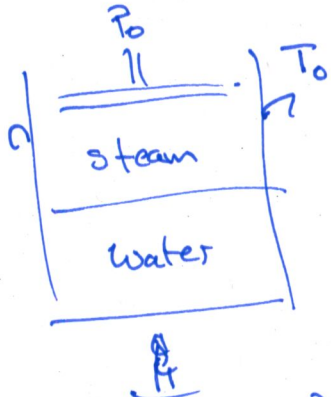
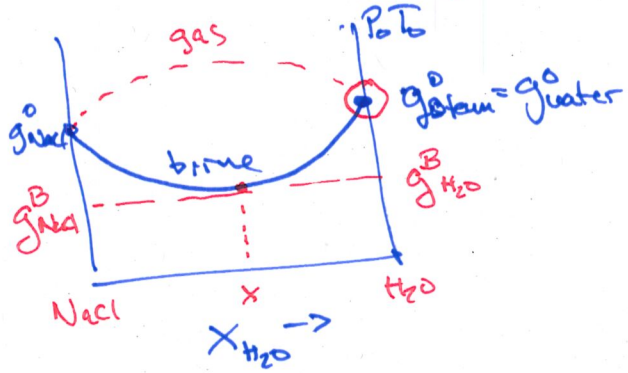
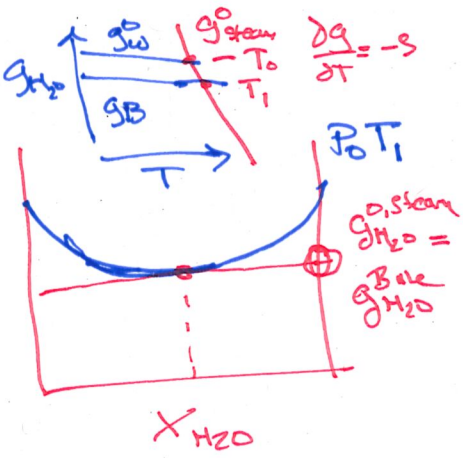
L 13.1 2021

Thermobarometry → Problem 8.2





$S^{gas} >> S^{brine}$

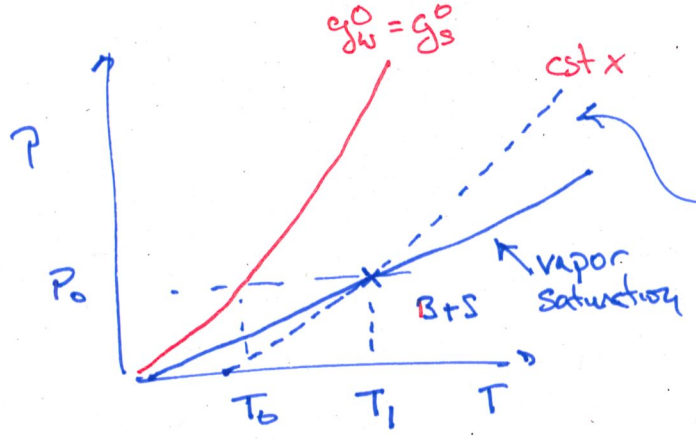


why add salt?

$$\mu_{H_2O} = \frac{\partial G^{steam}}{\partial N_{H_2O}} = g^0_{steam} = g^{H_2O}_{steam}$$

$$= \frac{\partial G^B}{\partial N_{H_2O}} = g^0_{H_2O} + S(x) = g^{brine}_{H_2O}$$

