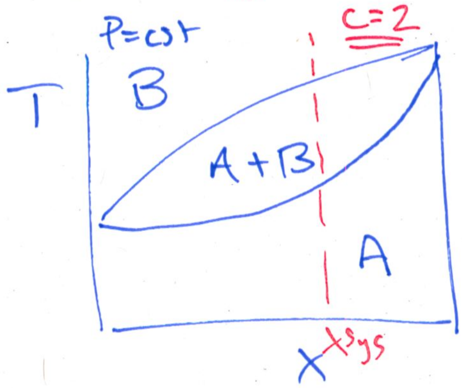
2° props: easily measured or reasonably approximated

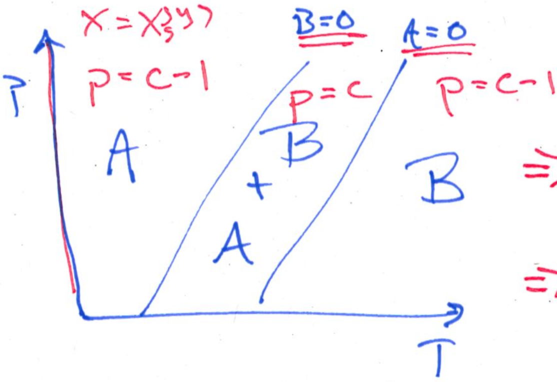
S_0 → C_p → vibrational entropy

$S^0 = S^0_{conf} + \int \frac{C_p}{T} dT$

S^0_{conf} → crystallography, phase eq

2) heterogeneous vs homogeneous ⇒ a matter of perspective (determinative variables)



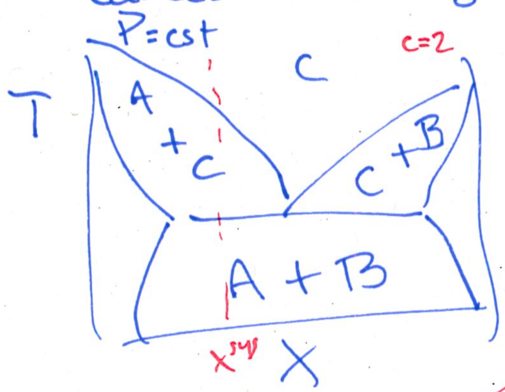


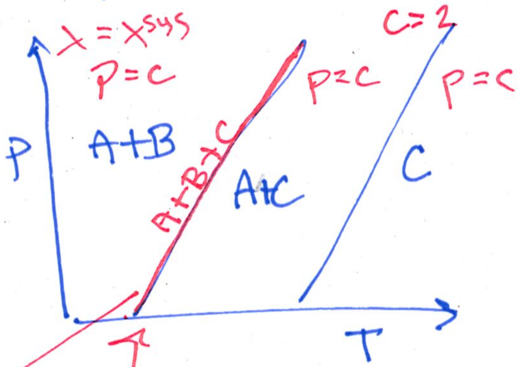
⇒ no discontinuity in system properties

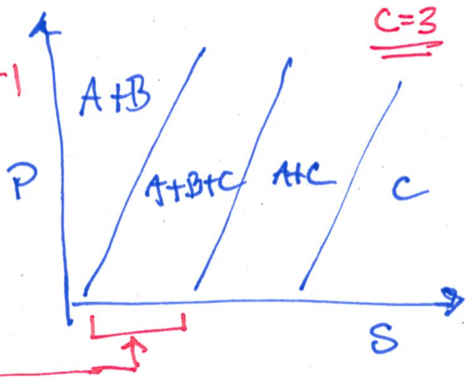
⇒ if A → B is a homogeneous reaction then any assemblage of p>1 phases represents a "reaction"

Maessing-Palatnik Rule

3) heterogeneous reactions ⇒ a process that (under equilibrium) causes a change of phase w/o changing the number of phases (p)







reaction equation
$\nu_A A + \nu_B B + \nu_C C = 0$

the "reaction" is "discontinuous" in S & T

4) So what is $A + B = C$?

a conservation eq among $p \leq c+1$ phases, φ^i is a c-dimensional vector of the phase properties (the components) that must be conserved by the system.

