10 [12] possible problemsets ⇒ 9 count
0, 1, 2, 4a, 4b, 5, 6, 8a, 8b, 11, [9.1], [7]

Chapter 11.1 2022
↓
Note correction (yesterday) to Eq 11.11 $g = g'/\boxed{\ }$

Problem 0.1 → solvus → Chp 8.1 (solvus can be calculated quantitatively w/script for problem 9.1)

Problem 0.3, 0.4 → Chp 6 (9)

Problem 0.2

→ ergodic hypothesis does not allow variable order

$X = \frac{1}{2}$ < Dolomite $Ca^{M1}Mg^{M2}(CO_3)_2$; MgCc $(CaMg)_2^{M}(CO_3)_2$

Why?	S^{conf}	S^{vib}
Do	Low	high
MgCc	high	low

S^{vib} → measured by C_p usually referred to as "enthalpic stabilization

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Speciation (aka order-disorder or compound formation) models. Components vs. Species

Water → $c = 1 \rightarrow H_2O$ if stoichiometric | , max $c = 2 \rightarrow H_2, O_2$ if nonstoichiometric → $c \leq$ # of elements

physics → t - species H_2O, H_2, O_2, OH^-, H^+, H_2O_2 ..... there is no thermodynamic restriction on species → used in thermo only to facilitate (simplify) empirical solution models

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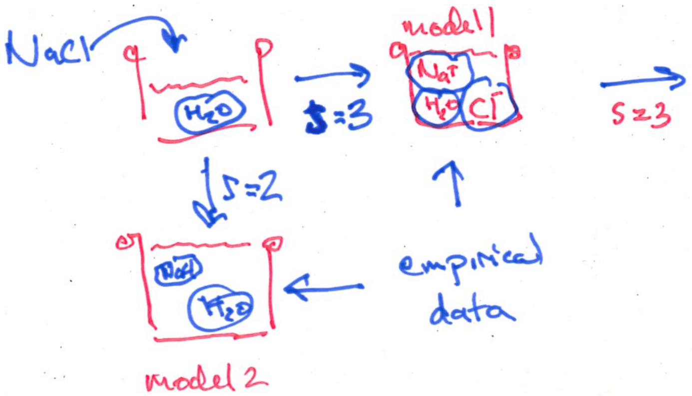
Two kinds of speciation models → Primitive → $t = c$ endmembers

→ microscopic speciation stoichiometrically prescribed (ergodic)

→ nothing new (plagioclase) → looks different for fluids and melts: $NaCl + H_2O \Rightarrow c = 2$ (!)



y → endmember fraction ($\Sigma = 1$)

z → species fraction ($\Sigma = 1$)

n_{TOT} → total number of mols of species

$n_{TOT} = y_{H_2O} + 2y_{NaCl} \Rightarrow y_{H_2O} = 1 - y_{NaCl}$

$= 1 + y_{NaCl}$

s=3 cont'd $\Rightarrow$ $z^*_{Na^+} = \frac{n_{Na^+}}{n_{TOT}} = \frac{y_{NaCl}}{1+y_{NaCl}} \left[= z_{Cl^-}\right]$

$$z_{H_2O} = \frac{n_{H_2O}}{n_{TOT}} = \frac{1-y_{NaCl}}{1+y_{NaCl}}$$

$$-\frac{S^{conf}}{R} = z_{Na^+}\ln z_{Na^+} + z_{Cl^-}\ln z_{Cl^-} + z_{H_2O}\ln z_{H_2O}$$

$$= 2\,\underbrace{\frac{y_{NaCl}}{1+y_{NaCl}}}_{y_{NaCl}}\ln\underbrace{\left(\frac{y_{NaCl}}{1+y_{NaCl}}\right)}_{y_{NaCl}} + \underbrace{\frac{1-y_{NaCl}}{1+y_{NaCl}}\ln\left(\frac{1-y_{NaCl}}{1+y_{NaCl}}\right)}_{0} \quad y_{NaCl}\rightarrow 0$$

