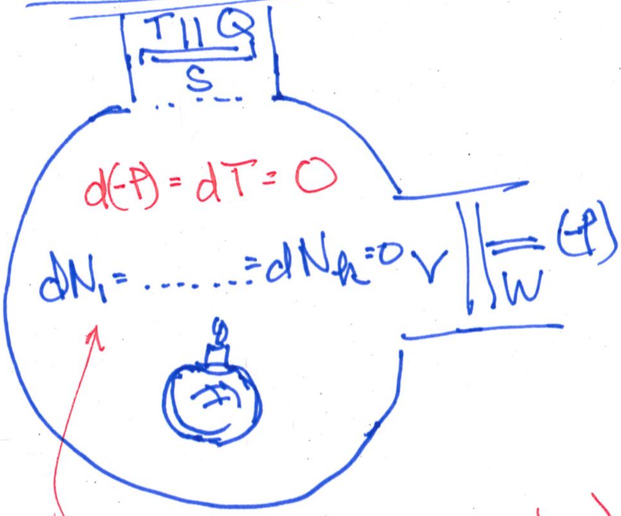
Problem 1.3 → is $f = x + y$ exact ?

Chapter 4 → Stability in open systems

Rules : 1) System variables only ⇒ ergo enviromental variables must be potentials

2) If the system and its environment are in eq w/ respect to Θ_i then the transfer of Ψ_i must be reversible ⇒ all interactions of the system and with its enviroment do not create entropy (though it may be transfered).



k - independent (conservative) properties

$dW = (-P)dV$ → only at cst P

$dQ = TdS^{ext}$ → only at cst T entropy transfer

$$(dU - dQ + dW)_{P,T} \equiv 0$$

$$\downarrow$$

$$dU - TdS^{ext} + \underbrace{pdV}_{-(-P)} = 0 < TdS^{int}$$

$$dG_{P,T,N} \equiv dU - T(dS^{ext} + dS^{int}) - (-P)dV \leq 0$$

G is a state function ⇒ $G = \int dG = U - TS - (-P)V$

$$U = TS + (-P)V + \sum \mu N$$

$$G = \sum_i^k \mu_i N_i$$

$$\frac{\partial}{\partial T}\frac{\partial G}{\partial P} = \frac{\partial}{\partial(-P)}\frac{\partial G}{\partial T} = \frac{\partial V}{\partial T} = -\frac{\partial S}{\partial P}$$

Maxwell relation problem $\boxed{4.1}$

$$dG = dU - d(TS) - d(-PV)$$

$$dU = TdS + (-P)dV + \sum \mu dN$$

$$dG = -SdT - Vd(-P) + \sum \mu dN$$

heterogeneous system at cst$(-P, T, N_1, \ldots N_k)$

$$G^1 = \mu_1 N_1^1 + \ldots\ldots + \mu_k N_k^1$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$G^p = \mu_1 N_1^p + \ldots\ldots + \mu_k N_k^p$$

$$G(-P, T, N_1, \ldots\ldots, N_k)$$

$$G\left(\frac{\partial U}{\partial V}, \frac{\partial U}{\partial S}, N_1, \ldots\ldots N_k\right)$$

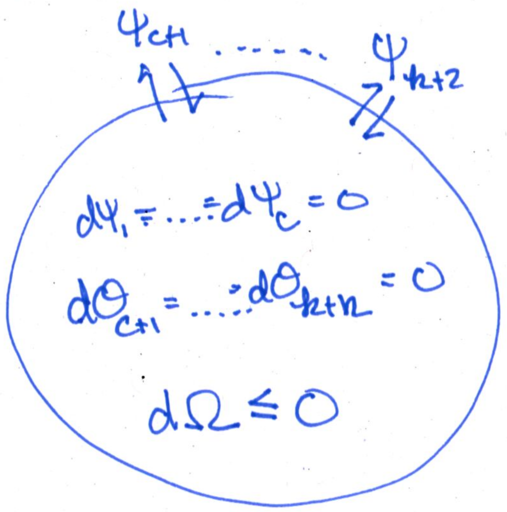
$$U(V, S, N_1, \ldots\ldots N_k)$$

$p \leq k$ → Goldschmidt's mineralogical phase rule.

Legendre transform

What is G → it is the energy that can be extracted from a system at constant P, T → the "free" energy.