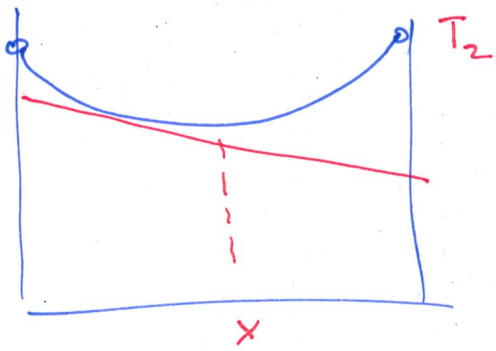
a activity

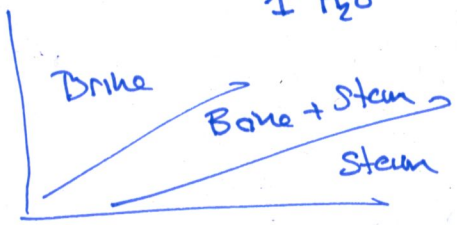


thermobarometric curve assumes x is fixed (observed) and $g^{brine}_{H_2O} = g^{steam}_{H_2O}$

necessary condition

$$1\ H_2O^{steam} = 1\ H_2O^{water}$$





Generalization: the change in partial molar g's must be zero for any stoichiometric reaction that can be written among the species/endmembers of an eq system

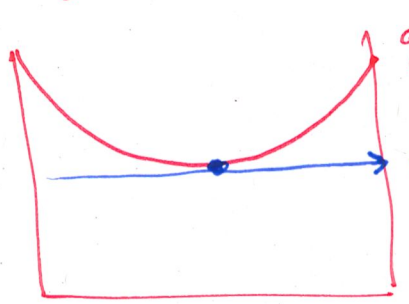
$$\Delta g = \sum_j^S \nu^j g^j \Rightarrow g^j = \sum_i^C n^j_i \mu_i \text{ at eq } g^j_i = \mu_i^*$$

$$\Delta g = \sum_j^S \nu^j \left(\sum_i^C n^j_i \mu_i\right) = \sum_j^S \sum_i^C \nu^j n^j_i \mu_i$$

$$\Delta g = \sum_i^C \mu_i \left(\sum_j^S \nu^j n^j_i\right) \Rightarrow \sum \nu^j n^j_i = \Delta n_i \equiv 0$$

* assuming for simplicity, in general g^j_i can be written as a linear comb of μ

activity ⇔



$\equiv -RT \ln a^{brine}_{H_2O}$

$g^{brine}_{H_2O} = g^{0}_{H_2O} + RT \ln a_{H_2O}$

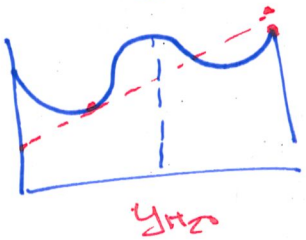
$a_{H_2O} \equiv \exp\left(\frac{g^{Brine}_{H_2O} - g^{0,w}_{H_2O}}{RT}\right)$

1) if $g^{ex} = 0$ and $g^{conf} = -R\sum y_i \ln y_i$ (ie a molecular model) then $a = y$ ⇒ hence the notion of "thermodynamic concentration."

2) in general $a \neq y$ but always $a(y)$ such that $y \to 1$ $a \to 1$

TEST #1 ⇒ [[1st test]] for any activity formulation

3) For any stable composition of a solution $a(y) \leq 1$



it is not required that $a_{H_2O} \to 0$ when $y_{H_2O} \to 0$

---

fugacity vs activity

ideal

activity $g_i = g^0_i(P,T) + RT \ln a_i$ $a_i = y_i$

fugacity $g_i = g^0_i(P_r,T) + RT \ln f_i$

$= g^0_i(P_r,T) + \int_{P_r}^{P} V^0_i dP$ → $RT \ln(P/P_r)$

$+ RT \ln a_i$

$f_i = y_i \cdot P$

$g^0_i(P,T) = g^0_i(P_r,T) + \int V dP$

$V_i = RT/P$ ⇐ ideal gas

technically

$\frac{f_{i,P}}{f_{i,P_r}} = y_i \frac{P}{P_r}$

but at 1 bar

$f_{i,P_r} = P_i$

~~$g^{sol} = g^{mech} + g^{conf}$~~

L 13.3 2021

geologically formulated solution models

$$g^{sol} = g^{mech} + g^{conf} + g^{ex}$$

$$\Rightarrow \text{irrationally} \quad g^{sol} = \sum^{\pm} y_i g_i^{sol} \Rightarrow g_i = g_i^0 + RT \ln a_i$$