1

$$-\frac{S^{conf}}{R} = y_{NaCl}\ln y^2_{NaCl} = y_{NaCl}\ln\left(a^{ideal}_{NaCl}\right) \qquad a^{ideal}_{NaCl} = y^2_{NaCl}$$

intro chemistry

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model 2 s=2

$$-\frac{S^{conf}}{R} = y_{NaCl}\ln y_{NaCl} + \cancel{y_{H_2O}\ln y_{H_2O}}^{\,0} \qquad y_{NaCl}\rightarrow 0$$

$$= y_{NaCl}\ln a_{NaCl} \qquad a_{NaCl} = y_{NaCl}$$

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silicate melt models are generally of this form (t=c)

Non-ergodic speciation models (order-disorder, compound formation)

$\Rightarrow$ t>c endmembers (species)

$\Rightarrow$ t-c speciation reactions

eg H_2O $\Rightarrow$ components $C=2$, species $t=\{H_2, O_2, H_2O\}=3$, speciation reaction $H_2+\frac{1}{2}O_2 = H_2O$

$\Delta G^o \neq 0$

$c = 1 \Rightarrow$ solution model $\Rightarrow$ oxygen $O\ [O_2, O_3, \ldots]$ ← Thermodynamics

$t = 2 \Rightarrow O_2, O_3$ species ← physics

$t - c = 1 \Rightarrow$ speciation reactions $\quad \frac{3}{2}O_2 - \frac{2}{2}O_3 = 0 \quad \Delta\alpha = 3-2 = 1$

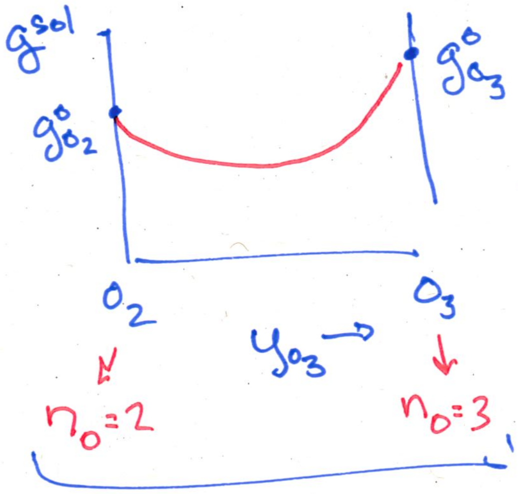
$$g^{sol} = \cancel{\sum_{i=1}^{t} y_i g_i^o} - Ts^{conf} + \cancel{g^{ex}} \rightarrow 0 \text{ for simplicity}$$

for ~~homogeneous~~ internal phase relations C of the g_i^o values may be set $= 0 \Rightarrow \sum_{c+1}^{t} y_i \Delta g_i^o$

$$= y_{O_3} \Delta g^o_{O_3}$$

$$g^{sol} = y_{O_3} \Delta g^o_{O_3} - RT\left(y_{O_3} \ln y_{O_3} + y_{O_2} \ln y_{O_2}\right)$$

