

Lecture 6

- Helmholtz and Gibbs free energies
- Thermodynamic potentials: U , H , F , G
- Second law in terms of thermodynamic potentials
- Fundamental equations: characteristic function, characteristic variables
- Euler equation and thermodynamic conjugates
- Gibbs-Helmholtz equation
- Why are H , F , G special?
- Legendre transform

Read Ch. 6 Callen, Ch. 7.1-7.3 Sandler

Objectives

- Know the definition, motivation and use of Helmholtz and Gibbs free energies
- Be able to rephrase second law in terms of thermodynamic potentials under appropriate conditions
- Know the four fundamental equations
- Know the mathematical and physical reasons for introducing H , F , G

Helmholtz Free Energy

By combining energy and entropy balance, for an isothermal process

$$TdS > \delta Q = dU - \delta W$$

$$-\delta W \leq -dU + TdS = -d(U - TS)$$

Define $F = U - TS$ Helmholtz *free* energy

$$-\delta W \leq -dF$$

In an isothermal process, the maximum work done by system equals the decrease in Helmholtz free energy. In the absence of work, a spontaneous process always decreases Helmholtz free energy

$$dF \leq 0$$

2nd law in terms of F

Gibbs Free Energy

For isothermal, isobaric process, the non-PV work

$$-\delta W' \leq -dU + TdS - PdV = -d(U - TS + pV)$$

Define $G = U - TS + PV = H - TS = F + PV$

$$-\delta W' \leq -dG \quad \text{Gibbs free energy}$$

In an isothermal, isobaric process, the maximum non-PV work done by system equals the decrease in Gibbs free energy. In the absence of any non-PV work, a spontaneous process always decreases Gibbs free energy

$$dG \leq 0$$

2nd law in terms of F

Combined 1st and 2nd Law for Simple, Open System in Reversible Process

$$dU = h_{in}\delta n_{in} - h_{out}\delta n_{out} + \delta Q - pdV = hdn + \delta Q - pdV$$

$$\delta Q = TdS - T(s_{in}\delta n_{in} - s_{out}\delta n_{out}) = TdS - Tsdn$$

$$\longrightarrow dU = TdS - pdV + \mu dn$$

Generalize:

$$dU = TdS - pdV + \sum_i \mu_i dn_i$$

Fundamental eqn.

Subtle change in the
meaning of differential

$$T = \left(\frac{\partial U}{\partial S}\right)_{v,\{n_i\}} \quad P = -\left(\frac{\partial U}{\partial V}\right)_{s,\{n_i\}} \quad \mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{s,v,n_{j \neq i}}$$

Four Common Fundamental Equations

$$dU = TdS - PdV + \sum_i \mu_i dn_i \quad U = U(S, V, \{n_i\})$$

$$T = \left(\frac{\partial U}{\partial S}\right)_{V, \{n_i\}}, -P = \left(\frac{\partial U}{\partial V}\right)_{S, \{n_i\}}, \mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_{i \neq j}}$$

$$H = U + PV \quad dH = TdS + VdP + \sum_i \mu_i dn_i \quad H = H(S, P, \{n_i\})$$

$$T = \left(\frac{\partial H}{\partial S}\right)_{P, \{n_i\}}, V = \left(\frac{\partial H}{\partial P}\right)_{S, \{n_i\}}, \mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S, P, n_{i \neq j}}$$

Four Common Fundamental Equations

$$F = U - TS \quad dF = -SdT - PdV + \sum_i \mu_i dn_i \quad F = F(T, V, \{n_i\})$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V, \{n_i\}}, -P = \left(\frac{\partial F}{\partial V}\right)_{T, \{n_i\}}, \mu_i = \left(\frac{\partial F}{\partial n_i}\right)_{T, V, n_{i \neq j}}$$

$$G = H - TS \quad dG = -SdT + VdP + \sum_i \mu_i dn_i \quad G = G(T, P, \{n_i\})$$
$$G = U - TS + PV$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P, \{n_i\}}, V = \left(\frac{\partial G}{\partial P}\right)_{T, \{n_i\}}, \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_{i \neq j}}$$

Each fundamental eq. contains **complete thermodynamic info.**

Specialness about U, H, F, G

These functions relate directly to heat and work under special conditions

$$dU = (\delta Q)_V \quad dU = (\delta W)_{ad}$$

$$dH = (\delta Q)_P \quad dH = (\delta W')_{P,ad}$$

$$dF = (\delta W)_T$$

$$dG = (\delta W')_{T,P}$$

They account for effects of the environment/surrounding

Euler Equation

Extensivity of U and all its dependent variables

$$U = U(\{n_i\}, S, V)$$

$$\lambda U = U(\lambda S, \lambda V, \{\lambda n_i\}) \quad \text{First order homogeneous function}$$

Taking derivative with respect to λ $\lambda = 1$

$$\begin{aligned} U &= \left(\frac{\partial U}{\partial \lambda S} \right) \left(\frac{\partial \lambda S}{\partial \lambda} \right) + \left(\frac{\partial U}{\partial \lambda V} \right) \left(\frac{\partial \lambda V}{\partial \lambda} \right) + \sum_i \left(\frac{\partial U}{\partial \lambda n_i} \right) \left(\frac{\partial \lambda n_i}{\partial \lambda} \right) \\ &= \left(\frac{\partial U}{\partial S} \right) S + \left(\frac{\partial U}{\partial V} \right) V + \sum_i \left(\frac{\partial U}{\partial n_i} \right) n_i \\ &= TS - PV + \sum_i \mu_i n_i \end{aligned}$$