$\nu_A \varphi^A + \nu_B \varphi^B + \nu_C^C \varphi_C = 0$

$\Rightarrow \sum^p \nu_i^j \varphi^j = 0$

$\Rightarrow$ one coefficient is arbitrary so define $\nu^p \equiv -1$, then if $p = c+1$ (!)

$$\begin{bmatrix} \varphi^1 \ldots\ldots \varphi^c \end{bmatrix} \begin{bmatrix} \nu^1 \\ \vdots \\ \nu^c \end{bmatrix} = \varphi^{c+1}$$

$\Rightarrow$ if $p < c+1$ (eg: garnet + qtz + coes) The system is locally degenerate and one or more components must be eliminated.

$\nu(\Theta_{c+1} \ldots \Theta_{k+2})$!!

complexity in real systems $\Rightarrow$ illustrate!

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5) $$\sum^p \nu^j \Psi_i^j \equiv \Delta\Psi_i \begin{cases} = 0 & i = 1 \ldots c \\ \neq 0 & i = c+1 \ldots k+2 \end{cases}$$

regardless of degeneracy!

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6) $$d\omega = \sum_i^c \Theta_i d\Psi_i - \sum_{c+1}^{k+2} \Psi_i d\Theta_i$$

$$d\Delta\omega = \sum^c \Theta_i d\Delta\Psi_i - \sum_{c+1}^{k+2} \Delta\Psi_i d\Theta_i = \Delta\omega = f(\Theta_{c+1} \ldots \Theta_{k+2})$$

0

(remember $\nu(\Theta_{c+1} \ldots \Theta_{k+2})$)

Eulerian form: $$\Delta\omega = \sum_{j=1}^p \nu^j \omega^j = \sum_j^p \nu^j \left(\sum_{i=1}^c \Theta_i \Psi_i^j\right)$$

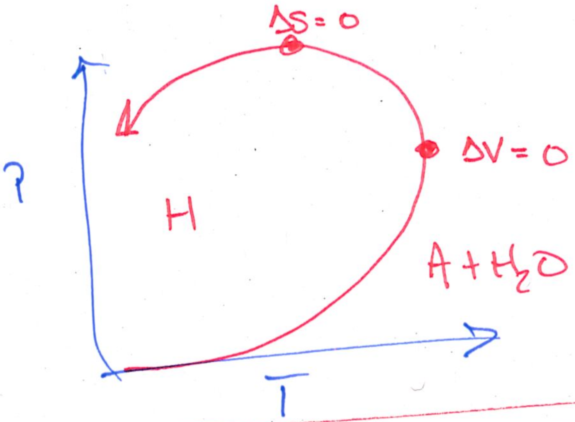
$$= \sum_i^c \Theta_i \sum_j^p \nu^j \Psi_i^j$$

$$= \sum_{i=1}^c \Theta_i \Delta_c \Psi_i \quad \text{na und?}$$

2021 12.3

7) chemically closed isothermal isobaric system

$c = k \qquad \omega = g$



$$\Delta g = -\Delta s\, dT - \Delta v\, d(-P)$$

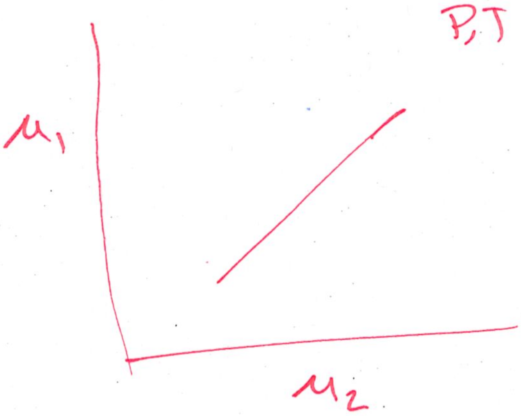
$$\Delta g = 0 \Rightarrow \frac{dP}{dT} = \frac{\Delta s}{\Delta v} \Rightarrow \text{Clapeyron slope}$$

