finish lecture 4 notes. subs(x, y, [f(x,y)])
solutions to chap 0 problems on web.

Lecture 5.1 2022

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Dilemma $du = Tds - pdv$ ?

The gibbs differential has k+2 independent variables

The gibbs-duhem says there are only k+1 independent state variables.

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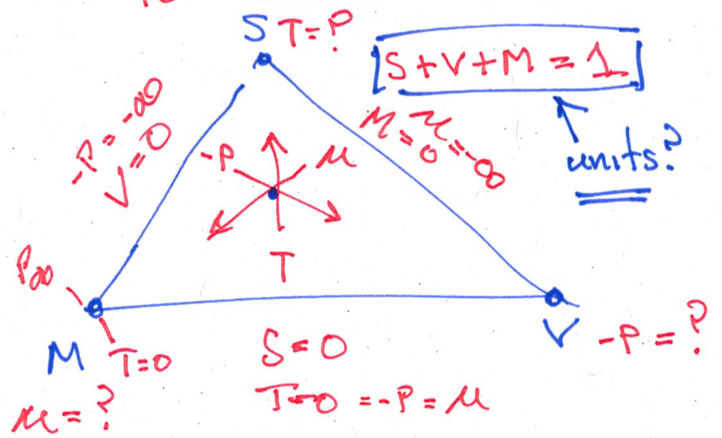
1) What is state? The arrangement of matter without regard to extent $\Rightarrow$ the relative proportions of S, V, M




$$\frac{\partial T}{\partial S} = \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial S}\right) > 0 \quad \text{to be proved}$$

$$\Rightarrow \frac{\partial(-P)}{\partial V}, \frac{\partial \mu}{\partial M}, \frac{\partial \Theta_i}{\partial \Psi_i} > 0$$

$\Rightarrow$ potentials measure the intensity (~ concentration) of their conjugate extensity

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2) The fundamental variables are extensive $\sum \psi^i \overset{?}{=} \psi^{system}$

$\alpha U = U(\alpha S, \alpha V, \alpha M) \Rightarrow 1°$ homogeneous function

Euler's th'm on homogeneous functions

$u = \overbrace{U/\alpha = u(S/\alpha, V/\alpha, M/\alpha)}^{\text{intensive}} \Rightarrow 0°$ homogeneous function

$u = u(s, v, m) \Leftarrow$ an equation of state

$\Rightarrow U = \alpha u \rightarrow$ ~~constant~~ $dU = \alpha du + u d\alpha \rightarrow$ constant extent $d\alpha$

$$du = \frac{dU}{\alpha} = \frac{1}{\alpha}(TdS + \ldots$$

$$= Tds + (-P)dv + \mu dm$$

in the above diagram $\alpha = S + V + M \Rightarrow ds + dv + dm = 0$

$$du = Tds + (-P)dv + (1 - ds - dv)\mu \leftarrow$$

$u(s,v) \Rightarrow dm = 1 - ds - dv$

$u(s,m) \Rightarrow dv = 1 - ds - dm$

$u(m,v) \Rightarrow \ldots$

$$\Rightarrow d(u - \mu) = (T - \mu)ds + [(-P) - \mu]$$

Lecture 5.2 2022

2a) $\Psi/\alpha$ $\rightarrow$ intensive state variables without a name, or rather many names

$\longrightarrow$ barycentric coordinates

$\longrightarrow$ specific variables (my favorite)

$\longrightarrow$ compositions (in the general sense)

$\longrightarrow$ densities

$\longrightarrow$ molar variables

$\longrightarrow$ normalized extensive variables (my least favorite) lecture. 5.3 2022

3) $\alpha$ can be chosen to be any extensive property or even a linear combination of extensive properties

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Physics / Gibbs $\quad \alpha \equiv M_k \Rightarrow du = Tds + (-p)dv + \mu_1 dm_1 + \dots + \cancel{\mu_k dm_k}$ $\rightarrow 0$

$d\alpha = dm_k = 0 \rightarrow u(s, v, m_1 \dots m_{k-1})$

$$\frac{\partial u}{\partial s} = T, \quad \frac{\partial u}{\partial v} = -P, \quad \oint_{P,T} du = 0$$

But: $\int_0^{s,v} du \neq Ts + (-P)v \Rightarrow$ because $s, v$ cannot change at constant $m$ w/o changing state.

rather $(k=1)$ $\quad u = U/\alpha = U/M_k = Ts + (-P)v + \mu$

relevant to problem 2.1

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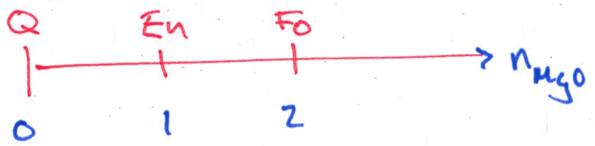
Chemists / geologists $\Rightarrow M \rightarrow N$ - number of moles instead of mass

$MgO - SiO_2 \Rightarrow \alpha = N_{SiO_2}, n_{SiO_2} = 1, n_{MgO} = N_{MgO}/N_{SiO_2}$



$Q = SiO_2 \Rightarrow n_{MgO} = 0$

$Fo = Mg_2SiO_4 \Rightarrow n_{MgO} = 2$

$En = MgSiO_3 \Rightarrow n_{MgO} = 1$

Periclase $\Rightarrow n_{MgO} = \infty$

so instead $\alpha = \sum_{i=1}^{k} N_i$

$$\Rightarrow \frac{N_{MgO}}{N_{MgO} + N_{SiO_2}} + \frac{N_{SiO_2}}{N_{MgO} + N_{SiO_2}} = 1 \Rightarrow \sum n = 1 \quad \sum dn = 0$$

usually denoted $x$ and called mol fractions.

$dn_{SiO_2} = -dn_{MgO}$

$$du = Tds + (-p)dv + \mu_{MgO}\, dn_{MgO} + \mu_{SiO_2}\, dn_{SiO_2}$$

$$= Tds + (-p)dv + (\mu_{MgO} - \mu_{SiO_2})\, dn_{MgO}$$

$$\frac{\partial u}{\partial s} = T, \quad \frac{\partial u}{\partial v} = (-p), \quad \frac{\partial u}{\partial n_i} = (\mu_i - \mu_k) \neq \frac{\partial U}{\partial N_i}$$

$$u = Ts + (-p)v + \mu_1 n_1 + \dots + \mu_k n_k$$

$$n_k = 1 - \sum_i^{k-1} n_i$$