$$= \sum^{\pm} y_i (g_i^0 + RT \ln a_i)$$

$$= \sum^{\pm} y_i g_i^0 + \sum y_i RT \ln a_i$$

(g^{mech})

$$g^{conf} = +RT \sum y_i \ln a_i^{ideal} \Leftarrow$$ (g^{conf})

$$g^{ex} = RT \sum y \ln \gamma_i$$

$$RT\left(\sum y_i \left(\ln a_i^{ideal} + \ln a_i^{non\text{-}ideal}\right)\right)$$ (a^{ex}; g^{conf})

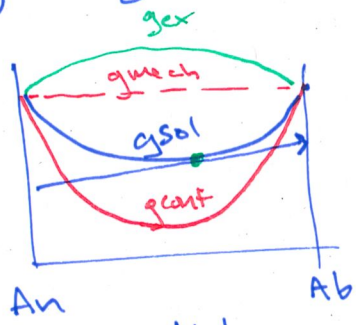
γ_i the activity coefficient

---

getting g_i, a_i, f_i from g

$$g_i^{sol} \equiv \frac{\partial G^{sol}}{\partial N_i} \neq \frac{\partial g}{\partial y_i}$$

only $z-1$ independent y's !!!



$g^{sol}(y_{ab})$

$$g^{Pl}_{Ab} = g^{Pl}(y_{ab})\Big|_y + \frac{\partial g^{Pl}}{\partial y_{Ab}}\Big|_y (1 - y_{ab})$$

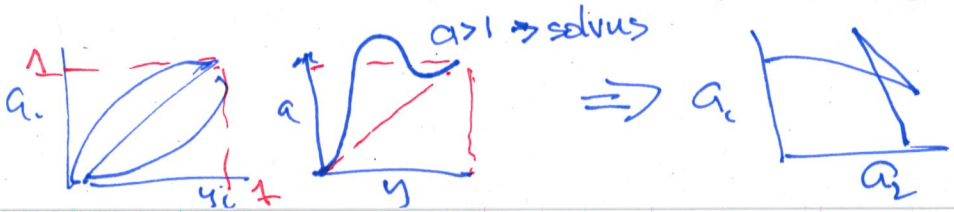
preferable because of symmetry →

$$g^{Pl}_{An} = g^{Pl}(y_{ab})\Big|_y + \frac{\partial G^{Pl}}{\partial y_{Ab}} (0 - y_{Ab})$$

↳ for $g^{sol}(y_{\hat{j}})$ → ie $i \neq j$

$$g_{\hat{j}}^{sol} = g^{sol}(y_{\hat{j}}) - \sum_{i=\hat{j}} y_i \frac{\partial g}{\partial y_i}$$

[[Test #2]] → $a_i \neq F(g_i^0)$ [for simple solution models]



L 13.4 2021

Back to Thermobarometry => problem 8.2

garnet (Mg, Fe : $Ca_3Al_2Si_3O_{12}$) + plagioclase (Na, Ca : $CaAl_2Si_2O_8$) + q (SiO_2) + ky (Al_2SiO_5)

$\Rightarrow C = 6 \Rightarrow$ reaction = C+1 phases

all 4 phases exist in $CaO-Al_2O_3-SiO_2$ $\quad k = 3$ $\quad$ reaction = 3+1 phases

(GASP) $\quad 3an - gr - 2ky - q = 0$ $\qquad \Delta g = 0$

necessary condition!

