2022 6.1

Recap

Extensive	Intensive: Potential	Intensive: Specific
S	$T \equiv \partial U/\partial S$	$s = S/\alpha$
Ψ	$\Theta \equiv \partial U/\partial \Psi$	$\psi = \Psi/\alpha$
$k+2$	$k+1$ $\sum \Psi d\Theta = 0$	$k+1$ $\alpha(\Psi)$

variables of state

$$U(S,V,N) \rightarrow U(\Psi_1, \dots, \Psi_{k+2})$$

$$a \equiv N \rightarrow u(s,v) \qquad u(\psi_1, \dots, \psi_{k+2})$$

$$\alpha \equiv V \rightarrow u(s,n)$$

$$\alpha \equiv S \rightarrow u(v,n)$$

$(a = N)$

$du = T ds + (-P) dv \Rightarrow$ for now

$u = Ts + (-P)v + \mu n \Rightarrow$ regardless of α

Why? Heterogeneous systems $\Rightarrow$ matter in different states $\Rightarrow$ potentials don't distinguish the equilibrium states.

Convenience J/kg vs J for X kg

State of a heterogeneous system is defined if the state and relative amounts of every phase is known.

Heterogeneous system of p-phases, how many phases can there be? $\Rightarrow$

Equality of potentials is a condition of internal equilibrium

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

$$\vdots$$

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

$$\Downarrow$$

$$y^1 = x_1 c_1^1 + \dots + x_n c_n^1$$

$$\vdots$$

$$y^m = x_1 c_1^m + \dots + x_n c_n^m$$

rank $k+2$

$1 \leq p \leq k+2$

if $p = k+1 \Rightarrow$ 1 potential can be arbitrarily specified

if $p = k \Rightarrow$ 2 potentials

...

$\Rightarrow$ $k+2-p$ - The number of potentials that can be independently changed

$\Rightarrow f = k+2-p$ - is NOT the number of intensive degrees of freedom; it IS the number of potentials that can be changed without requiring a phase change

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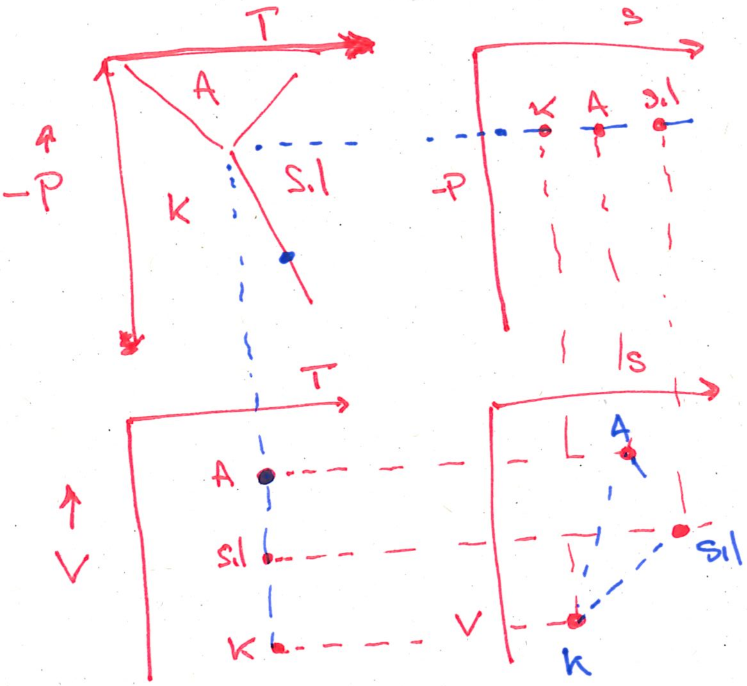
Phase proportions (AKA "the lever rule"):

For any extensive property $N^{sys} = \sum_j^p N^j = \sum_j^p \alpha^j n^j$ — α^j: extensive, n^j: specific (intensive)

$$\frac{N^{sys}}{\alpha^{sys}} = n^{sys} = \sum_j^p \frac{\alpha^j}{\alpha^{sys}} n^j = \sum_j^p \underbrace{x^j}_{\text{relative amount}} n^j$$

Each specific variable provides an equation in p-unknown proportions ⇒ to determine the state of a system containing p-phases the system must be described by p-specific variables.