Euler Equation

$$U = TS - PV + \sum_i \mu_i n_i$$

$$T \Leftrightarrow S$$

$$-P \Leftrightarrow V$$

$$\mu_i \Leftrightarrow n_i$$

Thermodynamic
conjugates

$$H = U + PV = U - \left(\frac{\partial U}{\partial V} \right) V$$

$$F = U - TS = U - \left(\frac{\partial U}{\partial S} \right) S$$

$$G = U - TS + PV = U - \left(\frac{\partial U}{\partial S} \right) S - \left(\frac{\partial U}{\partial V} \right) V = H - TS = F + PV$$

Legendre Transform

- Typically a function is represented by an abscissa–ordinate relation (x, f)

$$f = f(x) \quad \text{slope} \quad y = \left(\frac{\partial f}{\partial x}\right)$$

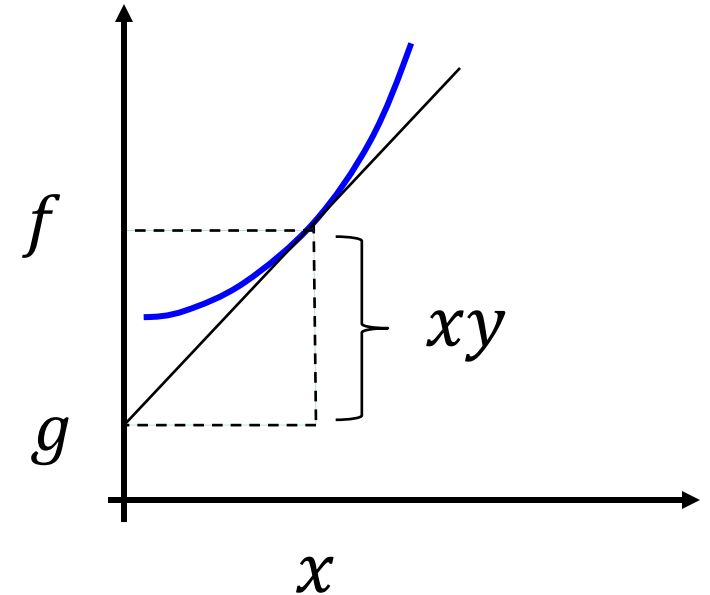
$$g(y) = f(x) - xy$$

$$dg = df - xdy - ydx = -xdy$$

$$\text{So} \quad x = -\left(\frac{\partial g}{\partial y}\right)$$

$$\text{Legendre transform} \quad x \rightarrow y, f \rightarrow g$$

$$g = f - xf'$$



- Representing a function by its slope and intercept
- Contains exactly the **same amount of info as original function**

Legendre Transform

Example: harmonic spring

Energy: $u = \frac{1}{2} k x^2$

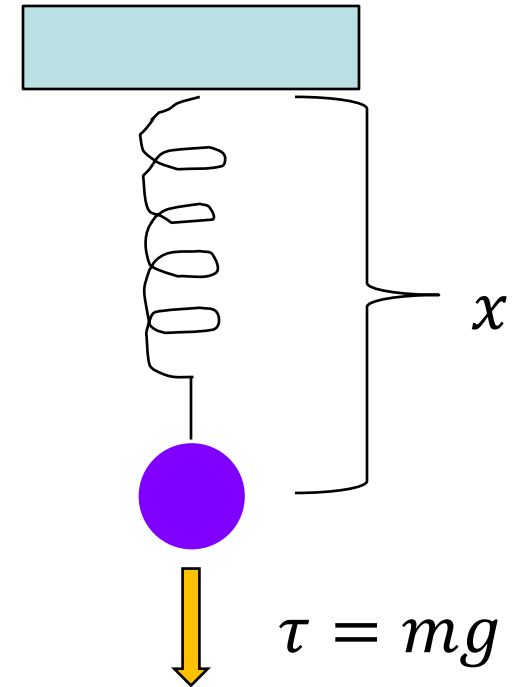
Tension: $\tau = u' = kx$

Define $h \equiv u - \tau x = -\frac{1}{2k} \tau^2$ “enthalpy”

so $x = -\left(\frac{\partial h}{\partial \tau}\right)$

h is the total energy including the gravitation energy of the weight

Legendre transform accounts for effects of environments/surrounding



Legendre Transform

- Mathematically preserves information
- Physically accounts for environmental effects

Gibbs-Helmholtz Equation

From

$$U = F + TS = F - T \left(\frac{\partial F}{\partial T} \right)$$

$$U = \frac{\partial(F/T)}{\partial(1/T)} = -T^2 \frac{\partial(F/T)}{\partial T}$$

Useful for obtaining F from temperature integration of internal energy in molecular simulation

Similarly

$$H = \frac{\partial(G/T)}{\partial(1/T)} = -T^2 \frac{\partial(G/T)}{\partial T}$$

Useful for determining shift in equilibrium constant in chemical rxns

Gibbs-Duhem Equation

Total Legendre transform

$$J = U - TS + PV - \sum_i \mu_i n_i = 0$$

$$-SdT + VdP - \sum_i n_i d\mu_i = 0$$

Constant T, P

$$\sum_i n_i d\mu_i = 0$$

Constant T, P; binary mixture

$$n_A d\mu_A + n_B d\mu_B = 0$$

Chemical potential for two species can't change independently

$$\frac{d\mu_A}{d\mu_B} = -\frac{n_B}{n_A} = -\frac{1 - x_A}{x_A}$$

Chemical potential changes faster for the dilute species

Questions to Think about

- What's special about H , F and G as thermodynamic potentials?
- Why F and G are called free energy? *Free* in what sense?
- What's so fundamental about the fundamental equations?
- Starting from the internal energy, how many Legendre transforms, i.e., how many thermodynamic potentials, can one construct?