Generalization of the Legendre transform



$$U(\Psi_1 \dots \Psi_{k+2}) \Rightarrow \Omega(\Psi_1 \dots \Psi_c, \Theta_{c+1} \dots \Theta_{k+2})$$

1) System is closed with respect to $\Psi_1 \dots \Psi_c$
2) System can do reversible work by exchanging $\Psi_{c+1} \dots \Psi_{k+2}$ with its environment. $dW = \sum_{c+1}^{k+2} -\Theta_i d\Psi_i \Rightarrow$

$$(dU + dW)_{\Psi_1 \dots \Psi_c, \Theta_{c+1} \dots \Theta_{k+2}} \equiv 0 \le T dS^{int}$$

adiabatic $dQ = 0$

diathermal $dT = 0$

$d\Omega \equiv dU + dW \equiv 0$

$dS \ge 0$

the $k+2$ conservative properties are $\Omega, \Psi_1 \dots \Psi_{c-1}$

$\Psi_c \equiv S$

$S = \Psi_{c+1}$, $T = \Theta_{c+1}$

$dQ = -dW_T = T dS^{ext}$

$d\Omega = dU - T dS^{ext} - \sum_{c+2}^{k+2} \Theta_i d\Psi_i$

$= 0 \le T dS^{int}$

$d\Omega = dU - T dS - \sum_{c+2}^{k+2} \Theta d\Psi_i$

$d\Omega_{\Psi_1 \dots \Psi_c, T, \Theta_{c+2} \dots \Theta_{k+2}} \le 0$

$$\Omega = U - \sum_{i=c+1}^{k+2} \Theta_i \Psi_i = \sum_{i=1}^{c} \Theta_i \Psi_i \Rightarrow P \le C$$

$$d\Omega = dU - \sum d(\Theta_i \Psi_i)$$

$$dU = \sum^{k+2} \Theta_i d\Psi_i$$

$$d\Omega = dU - \sum_{c+1}^{k+2} \Theta_i d\Psi_i - \sum_{c+1}^{k+2} \Psi_i d\Theta_i$$

$$= \sum_{i=1}^{c} \Theta_i d\Psi_i - \sum_{c+1}^{k+2} \Psi_i d\Theta_i \Rightarrow \Omega(\Psi_1 \dots \Psi_c, \Theta_{c+1} \dots \Theta_{k+2})$$

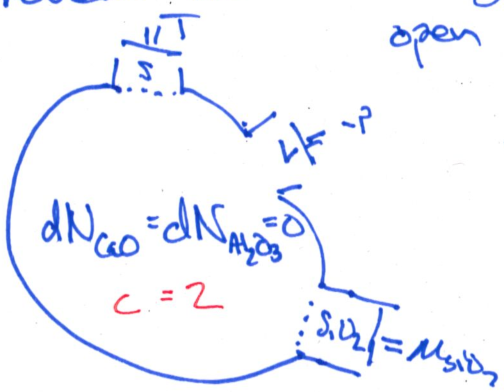
Standard Legendre Transforms: stability criterion

adiabatic	$U(S,V,N_1,\ldots,N_k)$	$c=k+2$	$\delta S_{U,V,M}<0 \quad (\delta U_{S,V,M}>0)$
diatermal	$A(T,V,N_1,\ldots,N_k)$	$c=k+1$	$\delta A_{T,V,N}>0$
adiatatic	$H(S,-P,N_1,\ldots N_k)$	$c=k+1$	$\delta S_{H,V,M}<0 \quad (\delta H_{S,-P,N}>0)$
diathermal	$G(T,-P,N_1,\ldots N_k)$	$c=k$	$\delta G_{T,-P,N}>0$
diathermal	$K(T,-P,\mu_1,N_2\ldots N_k)$	$c=k-1$	$\delta K_{T,-P,\mu_1,N}>0$

or activity / fuagacity

The Legendre transform of the Gibbs differential yields the only choices of independent variables for which it is possible to predict stability. These sets are known as the "natural variables" of the transformed function (Ω). $\Rightarrow$ $H(-P,T,N)$ $H(-P,S,N)$

Problem 4.2 $\Rightarrow$ analog $k=3$, CaO, Al_2O_3, SiO_2 $\Rightarrow$ system open with respect to SiO_2, S, V $\Rightarrow \Omega(\mu_{SiO_2},T,-P,\ldots)$



$$\Omega = U - TS - (-P)V - \mu_{SiO_2}N_{SiO_2}$$

$$d\Omega = \mu_{CaO}dN_{CaO} + \mu_{Al_2O_3}dN_{Al_2O_3} - SdT - Vd(-P)$$

$$d\Omega_{-P,T,\mu_{SiO_2}} > 0 \qquad p < (c=2)$$

Problem 4.3 a-$v \Rightarrow h$-s analog $\Rightarrow H(S,-P,N) \Rightarrow$ Enthalpy

