CHAPTER #2  Thermodynamics, Equilibrium and Stability

Ch1: Behavior of systems in terms of microscopic processes & variables
Ch2: Describe behavior of systems in terms of measurable quantities

1. The Energy Minimization Principle
2. Equilibrium and Stability
3. Legendre transforms, Free Energies, and Extrema principle
4. Functions
5. Heat capacities and Maxwell's relations
6. Phase Equilibria

Note about reversibility and quasi-static processes ⇒

A process that consists of a sequence of reversible steps.

A process through a manifold of equilibrium states.

Equilibrium states require very few variables (e.g., E, V, N, T, P, μ, S) to be described. Non-equilibrium processes require a large no. of variables (T, P, μ for whole system ill-defined).

Only a quasi-static process can be depicted on a graphical plot like the one below.

Real processes ⇒ Non-equilibrium steps cannot be represented on such a diagram. These steps lift the system off this manifold of states.
The fundamental energy and entropy equations in differential form:

\[ dE = TdS - pdV + \sum_i \phi_i \, dN_i \]

is valid only for the reversible microsteps. Only for reversible microsteps, we can expand heat absorbed as \( TdS \) and work done by system as \( -pdV \) and chemical work as \( \sum \phi_i \, dN_i \).

Real processes are lifted off the manifold of equilibrium P-V states, even though initial (\( P_1, V_1 \)) and final states (\( P_2, V_2 \)) can be depicted on the chart.

State properties depend only on initial and final state.

Non-state properties depend on whether quasi-static or some other path. Rates and driving forces matter.

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If we transfer heat in manageable microsteps:

\[ dS = \frac{dQ_i}{T_i} = C_i(T_i) \frac{dT_i}{T_i}; \quad dS_2 = \frac{dQ_2}{T_2} = C_2(T_2) \frac{dT_2}{T_2} \]

\[ \Delta U = \int_{T_{i1}}^{T_{f}} C_1(T_i) \, dT_i + \int_{T_{i2}}^{T_{f}} C_2(T_2) \, dT_2 = 0 \]

If heat capacities independent of temperature:

\[ 0 = C_1(T_2 - T_{i1}) + C_2(T_2 - T_{i2}) \]

\[ T_2 = \frac{C_1T_{i1} + C_2T_{i2}}{C_1 + C_2} \]

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\[ \Delta S = \frac{dS_1 + dS_2}{C_1 + C_2} = \int_{T_{i1}}^{T_f} dS_1 + \int_{T_{i2}}^{T_f} dS_2 = C_1 \ln \frac{T_f}{T_{i1}} + C_2 \ln \frac{T_f}{T_{i2}} \]

This condition can be written only if at each point, temperature is defined.

\( \Delta S = C_1 \ln \left( \frac{T_f}{T_{i1}} \right) + C_2 \ln \left( \frac{T_f}{T_{i2}} \right) \Rightarrow \text{always} > 0 \) (prove)
Maximum Work Theorem

Maximum work is done in a reversible process.

For any process,
\[ \Delta E = q - W \]
\[ W = q - \Delta E \]

\( q \) = heat absorbed by system
\( W \) = work done by system

For any spontaneous process,
\[ \Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surr bath}} \]
\[ \Delta S_{\text{universe}} = \Delta S_{\text{system}} + \frac{q}{T} \]

\( \Delta S_{\text{universe}} \) for a reversible path

\[ q = -T (\Delta S_{\text{universe}} - \Delta S_{\text{system}}) \]

\[ W = -T \Delta S_{\text{universe}} + T \Delta S_{\text{system}} - \Delta E \]

\( T \) = state properties, not dependent on the path.

\[ W = - (\Delta E - T \Delta S_{\text{system}}) - T \Delta S_{\text{universe}}. \]

\[ \Delta S_{\text{universe}} \geq 0 \]
\[ W \leq - (\Delta E - T \Delta S_{\text{system}}) \]
\[ W \leq T \Delta S_{\text{system}} - \Delta E \]

with the maximum value \( W_{\text{max}} = T \Delta S_{\text{system}} - \Delta E \) when \( \Delta S_{\text{universe}} = 0 \)
i.e. for a reversible process.