→ geophysical "Clapeyron" slopes

8) $\omega = f(\varphi_1 \ldots \varphi_c, T, P, \mu_1, \mu_2)$

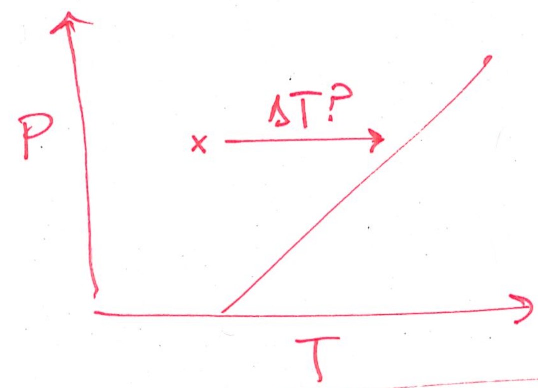
$c = k - 2$

system open with respect to n_1 and n_2, i.e. reactions dont conserve n_1, n_2



$$\frac{\partial \mu_1}{\partial \mu_2} = -\frac{\Delta n_2}{\Delta n_1}$$

9)



$$d\Delta g = -\Delta s\, dT - \Delta v\, d(-P)$$

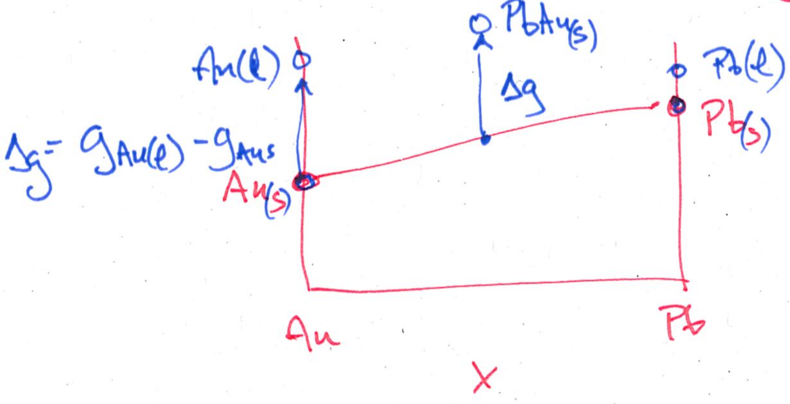
$$\Rightarrow \delta \Delta g \approx -\Delta s\, \delta T - \Delta v\, \delta P$$

$$\delta T = \frac{\delta \Delta g}{-\Delta s}$$

So why have we wasted 2 hours?

