

Exam II Study Guide

Chapter 3

The fundamental concept of chapter 3 really is the thermodynamic identity:

$$dU = TdS - PdV + \mu dN \quad (1)$$

which we can combine with the definition of the total derivative of $U(S, V, N)$:

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN \quad (2)$$

To derive:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \quad (3)$$

$$-P = \left(\frac{\partial U}{\partial V}\right)_{S,N} \quad (4)$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \quad (5)$$

Equation 1 is the same as:

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN \quad (6)$$

from which we derive:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} \quad (7)$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N} \quad (8)$$

$$\mu = \left(\frac{\partial S}{\partial N}\right)_{U,V} \quad (9)$$

$$(10)$$

You should be able to start at equation 1 and derive 2-10!

The basic idea of chapter 3 is this:

1. Start with (or derive) a system's multiplicity $\Omega(U, V, N)$
2. Take the logarithm of Ω to find the entropy S
3. Once you have S , you can take derivatives to find any macroscopic quantity you want. For example, in class (and in the book) we used equation 8 (which you should know as the *definition* of temperature) to obtain U as a function of T for the Einstein solid and the ideal gas. Once you know $U(T, V, N)$, you can also find the heat capacity by differentiating with respect to temperature.

We used the above formula to find $U(T)$ and C_V for the ideal gas, the Einstein solid, and the paramagnet. The results themselves are not as important as knowing how to obtain them. (If I give you a function for Ω , you should be able to find relations between energy, temperature, pressure, etc using eqns 1-10 above.)

You should also know that (for quasistatic processes¹) $dS = \frac{Q}{T} = \int \frac{C_V}{T} dT$, and be able to use this to calculate ΔS given a know ΔT or Q .

¹Know what this means!

Chapter 4

- You should be familiar with the basic operating principle of a heat engine (create a temperature difference causing heat to flow from hot to cold, capture some of the heat and use it to do work).
- You should be able to qualitatively describe why the efficiency of a heat engine is fundamentally limited (you should be able to show that if you *could* convert all of the heat leaving the hot reservoir into work, this would violate the second law).
- You should be able to use the basic results derived in class and in the book to calculate unknown quantities, like in the homework problems (if the engine operates at these temperatures, how much waste heat must be expelled to obtain some given amount of work?, etc...)

Chapter 5

Be very familiar with the Helmholtz energy F , the Gibbs energy G , and their corresponding thermodynamic identities:

$$F = U - TS \quad (11)$$

$$dF = -SdT - PdV + \mu dN \quad (12)$$

$$G = U - TS + PV \quad (13)$$

$$dG = -SdT + VdP + \mu dN \quad (14)$$

You should be able to derive dF from the definition of F and dG from G .

With equations 11-14, we can then say (make sure you know how to derive these!):

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

Know the importance of F and G : in a non isolated system, S of the system does not necessarily need to always increase. Instead, F or G need to *decrease*.

- If the system is isolated from the environment (constant energy, volume, N): S tends to increase
- If the system exchanges energy with the environment at constant T and V , then F tends to decrease
- If the system exchanges energy and volume with the environment at constant T and P , then G tends to decrease

At constant T and V , $\Delta F = \Delta U - T\Delta S$: F balances the systems inclination to minimize its energy with the second law.

Phase Transitions

At constant T and P , $\Delta G = \Delta H - T\Delta S$. ΔG determines whether or not a substance will transition to a different phase. For example: if $Q_{\ell \rightarrow g}$ is the heat required to vaporize a liquid at constant pressure, and $\Delta S_{\ell \rightarrow g}$ is the change in entropy from a liquid to a gaseous state (which will be positive): then the liquid will vaporize if

$$\Delta G = \Delta H - T\Delta S = Q_{\ell \rightarrow g} - T\Delta S_{\ell \rightarrow g} < 0$$

In other words: vaporization is a *disfavored* process because it costs energy ($Q_{\ell \rightarrow g}$). On the other hand, it is *favoured* because it increases entropy. If the increase in entropy exceeds the cost in energy, the process will proceed:

$$Q_{\ell \rightarrow g} < T\Delta S_{\ell \rightarrow g}$$

If $\Delta G = 0$, then the two phases are in equilibrium. This can only occur for certain combinations of T and P_{vapor} . The set of (T, P_{vapor}) points for which two phases are in equilibrium are solutions to the **Clausius-Clapeyron** Relation:

$$\frac{dP}{dT} = \frac{mL}{T\Delta V} \quad (15)$$

Where L is the latent heat (per mass) required for the phase transition, m is the mass of the substance, and $\Delta V = V_f - V_i$ is the change in volume as a result of the phase transition. You should be able to use this relation as in problems 32, 35, etc in the book.

You should also know the definition of vapor pressure, be able to explain the difference between evaporation and boiling, and estimate the boiling temperature at different altitudes.