

Fri. 2/13	5.1 – 5.2 Free Energy & Equilibrium	HW14: 1,5,8,11,20,21,22	
Mon. 2/16	5.3 Phase transformation (not van der Waals)	HW15: 28, 30, 32, 35 (not d), 37	HW12,13,14
Wed. 2/18	5.3 van der Waals	HW16: 48, 51, 52	
Fri. 2/20	5.4 Free Energy of a Mixture	HW17: 56, 57	

Equipment

Hydrogen fuel-cell car. Make sure I've got de-ionized water.

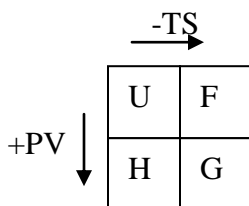
Transition. One major application of Thermodynamics is industrial – heat engines, air conditioners, refrigerators, cars,... Another is a bit smaller scale – the equilibria of solutions: different phases of the same material and different materials. That's where we're venturing now.

5 Free Energy and Chemical Thermodynamics

- **Introduction.** Now we apply the laws of thermodynamics to systems that undergo chemical transformations. First, we need to create specialized tools to facilitate this, tools that take into account not constant *energy* but the constant *temperature* and *pressure* that are characteristic of a system interacting with its surroundings (which are at constant T and P).
- In the pursuit of Physics, we have two goals: gain *fundamental* understanding, and do something *useful*. This chapter does a little of both. The tools of H, F, and G help us to tackle problems, and in so doing, allow us to address things we couldn't otherwise easily address.

5.1 Free Energy as Available Work

- **The Specialized Tools: Thermodynamic Potentials**
 - **Internal Energy: U. (energy in the system)**
 - **The Thermodynamic Potentials Table**



- **Enthalpy: H. (energy needed to create system in environment isobarically – constant pressure)**
 - Assume mechanical equilibrium with an environment at constant pressure.
 - The total energy that's expended when making a system in an environment at constant pressure is the energy that goes into the system itself, U, plus the energy that goes into the environment in making room for it under constant pressure, PV. We've seen and used this one a few times thus far.
 - $H \equiv U + PV$
 - (the change in volume here is the total volume since we want the work done in making room for the whole system)
 - Alternatively, this is the total energy that you would get out of *destroying* a system – some from the system, and some from the environment.

- **Helmholtz' Free Energy: F (energy that you put into system when creating it isothermally, regardless of isochoric or not)**
 - Assume thermal equilibrium with an environment at constant temperature.
 - Regardless of how much energy goes into the environment in the process of creating the system in its midst, the total amount of energy that you put into the system is the system energy minus what the environment puts in as heat.
 - $F \equiv U - TS$
 - Alternatively, the total amount of energy that you can get back out, is the energy in the system minus what the environment takes – irrecoverable heating.
- **Gibbs Free Energy: G. (energy needed to create system in environment isobarically and isothermally)**
 - Assume thermal and mechanical equilibrium with an environment at constant temperature and pressure.
 - The environment will put some energy into the system via heating, TS, so you are responsible for providing everything but that – and then some, for pushing out space in the environment.
 - $G \equiv U + PV - TS = H - TS$
 - So, this is the total amount of energy you could hope to recover if a system were destroyed at constant P and T.
- **Different tools for different tasks**
 - In a tool box, there's a big claw hammer, there's a little claw hammer, there's a ball-ping hammer, there's a wooden mallet, there's a raw-hide mallet,...
 - All these different energies are like the different hammers – depending on the task, one or another will be the best suited.

○ **Differential Changes & 5.1.2 Thermodynamic Identities**

- Pulling back from full-on creation and annihilation, we'll consider the differential forms of these, for when we're just tweaking the systems.

