

Physics 415 - Lecture 12: Thermodynamic Potentials

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Summary

- Fundamental relation (for simple system with V as external parameter): $dE = TdS - pdV$ [cite: 2]. Natural variables for E are (S, V) .
- First Law: $dE = dQ - dW$ [cite: 2].
- Second Law: For a thermally isolated system, $\Delta S \geq 0$ for any spontaneous process[cite: 2]. Equilibrium corresponds to $S = \max$ [cite: 2].

Thermodynamic Potentials

The thermodynamic variables include $\{E, S, T, V, p, \dots\}$ [cite: 3]. (More variables exist, e.g., chemical potential μ , particle number N , but focus on these for now).

For a closed system, we might specify (E, V) as independent variables [source: 4]. Other quantities are then determined, e.g., $S = S(E, V)$, $T = T(E, V)$, $p = p(E, V)$ [source: 4]. Equivalently, we can take (S, V) as independent variables, and then $E = E(S, V)$ is determined [source: 5]. From the fundamental relation $dE = TdS - pdV$, we can find T and p [source: 6]:

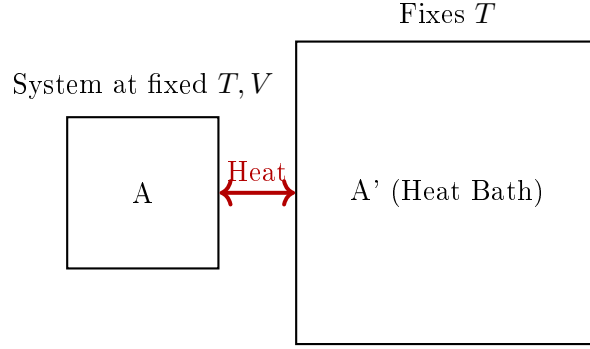
$$T = \left(\frac{\partial E}{\partial S} \right)_V, \quad p = - \left(\frac{\partial E}{\partial V} \right)_S \quad [\text{cite: 6}]$$

The pair (S, V) are the "natural variables" for the internal energy function E .

In practice, we would like to use variables that are more easily controlled experimentally, like temperature T and pressure p , as independent variables, instead of S and E [source: 7]. Thermodynamic potentials allow us to switch the set of independent variables while retaining all thermodynamic information.

Helmholtz Free Energy (F)

Consider putting a system A (of interest) in contact with a heat bath A', which is a much larger system that fixes the temperature T of system A [source: 8, 9]. The combined system A+A' is isolated, but A itself is not (it can exchange heat with A') [source: 9]. We are interested in system A at fixed (T, V) .



What is the work done *by* system A? From the first law $dE = dQ - dW$, we have $dW = dQ - dE$ [cite: 10]. For a quasi-static process occurring at constant temperature T , the heat absorbed by A is $dQ = TdS$ [cite: 11] (where S is the entropy of system A).

$$\implies dW = TdS - dE \text{ [cite: 11]}$$

Since T is constant, $TdS = d(TS)$ [cite: 11].

$$dW = d(TS) - dE = -d(E - TS) \text{ [cite: 11]}$$

We define the **Helmholtz Free Energy** F [cite: 11]:

$$F \equiv E - TS \text{ [cite: 11]}$$

Then, for a quasi-static, isothermal process[cite: 11]:

$$dW = -dF \text{ [cite: 11]}$$

The infinitesimal work done by the system equals the decrease in its Helmholtz free energy[cite: 12]. For a finite process from state i to f : $W_{if} = -\Delta F = F_i - F_f$.

F is a function of state[cite: 12]. What are its natural variables? $dF = dE - d(TS) = dE - TdS - SdT$ [cite: 14]. Substitute the fundamental relation $dE = TdS - pdV$ [cite: 14]:

$$dF = (TdS - pdV) - TdS - SdT$$

$$\implies dF = -SdT - pdV \text{ [cite: 14]}$$

This shows that the natural variables for F are (T, V) [cite: 14]. $F = F(T, V)$. From this differential form, we can find S and p [cite: 14]:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V, \quad p = -\left(\frac{\partial F}{\partial V}\right)_T \text{ [cite: 14]}$$

Knowing $F(T, V)$ allows us to find S and p [cite: 14]. We can also find E [cite: 15]:

$$E = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_V \text{ [cite: 15]}$$

This can also be written using a "Gibbs-Helmholtz" type relation[cite: 15]:

$$E = -T^2 \left(\frac{\partial}{\partial T} \frac{F}{T} \right)_V \text{ [cite: 15]}$$

The mathematical procedure used to pass from $E(S, V)$ to $F(T, V)$ is called a **Legendre Transform**[cite: 16]. We started with $E(S, V)$ and $T = (\partial E / \partial S)_V$ [cite: 16]. We defined $F = E - TS$ [cite: 16]. The new function F depends on T instead of S . This is analogous to passing from the Lagrangian $L(q, \dot{q})$ to the Hamiltonian $H(q, p)$ in classical mechanics, where $p = \partial L / \partial \dot{q}$ [cite: 17]: $H(q, p) = p\dot{q} - L(q, \dot{q})$ [cite: 17]. (Analogy: $S \leftrightarrow \dot{q}$, $T \leftrightarrow p$, $E \leftrightarrow L$, $F \leftrightarrow -H$)[cite: 17].

Enthalpy (H)

Just as we considered a system at fixed (controllable) T , we may consider a system maintained at fixed pressure p (e.g., open to atmosphere, or piston with constant external force)[cite: 17].

