Gibbs method – takes advantage of constraints from thermo. equilib. & mass balance.

equilib. constraints $\sum_{j=1}^{m} \nu_j \mu_j = 0$

$\Delta G_{rxn} = 0$

one for every stoichiometric equation written among the phase components of an equilibrium assemblage.

only necessary to write a linearly independent subset of ~~all~~ the possible reactions.

# of linearly indep. reactions = total # of phase components in all phases in an assemb. − # of system components

– stoichiometric constraints

$$\sum_{j=1}^{npc^k} X_j^k = 1 \leftarrow X_j^k \text{ is the mole frac. of component } j \text{ in phase } k$$

– mass balance constraint

one for each independent system component

specifies the bulk comp. of the rock by describing the amt. of each component present

$$m_i = \sum_{k=1}^{nph} n_i^k M^k \leftarrow \text{one for each component}$$

n_i^k = # of moles of sys comp. i in phase k.

M_k = # of moles of k in the rock

m_i - the number of moles of system component i is generally known, because it defines the bulk composition

the variable n_i^k can be expressed in terms of

X_j^k - it is the sum of the # of moles of system component i in one mole of each phase component j - ($n_{i,j}^k$) x the mole fraction of phase component j in the mineral or melt... X_j^k

or

$$n_i^k = \sum_{j=1}^{npc^k} n_{i,j}^k X_j^k$$

and the full mass balance becomes

$$m_i = \sum_{k=1}^{nph} m^k \sum_{j=1} n_{i,j}^k X_j^k$$

intensive variables in the Gibbs minimization of free energy are T, P and X

the number of independent variables is given by the Gibbs phase rule

$$F = nsc + 2 - nph$$

for each phase in the system there is a Gibbs - Duhem equation that can be used to specify relations of T, P and μ (3)

$$0 = S\,dT - V\,dP + \sum n_i\, d\mu_i$$

one for each phase

number of reactions

for any stoichiometry reaction among the phases in these system

$$\sum_{j=1}^{m} \nu_j \mu_i = 0$$

and there are $nrx = npct - nsc$ independent reactions of this type

# of phase components

# of sys. components

(4)

for system $MgO - FeO - SiO_2$ | phase components

Qtz
Opx
Oliv

2 linearly independent reactions

(20) $2\,MgSiO_3 = Mg_2SiO_4 + SiO_2$

(21) $2\,MgSiO_3 + Fe_2SiO_4 = 2\,FeSiO_3 + Mg_2SiO_4$

---

conditions of equilib.

(20) $-RT\ln K_{20} = \Delta H_{298} + \int_{298}^{T} \Delta C_p\, dT + \int_1^2 \Delta V\, dP - T\left(\Delta S_{298}\ \int_{298}^{T} \frac{\Delta C_p}{T} dT\right.$

(21) $-RT\ln K_{21} =$ " " "

Stoichiometric constraints

$X_{SiO_2}^{Qtz} = 1$

$X_{Fa}^{ol} + X_{Fo}^{ol} = 1$

$X_{En}^{opx} + X_{Fs}^{opx} = 1$

# of intensive variables = 7

$T, P, X_{Fo}, X_{Fa}, X_{En}, X_{Fs}, X_{SiO_2}$

# of constraints = 5 $\therefore$ 2 degrees of freedom

also mass balance constraints

$m_{SiO_2} = m_{Qtz} + m^{ol}(X_{Fo}^{ol} + X_{Fa}^{ol}) + m^{px}(X_{En}^{px} + X_{Fs}^{px})$

$m_{FeO} = 0 + m^{ol}(2X_{Fa}) + m^{ol}(X_{Fs})$

[illegible]

so the total # of constraints (5)

thermodynamic	2
stiochiometric	3
mass balance	3
	8

Total # of variables

10

T, P

X_{qtz}

X_{En}^{px}

X_{Fs}^{px}

X_{Fo}^{ol}

X_{Fa}^{ol}

M_{FeO}

M_{MgO}

M_{SiO_2}

for a variance of 2 - so - any 2 variables can be taken as independent

$$\boxed{F = c + 2 - \phi = 5 - 3 = 2}$$

now -
what to do with all of this information

1) choose variables as independent = to the variance

2.) specify values for each independent variable

3.) solve for dependent variables

we have been doing this graphically throughout the semester showing a T-X diagram and fixing $\underline{P}$