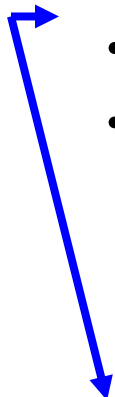
Book jumps straight in with constant pressure, then later returns for general case

Enthalpy

- $dH = dU + PdV + VdP$
 - Where $dU = TdS - PdV + \mu dN + \frac{\partial u}{\partial X} dX = Q + W_{mech} + W_{other}$
 - So, $dH = TdS - PdV + \mu dN + \frac{\partial u}{\partial X} dX + PdV + VdP$
 - $dH = TdS + \mu dN + \frac{\partial U}{\partial X} dX + VdP$
- **Constant Pressure and Number**
 - $dH_{p,N} = TdS + \frac{dU}{dX} dX$
 - **quasistatic / reversible**
 - $Q = TdS, W_{mech} = -PdV, W_{other} = \frac{dU}{dX} dX$
 - So $dH_{p,N} = Q + W_{other}$
 - **Non-quasistatically**

For example, a magnetic term

Pr. 5.8, you'll do this for G.



- $W_{mech} > -PdV$, so
 $TdS - PdV + \frac{\partial u}{\partial X} dX = Q + W_{mech} + W_{other}$ suggests
 $TdS + \frac{\partial u}{\partial X} dX - Q + W_{other} \stackrel{?}{=} W_{mech} + PdV > 0$
 $TdS + \frac{\partial u}{\partial X} dX > Q + W_{other}$
- But the left is dH , so
- $dH_{P,N} \geq Q + W_{other}$

• **Partial Derivatives**

- Looking back at our full differential form of enthalpy, we

$$\text{have } T = \frac{\partial H}{\partial S}_{N,P,X} \quad V = \frac{\partial H}{\partial P}_{N,S,X} \quad \mu = \frac{\partial H}{\partial N}_{S,P,X}$$

Gibbs

▪ $dG = dU + PdV + VdP - TdS - SdT$

- Similarly, $dG = \mu dN + \frac{dU}{dX} dX + VdP - SdT$

• **Constant Pressure, Temperature, and Number**

- $dG_{P,T,N} = \frac{dU}{dX} dX$

- **Quasistatic / Reversible** $Q = TdS$

- $dG_{P,T,N} = W_{other}$

- **Non-quasistatically** (similar argument to that for dH)

- $dG_{P,T,N} \leq W_{other}$

• **Partial Derivatives**

- $S = -\frac{\partial G}{\partial T}_{N,P,X} \quad V = \frac{\partial G}{\partial P}_{N,T,X} \quad \mu = \frac{\partial G}{\partial N}_{T,P,X}$

You'll use reasoning like this on pr. 5.11.

• **Example:** the volume of a mole of graphite is $5.3 \times 10^{-6} \text{m}^3$. Under constant volume, temperature, and number conditions then $5.3 \times 10^{-6} \text{m}^3 \Delta P = \Delta G_{N,T,X}$ and so an increase in pressure of 1 Pa means an increase in Gibbs Free Energy of $5.3 \times 10^{-6} \text{J}$.

Helmholtz

▪ $dF = dU - TdS - SdT$

- Similarly, $dF = -PdV + \mu dN - \frac{dU}{dX} dX - SdT$

• **Constant Temperature and Number**

- $dF_{T,N} = -PdV - \frac{dU}{dX} dX$

- **Quasistatic / Reversible**

- $dF_{T,N} = W$

- **Non-quasistatically**

- $dF_{T,N} \leq W$

• **Partial derivatives**

- $S = -\frac{\partial F}{\partial T}_{N,V,X} \quad P = -\frac{\partial F}{\partial V}_{N,T,X} \quad \mu = \frac{\partial F}{\partial N}_{T,V,X}$

Ask them to do



- **Energy Reference Points**

- All we're usually interested in is how the energies *change* through a process; so we don't care about the absolute values of the energies, as long as they are all referenced to the same (arbitrarily chosen) point.