$$\Delta g = \sum_{i}^{P} \nu_i g^i = \sum \nu_i (g_i^\circ + RT \ln a_i)$$

(technically $g^i_{j(i)}$)

$$= \sum \nu_i g_i^\circ + \sum \nu_i RT \ln a_i$$

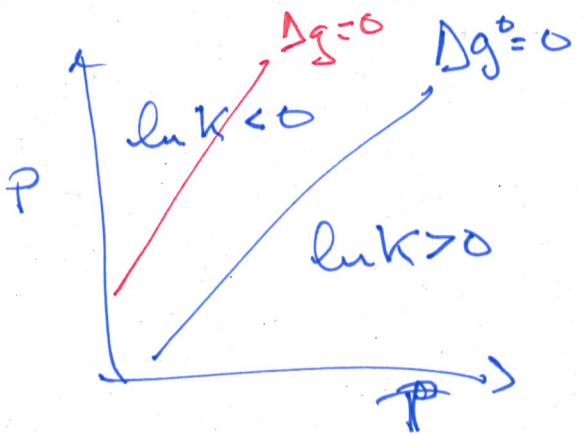
$$= \Delta g^\circ + \sum RT \ln a_i^{\nu_i}$$

$$= \Delta g^\circ + RT \ln \left(\Pi a_i^{\nu_i} \right)$$

eq constant:

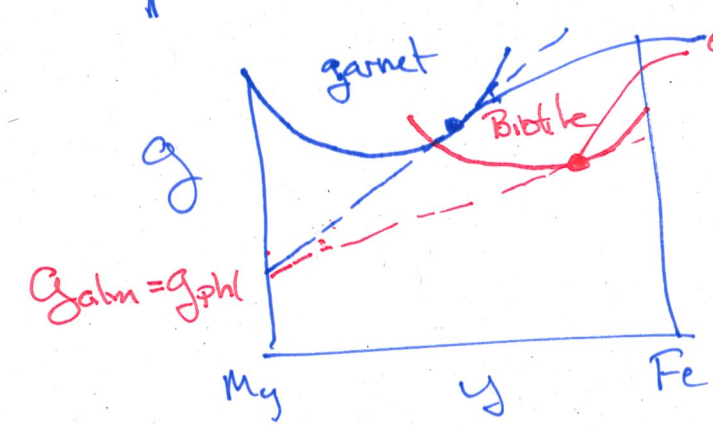
$$K \equiv \Pi a_i^{\nu_i} = a_{an}^3 / a_{gr} / a_{ky}^1 / a_q^1$$

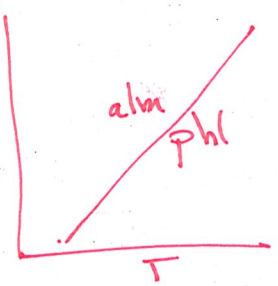
$K(P, T, y_i) \Rightarrow y_i$ observed.



Inverse method

1) plug in observed compositions
   compute $\Delta g(P,T) = 0 \Rightarrow$ gives "curve"
2) introduce 2nd constraint
3) always works $\Leftarrow$ why it's bad
5) empirical calibration $\Leftarrow$ why it's good

