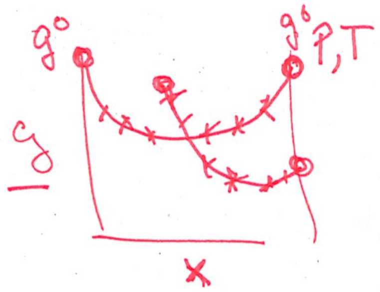


1) construct the curves -> chp 8

2) obtain g^0's -> chp 7

$g(P,T) \rightarrow g(P,T,y)$

$\rightarrow$ mixture of t endmembers, Olivine (fo, fa), Plagioclase (An, Ab)

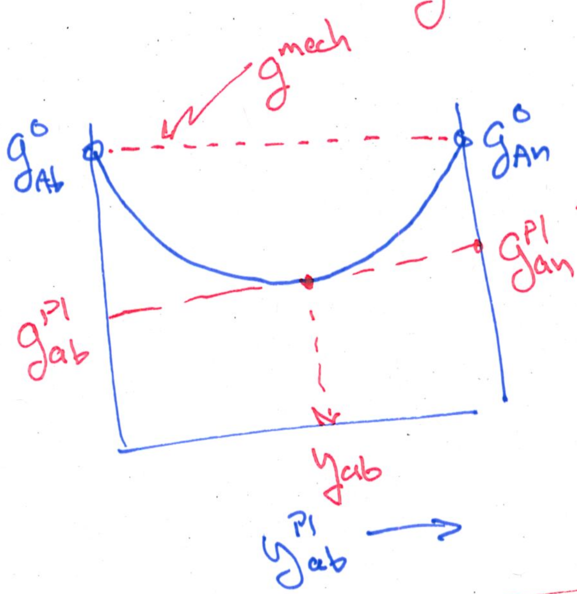
$\rightarrow$ composition $\rightarrow$ molar endmember fractions, $y_i = N_i / \sum^t_i N_i$

$\rightarrow$ $g^{sol} = g^{mech} + g^{conf} + g^{strain}$ $\quad \alpha = \sum^t N_i$

$\sim \quad \Delta u \quad - T\Delta s^{conf} + p\Delta v^{strain}$

$$G^{sol} = \sum^c \mu_i x_i = \sum^t g_i^{sol} y_i^{sol}$$

$\uparrow$ system $\qquad$ $\uparrow$ phase



$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{P,T\ldots} \qquad g_i^{sol} = \left(\frac{\partial G^{sol}}{\partial N_i^{sol}}\right)_{P,T\ldots}$$

$\Leftarrow$ partial molar gibbs energy of of i in "sol"

$g^{mech} = \sum y_i g_i^0 \Rightarrow$ bookkeeping term, can be dropped for homogeneous phase relations

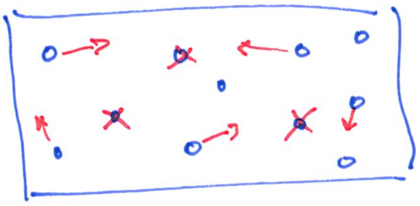
---

g^{conf} $\rightarrow$ theoretical entropic stabilization $= -T\Delta s^{conf}$

$\rightarrow$ $s^{conf} \propto$ to the total number of microstates W $\rightarrow$ ergodic hypothesis

2021 11.2

$\rightarrow W = 1,\ S^{conf} = 0$, ergo $S^{conf} = k \ln W$ Boltzman!



What are we counting?

$S^{vib} + S^{pos} + S^{conf} + \ldots$

$S^{conf} \rightarrow$ how many ways the atoms can be painted x or o

$N = N_o + N_x$

$W^{conf} = N! \,/\, N_o!\, N_x!$ a wee bit problematic if $N \sim N_A = 6 \times 10^{23}$

$$N! = N \ln N - N$$

$$\ln W^{conf} = \ln(N!) - \ln(N_o!) - \ln(N_x!)$$

$$= N \ln N - N_o \ln N_o - N_x \ln N_x - \cancel{N + N_o + N_x} \rightarrow 0$$

$\Rightarrow z_x = N_x / N \rightarrow N_x = z_x N,\ N_o = \ldots$

$$= N \ln N - z_o N [\ln N + \ln z_o] - z_x N [\ln N + \ln z_x]$$

$$= \Big[N \ln N - [\cancel{z_o N \ln N + z_x N \ln N}]\Big] \rightarrow 0$$

$$- z_o N \ln z_o - z_x N \ln z_x$$

$$= -N \sum^{t} z_i \ln z_i$$

$$S^{conf} = k \ln W = \cancel{Nk \ln} \; \underline{-Nk \sum^{t} z_i \ln z_i}$$

always positive because $z < 1$ ← the "Gibbs Formula"

if $N = N_A$ then $Nk = R$ ← universal gas constant

↑ Boltzmans cst.

