Order/disorder, aka speciation, models

Water → 1 component → H_2O, max 2 → $H_2 + O_2$ → $c \leq$ # of elements

n-species $H_2O, H_2, O_2, OH^-, H^+, H_2O_2, \ldots$ no Thermodynamic restriction

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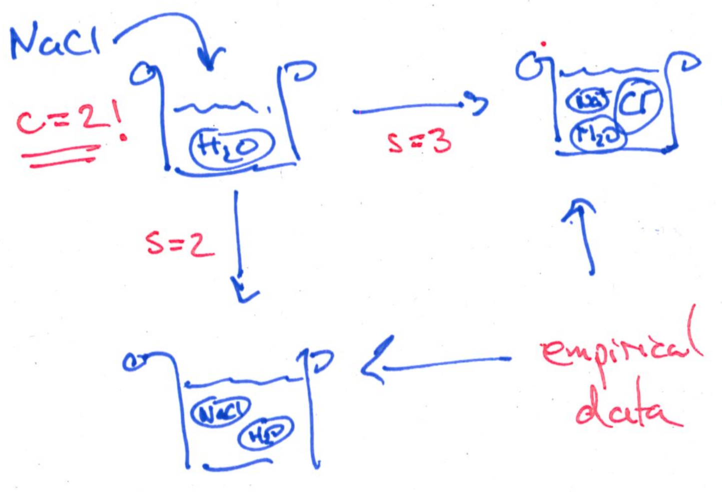
Primitive speciation models → t = c endmember → microscopic speciation stoichiometrically prescribed

→ nothing new (plagioclase) → looks different for fluids and melts



y → endmember fraction

z → species fraction ($\Sigma = 1$)

n_{TOT} → total number of mols of species

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

$$z_{Na^+} = z_{Cl^-} = y_{NaCl}/(1+y_{NaCl})$$

$$z_{H_2O} = (1-y_{NaCl})/(1+y_{NaCl})$$

$$y_{NaCl} = 1 - y_{H_2O}$$

$$-\frac{S^{conf}}{R} = y_{NaCl}\ln y_{NaCl} + y_{H_2O}\ln y_{H_2O}$$

$$a_{NaCl} = y_{NaCl}$$

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

$$= 2\frac{y_{NaCl}}{(1+y_{NaCl})}\ln\left(\frac{y_{NaCl}}{1+y_{NaCl}}\right) + \frac{(1-y_{NaCl})}{(1+y_{NaCl})}\ln\frac{(1-y_{NaCl})}{(1+y_{NaCl})}$$

introchem $\xleftarrow[y_{NaCl} \to 0]{}$

$$-\frac{S^{conf}}{R} = y_{NaCl}\ln y_{NaCl}^2$$

$$a_{NaCl} = y_{NaCl}^2$$

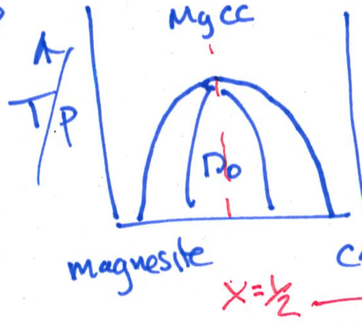
Silicate melts are generally of this form.

0, 1, 2, 4a, 4b, 5, 6, 8a, 8b, 11. 9 problemsets

Problem 0.1 → solvus → Chp 8.11

0.4, 0.3 → Chp 6 (9), 9.1 possible problem

0.2 →



→ ergodic hypothesis does not allow variable order

Do → $Ca^{M1}Mg^{M2}(CO_3)_2$

MgCc → $(Ca,Mg)_2(CO_3)_2$

	g_{conf}	g_{vib}
Why? Do	low	high
MgCc	high	low

↓ measured by C_p usually referred to as "enthalpic" stabilization.

Variable speciation models = order-disorder

= cpd formation models $t>c$

endmembers ⇒ $t-c$ reactions

eg H_2O → $t=3$, $c=2$ (or 1) $H_2 + O_2 = H_2O$ $\Delta g^o \neq 0$!!