- **Prep for HW 5.1**

- You *compute* the thermal energy, entropy, enthalpy, Helmholtz free energy, and Gibbs free energy for a mole of argon at room temperature and atmospheric pressure. Let's do part A.
 - Draw on argon being pretty nearly an *ideal* gas. Thermal energy: U .

$$U = \frac{3}{2} nRT = \frac{3}{2} \cdot (1) \cdot (8.31 J / K) \cdot 300 K = 3.74 kJ$$
 - Note: it does say "compute", so don't just look up in the table at the back of the book (though that will give you values to shoot for). Again, since it's an ideal gas, you can use the ideal-gas, S-T entropy relation we'd developed in chapter 2. For the entropy you'll need the mass of an argon atom which can be found in the periodic table at the back of the book and converted into kg using the conversion on the opposite page.

5.1.1 Electrolysis, Fuel Cells, and Batteries

- **Electrolysis**

You'll build on this example in Pr. 5.11

- Our first example of a process involving *other* work, and necessitating the use of these free energies is electrolysis: splitting water into hydrogen and oxygen gas. $H_2O \rightarrow H_2 + \frac{1}{2} O_2$
- **Q:** How much energy will it take to split one mole of water? ΔH
 - There's the change in the internal energy of the system, ΔU , and then there's the change in energy of the environment which is pressed out as the products expand from liquid to gas phase, $P\Delta V$. So the total energy required is $\Delta H_p = \Delta U + P\Delta V$.
 - The book quotes a table as 286 kJ for this process.
- **Q:** How much energy will *you* need to provide? $\Delta H - T\Delta S = \Delta G = W_{\text{other}}$, (work of splitting molecules)
 - Say that enthalpies and entropies are tabulated for the products and reactants at your given temperature, then you'd proceed as follows.
 - $\Delta G_{p,T} = \Delta H - T\Delta S$ Could look up in the table in the back of the book., or show yourself how the ΔG values were generated by the following:
 - $\Delta H = \Delta_f H_{\text{products}} - \Delta_f H_{\text{reactants}} = 286 \text{ kJ (per mole)}$
 - Look up in table at back of book. In this case, the products are elemental, so

$$\Delta_f H_{\text{products}} = 0$$
 - $\Delta S = S_{\text{products}} - S_{\text{reactants}}$

$$\Delta S = S_{1\text{mole},H_2} + \frac{1}{2} S_{1\text{mole},O_2} - S_{1\text{mole},H_2O}$$

$$= 131 J / K + \frac{1}{2} (205 J / K) - 70 J / K = 163 J / K \quad (\text{per mole})$$
 - Taking $T = 298K$, the total energy that *you* must provide is
 - $\Delta G_{p,T} = \Delta H - T\Delta S = 286 \text{ kJ} - 298K (163J/K) = 237kJ$

- **Fuel Cells**

- If you put in $\Delta G=237$ J to split water, you could, ideally, recover 237 J when it recombines. Again, the system and environment release $\Delta H=286$ J of energy, but $T\Delta S$ of that is lost as heating in the process.
- The principle of a fuel cell is to allow H and O to recombine, but to force them to do some work, generate some electricity along the way.
- **Efficiency:** $\frac{\text{usable}}{\text{released}} = \frac{\Delta G}{\Delta H} = \frac{\Delta H - T\Delta S}{\Delta H} = \frac{237\text{kJ}}{286\text{kJ}} = 83\%$.
 - **Note:** the key is that the $T\Delta S$ term is small – *the lower the temperature, the better.*
- In a fuel cell, the energy is put to use in driving a current, like in a battery.
 - At the negative electrode: $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$
 - At the positive electrode: $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$
 - The OH^- ions generated at the one electrode help burn the H^2 at the other. The electrons generated at one electrode are siphoned off and forced to do a bit of electrical work for us before returning to the other electrode.
- This is the basic operation of a fuel cell. In a hydrogen fuel cell, oxygen is taken in from the environment, hydrogen is provided as the fuel (sometimes it's initially bound up in a hydrocarbon), and the two are allowed to combine in a cell. The energy drives a current; the resulting water is expelled.
- The phrase '**hydrogen fuel economy**' references a future in which hydrogen rather than complex fossil hydrocarbons are burned to run cars. The burning process in a fuel cell has a *much* higher ideal efficiency than, say, the otto cycle. Of course, the current fuel system has to invest relatively little in producing the fuel (we only have to drill and refine it). In this imagined fuel system we'd have to produce the fuel, either by burning fossil fuels elsewhere, or by drawing energy from photovoltaics, hydroelectric, etc.