choosing T and X as independent variables

solving series of non-linear equations

To use Newton-Raphson - need to take total derivative of each equation with respect to the independent variables, e.g. T, P, X_j

so for each μ in our stoichiometric constraints

$$\sum_{j=1}^{m} \nu_j \mu_j \quad , \quad \left.\frac{\partial \mu_j}{\partial T}\right|_{P,X} = -\bar{S}_j$$

$$\left.\frac{\partial \mu_j}{\partial P}\right|_{T,X} = \bar{V}_j$$

$$\left.\frac{\partial \mu_j}{\partial X_j}\right|_{T,P\,x_i \neq x_j} = \frac{RT\alpha_j}{X_j} + \frac{RT\alpha_j}{\gamma_j}\left(\frac{\partial \gamma_j}{\partial X_j}\right)_{T,P,x_i \neq x_j}$$

since the nonideal term $RT \ln \gamma_j$ is a function of the composition of the phase - all the other X_j's change its value

$$\left.\frac{\partial \mu_j}{\partial X_i}\right)_{T,P,X_i \neq X_j} = \frac{RT\alpha_j}{\gamma_j} \left.\frac{\partial \mu_j}{\partial X_i}\right|_{T,P\,X_i \neq X_j}$$

plug these constraints into the original

2 stoic. coefficients

$$-\Delta S \, dT + \Delta V \, dP + \sum_{j=1}^{m} \nu_j \frac{RT\alpha_j}{X_j} dX_j$$

$$+ \sum_{j=1}^{m} \nu_j \left(\sum_{i=1}^{npct} \frac{RT\alpha_j}{\gamma_j} \left.\frac{\partial \gamma_j}{\partial X_i}\right|_{T, P, X_j \neq X_i} \right) dX_i$$

stoic constraints

$$\sum_{j=1}^{npc^k} dX_j^k = 0$$

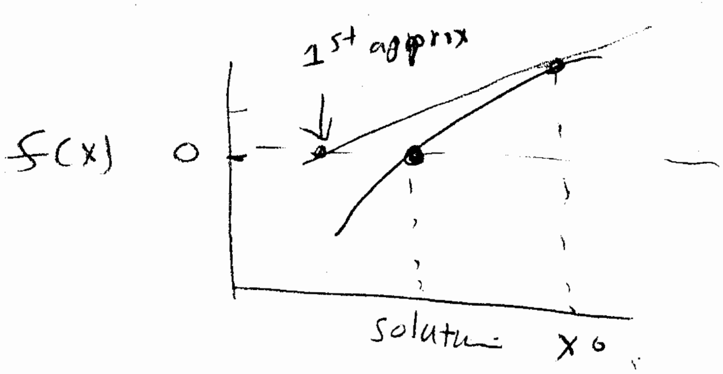
mass balance constraints for a closed system

$$\sum_{k=1}^{nph} m^k \sum_{j=1}^{npck} n_{i,j}^k \, dX_j^k + \sum_{k=1}^{nph} dM_k \sum_{j=1}^{npck} n_{i,j}^k X_j^k$$

solve using Newton-Raphson

find $f(x) = 0$

where $f(x) = f(x^0) + \frac{\partial f(x^0)}{\partial x} \Delta x$



p. 562 - shows it for our system

two variables must be specified often T & P, but not necessary might be better to specify P & bulk comp.

for the ex. in Spear -

he chooses T and X_{Fs}^{px} and solves for pressure and comp. of olivine and moles of qtz, px and oliv in assemb.

substitute in for $\Delta T = \Delta X_{Fs} = 0$

16-2 shows resulting equations

Jacobian soln method useful if you don't have complete thermo info

Table 16-5 shows problem where the trivial constraint for qtz has been relieved..

Spear constructions

T-X, P-X and P-T diagrams

rearrange eqns in 16.6 to show selected dependent variable

need to fix X_{Fs} and then start at a reference condition

16-2 shows P-X, T-X and T-P diagrams

pg. 571

when you add mass balance constraints always have 2 degrees of freedom.

— can track reactions ~~completely~~

16-4 - shows modal proportions

for fixed modal proportions

px used up first on decompression

oliv used up first on cooling