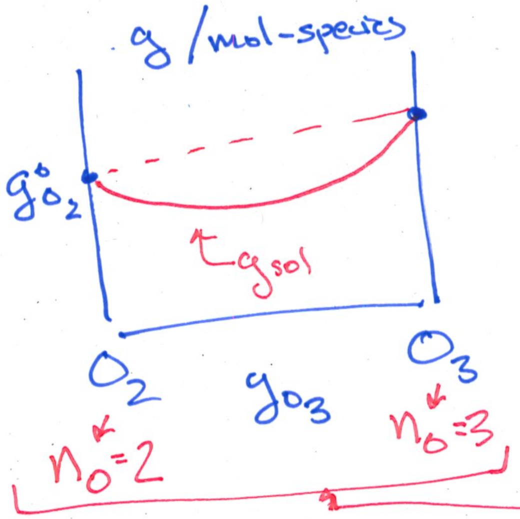
~~$t=5$, $c=2$ $H_2 = 2H^+$~~ → back off to $c=1$

$c=1$ ⇒ oxygen O $[O_2, O_3 \dots]$ ← thermodynamics

$t=2$ ⇒ O_2, O_3 species $[O \dots]$ ← physics

$t-c=1$ independent reaction $3O_2 = 2O_3$ $\Delta g^o \neq 0$ $(>>0)$

$3O_2 - 2O_3 = 0$ $\Delta \nu = 3-2=1$



$$g^{sol} = \sum_{i=1}^{t} y_i g^o_i - T s^{conf} + g^{ex}$$

$\to y_{O_3}\Delta g_{O_3}$; $g^{ex} \to 0$

$$s^{conf} = -R\sum_{i=1}^{t} y_i \ln y_i$$

⇒ eliminate y_{O_2}

⇒ $g(y_{O_2})$

⇒ g^{sol} is per mol-species

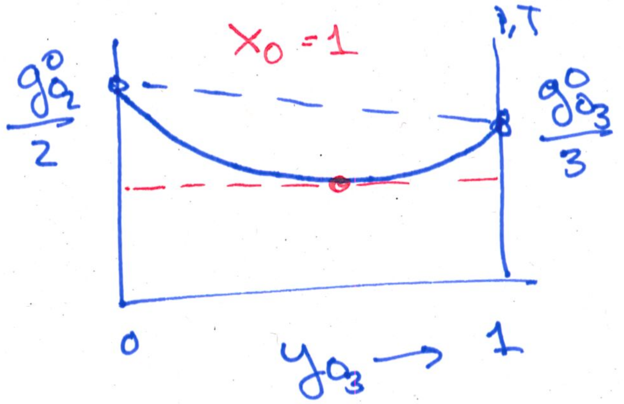
we need g' per mol-atom →

$n_O = 2 + y_{O_3}$ $\qquad g' = g^{sol}/n_O \Rightarrow$ in chp 11 $\rightarrow$ chapter 11 Eqs 6-11