- **Batteries**

- A battery is like a fully self-contained fuel cell.
- **Pr. 5.5** you'll do the following kind of analysis
- **The process:** the common lead acid battery
 - At – electrode: $Pb + HSO_4^- \rightarrow PbSO_4 + H^+ + 2e^-$
 - In solution: $2SO_4^{2-} + 2H^+ \rightarrow 2HSO_4^-$
 - At + electrode: $PbO_2 + HSO_4^- + 3H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$
 - The net effect: $Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \rightarrow 2PbSO_4 + 2H_2O$
- **Question:** If it runs at room temp and atmospheric pressure, what's the voltage?
 - $q_{\text{charge}} \Delta V_{\text{oltage}} = \Delta \text{Energy}_{\text{charges}} \Rightarrow \Delta V_{\text{oltage}} = \frac{\Delta \text{Energy}_{\text{charges}}}{q_{\text{charge}}}$
 - **What's q?** For one cycle, 2 electrons are transferred, so $q = 2e = 2 \bullet 1.6 \times 10^{-19} \text{Coul} / \text{cycle}$
 - **What's $\Delta \text{Energy}_{\text{charge}}$?** Ideally, all recoupable energy released during the chemical process is invested in moving the charges. Assuming that the battery operates at constant temperature and

pressure (via interactions with the environment), then the energy gained by the electrons is that liberated by the reaction: $-\Delta G_{\text{system}}$

- $\Delta E_{\text{charge}} = -\Delta G_{\text{system}} = -G_{\text{products}} - G_{\text{reactants}}$
 - In practice, G 's aren't tabulated, $\Delta_f G$'s are – the change in Gibbs free energy for forming a substance from its constituent elements, that is, $G - G_0$. Since both the reactants and products have the *same* constituent elements, thus the same G_0 ,

$$G_{\text{products}} - G_{\text{reactants}} = \Delta_f G_{\text{products}} - \Delta_f G_{\text{reactants}}$$
- $\Delta E_{\text{charge}} = -\Delta G_{\text{system}} = -\left(\Delta_f G_{\text{products}} - \Delta_f G_{\text{reactants}} \right)$

$$= -\left(\Delta_f G_{\text{PbSO}_4} + 2\Delta_f G_{\text{H}_2\text{O}} - \left(\Delta_f G_{\text{Pb}} + \Delta_f G_{\text{PbO}_2} + 4\Delta_f G_{\text{H}^+} + 2\Delta_f G_{\text{SO}_4^{2-}} \right) \right)$$
 - Each of these $\Delta_f G$'s are in the table in the back of the book for *one mole* of reactants, or *one mole* of cycles. Since we want the energy for just one cycle (and the 2 electrons moved during it), we'll divide by 6.02×10^{23} cycles/mole.
 - $\Delta_f G_{\text{Pb}} = 0$ since Pb is the substance's elemental form.

- $\Delta E_{\text{charge}} = -\Delta G_{\text{system}} = -\left(\frac{-394 \text{kJ/mole}}{6.02 \times 10^{23} \text{cycles/mole}} \right)$

$$q_{\text{charge}} \Delta V_{\text{oltage}} = \Delta \text{Energy} \Rightarrow \Delta V_{\text{oltage}} = \frac{\Delta \text{Energy}}{q_{\text{charge}}}$$

$$\frac{394 \text{kJ/mole}}{\left(e^- / \text{cycle} \right) \left(6.02 \times 10^{23} \text{cycles/mole} \right)} = \frac{394 \text{kJ} / \left(6.02 \times 10^{23} \right)}{2 \cdot \left(1.6 \times 10^{-19} \text{Coul} \right)} = 2.04 \text{Volts}$$