$\Rightarrow$ eliminate $y_{O_2}\ (= 1 - y_{O_3}) \Rightarrow g(y_{O_3})$



$g^{sol} \rightarrow$ is g/mole-of-species

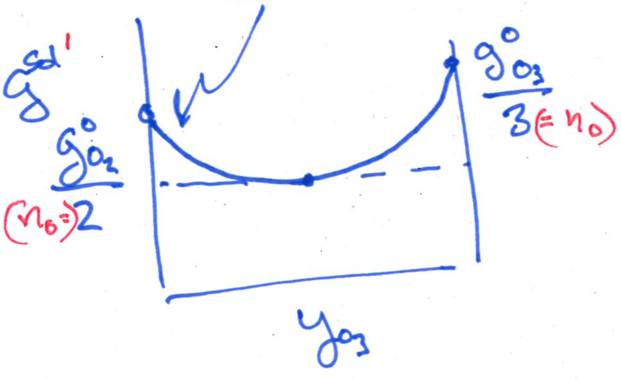
we need g/mole-of-atoms

~~For an initial~~ $n_O = 2 + y_{O_3}$

$$g^{sol'} = g^{sol}/n_O = g^{sol}/2 + y_{O_3}$$

↳ generalization in Chp11 eqs 6-11

all values are for 1mol of O atoms



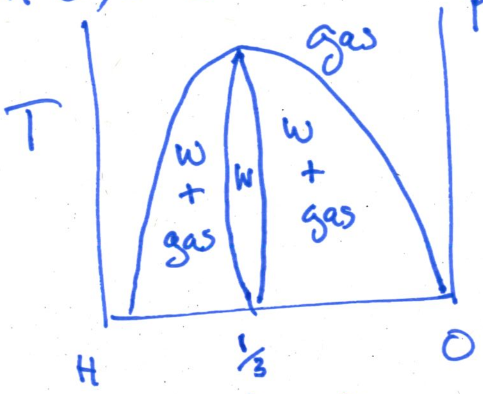
$$\mathrm{min}\left(g^{sol'}(y_{O_3})\right) \Rightarrow$$

$$\mathrm{solve}\left(\mathrm{diff}\left(g^{sol'}, y_{O_3}\right)\right)$$

$c > 2$ $t > c$ convergent ordering

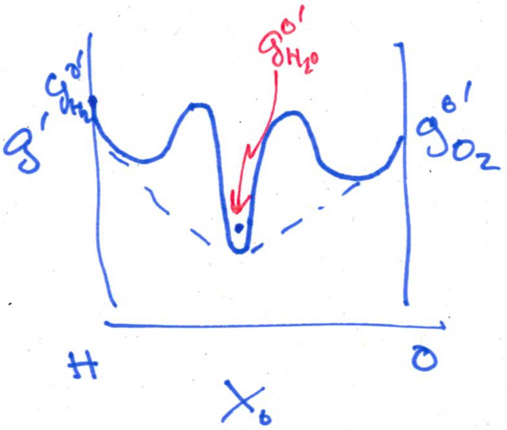
H-O, $c = 2$

$P < P_{crit} \approx 221$ bar



$c = 2$

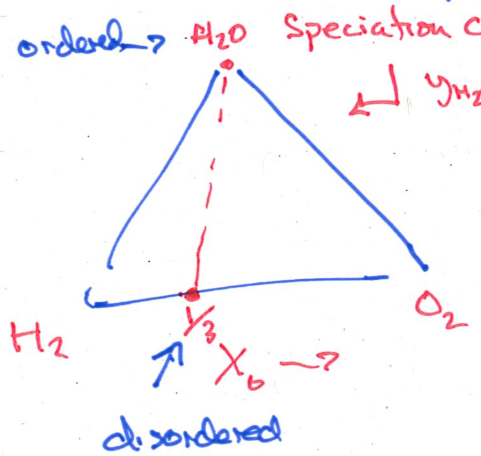
$t = 3 = \{H_2, O_2, H_2O\}$



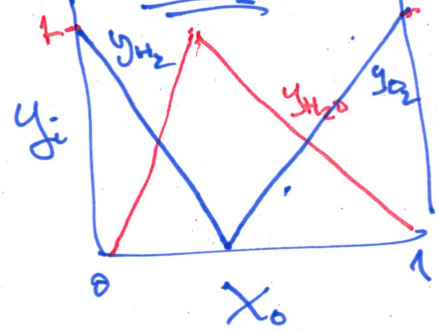
X_O → Bulk composition

ordered → H_2O Speciation composition

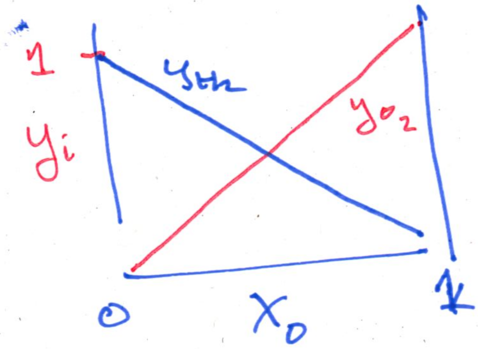
↵ $y_{H_2O}, y_{H_2}, y_{O_2}$



low T ($T < T^{crit} < 374°C$)