$g' = \Xi\, g^{sol}$

$\sum \nu_i = 0 \Rightarrow \Xi = 1$

usually the case for solids



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

$\min(g'(y_{O_3})) \Rightarrow \text{solve}(\text{diff}(g', y_{O_3}))$

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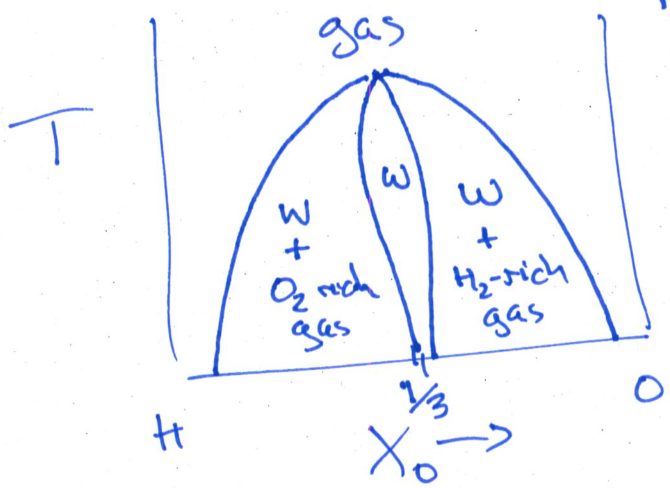
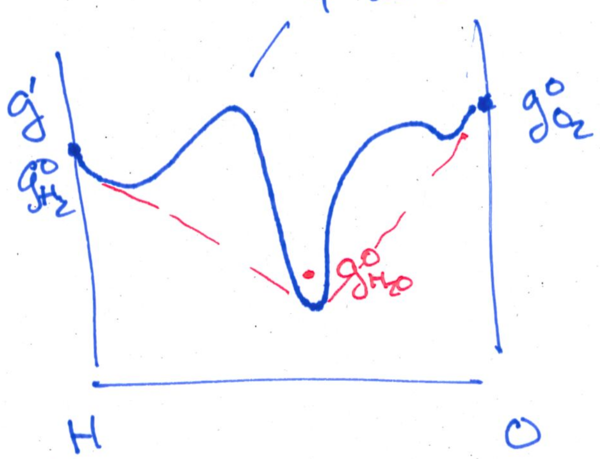
multicomponent speciation

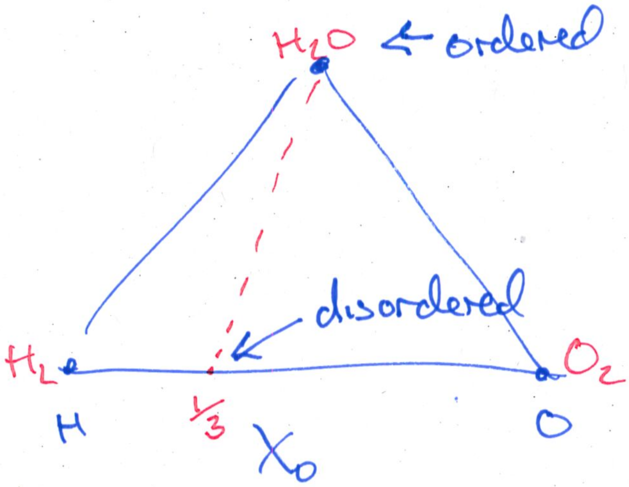


$P_{cs1} < 21216$

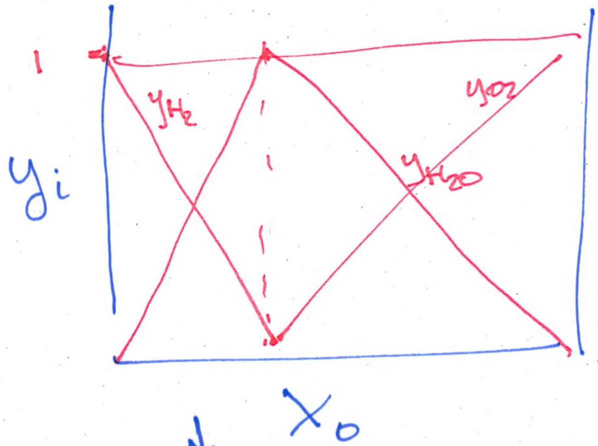
$c = 2$

$t = 3$ $\quad H_2O$, H_2, O_2

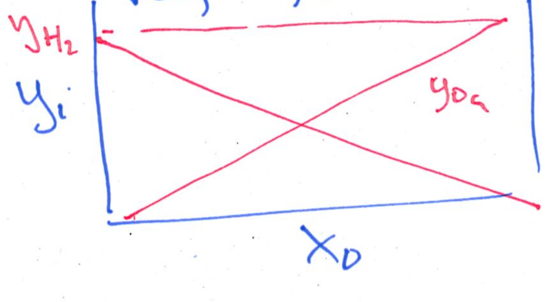




not so high T (> 374°C)



very high T



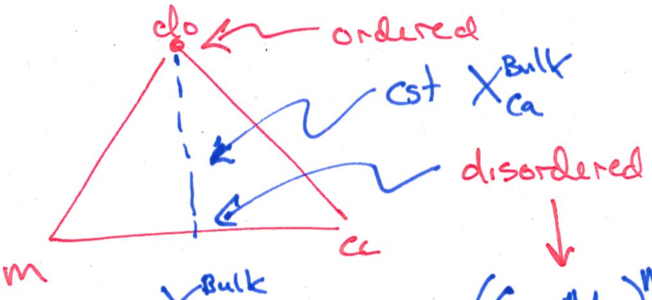
solids do-cc-m (problem 11.1 jcl-di-om)