▪ Got this Far

5.1.2 Extensive and Intensive Quantities

- A spot of vocabulary:
 - **Extensive** = depends on amount in system
 - U, V, N, S, H, F, G, m
 - **Rule of Thumb:** if adding a second, identical system doubles a value, it's extensive.
 - **Intensive** = does not depend on amount of stuff
 - T, P, μ , density
- **Example:** Say you have one Einstein solid with its energy, volume, ... Now you get another identical Einstein solid. You've doubled your total energy, volume, ... but the temperature, pressure... are unchanged.
- **Simple relations.** Since all extensive properties are proportional to the amount of material, one divided by the other cancels off that dependence, leaving an intensive quantity. Ex. $G \propto \text{amount}$, $N \propto \text{amount}$ $\frac{G}{N} \propto \frac{\text{amount}}{\text{amount}} = \text{intensive}$.

5.1.3 Gibbs Free Energy and Chemical Potential

- $\mu = \frac{\partial G}{\partial N_{T,P}}$ says that, holding intensive properties T and P constant, then the ratio of a change in G to a change in N is μ . But if G/N is intensive and the only constants we're holding constant are inherently intensive, then the whole right hand side is intensive, meaning that the left hand side is intensive, i.e. μ doesn't depend upon the amount, μ doesn't depend upon N.
- So, $\int \mu \partial N_{T,P} = \partial G \Rightarrow \mu N = G$ or $\mu = \frac{G}{N}$
- This argues that, under these conditions, the chemical potential is a constant, simply the Gibbs free energy per particle.
- This result may seem a bit surprising, but let's compare it with the definition of Gibbs Free energy and see if it makes sense.
 - $\mu N = G \equiv U - TS + PV$
 - Eliminating G and solving for U, we have
 - $U = TS - PV + \mu N$
 - Now, if we say hold T and P constant while varying U, we get
 - $dU = TdS - PdV + \mu dN + Nd\mu$
 - First, assume that there is no other work done (just mechanical), then we have
 - $dU = TdS - PdV + \mu dN$
 - These are equal under the condition that $d\mu = 0$, i.e., chemical potential is constant.
 - On the other hand, if we allow that *other* work happens (say chemical work), then
 - $dU = TdS - PdV + \mu dN + \frac{\partial U}{\partial X} dX$,
 - And the two relations are equal only if
 - $Nd\mu = \frac{\partial U}{\partial X} dX \Rightarrow \frac{d\mu}{dX} = \frac{1}{N} \left(\frac{\partial U}{\partial X} \right)_{S,V,N}$ so the chemical potential depends on the external influence X (say, magnetic field).
- **Application: Back to the Battery**
 - In the battery example that we examined, recall that it was a difference in Gibbs free energies that drove/drew the electrons from one electrode to the other. Now seeing how Gibbs free energy is related to chemical potential, we could say, as is often said, it's the battery's *chemical potential difference* for electrons that drives them.
 - In particular, the Gibbs free energy per cycle was
 - $\Delta G = -\frac{394 \text{ kJ/mole}}{6.02 \times 10^{23} \text{ cycles/mole}} = -6.54 \times 10^{-22} \text{ J} = -4.08 \text{ eV}$
 - There were N = 2 electrons per cycle, so
 - $\Delta \mu_{e^-} = \frac{\Delta G}{N_{e^-}} = -\frac{4.08 \text{ eV}}{2} = -2.04 \text{ eV}$
 - **Bad Plumbing**
 - Inadvertently, little 'batteries' can be created when pipes of two different metals are mated in plumbing. The different metals have different electronic chemical potentials, so electrons will flow

between them, they interact with ions in the water contained in the pipes and promote chemical reactions / corrosion on the two 'electrodes.'

- **Counter Example**

- $\mu = \frac{\partial F}{\partial N_{T,V}}$ Again, both F and N are extensive, so their ratio is intensive; but that doesn't guarantee that their derivative is. In fact, this derivative implies holding constant another extensive variable, V. The effect is that extensivity is preserved. So under these conditions μ is extensive, as is N, so they depend upon each other and the integral is not trivial.
- Qualitatively this can be understood because, holding the volume constant while putting in more particles would surely increase the density, and likely make it harder to squeeze in each subsequent particle (raising μ).

