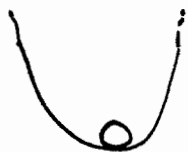


Reference: T + M Chapter 6

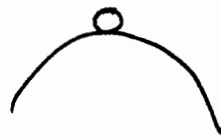
Classification of equilibrium states - mechanical analogy



stable



metastable



unstable



marginally stable

stable in some directions only

Practically all thermodynamic systems are metastable with respect to some perturbations for sufficiently long time scales

[  $H_2 + O_2$   
any atom other than  $Fe^{56}$  ]

Because of this, the specification of internal barriers (perturbations that are not allowable) is an integral part of the specification of equilibrium states

### Stable equilibrium states

Remember discussion of entropy in class:

for an adiabatic process between states I and II of a closed system,  $\Delta S \geq 0$

For an isolated system, the removal of internal restraints and subsequent equilibration results in  $\Delta S \geq 0$ .

Therefore, for the system at equilibrium, the entropy must be a maximum (at const.  $u, v, N_i$ )

For any virtual process of a system in a SES, we must have  $\Delta S \leq 0$  for virtual process starting from SES  $\Delta$ : total change

write  $\underline{S}$  as a Taylor series expansion

$$\underline{x}^0 = (\underline{u}^0, \underline{v}^0, \mu_1^0, \mu_2^0, \dots, \mu_n^0)$$

$$\underline{S} = \underline{S}(\underline{x}) \quad \Delta \underline{S} = \underline{S} - \underline{S}^0 = \underset{\substack{\downarrow \\ \text{1st order}}}{\delta \underline{S}} + \frac{1}{2!} \underset{\substack{\downarrow \\ \text{2nd order}}}{\delta^2 \underline{S}} + \frac{1}{3!} \delta^3 \underline{S} + \dots \text{ etc}$$

where:  $\delta \underline{S} = \frac{\partial \underline{S}}{\partial \underline{u}} (\underline{u} - \underline{u}^0) + \frac{\partial \underline{S}}{\partial \underline{v}} (\underline{v} - \underline{v}^0) + \dots$

$$\delta^2 \underline{S} = \frac{\partial^2 \underline{S}}{\partial \underline{u}^2} (\underline{u} - \underline{u}^0)^2 + \frac{\partial^2 \underline{S}}{\partial \underline{u} \partial \underline{v}} (\underline{u} - \underline{u}^0)(\underline{v} - \underline{v}^0) + \dots$$

mathematical conditions for equilibrium:

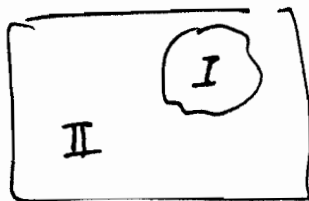
$$\delta \underline{S} = 0 \quad \delta^2 \underline{S} \leq 0 \quad \text{but if } = 0, \text{ then must have}$$

$$\delta^3 \underline{S} \leq 0, \quad \dots$$

what can we get out of this?

→ Prove that for a system at equilibrium,  $T, P, \mu_i$  are constant throughout.

Proof



split system into two subsystems,

$$\delta \underline{u}^I + \delta \underline{u}^II = 0$$

$$\delta \underline{v}^I + \delta \underline{v}^II = 0$$

$$\delta N_i^I + \delta N_i^{II} = 0$$

$$\delta \underline{S} = \frac{\partial \underline{S}^I}{\partial \underline{u}^I} \delta \underline{u}^I + \frac{\partial \underline{S}^{II}}{\partial \underline{u}^{II}} \delta \underline{u}^{II} + \frac{\partial \underline{S}^I}{\partial \underline{v}^I} \delta \underline{v}^I + \dots = 0$$

$$\Rightarrow \left( \frac{1}{T^I} - \frac{1}{T^{II}} \right) \delta \underline{u}^I + \left( \frac{P^I}{T^I} - \frac{P^{II}}{T^{II}} \right) \delta \underline{v}^I + \left( \frac{\mu_i^I}{T^I} - \frac{\mu_i^{II}}{T^{II}} \right) \delta N_i^I = 0$$

$$\Rightarrow \begin{aligned} T^I &= T^{II} & \mu_i^I &= \mu_i^{II} \\ P^I &= P^{II} \end{aligned}$$

In energy representation: system at constant  $\underline{S}, \underline{V}, N_1, \dots, N_n$

Does  $\underline{S}$  constant mean that we can only consider reversible changes?  $\rightarrow$  No, can interact w/ environment, not isolated.