high T ⇒ $y_{H_2O} = 0$



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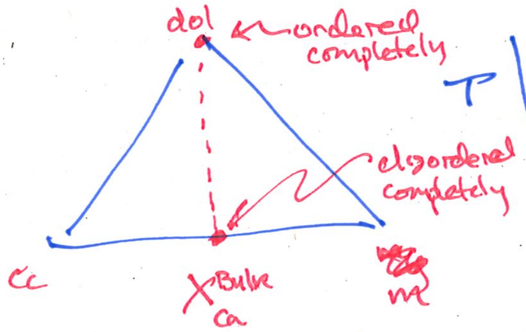
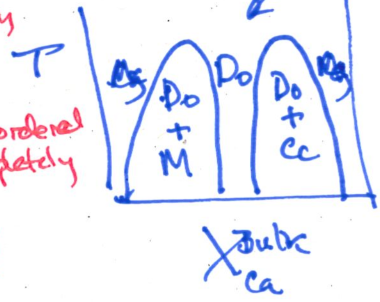
solids do-cc-m (problem 11.1 omphacite jd-di-om)

$c = 2$ $\{CaCO_3, MgCO_3\}$ — means there MUST be 2 crystallographically distinct sites for Ca, Mg

$t = 3$ $\{\overset{cc}{CaCO_3}, \overset{m}{MgCO_3}, \underbrace{Ca_{.5}Mg_{.5}CO_3}_{dol}\}$



non-convergent (no transition to completely disordered phase)



⇒ we need $g^{sol}(X_{Ca}, y_{do})$

Chap 11.5 2022

Endmember site occupancies and multiplicities

	M1	M2
cc	Ca	Ca
m	Mg	Mg
do	Mg	Ca
f^j	1/2	1/2

1) formulate $g^{sol}(y)$

$g^{mech} = y_{cc} g^o_{cc} + y_m g^o_m + y_{do} g^o_{do} \Rightarrow c=2 \rightarrow so$

For internal phase relations we may set $g^o_{cc} = g^o_m = 0$

and $g^{mech} = y_{do} g^o_{do}$ ($g^o_{do} = \Delta g^o$ for the pure ordering rxn)

$$g^{conf} = -RT \left\{ \tfrac{1}{2} \left[z^{M1}_{Ca} \ln z^{M1}_{Ca} + z^{M1}_{Mg} \ln z^{M1}_{Mg} \right] + \tfrac{1}{2} \left[z^{M2}_{Ca} \ln z^{M2}_{Ca} + z^{M2}_{Mg} \ln z^{M2}_{Mg} \right] \right\}$$

From site occupancy table $z^{M1}_{Ca} = y_{cc}$ $z^{M1}_{Mg} = 1 - y_{cc}$

$z^{M2}_{Mg} = y_m$ $z^{M2}_{Ca} = 1 - y_m$

$g^{ex} = 0$ for simplicity, in general an excess function as in normal solutions (and in problem 11.1)

2) convert to $g^{sol}(X_{Ca}, y_{do})$

a) $X_{Ca} = \dfrac{n_{Ca}}{n_{Ca} + n_{Mg}}$ $n_{Ca} = y_{cc} + \tfrac{1}{2} y_{do}$

$n_{Mg} = y_m + \tfrac{1}{2} y_{do}$

$n_{tot} = y_{cc} + y_{mg} + y_{do} = 1$

$X_{Ca} = y_{cc} + \tfrac{1}{2} y_{do}$

$g(X_{Ca}, y_{do}, y_m) \Leftarrow$ $\Rightarrow y_{cc} = X_{Ca} - \tfrac{1}{2} y_{do}$

