maple hints ? ⇒ problem 1.4 2021.4.1

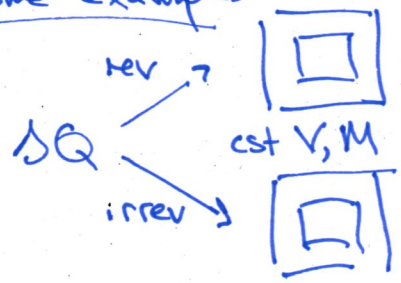
Recap $dU = TdS + (-p)dV + \mu dM \quad U(S,V,M)$

$T \equiv \partial U/\partial S \quad -p \equiv \partial U/\partial V \quad \mu \equiv \partial U/\partial M$

utility : 1) reversible processes (Rev)

2) irreversible processes between eq states

Some examples



$U_{rev} = T_r S_r + (-P_r) V_0 + \sum \mu_r M_0$

$U_{irrev} = T_i S_i + (-P_i) V_0 + \mu_i M_0$

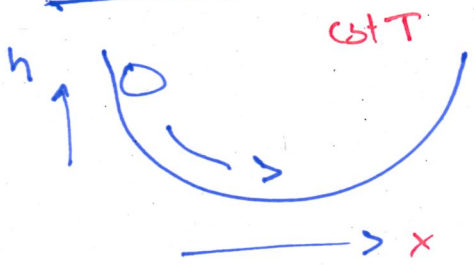
$\Delta U_{rev-irrev} = \Delta T \Delta S + (-\Delta P) V_0 + \Delta\mu M_0$

ideal gas - non-interacting particles $U(S,V,M_0,M_x)$

$\Delta T = \Delta P = \Delta U = 0$

$= \Delta M_0 = \Delta V = \Delta M_x$

$\Delta U_{final-initial} = 0 = \underbrace{T\Delta S}_{>0} + \underbrace{\Delta\mu_0 M_0 + \Delta\mu_x M_x}_{<0}$



$E = \frac{1}{2}Mv^2 + Mgh \; [+TS]$

$v(x), h(x)$

$E = M, x, S$

you cannot do any real process w/o creating entropy ⇒ damage ⇒ lowering the quality of the system's energy, ie the potential to do useful work

eg convert kinetic energy to potential energy

Rheology

elastic → "reversible" → no damage ⇔ thermodynamic

viscous, plastic → irreversible → damage ⇔ permanent

inviscid → deformation w/o work ⇒ thermodynamic

2021 4.12

3rd Law - Nernst's Law - it is impossible to reach 0K
→ a real process is possible if S can increase
→ no process is possible at 0K
→ ergo all states at 0K must have the same entropy
→ might as well define that S to be 0.

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exception 1

vibrational disorder = 0
configurational order →
like damage ≠ 0

→ the "perfect crystal"
@qualification

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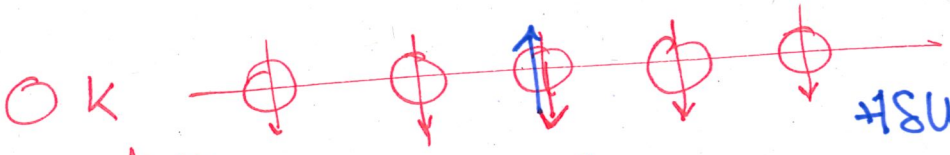
exception 2 quantum gas on a wire

$\frac{\partial U}{\partial S} = T \Rightarrow \frac{\partial S}{\partial U} = \frac{1}{T}$



ΔU_{spin} $\frac{\Delta S}{\Delta U} > 0$?

$\Delta U_{spin} \ll \Delta U_{electronic}$

ΔS is purely configurational (up/down)

C.P. Snow → Geologist (Crystallographer) → Novelist →
Scientific philosopher:

Thermodynamics vs Economics

0 - you must play
1 - you can't win
2 - you can't break even
3 - you can't quit

MVT ↔ μ,P,T ↔ k+2 state variables

State vs Extent $\oint dU = \oint dU = 0$ 1st law

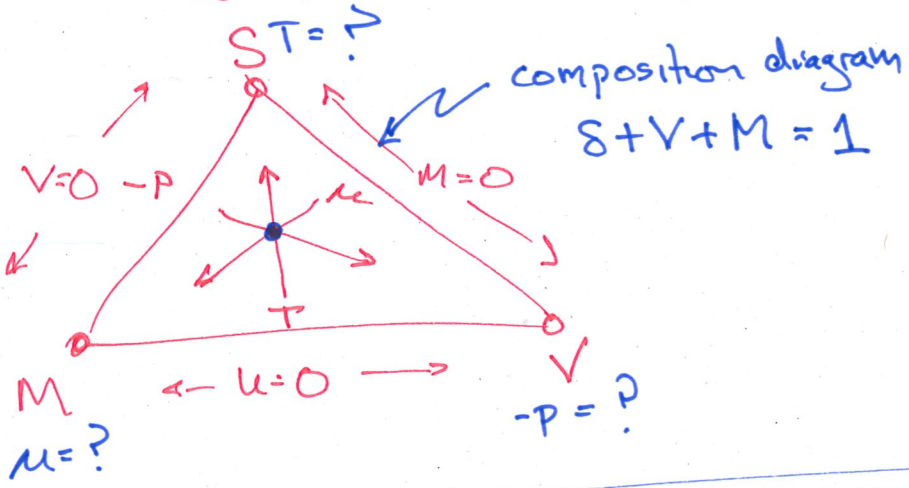
Gibbs-Duhem $0 = SdT + Vd(-P) + Nd\mu$
$= \sum_{i=1}^{k+2} \psi_i d\Theta_i$ ⇒ only k+1 ind state variables

Chapter 2

Physics: $dU = TdS - pdV$ Chemistry: $dU = TdS - pdV + \mu dN$

2021 4.3

1) What is state? The arrangement of matter w/o regard to its extent $U(S,V,M)$



to be proved.

$$\frac{\partial T}{\partial S} = \left[\frac{\partial}{\partial S}\frac{\partial U}{\partial S} > 0\right]$$

$$\frac{\partial(-P)}{\partial V}, \frac{\partial M}{\partial M}, \frac{\partial \Psi}{\partial \Psi} > 0$$

intuitive for now

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2) The fundamental variables are extensive, additive

$$\sum_j^P V^j = V^{system} \quad \dots \quad \sum_j^P \Psi^j = \Psi_{system}$$

extensive → $\alpha U = U(\alpha S, \alpha V, \alpha M) \Rightarrow 1^\circ$ homogeneous function

Eulers theorem →

intensive → $u = U/\alpha = u(S/\alpha, V/\alpha, M/\alpha) \Rightarrow 0^\circ$ homogeneous function

$u = u(s,v,m)$ ⇐ an equation of state

$U = \alpha u$ $\quad dU = \alpha du + u d\alpha$ → constant extent $d\alpha = 0$

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

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

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3) s, v, m, u, ψ are ← barycentric coordinates
- specific variables
- compositions
- densities
- molar variables
- "normalized extensive variables"

Tolman

2021 4.4

Physics / Gibbs $\alpha = M_k \Rightarrow du = Tds + (-p)dv + \mu_1 dm_1 + \dots + \mu_k dm_k$

$dM_k = d\alpha = 0$

$u = u(s, v, m_1, \dots m_{k-1}) \leftarrow du = Tds + (-p)dv + \mu_1 dm_1 + \dots + \mu_{k-1} dm_{k-1}$

$\frac{\partial u}{\partial s} = T, \quad \frac{\partial u}{\partial v} = (-p), \quad \oint du = 0$

But! $\oint du \neq Ts + (-p)v + \sum_i^{k-1} \mu_i m_i$

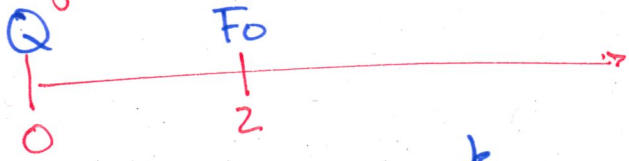
$u = U/M_k = Ts + (-p)v + \sum_i^{k-1} \mu_i m_i + \mu_k$

$k = 1 \Rightarrow \boxed{u = Ts + (-p)v + \mu}$ → remember for problem 2.1

$(u - \mu) = Ts + (-p)v$

Chemists / geologists $M \to N$ - number of moles

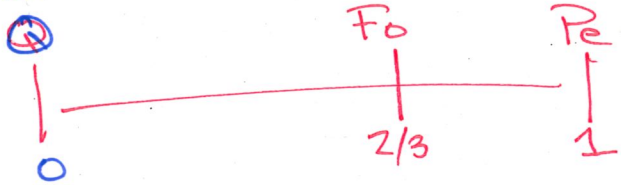
$MgO\text{-}SiO_2 \Rightarrow \alpha = N_{SiO_2}$ $\quad Q \to SiO_2$, $Fo \to Mg_2SiO_4$, $Pe \to MgO$