Problem 2.1 $\frac{\partial \Omega}{\partial \Psi} > 0$ for reversible processes (to be proven)



$-P, T \rightarrow p_{max} = 1$

V, T ; $-P, S \rightarrow p_{max} = 2$

$S, V \rightarrow p_{max} = 3 = k+2$

$u^i = Ts^i + (-P)v^i + \mu n^i$

$$\begin{vmatrix} s^A & v^A & n^A \\ s^K & v^K & n^K \\ s^{sl} & v^{sl} & n^{sl} \end{vmatrix} \begin{vmatrix} T \\ -P \\ \mu \end{vmatrix} = \begin{vmatrix} u^A \\ u^K \\ s^{sl} \end{vmatrix}$$

$$\Downarrow$$

$$\bar{A}\bar{x} = \bar{b}$$

$$\Downarrow$$

$$\begin{vmatrix} s^A & s^K & s^{sl} \\ v^A & v^K & v^{sl} \\ \cancel{n^A} & \cancel{n^K} & \cancel{n^{sl}} \end{vmatrix} \begin{vmatrix} x^A \\ x^K \\ x^{sl} \end{vmatrix} = \begin{vmatrix} s^{sys} \\ v^{sys} \\ \cancel{n^{sys}} \end{vmatrix}$$

if $\alpha = N$ then $1 \leftarrow n^A\, n^K\, n^{sl}$, $n^{sys} \rightarrow 1$
and the x's are molar proportions

if $\alpha = V$?

$$\bar{A}^t \bar{x} = \bar{b}$$

Stability (chapter 3)

Reversible processes ⇒ $du = \ldots$ ⇒ external influence required !!

Spontaneous processes ⇒ $dS^{\text{universe}} > 0$ ⇒ possible with no external influence.

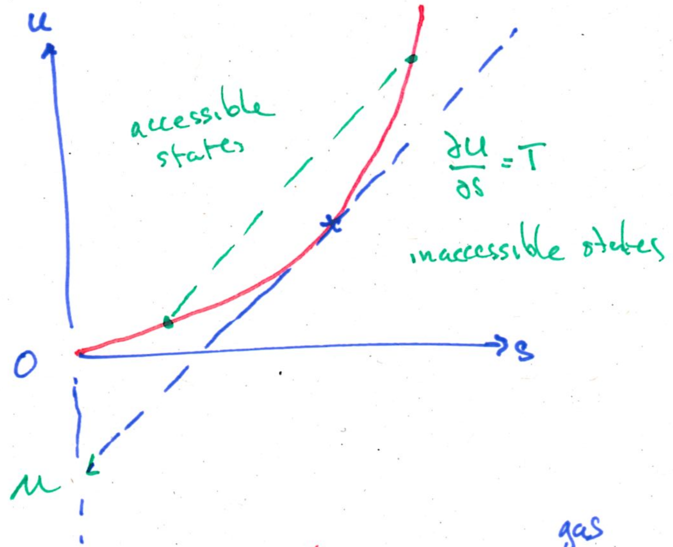
Isolated system ⇒ no external influence possible, $dQ = dW = 0$ ⇒ $\underline{dS > 0}$

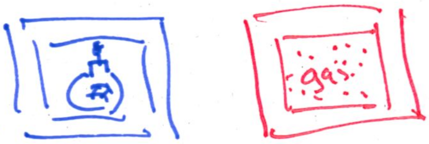
a simplified universe with no mechanical processes:

$U = TS + \mu N$ ⇒ $a = N$

$u = Ts + \mu$ ⇒ $k = 1$, $p_{max} = ?$

$du = T ds$

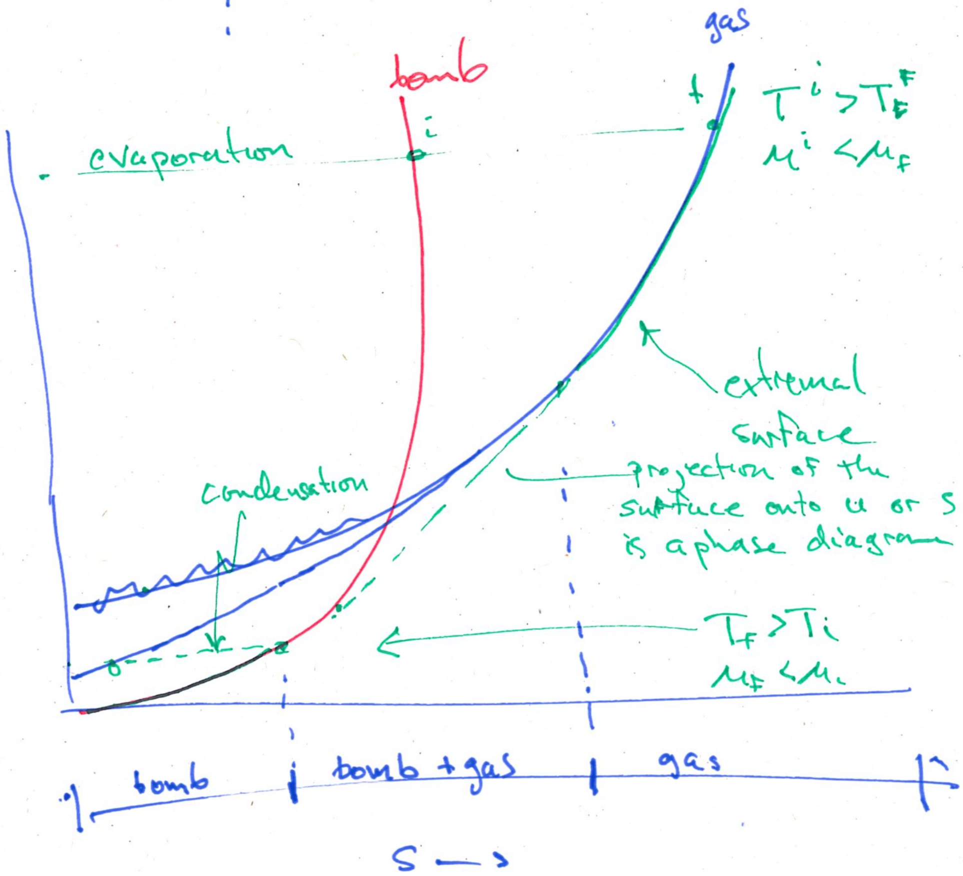




max(s) is a sufficient condition for equilibrium, equality of potentials is a necessary condition

aka Kuhn-Tucker-Karush conditions

$$\frac{\partial^2 u}{\partial s^2} = \frac{\partial}{\partial s}\left(\frac{\partial u}{\partial s}\right) = \frac{\partial T}{\partial s} \geq 0$$



$$\frac{\partial^2 u}{\partial s^2} = 0 \text{ when } p = p_{max} \text{ (here } k+1 = 2)$$

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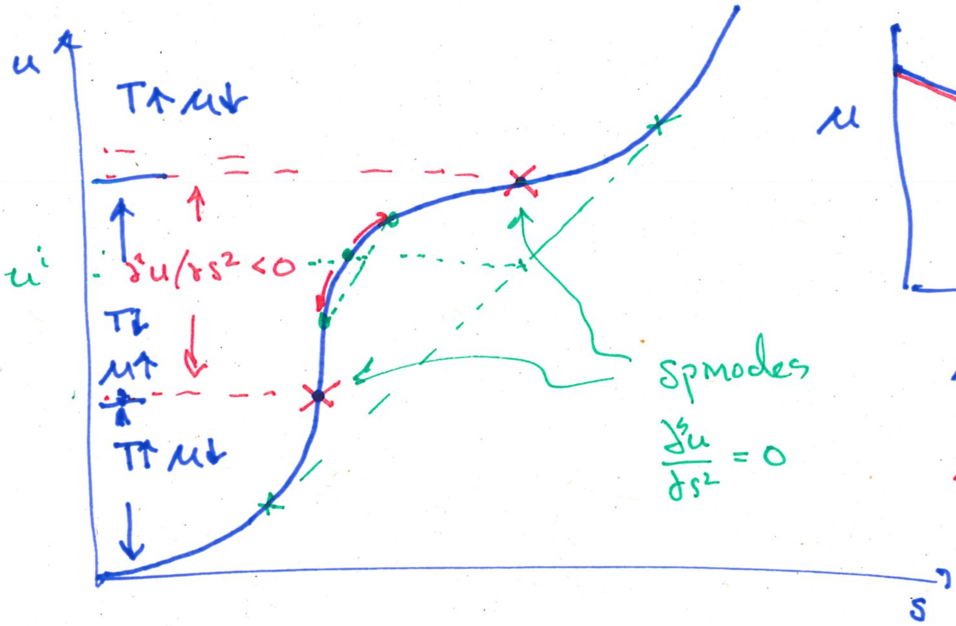
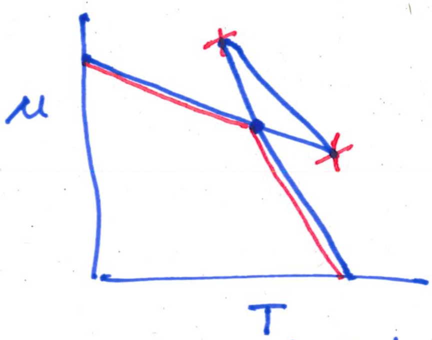
Why can't $\partial^2 u/\partial s^2$ be < 0 ?