$$H = U - (-P)V = TS + \mu N$$

$$dH = TdS + \mu dN - Vd(-P) \Rightarrow \alpha \equiv N$$

specific $\Rightarrow dh = Tds + \cancel{\mu dn} - vd(-P) \Rightarrow h(s,-P)$

$\qquad 0$

$$h = Ts + \mu \cancel{n} = u + pv$$

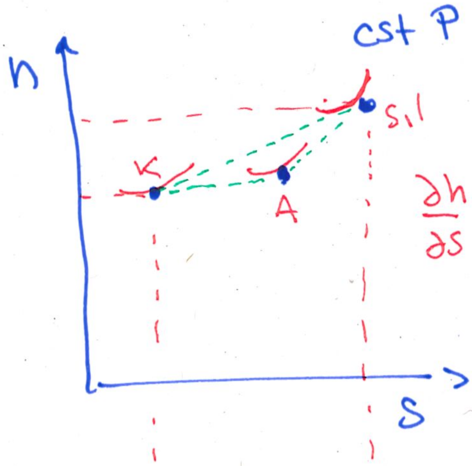
given $u^i, s^i, v^i, \cancel{n^i}$ for the aluminosilicates

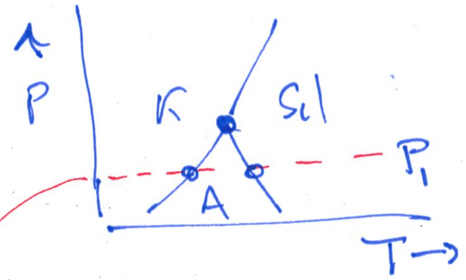
construct an h-s diagram at cst P

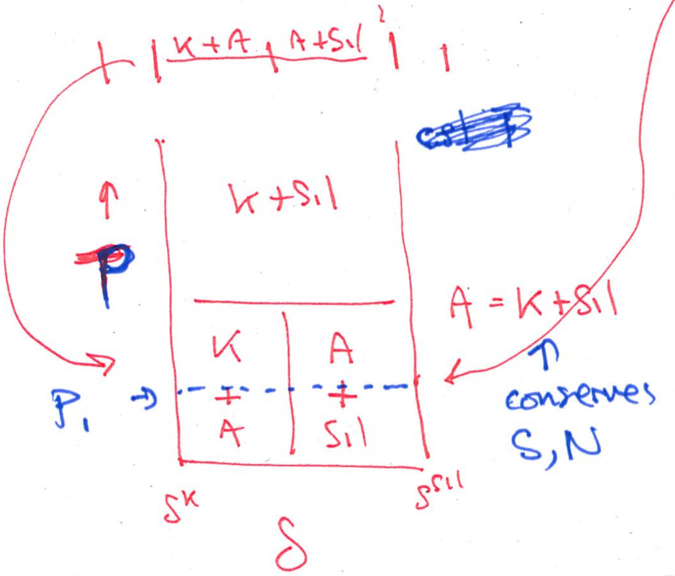
$$h^A = [u^A - (-p)v^A] = Ts^A + \cancel{\mu n^A}$$

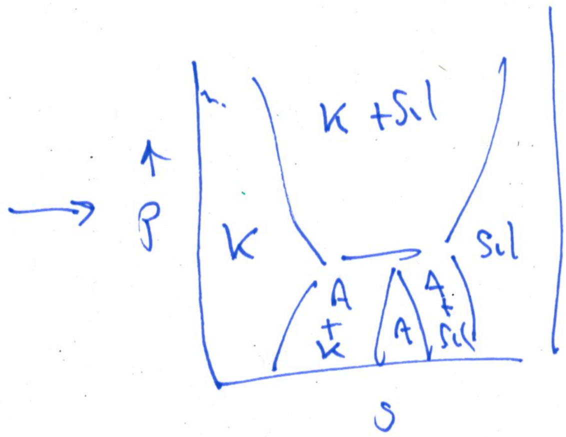
$$h^K = [\quad] =$$

$$\begin{bmatrix} s^A & n^A \\ s^K & n^K \end{bmatrix} \begin{bmatrix} T \\ \mu \end{bmatrix} = \begin{bmatrix} h^A \\ h^K \end{bmatrix}$$



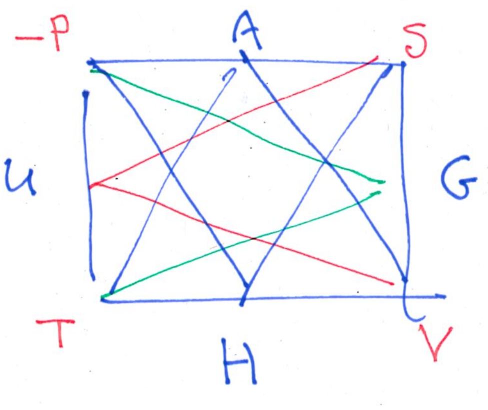






Problems 4.1-3 constitute 1 problem set.

Born Square



why ?