$\Delta \underline{U} \geq 0$  <sup>by a</sup> <sub>virtual process</sub>  $\rightarrow$  energy is minimized at equil.   
 away from equil. at const  $\underline{S}, \underline{V}, N_i$

Two steps in proof: const  $-\underline{U}$  change  $\Delta \underline{S} =$   
 $= \underline{S}_{final} - \underline{S}_{initial} \leq 0$

Change from  $\underline{S}_{final}$  back to  $\underline{S}_{initial}$

$\underline{S}_{final} \geq \underline{S}_{initial} \Rightarrow \frac{\partial \underline{U}}{\partial \underline{S}} = T > 0 \Rightarrow \underline{U}_{final} \geq \underline{U}_{initial}$

$\Rightarrow \Delta \underline{U} \geq 0$  Q.E.D.

Conditions of equilibrium are same as before, opposite sign:

$$\delta \underline{U} = 0$$

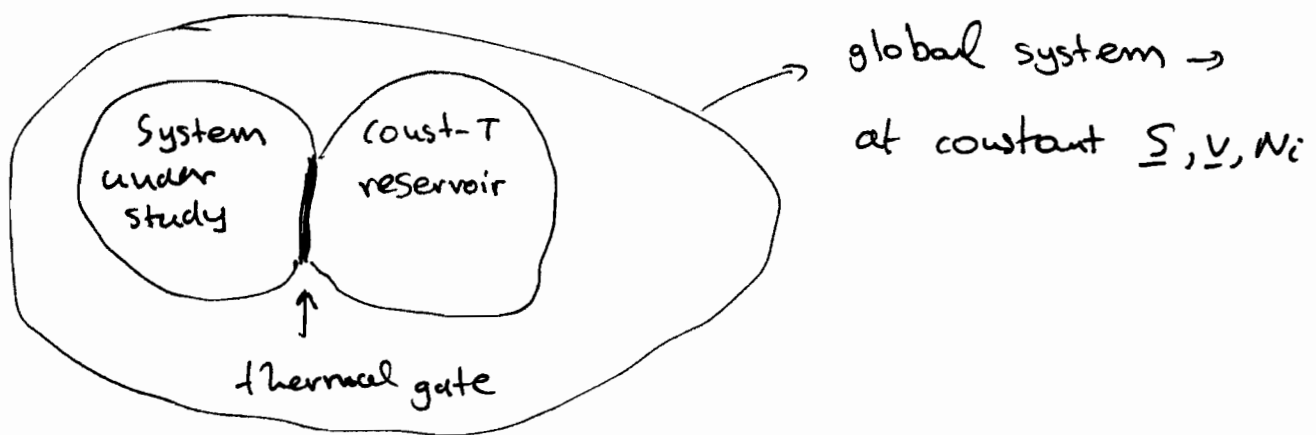
$$\delta^2 \underline{U} \geq 0 \text{ but if } \neq,$$

$$\delta^3 \underline{U} \geq 0$$

Recap: If  $\underline{S}, \underline{V}, N_i$  const.  $\Rightarrow \underline{U}$  minimized

If  $\underline{U}, \underline{V}, N_i$  const  $\Rightarrow \underline{S}$  maximum

What happens if we consider a system at constant  $T, \underline{V}, N_i$ ? or  $T, P, N_i$ ?