Stefan → Boltzman → Nernst, Ehrenfest, Arrhenius

Euler, Bernoulli, → atoms

Mueller - Tragicomedy

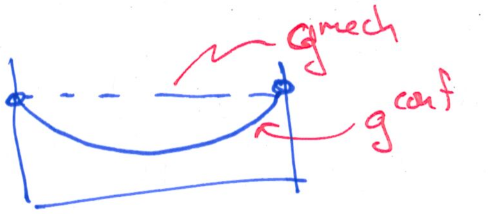
→ 1900 → Ether revival → duality → depression, † 1906.

Mach, applied math

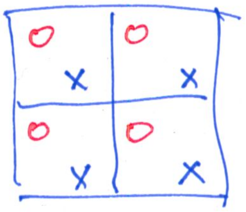
2021 11.3

Crystals $\rightarrow$ molecular model

$$g^{conf} = -Ts^{conf} \rightarrow S^{conf} = -R\left[y_{ab}\ln y_{ab} + y_{an}\ln y_{an}\right]$$

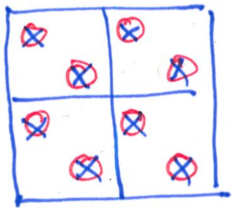


feldspar T2 $\rightarrow$ sub-lattice model



"~~Ideal~~" misnomer
↓
Experimental !!
↓
crystallography
phase equilibria

	M	T2	T1	O
Albite	[Na]	[Al Si]	[Si Si]	$[O]_8$
Anorthite	[Ca]	[Al Al]	[Si Si]	$[O]_8$
multiplicity	$g^{M1}=1$	$g^{T2}=2$	$g^{T1}=2$	$g^{O}=8$



$$S^{M} = -\cancel{g^{M}}\,R\left(Z^{M}_{Ca}\ln Z^{M}_{Ca} + Z^{M}_{Na}\ln Z^{M}_{Na}\right) \Rightarrow Z^{M}_{Ca} = f(y)$$

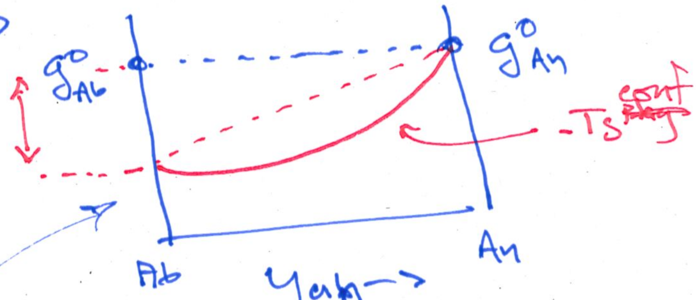
1

$$S^{T2} = -\cancel{g^{T2}}\,R\left(Z^{T2}_{Al}\ln Z^{T2}_{Al} + Z^{T2}_{Si}\ln Z^{T2}_{Si}\right) \Rightarrow Z^{T2}_{Al}\ ?$$

2

$$S^{Plag} = S^{M} + S^{T2} + S^{T1} + S^{O} \qquad S^{T1} = S^{O} = 0$$

The fly in the ointment $\Rightarrow$



$$g^{o}_{i} = u^{o}_{i} - Ts^{o}_{i} + Pv^{o}_{i}$$

↓

$$\left(s^{o,vib}_{i} + s^{o,conf}_{i}\right)$$

$$g^{mech} = \sum^{t} y_i g^{o}_{i} \Rightarrow \text{includes } -T\sum^{t} y_i s^{o,conf}_{i}$$

$$g^{sol} = g^{mech} + T\sum^{t} y_i s^{o,conf}_{i} - Ts^{conf} + g^{strain}$$

$$= g^{mech} - T\left(s^{conf} - \sum y_i s^{o,conf}_{i}\right) + g^{strain}$$

$$= g^{mech} - T\Delta s^{conf} + g^{strain}$$

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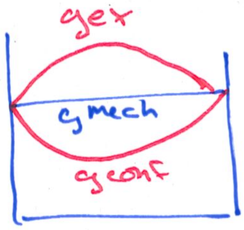
g^{strain} or g^{excess} because in practice it's a fudge factor accounting for the inadequacy of g^{conf} as well as strain $\Rightarrow$ taylor in y



$$g^{ex} = W_0 + \cancel{W_1 y_1 + W_2 y_2 \ldots} \rightarrow 0$$

$$+ W_{12} y_1 y_2 + \cancel{W_{21} y_2 y_1 \ldots} \rightarrow \text{collapse by symmetry to } W_{12} y_1 y_2$$

$2^o \rightarrow g^{ex} = \sum_{i}^{t-1} \sum_{j=i+1}^{t} W_{ij} y_i y_j \Rightarrow$ regular if $W \neq f(P,T)$ ← elastic

subregular if $W(P,T)$

symmetric on y

$3^o \rightarrow g^{ex} = W_{ananab} y_{an} y_{an} y_{ab} + W_{anabab} y_{an} y_{ab} y_{ab}$

asymmetric on y

van Laar $\quad g^{ex} = W_{ij} \varphi_i \varphi_j \rightarrow \varphi_i$ = "volume" fraction

Redlich-Kistler $\rightarrow$ asymmetric better theory $\rightarrow$ metallurgy

---

$g^{sol} = g^{conf} + g^{ex}$ who wins when?