\[ W_{\text{max}} = - \Delta F \]
\( \Delta F \) = change in Helmholtz free energy.
Meaning of fundamental equations and differential form of functions

Fundamental energy equation

\[ dE = TdS - pdV + \sum_{i} \mu_i dN_i \]

\[ \left( \frac{\partial E}{\partial V} \right)_{S,N_i} = -p \]

\[ \left( \frac{\partial E}{\partial N_i} \right)_{S,V,N_i} = \mu_i \]

\[ \left( \frac{\partial E}{\partial S} \right)_{V,N_i} = T \]

\[ E = E(S,V,N) \]

Any allowed partitioning of S,V,N for constant total S,V,N minimizes E.

Fundamental entropy equation

\[ ds = \frac{dE}{T} + \frac{pdV}{T} - \sum_N \frac{\mu_i}{T} dN_i \]

\[ \left( \frac{\partial s}{\partial E} \right)_{V,N_i} = \frac{1}{T} \]

\[ \left( \frac{\partial s}{\partial V} \right)_{E,N_i} = \frac{p}{T} \]

\[ \left( \frac{\partial s}{\partial N_i} \right)_{E,V,N_i} = -\frac{\mu_i}{T} \]

\[ s = s(E,V,N) \]

Any allowed partitioning of E,V,N for constant total E,V,N maximizes s.

Differential form of a function tells you how the value of the function changes in response to a small change in the partitioning of the system.

Multiphase Equilibrium

For r phases

\[ ds = \sum_{r} dS_r = \sum_{r} \frac{E dE_r}{T_r} + \sum_{r} \frac{P_r dV_r}{T_r} - \sum_{r} \mu_r dN_r \]
For 2 phases 1 and 2

\[ ds = \frac{dE_1}{T_1} + \frac{dE_2}{T_2} + \left( \frac{dV_1}{T_1} + \frac{dV_2}{T_2} \right) - \sum_j \left( \frac{N_j^1}{T_1} - \frac{N_j^2}{T_2} \right) \]

\[ \cdot \quad E, V, N = \text{constant} \]

\[ dE_1 + dE_2 = 0 \quad \Rightarrow \quad dE_2 = -dE_1 \]

\[ dV_2 = -dV_1 \]

\[ dN_2^j = -dN_1^j \]

\[ ds = dE_1 \left( \frac{1}{T_1} - \frac{1}{T_2} \right) + dV_1 \left( \frac{P_1}{T_1} \right) \left( \frac{P_2}{T_2} \right) - \sum_j \left( \frac{N_j^1}{T_1} - \frac{N_j^2}{T_2} \right) \]

At equilibrium, \( S \) is maximized w.r.t. the partitioning \( E^1, E^2, V^1, V^2, N_i^1, N_i^2 \)

\[ ds = 0 \quad \text{for small } dE_1, \ dV_1, \ \text{or } dN_1 \]

This can be true only if

\[ \frac{1}{T_1} - \frac{1}{T_2} = 0 \quad \Rightarrow \quad \frac{P_1}{T_1} - \frac{P_2}{T_2} = 0 \quad \Rightarrow \quad \frac{N_j^1}{T_1} - \frac{N_j^2}{T_2} = 0 \]

or

\[ T_1 = T_2 \]

\[ P_1 = P_2 \]

\[ M_1 = M_2 \]

For \( r \) phases

\[ T_1 = T_2 = T_3 = \ldots = T_r \]

\[ P_1 = P_2 = P_3 = \ldots = P_r \]

\[ M_1^j = M_2^j = M_3^j = \ldots = M_r^j \quad \text{(for each species } 1 \text{ to } j) \]

This is the same kind of treatment as we did in

first lecture.
An Energy Extremum Principle

For an isolated system:
\[ S(E,N,V) > S(E,N,V,\text{internal constraint}) \]

When an internal constraint is removed, \( E, V \), and \( N \) are re-partitioned so as to maximize \( S \) of the isolated system.

