Reference: T+M Chapter 6

Classification of equilibrium states - mechanical analogy

stable  metastable  unstable  marginally stable

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

\[ \text{H}_2 + \text{O}_2 \]
\[ \text{any atom other than } \text{Fe}^{56} \]

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 constant \( U, V, N \)).

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 $s$ as a Taylor series expansion:

$$\xi^0 = (u^0, v^0, u_1^0, u_2^0, \ldots, u_n^0)$$

$$s = s(x) \quad \Delta s = s - s^0 = \delta s + \frac{1}{2!} \delta^2 s + \frac{1}{3!} \delta^3 s + \ldots$$

Where:

$$\delta s = \frac{\partial s}{\partial u} (u-u_0^0) + \frac{\partial s}{\partial v} (v-v_0^0) + \ldots$$

$$\delta^2 s = \frac{\partial^2 s}{\partial u^2} (u-u_0^0)^2 + \frac{\partial^2 s}{\partial u \partial v} (u-u_0^0)(v-v_0^0) + \ldots$$

Mathematical condition for equilibrium:

$$\delta s = 0 \quad \delta^2 s \leq 0$$

But if $\delta = 0$, then must we have

$$\delta^2 s \leq 0 \quad \ldots$$

What can we get out of this?

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

**Proof**

Split system into two subsystems,

$$\delta u_I + \delta u_{\Pi} = 0$$

$$\delta u_I + \delta v_{\Pi} = 0$$

$$\delta u_{I} + \delta u_{\Pi} = 0$$

$$\delta u_{I} + \delta u_{\Pi} = 0$$

$$\delta u_{I} + \delta u_{\Pi} = 0$$

$$\Rightarrow \left(\frac{1}{I} - \frac{1}{\Pi}\right) \delta u_I + \left(\frac{P_I}{T_I} - \frac{P_{\Pi}}{T_{\Pi}}\right) \delta v_I = 0$$

$$\Rightarrow \frac{T_I}{P_I} = \frac{T_{\Pi}}{P_{\Pi}} \quad H = H_{\Pi}$$
In energy representation: system at constant $S, V, N_1, \ldots, N_n$.

Does $S$ constant mean that we can only consider reversible changes? → No, can interact with environment, not isolated.

\[
\Delta U \underset{\text{Bray}}{\geq} 0 \quad \Rightarrow \quad \text{energy is minimized at equil. at const. } S, V, N_i
\]

Two steps in proof:
- Constant $U$ change $\Delta S = -S_i\Delta U - S_i\text{init} \leq 0$
- Change from $S_i\text{final}$ back to $S_i\text{initial}$

\[
S_i\text{final} \geq S_i\text{initial} \Rightarrow \frac{\partial U}{\partial S} = T \geq 0 \Rightarrow U_i\text{final} \geq U_i\text{initial}
\]

$\Rightarrow \Delta U \geq 0$ Q.E.D.

Conditions on equilibrium are same as before, opposite sign:

\[
\begin{align*}
\delta U &= 0 \\
\frac{\delta^2 U}{\delta S^2} &= 0 \quad \text{but } \delta^3 U \\
\delta^3 U &> 0
\end{align*}
\]

Recap: if $S, V, N_i$ const. $\Rightarrow U$ minimized
if $U, V, N_i$ const. $\Rightarrow S$ maximum

What happens if we consider a system at constant $T, U, N_i$? or $T, P, N_i$?
For global system, energy must be a minimum:

$$\Delta U_{\text{GLOBAL}} > 0 \quad \text{for any change away from equilibrium}$$

$$\Delta U = \Delta U_{\text{SYSTEM}} + \Delta U_{\text{RESERVOIR}} =$$

$$= \Delta U_{\text{SYSTEM}} + T \cdot \Delta S_{\text{RESERVOIR}} = \Delta U_{\text{SYSTEM}} - T \Delta S_{\text{SYSTEM}}$$

(since $$\Delta S_{\text{GLOBAL}} = \Delta S_{\text{SYSTEM}} + \Delta S_{\text{RESERVOIR}} = 0$$)

$$\Rightarrow \boxed{\Delta A_{\text{SYSTEM}} > 0}$$ or $$\Delta A$$ is minimum at constant $$T, V, N_i$$

Same way, we can show:

constant - $$T, P, N_i$$ => $$G$$ min
constant - $$S, P, N_i$$ => $$H$$ min

:: The thermodynamic function being maximized is the Legendre Transform of the Fundamental Equation that corresponds to the set of variables held constant.
Membrane Equilibria

Rigid partition, permeable only to $A \rightarrow$ only $S_I^\text{I}, S_I^\text{II}$, $N_A^\text{I}, N_A^\text{II}$ can vary

To 1st order:

\[ \Delta U^{\text{glob}} = 0 = \Delta U_I^\text{I} + \Delta U_I^\text{II} = \]

\[ = T^\text{I} \Delta S_I^\text{I} + T^\text{II} \Delta S_I^\text{II} + T^\text{I} \Delta N_A^\text{I} + T^\text{II} \Delta N_A^\text{II} + \]

\[ (T^\text{I} - T^\text{II}) \Delta S_I^\text{I} + (\mu_A^\text{I} - \mu_A^\text{II}) \Delta N_A^\text{II} = 0 \]

\[ \Rightarrow \begin{cases} T^\text{I} = T^\text{II} \\ \mu_A^\text{I} = \mu_A^\text{II} \end{cases} \]

Chemical Reaction Equilibria

\[ V_1 C_1 + V_2 C_2 + \ldots + V_i C_i = 0 \]

\[ \Rightarrow \text{component i} \]

\[ \Rightarrow \text{stoichiometric coefficient.} \]

\[ \text{must have } \frac{\Delta N_1}{V_1} = \frac{\Delta N_2}{V_2} = \ldots = \frac{\Delta N_i}{V_i} = \delta \]

For a change in composition (at const. $S$, $V$)

\[ \Delta U = 0 \Rightarrow \sum_i \mu_i \Delta N_i = (\sum_i \mu_i V_i) \Delta S \]

\[ \Rightarrow \sum_i \mu_i V_i = 0 \text{ at equilibrium} \]