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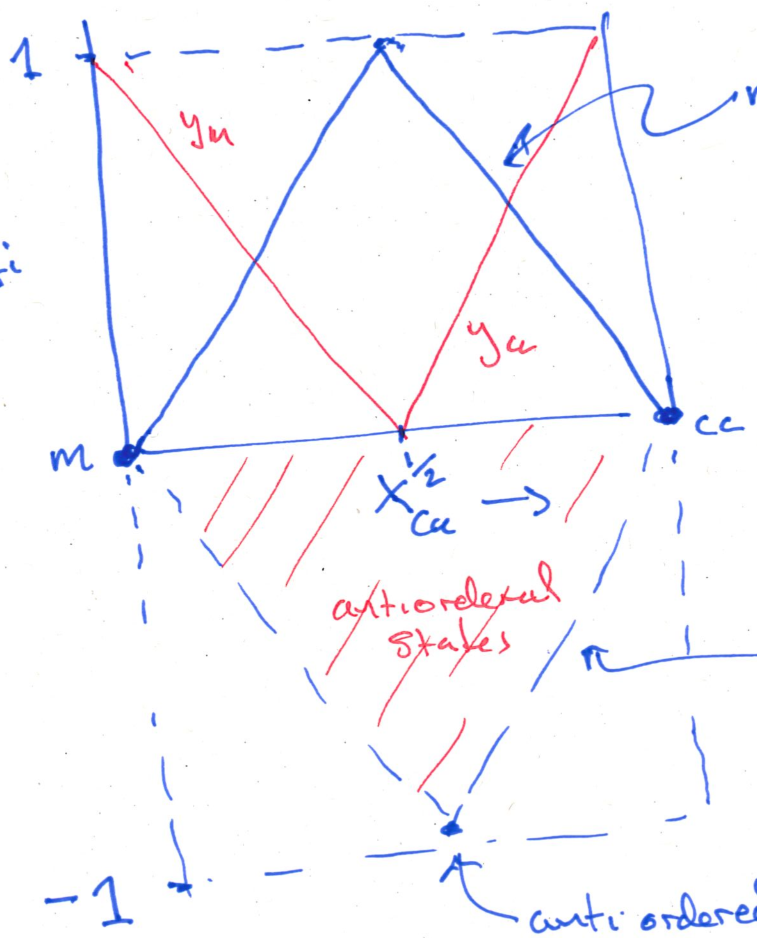
b) use closure to eliminate y_m $\Rightarrow$

$y_m = 1 - y_{cc} - y_{do}$ $\Rightarrow$ $y_{cc} = X_{ca} - \frac{1}{2} y_{do}$

$y_m = 1 - X_{ca} - \frac{1}{2} y_{do}$ $\Rightarrow$ $g(X_{ca}, y_{do})$



max(y_{do}) – fully ordered

ignoring anti ordered states

if $X_{ca} < \frac{1}{2}$

$y_{do,max} = 2X_{ca}$

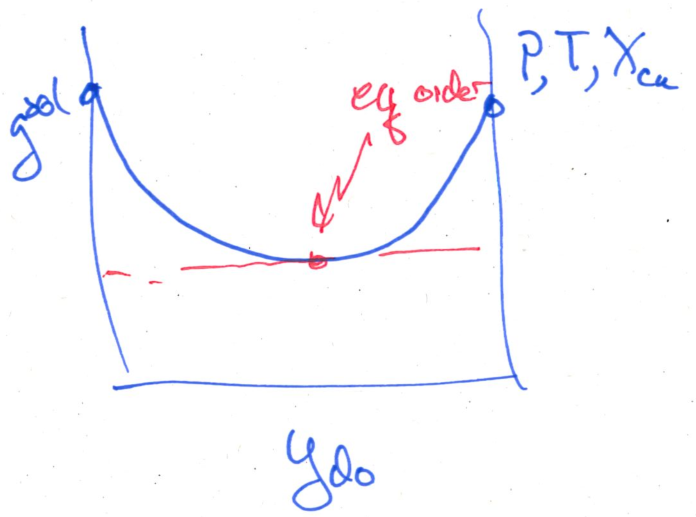
if $X_{ca} > \frac{1}{2}$

$y_{do,max} = 2(1 - X_{ca})$

anti ordered (true min y_{do})

($y_{do,min} = -y_{do,max}$)

anti ordered dolomite = m + cc – do



min (g^{sol}) at cst P, T, X_{ca}

$\Rightarrow$

solve (diff ($g, y_{do} = \cancel{0} \ldots y_{do,max}$))

or $y_{do,min}$

given ~~y_{do}~~ and X_{ca}; y_{cc} and y_m can be obtained by back substitution

Order parameters $Q = [-1, 1]$

$-1 \rightarrow$ antiordered

$0 \rightarrow$ disordered

$1 \rightarrow$ ordered

usually expressed as the difference in site fractions for some element, eg here (and in problem 11.1)

$$Q = Z^{M1}_{Mg} - Z^{M2}_{Mg} = (y_m + y_{do}) - (y_m) = y_{do}$$

Why bother?