μ - not single valued f(T)

μ' = min(μ) - single valued, not path dependent, dμ' ?

Stability criterion: a system is stable when <u>NO</u> processes are possible → 0

logic / good

thermodynamics / evil

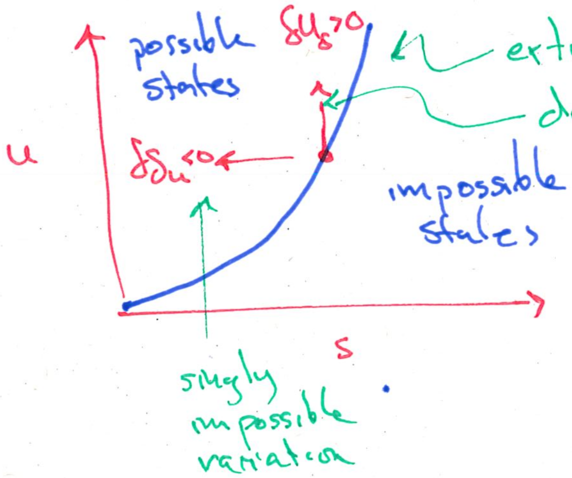
If there is an accessible state such that $\delta S_{u,V,M} > 0$ then a process <u>is</u> possible.

$\delta S_{u,V,M} > 0$ is a criterion for possible processes [Clausius]

A system is stable when any variation [by definition an impossible variation] to a possible state at cst u,V,M decreases entropy, ie

$$\delta S_{u,V,M} < 0$$

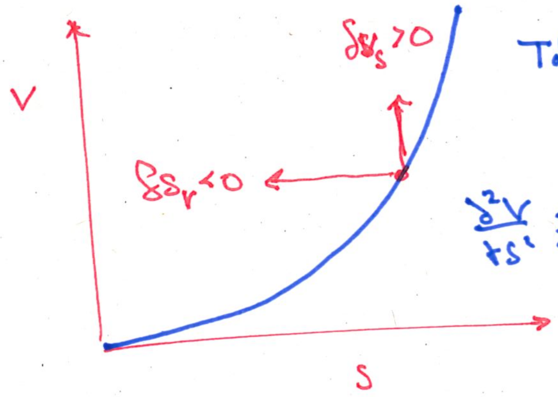
A family of irrational stability criteria



extremal surface $\frac{\partial^2 u}{\partial s^2} \geq 0$

doubly impossible variation $\rightarrow$ the seed of energy minimization

virtual differentials, Tunell



$$T ds - p dv = 0$$

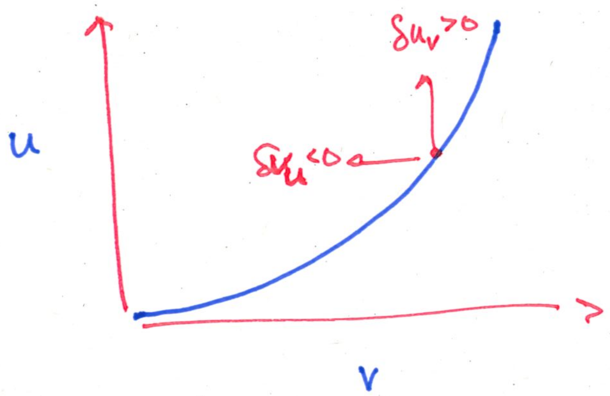
$$ds = \left(\frac{-p}{T}\right) dv$$

← a potential for entropy

$$\frac{\partial^2 v}{\partial s^2} \geq 0$$

$$ds = \frac{1}{T} du + \frac{p}{T} dV - \frac{\mu}{T} dM$$

entropy potentials > 0



$du = (-p) dv$ if u is a minimum

$$\frac{\partial^2 u}{\partial v^2} = \frac{\partial}{\partial v}\frac{\partial u}{\partial v} = \frac{\partial(-p)}{\partial V} > 0$$

if $s(v, u, N)$ is convex

$\partial^2 s / \partial \psi^2 < 0$

then

$u(s, v, N) \rightarrow \partial^2 u / \partial \psi^2 > 0$

$v(s, u, N)$

$N(s, u, v)$

must be concave