$n_{MgO} = \frac{N_{MgO}}{N_{SiO_2}} \to \infty$ Pe

instead $\alpha = \sum_k^k N_k$ → are N_i additive? Leave for later 4.5

so



$\sum n = 1 \to = dn_{MgO} + n_{SiO_2}$

$n_{MgO} \to$

$X_{MgO} \to$

$n_{SiO_2} = 1 - n_{MgO}$

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

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

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

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

$u(s, v, n_1 \dots n_{k-1})$

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

2021
2020 4.5

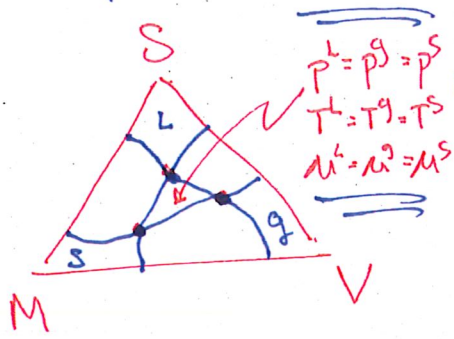
are X's ie $n_i = N_i / \Sigma N$ unitless? $N_1 \dots N_k$ are orthogonal

ΣN is a variable but not our variable!

$\alpha = \frac{N_1}{c_1} + \dots + \frac{N_k}{c_k}$ makes α scalar, also for $\frac{S}{c_S} + \frac{V}{c_V} + \frac{M}{c_M}$

hence the unpleasant notation in the script.

State of a heterogeneous system - is determined if the state and relative amounts of every phase is known (a phase is all parts of the system in the same state)



$T^L = T^g = T^s$

$\mu^L = \mu^g = \mu^s$

$u^i = u(s^i, v^i, m^i) \Rightarrow$ Eos for phase i

$u^1 = Ts^1 + (-p)v^1 + \mu_1 n_1^1 + \dots + \mu_k n_k^1$

$\vdots$

$u^p = Ts^p + \dots + \mu_k n_k^p$

Equality of potentials = condition of internal eq

$y^k = C_1^1 x_1 + \dots + C_m^m x_m$

$\vdots$

$y^j = C_1^n x_1 + \dots + C_M^m x_n$

p - k+2 potentials can be changed without causing a change in phase $\longrightarrow$ $1 \le p \le k+2$

Phase proportions (Aka "the Lever Rule")

for any extensive property, eg S here.

$\rightarrow S^{sys} = \sum_i^p S^i = \sum^p \alpha^i s^i$ ← α^i the absolute amount of phase i

$s^{sys} = S^{sys} / \alpha^{sys} = \sum^p \frac{\alpha^i}{\alpha^{sys}} s^i = \sum^p x_i^i s^i$

$\Rightarrow x_i^i$ is the relative amount of phase i.

$\Rightarrow \sum x_i^i = 1 \Rightarrow$ ~~k+1 equations~~

Since each specific variable provides an independent equation in $\{x^1 \dots x^p\}$ it follows that the state of a heterogeneous system can only be determined in terms of $p-1$ specific variables. Eg. The amounts of the phases at the L+S+G triple point are not known if only the triple point P-T is specified, but are known in terms of s-v

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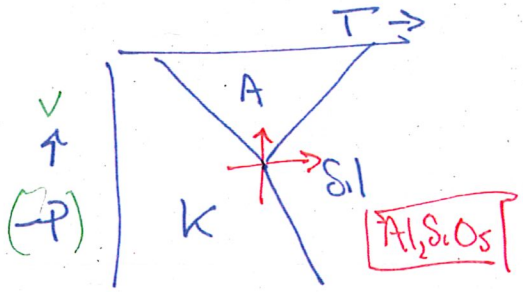
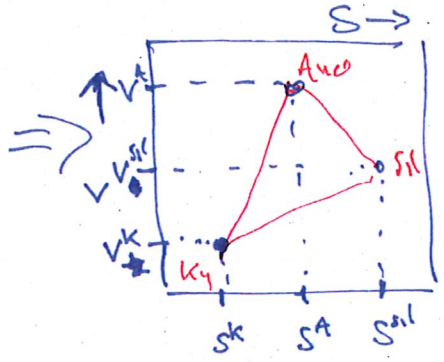
Chapter 2 $\frac{\partial(-P)}{\partial V} > 0$ $\frac{\partial T}{\partial S} > 0$ $\Rightarrow$ Problem 2.1





$S^{Sil} > S^K$ $V^A > V^K$
$S^A > S^K$ $V^{Sil} > V^K$

potentials → $U^A = TS^A + (-P)V^A + \mu n^A$
$U^K = \dots$
$U^{Sil} = \dots$

relative amounts → ~~X^A~~ X^K X^{Sil} $\Rightarrow$ $S^{sys} = X^A S^A + X^K S^K + X^{Sil} S^{Sil}$
$V^{sys} = \dots$

The data is for $\alpha = N^{Al_2Si_2O_5}$
Therefore the amounts are mole fractions.
To get volume fractions you must convert ~~specific~~ the molar specific properties to volumetric specific properties