Let's consider the following isolated system where the inner boundary is made conducting. Energy \( \Delta E \) flows from one system to another until equilibrium is reached. At equilibrium, we say left system has energy \( E_1 \) and right one \( E_2 \):

\[
S(E_1 + \Delta E, V_1, N_1) + S(E_2 - \Delta E, V_2, N_2) < S(E_1 + E_2, V_1 + V_2, N_1 + N_2)
\]

Since \( S \) is monotonic w.r.t. \( E \), there must be an energy \( E^* < E_1 + E_2 \) such that:

\[
S(E_1 + \Delta E, V_1, N_1) + S(E_2 - \Delta E, V_2, N_2) = S(E^*, V_1 + V_2, N_1 + N_2)
\]

Thus if we constrain entropy of composite system to remain constant, then the total energy of the system must decrease:

\[
\text{of course by releasing energy to the rest of the universe.}
\]

Thus there is another corollary for the second law:

\[
E(S,N,V) < E(S,N,V,\text{internal constraint})
\]

Energy is minimized when \( S \) constrained energy minimum principle.

Entropy maximization principle arrived at by constraining total energy of a system total entropy.
You can also constrain temperature or pressure as is often done in experiments in the lab (e.g., test tube in a heat bath). We'll see this soon.

**Describing equilibrium and stability in terms of energy minimization**

\[ E(S, V, N) < E(S, V, N, \text{internal constraint}) \]

Let \( SY \) be variation or partitioning of the system away from equilibrium.

\[ E(S, V, N, SY) = E(S, V, N, 0) + \frac{\partial E}{\partial Y} \bigg|_{S,V,N,Y=0} SY + \frac{1}{2} \frac{\partial^2 E}{\partial Y^2} \bigg|_{S,V,N,Y=0} SY^2 + \ldots. \]

Taylor's series

For small displacements \( SY \), higher order terms negligible.

\[ \frac{\partial E}{\partial Y} \bigg|_{S,V,N,Y=0} = 0, \quad \frac{\partial^2 E}{\partial Y^2} \bigg|_{S,V,N,Y=0} \geq 0 \text{ since we have } (\Delta E),_Y > 0 \text{ for a small displacement away from a stable equilibrium state in other words non-spontaneous.} \]

\[ \frac{\partial^2 E}{\partial Y^2} \bigg|_{S,V,N,Y=0} > 0 \text{ guarantees stable equilibrium.} \]

But if \( \frac{\partial^2 E}{\partial Y^2} \bigg|_{S,V,N,Y=0} = 0 \), then we have to investigate \( \Delta E \) and only if that is \( > 0 \), then we have stable equilibrium.

\[ \frac{\partial E}{\partial Y} \bigg|_{S,V,N,Y=0} = 0 \text{ for all four cases above.} \]

\[ \frac{\partial^2 E}{\partial Y^2} \bigg|_{S,V,N,Y=0} > 0 \]

\[ \frac{\partial^2 E}{\partial Y^2} \bigg|_{S,V,N,Y=0} < 0 \]

\[ \frac{\partial^2 E}{\partial Y^2} \bigg|_{S,V,N,Y=0} > 0 \]

but \( \frac{\partial^2 E}{\partial Y^2} \bigg|_{S,V,N,Y=0} < 0 \).
Entropy maximization is equivalent to energy minimization (at constant energy).

The shape arises from the facts:
\[
\frac{dS}{dE} > 0 \quad \text{and}\quad E \text{ is a single-valued continuous function of } S.
\]

Equilibrium state $A$ is a point of maximum $S$ at constant total $E$.

\[ \Rightarrow \text{This situation matches the universe since the total energy of universe is constant. Some holds for any isolated system.} \]

\[ E_i \quad \text{increasing} \]

$X_j$ is one of many possible unconstrained parameters.

Equilibrium state $X$ is a point of minimum $E$ for constant total $S$.

**Stable equilibrium**
\[ \frac{dS_{\text{tot}}}{dx} = 0, \quad \frac{d^2S_{\text{tot}}}{dx^2} < 0. \quad S_{\text{tot}} = \frac{dS_1}{dx} DX + \frac{dS_2}{dx} DX^2 \quad \Rightarrow \text{this gives} \]

the required $\delta S_{\text{tot}} < 0$ for a step away from equilibrium.