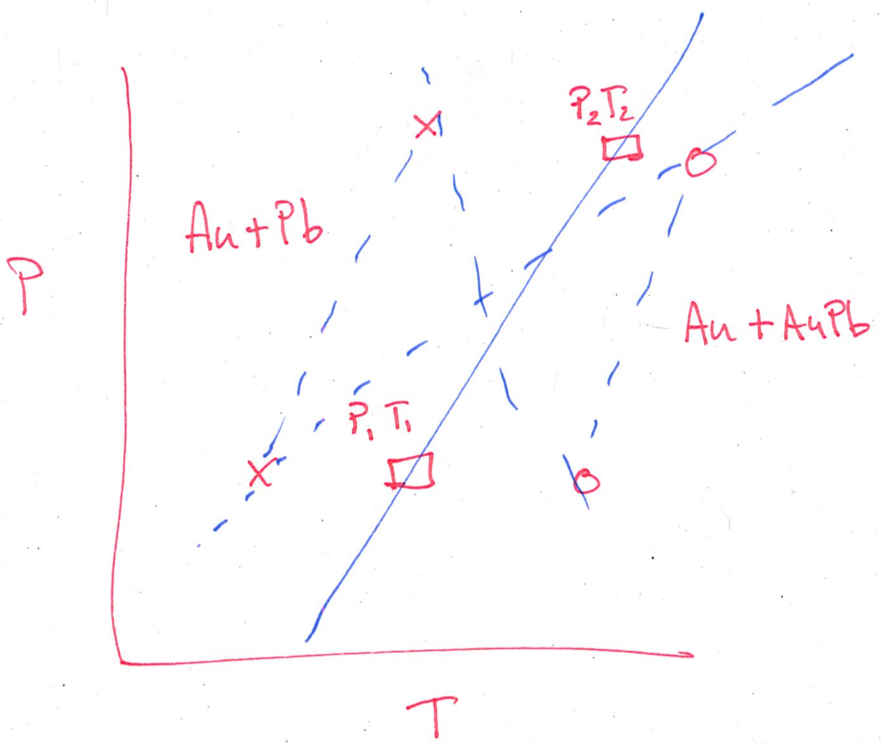
Lecture 12.4 2021

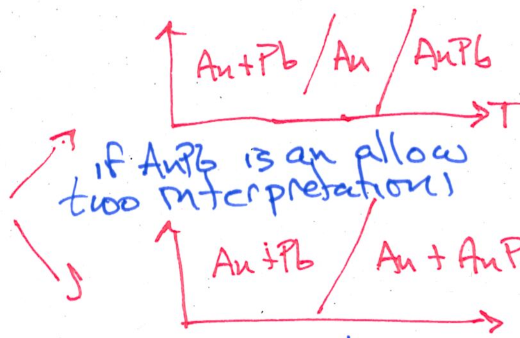
9) The arbitrariness of g_0



→ from a phase equilibrium perspective there are always k-arbitrary g_0 values. How these are assigned is a matter of convention and mixing conventions is disastrous.

10) $g_0^{Au(s)} = g_0^{Pb(s)} \Rightarrow$ how do we get $g_0^{PbAu(s)}$?





if AuPb is stoichiomet

$$\nu_{Au} Au + \nu_{Pb} Pb = \cancel{\nu_{AuPb}} AuPb \quad \equiv 1$$

$$0 \Leftarrow \Delta g_{AuPb} = g_{AuPb} + \nu_{Au} g_{Au} + \nu_{Pb} g_{Pb}$$

$$\Delta g = 0 = g^0_{AuPb} + \int_{P_0}^{P} V_{AuPb,T}\, dP - \int_{T_0}^{T} \left(S_0 + \int_{T_0}^{T} \frac{C_P}{T} dT \right) dT + f_1(P,T)$$

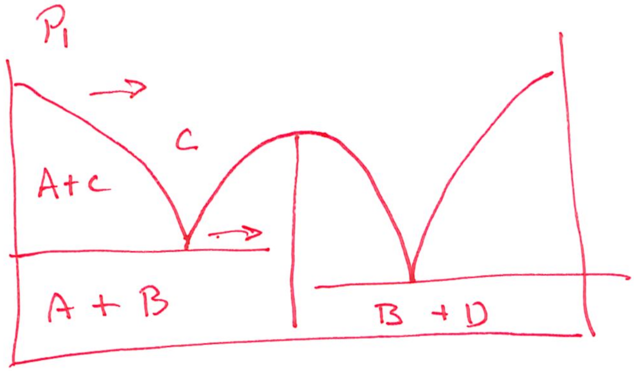
$$\iint \frac{C_P}{T} dT$$

$$= g^0 + f_2(P,T) - S_0(T-T_0) + f_3(P,T) + f_1(P,T)$$

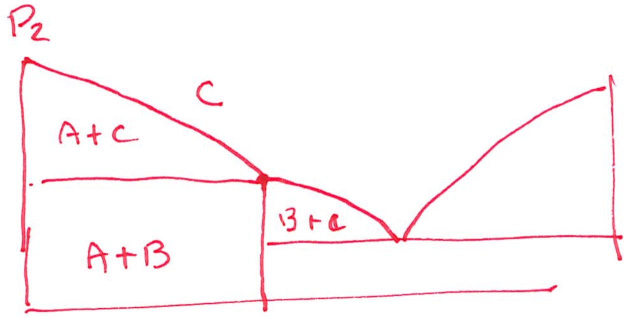
$$= g^0 - s^0(T-T_0) + f(P,T) \quad (= f_1 + f_2 + f_3)$$

eq1 := $0 = g_0 - S_0(T_1 - T_0) + f(P_1, T_1)$

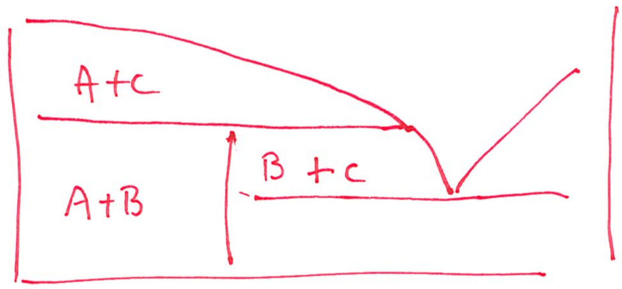
eq2 := $0 = g_0 - S_0(T_2 - T_0) + f(P_2 T_2)$



C = A + B



B = C



A + C = B

~~B = A + C~~

$$\frac{N!}{\prod^{t} N_i!}$$