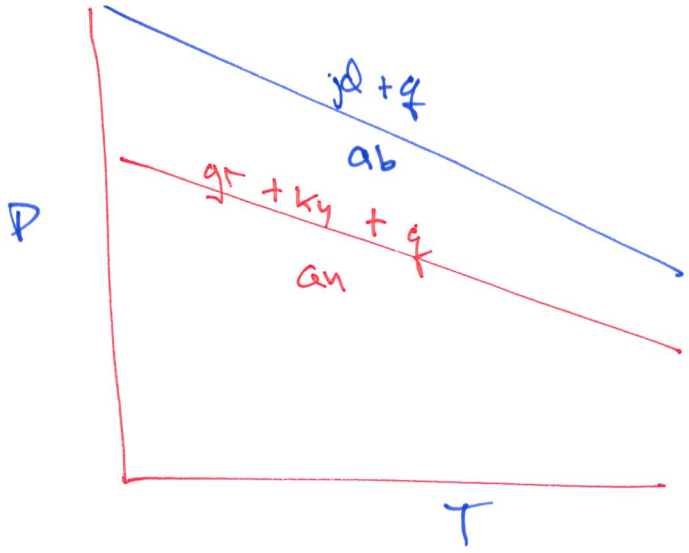




L13.5 2021

+ Cpx Gt + Pl + Cpx + Q + K

The Problem → necessary but not sufficient



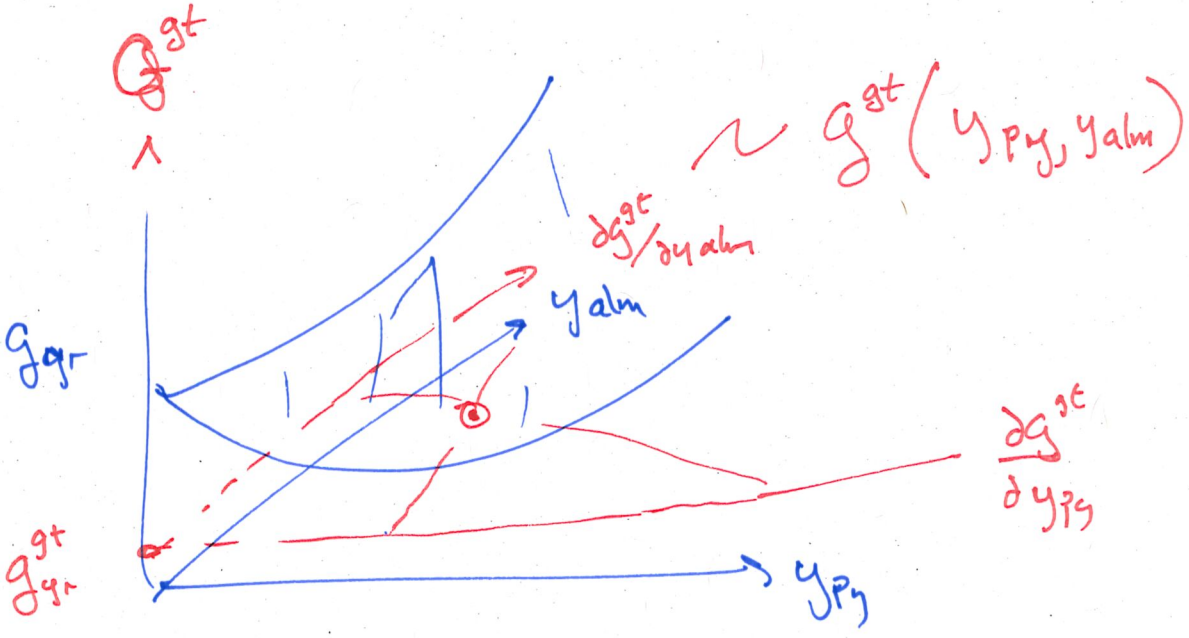
an = gr + ky + q hi P

ab = jd + q hi P

uncertainty - non-equilibrium
- bad data

even if they do cross
- it only means the phases could have been stably

Problem 8.2



$$g^{Gt}_{Gr} = g^{Gt}\Big|_{y_{alm}\, y_{Py}} - y_{Py}\left(\frac{\partial g^{Gt}}{\partial y_{Py}}\right) - y_{alm}\left(\frac{\partial g^{Gt}}{\partial y_{alm}}\right)$$

$$g_i = g - \sum_{j \neq i} y_j \left(\frac{\partial g_j}{\partial y_j}\right)$$

---

problem 8.4

1) $g^{Pl}_{Ab} = f_1(y^{Pl}_{An})$, $g^{Pl}_{An} = f_2(y)$

2) $T < T_c \rightarrow$ $g^{Anss}_{Ab} = g^{Abss}_{Ab}$, $g^{Anss}_{An} = g^{Abss}_{An}$

3) glan = subs ($y = y_1$, gan)
   glab = " ($y = y_1$, gab)

4) fsolve ($\{g^{lan}_{y1} = g^{an}_{y}, g^{lab}_{y1} = g^{ab}_{y}\}, \{y_1 = 0 \ldots y_c, y = y_c \ldots 1\}$)