$c = 2$ $\{CaCO_3, MgCO_3\}$

$t = 3$ $\{CaCO_3, Ca_{1/2}Mg_{1/2}CO_3, MgCO_3\}$ $\Rightarrow$ 1 reaction $\frac{1}{2}cc + \frac{1}{2}m = do$

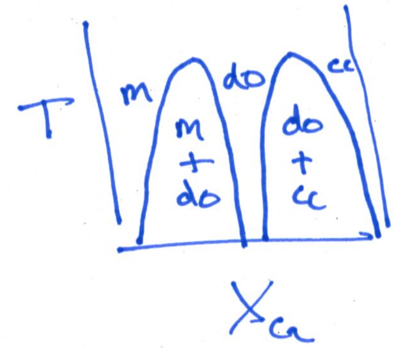
$\sum \nu = 0$

$\Delta g^o_{do} \neq 0$



$X^{Bulk}_{CaCO_3}$

$\longrightarrow$



disordered

$\downarrow$

$(Ca,Mg)^{M}CO_3$

$\downarrow$

$(Mg)^{M1}_{1/2}(Ca)^{M2}_{1/2}CO_3$

	M1	M2
cc	Ca	Ca
M	Mg	Mg
do	Mg	Ca
g	1/2	1/2

$X_{CaCO_3} = n_{Ca}/(n_{Ca}+n_{Mg})$

we need $g^{sol}(X_{CaCO_3}, y_{do})$

$\Rightarrow$ 1st formulate $g^{sol}(y)$

$g^{mech} = y_{cc}g^o_{cc} + y_m g^o_m + y_{do}g^o_{do}$ $\rightarrow$ since $c=2$ $\rightarrow$ two arbitrary g's $\rightarrow$ set $g^o_{cc} = g^o_m = 0$ then

$g^{mech} = y_{do}g^o_{do}$ $(\cancel{g^o_{do}}\ g^o_{do} = \Delta g^o_{do})$

$+\ g^{conf} = -RT \cdot \left\{ \frac{1}{2}\left[z^{M1}_{c}\ln z^{M1}_{c} + z^{M1}_{M}\ln z^{M1}_{M}\right] + \frac{1}{2}\left[z^{M2}_{c}\ln z^{M2}_{c} + z^{M2}_{M}\ln z^{M2}_{M}\right]\right\}$

from site occupancy table $z^{M1}_{Ca} = y_{cc}$,

$z^{M1}_{Mg} = y_{M} + y_{do}$, $z^{M2}_{Ca} = y_{cc} + y_{do}$, $z^{M2}_{Mg} = y_M$

$+\ g^{ex} = 0$ for simplicity, in general $= \sum W_{ij} y_i y_j$ as in normal solutions

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$= g^{sol}(y_{cc}, y_{do}, y_M) \Rightarrow$ need $g^{sol}(X, y_{do})$

