

## Recitation: 5

10/02/03

See Callen, first part.

### Legendre Transforms

In both the entropy and energy representations, the extensive parameters play the roles of mathematically independent variables, whereas intensive variables are derived concepts:

$$\begin{aligned}\left(\frac{\partial U}{\partial S}\right)_{V,N} &\equiv T \\ \left(\frac{\partial U}{\partial S}\right)_{S,N} &\equiv -P \\ \left(\frac{\partial U}{\partial N}\right)_{S,V} &\equiv \mu\end{aligned}$$

In experiments, the opposite is true.

The problem is equivalent to the following:

Given

$$\begin{aligned}Y &= Y(X) \\ P &= \frac{\partial Y}{\partial X}\end{aligned}$$

Find

$$Y = Y(P)$$

Problem: We lack information:

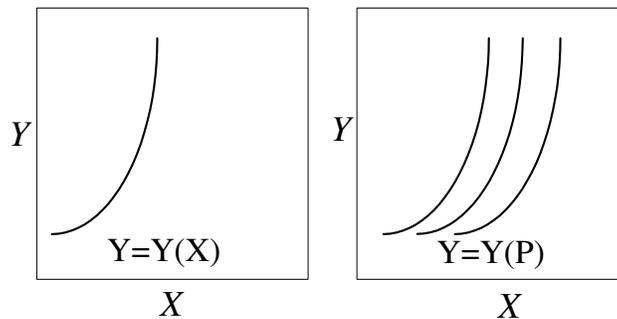


Figure 1: Legendre Transforms (1)

Solution: Need intercept,  $\psi$ :

From the Straight Line Equation:

$$P = \frac{Y-\psi}{X-0}$$

or

$$\psi = Y - PX$$

The same approach can be used in Thermodynamics!!!

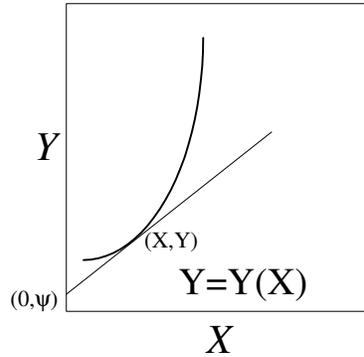


Figure 2: Legendre Transforms (2)

For example, let us say that we want to find a function that represents the thermodynamic state of a system in which we would like to control temperature,  $T$ , which is easy to measure and control, instead of the entropy,  $S$ , which cannot be measured or controlled using conventional experimental techniques.

In this case, we would have to perform the operation:

$$U(S, V, N) \rightarrow F(T, V, N)$$

So, using the analogies:

$$\begin{aligned} U &\rightarrow Y \\ X &\rightarrow S \\ P &\rightarrow \left(\frac{\partial U}{\partial S}\right)_{V,N} \equiv T \\ \psi &\rightarrow F \end{aligned}$$

we have,

$$F = U - TS$$

$F$ , called the Helmholtz Free Energy represents, then, a state function in which  $T$ , instead of  $S$  constitutes the independent variable.

The complete differential of this function is then given by:

$$\begin{aligned} dF &= dU - TdS - SdT \\ dF &= -SdT - PdV + \mu dN \end{aligned}$$

Similar Legendre transformations can be performed so different intensive variables take the place of their conjugate extensive variables, as independent variables:

$$\begin{aligned} H &\equiv U [P] \\ G &\equiv U [P, T] \\ \Phi &\equiv U [T, \mu] \end{aligned}$$

where  $H$  is called the enthalpy,  $G$  is the Gibbs Free Energy, and  $\Phi$  is the Grand Canonical Potential, which is of great use in Statistical Mechanics....(more later).

Above, extremum principles were stated for the entropy and energy representations. The same can be done for the Legendre transforms:

- *Helmholtz Potential Minimum Principle*: The equilibrium value of any unconstrained internal parameter in a system in diathermal contact with a heat reservoir minimizes the Helmholtz potential over the manifold of states for which  $T = T^r$ .
- *Enthalpy Minimum Principle*: The equilibrium value of any unconstrained internal parameter in a system in contact with a pressure reservoir minimizes the enthalpy over the manifold of states of constant pressure (equal to the pressure reservoir).
- *Gibbs Potential Minimum Principle*: The equilibrium value of any unconstrained internal parameter in a system in contact with a thermal and pressure reservoir minimizes the Gibbs potential at constant temperature and pressure (equal to those of respective reservoirs).

In general,

$$\begin{aligned}\delta F &\geq 0 \\ \delta H &\geq 0 \\ \delta G &\geq 0\end{aligned}$$

Note that

- $F$  is the work available at constant temperature.
- $H$  represents the heat added to the system at constant pressure.
- $G$  is the work available in a system at constant pressure and temperature. Only  $N_1, N_2, N_3$  can vary. This is very useful for chemical reactions!!!

Using the Euler relation, and the Legendre Transforms, we have that:

$$\begin{aligned}H &= U + PV = TS + \sum \mu_i n_i \\ F &= U - TS = -PV + \sum \mu_i n_i \\ G &= U - TS + PV = \sum \mu_i n_i\end{aligned}$$

### Maxwell Relations

Since  $S, U, H, G, F$  are state functions, their differentials are perfect differentials.