For global system, energy must be a minimum:

$\Delta \underline{U}^{\text{GLOBAL}} > 0$  for any change away from equilibrium

$$\Delta \underline{U}^{\text{GLOBAL}} = \Delta \underline{U}^{\text{SYSTEM}} + \Delta \underline{U}^{\text{RESERVOIR}} =$$

$$= \Delta \underline{U}^{\text{SYSTEM}} + T \cdot \Delta \underline{S}^{\text{RESERVOIR}} = \Delta \underline{U}^{\text{SYSTEM}} - T \Delta \underline{S}^{\text{SYSTEM}}$$

$$\left( \text{since } \Delta \underline{S}^{\text{GLOBAL}} = \Delta \underline{S}^{\text{SYSTEM}} + \Delta \underline{S}^{\text{RESERVOIR}} = 0 \right)$$

$$\Rightarrow \boxed{\Delta \underline{A}^{\text{SYSTEM}} > 0} \quad \text{or} \quad \underline{A} \text{ is minimum at } \text{const } T, \underline{V}, N_i$$

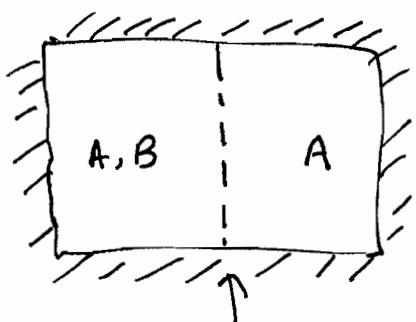
Same way, we can show:

$$\text{constant } - T, P, N_i \Rightarrow \underline{G} \text{ min}$$

$$\text{constant } - \underline{S}, P, N_i \Rightarrow \underline{H} \text{ min}$$

$\therefore$  The thermodynamic function being maximized <sup>or</sup> minimized is the Legendre Transform of the Fundamental Equation that corresponds to the set of variables held constant.

## APPLICATIONS

Membrane Equilibria

global system at constant  $\underline{S}, \underline{U}, N_A, N_B$

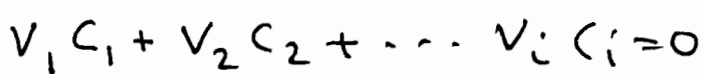
$$\therefore \left. \begin{aligned} \delta \underline{S}^I + \delta \underline{S}^II &= 0 \\ \delta N_A^I + \delta N_A^II &= 0 \end{aligned} \right\} \textcircled{1}$$

rigid partition, permeable only to A  $\rightarrow$  only  $\underline{S}^I, \underline{S}^II, N_A^I, N_A^II$  can vary

To 1st order:

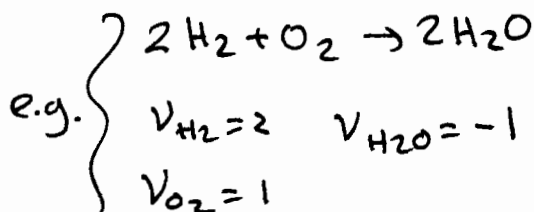
$$\begin{aligned} \delta \underline{u}^{\text{GLOBAL}} = 0 &= \delta \underline{u}^I + \delta \underline{u}^II = \\ &= T^I \cdot \delta \underline{S}^I + \mu_A^I \cdot \delta N_A^I + T^II \cdot \delta \underline{S}^II + \mu_A^II \cdot \delta N_A^II = 0 \quad \textcircled{1} \\ (T^I - T^II) \delta \underline{S}^I + (\mu_A^I - \mu_A^II) \delta N_A^II &= 0 \Rightarrow \end{aligned}$$

$$\begin{aligned} T^I &= T^II \\ \mu_A^I &= \mu_A^II \end{aligned}$$

Chemical Reaction Equilibria

$\hookrightarrow$  component 1

$\hookrightarrow$  stoichiometric coefficient.



must have  $\frac{\delta N_1}{v_1} = \frac{\delta N_2}{v_2} = \dots = \frac{\delta N_i}{v_i} = \delta \xi$

For a change in composition (at const.  $\underline{S}, \underline{U}$ )

$$\delta \underline{u} = 0 = \sum_i \mu_i \delta N_i = \left( \sum_i \mu_i v_i \right) \cdot \delta \xi \Rightarrow$$

$$\sum_i \mu_i v_i = 0 \quad \text{at equilibrium}$$