$X_{ca} = n_{ca} / (n_{ca} + n_{mg})$

$n_{ca} = y_{cc} + \frac{1}{2} y_{do}$

$n_{mg} = y_{m} + \frac{1}{2} y_{do}$

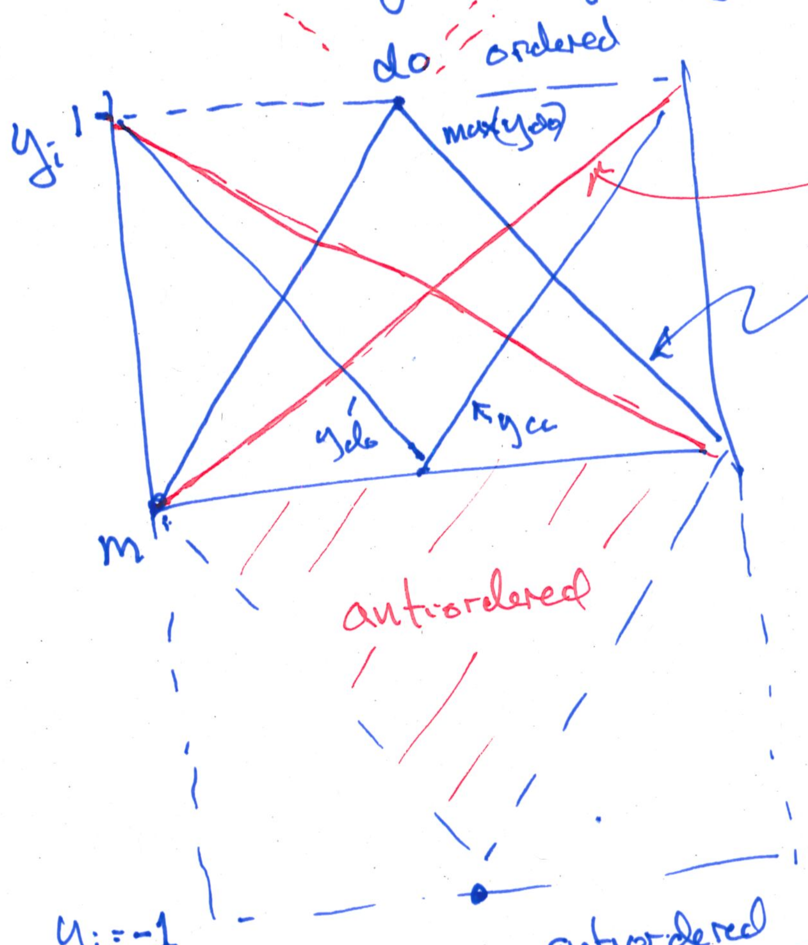
$n_{TOT} = n_{ca} + n_{mg} = y_{cc} + y_{mg} + y_{do} = 1$

$\downarrow$

$X_{ca} = n_{ca} = y_{cc} + \frac{1}{2} y_{do} \Rightarrow y_{cc} = X_{ca} - \frac{1}{2} y_{do} \Rightarrow g^{sol}(X, y_{do}, y_m)$

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

$\Rightarrow g^{sol}(X_{ca}, y_{do})$



max disorder ($y_{do} = 0$)

max order, ie max y_{do}

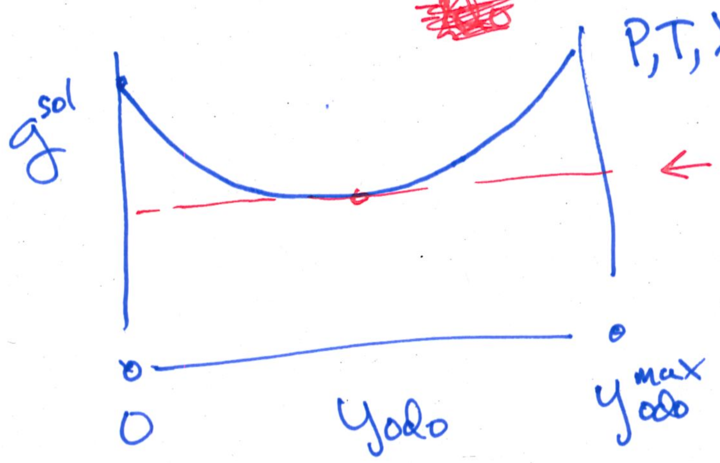
if $X < \frac{1}{2}$

$y_{do,max} = \cancel{X/2}\ 2X$

if $X > \frac{1}{2}$

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

antiordered dolomite $= m + cc - do$



$\leftarrow$ min (g^{sol})

$=$ diff $(g, y_{do} = 0..y_{do,max})$

$= 0 \Rightarrow y_{do}$

y_{cc}, y_m by back substitution

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

antiordered 0 ordered

disordered

$Z^{M1}_{Mg} - Z^{M2}_{Mg}$

$= (y_M + y_{do}) - (y_M) = y_{do}$

why bother?