For example,

$$\begin{aligned}dU &= TdS - PdV + \mu dN \\ dU &= \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial S}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN\end{aligned}$$

So,

$$\left( \frac{\partial^2 U}{\partial S \partial V} \right)_N = \left( \frac{\partial^2 U}{\partial V \partial S} \right)_N$$

or

$$\left( -\frac{\partial P}{\partial S} \right)_{V,N} = \left( \frac{\partial T}{\partial V} \right)_{S,N}$$

This is a Maxwell Relation for the Energy State Function.

For the Gibbs free energy, we have:

$$dG = -SdT + VdP + \mu dN$$

So the Maxwell relations would be:

$$\begin{aligned} \left( -\frac{\partial S}{\partial P} \right)_{T,N} &= \left( \frac{\partial V}{\partial T} \right)_{P,N} \\ \left( -\frac{\partial S}{\partial N} \right)_{T,P} &= \left( \frac{\partial \mu}{\partial T} \right)_{P,N} \\ \left( \frac{\partial V}{\partial N} \right)_{T,P} &= \left( \frac{\partial \mu}{\partial P} \right)_{T,N} \end{aligned}$$

Useful Rules:

$$\begin{aligned} \left( \frac{\partial X}{\partial Y} \right)_Z &= 1 / \left( \frac{\partial Y}{\partial X} \right)_Z \\ \left( \frac{\partial X}{\partial Y} \right)_Z &= \left( \frac{\partial X}{\partial W} \right)_Z / \left( \frac{\partial Y}{\partial W} \right)_Z \\ \left( \frac{\partial X}{\partial Y} \right)_Z &= - \left( \frac{\partial Z}{\partial Y} \right)_X / \left( \frac{\partial Z}{\partial X} \right)_Y \\ \left( \frac{\partial X}{\partial f} \right)_Z &= \left( \frac{\partial X}{\partial f} \right)_Y + \left( \frac{\partial X}{\partial Y} \right)_f \cdot \left( \frac{\partial Y}{\partial f} \right)_Z \end{aligned}$$

Important definitions:

$$\begin{aligned} \alpha &\equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \\ \kappa_T &\equiv -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \\ C_p &\equiv T \left( \frac{\partial S}{\partial T} \right)_P \\ C_V &\equiv T \left( \frac{\partial S}{\partial T} \right)_V \end{aligned}$$

### General Rule for Maxwell Relation

In class, Prof. Ceder gave you a general rule to determine Maxwell Relations:

$$\left( \frac{\partial X}{\partial Y} \right)_{CONJ(X)} = \pm \left( \frac{\partial CONJ(Y)}{\partial CONJ(X)} \right)_Y$$

In order to know the sign of the equality, there is a very simple technique:

$X$  and  $CONJ(Y)$  should be the dependent variables of the potentials. So, we need to find a potential that has  $CONJ(X)$  and  $Y$  as their dependent variables. Then we write down the differential form of the potential and find the appropriate sign.

For example, get the Maxwell Relation for  $\left(\frac{\partial P}{\partial S}\right)_V$ :

Using Prof. Ceder's Rule, we have:

$$\left(\frac{\partial P}{\partial S}\right)_V = \pm \left(\frac{\partial T}{\partial V}\right)_S$$

To find the sign, we recognize that this Maxwell Relation must come from a potential that has  $V$  and  $S$  as the independent variables.

We immediately recognize that  $U \rightarrow U(S, V)$  and from  $dU = TdS - PdV$  we find that:

$$\left(\frac{\partial P}{\partial S}\right)_V = - \left(\frac{\partial T}{\partial V}\right)_S$$

### Gibbs Free Energy:

At constant pressure and temperature, the condition for equilibrium in a system is obtained by minimizing the Gibbs free energy.

$$dG = -SdT + VdP + \sum_i N_i d\mu_i$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\frac{C_P}{T}$$

$$\left(\frac{\partial G}{\partial P}\right)_T = +V \quad \left(\frac{\partial^2 G}{\partial P^2}\right)_T = -\kappa_T V$$

At constant pressure and temperature:

$$dG = \sum_i N_i d\mu_i$$

### Gibbs-Duhem Equation

From first law:

$$dU = TdS - PdV + \mu dN$$

From Euler Relation:

$$dU = TdS + SdT - PdV - VdP + \mu dN + Nd\mu$$

Since  $dU = dU$

$$SdT - VdP + Nd\mu = 0$$

Intensive Variables are Not Independent!!!

### Clausius-Clapeyron Equation

If two phases are at equilibrium,

$$G^\alpha = G^\beta$$

At the coexistence line, any change in the Gibbs energy of  $\alpha$  must be matched by a corresponding change in the Gibbs energy of  $\beta$ :

$$dG^\alpha = dG^\beta$$

Therefore,

$$-S^\alpha dT + V^\alpha dP = -S^\beta dT + V^\beta dP$$

Consequently,

$$\frac{dT}{dP} = \frac{\Delta V^{\alpha \rightarrow \beta}}{\Delta S^{\alpha \rightarrow \beta}}$$

This is the Clausius-Clapeyron Equation.

### **Problem 1**

Consider an insulated and rigid chamber divided by one partition at the middle. One of the partitions is full with a gas. If the dividing wall suddenly breaks, please determine how the temperature of the system will change, as a function of properties such as specific heat, compressibilities, thermal conductivity, etc.

### **Problem 2**

In class we saw that, for an adiabatic pull, with force,  $F$ , the change in temperature under constant force is:

$$\left( \frac{\partial T}{\partial F} \right)_S = \frac{-L\alpha_L T}{C_F}$$

What is the relationship between  $C_F$  and  $C_P$ ?