For a system at fixed V , heat absorbed is $dQ_V = dE_V$ [cite: 18]. For a system undergoing a quasi-static process at fixed p [cite: 18]:

$$dQ|_p = dE|_p + dW|_p = dE|_p + pdV|_p \text{[cite: 18]}$$

Since p is constant, $pdV|_p = d(pV)|_p$ [cite: 19].

$$dQ|_p = dE|_p + d(pV)|_p = d(E + pV)|_p \text{[cite: 19]}$$

We define the **Enthalpy** H [cite: 19]:

$$H \equiv E + pV \text{[cite: 19]}$$

Then, for a quasi-static process at constant pressure[cite: 19]:

$$dQ|_p = dH|_p \text{[cite: 19]}$$

The heat absorbed at constant pressure equals the change in enthalpy[cite: 19]. H is a function of state[cite: 20]. What are its natural variables?

$$dH = dE + d(pV) = dE + pdV + Vdp \text{[cite: 21]}$$

Substitute $dE = TdS - pdV$ [cite: 21]:

$$dH = (TdS - pdV) + pdV + Vdp$$

$$\implies dH = TdS + Vdp \text{[cite: 21]}$$

The natural variables for H are (S, p) [cite: 20]. $H = H(S, p)$. From this, we can find T and V [cite: 21]:

$$T = \left(\frac{\partial H}{\partial S} \right)_p, \quad V = \left(\frac{\partial H}{\partial p} \right)_S \text{[cite: 21]}$$

If a process occurs at constant pressure and is thermally isolated ($dQ = 0$), then $dH = 0$ [cite: 21]. Enthalpy is conserved in such processes[cite: 22].

The heat capacity at constant pressure C_p [cite: 22]: $dQ|_p = C_p dT$ [cite: 22]. Since $dQ|_p = dH|_p$:

$$dH|_p = C_p dT \text{[cite: 22]}$$

Considering $H = H(T, p)$, $dH = (\partial H / \partial T)_p dT + (\partial H / \partial p)_T dp$. At constant p , $dH|_p = (\partial H / \partial T)_p dT$.

$$\implies C_p = \left(\frac{\partial H}{\partial T} \right)_p \text{[cite: 22]}$$

(Compare with $C_V = (\partial E / \partial T)_V$)[cite: 22].

Example: Monatomic ideal gas[cite: 22]. $E = \frac{3}{2}NT$ and $pV = NT$ [cite: 23]. (Using T in energy units). $H = E + pV = \frac{3}{2}NT + NT = \frac{5}{2}NT$ [cite: 23]. $C_p = (\partial H / \partial T)_p = \frac{5}{2}N$ [cite: 23]. In molar terms (with T in Kelvin): $E = \frac{3}{2}\nu RT$, $pV = \nu RT$. $H = E + pV = \frac{3}{2}\nu RT + \nu RT = \frac{5}{2}\nu RT$. $C_p = (\partial H / \partial T)_p = \frac{5}{2}\nu R$. Molar specific heat $c_p = C_p / \nu = \frac{5}{2}R$. Matches $c_p = c_v + R = \frac{3}{2}R + R = \frac{5}{2}R$ [cite: 23]. ✓

Gibbs Free Energy (G)

To describe a system at constant (externally specified) T and p , we use the **Gibbs Free Energy** G [cite: 24]:

$$G \equiv E - TS + pV = F + pV = H - TS[\text{cite: 24}]$$

G is a state function [source: 24]. What are its natural variables? $dG = dH - d(TS) = dH - TdS - SdT$ [source: 24]. Substitute $dH = TdS + Vdp$ [source: 24]:

$$\begin{aligned} dG &= (TdS + Vdp) - TdS - SdT \\ \implies dG &= -SdT + Vdp[\text{cite: 25}] \end{aligned}$$

The natural variables for G are (T, p) [cite: 24]. $G = G(T, p)$. From this, we can find S and V [cite: 25]:

$$S = -\left(\frac{\partial G}{\partial T}\right)_p, \quad V = \left(\frac{\partial G}{\partial p}\right)_T [\text{cite: 25}]$$

We can also find H [cite: 25]:

$$H = G + TS = G - T\left(\frac{\partial G}{\partial T}\right)_p [\text{cite: 25}]$$

This can also be written as[cite: 25]:

$$H = -T^2 \left(\frac{\partial}{\partial T} \frac{G}{T} \right)_p [\text{cite: 25}]$$

Summary of Potentials

The functions E, F, H, G are called "thermodynamic potentials"[cite: 26].

- Internal Energy: $E(S, V) \implies dE = TdS - pdV$
- Helmholtz Free Energy: $F(T, V) = E - TS \implies dF = -SdT - pdV$
- Enthalpy: $H(S, p) = E + pV \implies dH = TdS + Vdp$
- Gibbs Free Energy: $G(T, p) = E - TS + pV \implies dG = -SdT + Vdp$

From any one of these potentials, expressed as a function of its natural variables, we can obtain all other thermodynamic quantities (S, T, p, V) by taking appropriate partial derivatives[cite: 25].

Thermodynamic potentials are also important because they are minimized in equilibrium under certain conditions (analogous to S being maximized for an isolated system)[cite: 27].

- For closed system at fixed (T, V) : F is minimized in equilibrium.
- For closed system at fixed (T, p) : G is minimized in equilibrium.

(To be shown later)[cite: 27]. This tells us how systems approach equilibrium when they can exchange heat with, or do work on, their environments under these specific constraints[cite: 29].