The edges $\quad y \rightarrow 0 \quad 1-y \rightarrow 1 \Rightarrow g^{ex} \rightarrow Wy$

used to argue no pure phase $\Rightarrow g^{conf} \rightarrow +RTy\ln y \rightarrow -\infty$

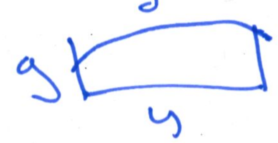
The extremes

$T \rightarrow \infty \quad g^{sol} = g^{conf} \Rightarrow$

$\frac{\partial^2 g}{\partial y^2} > 0$

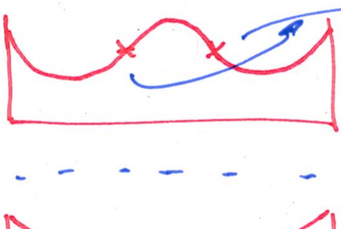
$T \rightarrow 0 \quad g^{sol} = g^{ex} \Rightarrow$

(only pure phases at 0K)



$\frac{\partial^2 g}{\partial y^2} < 0$

Low T



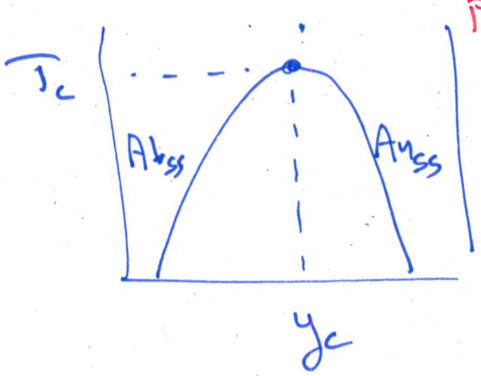
$\rightarrow$ spinodes $\frac{\partial^2 g}{\partial y^2} = 0$

T_{crit} $\quad \frac{\partial^2 g}{\partial y^2}, \frac{\partial^3 g}{\partial y^3}, \ldots = 0$, except $\frac{\partial g}{\partial y}$

high T

2021 11.5

Problem 8.1 → counts as a single problem set



P_{cst} $g^{Plag}\left(\cancel{g^{0}_{an}}, \cancel{g^{0}_{ab}}, y_{an}, \underline{\underline{W_{abanan}}}, \underline{\underline{W_{ababan}}}\right)$

$g^{0}_{an} \to 0$, $g^{0}_{ab} \to 0$

obtain W's by solving

$$\mathrm{diff}(g^{Pl}, y_{an}, y_{an}) = \mathrm{diff}(g^{Pl}, y_{an}, y_{an}, y_{an})$$

at $T = T_c$ $y = y_c$

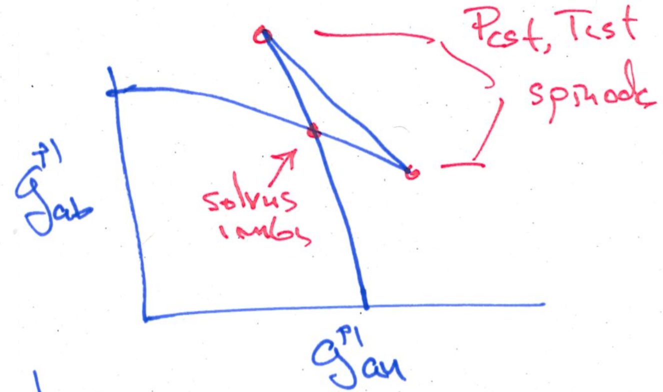
---

answer as in problem set 0, (ie sketch and estimate) alternatively:

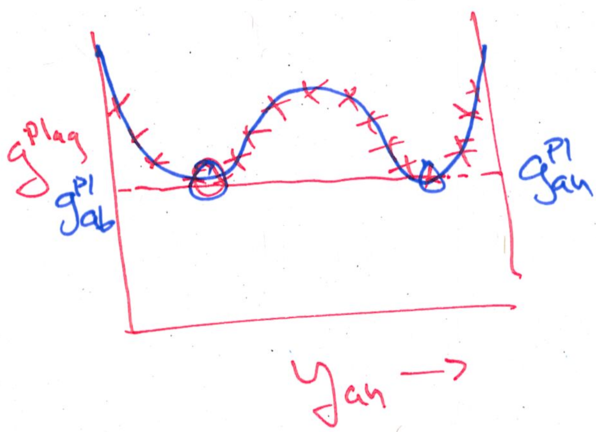
1) make use of $\left[g^{Abss}_{an} = g^{Anss}_{an}\right] + \left[g^{Abss}_{ab} = g^{Anss}_{an}\right]$ P_{cst}, T_{cst}

to compute the solvus.

2) make a parametric plot



3) use free energy minimization



→ LP → discretization

NLP → no discretization