- **Multiple Species**

- If there are multiple species, then each particle brings in the energy appropriate to its species, *given the environment into which they're coming*. If P and T are constant, then

$$dG = \mu_1 dN_1 + \mu_2 dN_2 + \dots \Rightarrow G = \mu_1 N_1 + \mu_2 N_2 + \dots$$
- As implied by the 'given the environment' business, while the chemical potentials are intensive (independent of *number*), they can depend upon the *ratios* of the different species. Thus the chemical potential for, say, hydrogen gas, is different if it's in a pure state or 50/50 mixed with oxygen.

- **Ex. Ideal Gas**

- $\frac{\partial G}{\partial P_{T,N}} = V$ so, $\partial G = V \partial P_{N,T}$
- By the Ideal Gas Law, $V = NkT/P$ so

$$\partial G = V \partial P_{N,T} = \frac{NkT}{P} \partial P_{N,T} \Rightarrow \underline{G - G^\circ = NkT \ln(P / P^\circ)}$$
- Taking P° to be atmospheric pressure, then if T = room temperature, the G° values can be found in tables of G at room temperature. So we can boot strap our way up from an initial value of G to a new one.
- This can be rephrased in terms of chemical potentials by substituting $G = N\mu$ we get
- $N\mu - N\mu^\circ = NkT \ln(P / P^\circ) \Rightarrow \underline{\mu - \mu^\circ = kT \ln(P / P^\circ)}$
- For a mixture of ideal gasses, with the pressures taken to be the partial pressures, this can be used for individual species. It is through the partial pressures that the μ 's implicitly depend upon the presence of the other species.

5.2 Free Energy as a Force toward Equilibrium

- Processes are driven by the increase in entropy; however, that's the *universal* entropy, not that of just your system. If your system is isolated, you need only track its entropy; but often it interacts with its environment. Then you need to track the total entropy. Here, we see how the total entropy can be rephrased in terms of the system's free energies, thus we can use the free energies to determine how *un-isolated* systems evolve.
- **Environment as Reservoir**

- We can treat the environment as a heat reservoir, for it is typically so much larger than the system that its temperature is virtually unaffected by transferring energy. In this argument, all of its properties will be subscripted with an R while the system's properties will be unsubscripted.
- Then the total entropy change is $dS_{total} = dS + dS_R$
- In general, $dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN$.
- **Constant T, V, and N** (ex. Gas in a container)
 - Considering the case in which V and N remain constant, only energy is transferred, then $dU = -dU_R$. So, $dS_R = \frac{1}{T} dU_R = -\frac{1}{T} dU$.
 - Then $dS_{total} = dS + dS_R = dS - \frac{1}{T} dU = \frac{1}{T} \left(dS - dU \right) = -\frac{1}{T} dF$.
 - So, under these conditions, as S_{total} increases the system's Helmholtz Free Energy, F, decreases.
- **Constant T, P, and N** (ex. Solid or gas that's open to the room)
 - In this case, both energy and volume can be exchanged, so $dU = -dU_R$ and $dV = -dV_R$. So $dS_R = \frac{1}{T} dU_R + \frac{P}{T} dV_R = -\left(\frac{1}{T} dU + \frac{P}{T} dV\right)$.
 - Then

$$dS_{total} = dS + dS_R = dS - \frac{1}{T} \left(dU + PdV \right) = -\frac{1}{T} \left(dU + PdV - TdS \right) = -\frac{1}{T} dG$$
 - Under these conditions, as S_{total} increases, the system's Gibbs Free Energy, G, decreases.
- **Conceptually:** Outside of thermodynamics, we're familiar with the rule of thumb that systems tend toward the lowest accessible energy state – for example, balls roll down hill and electrons settle into the ground state. In both cases, the decrease in potential energy is accompanied by a decrease in kinetic energy since that is given up to the environment (in heating and sound in the first case and in a photon in the second).
 - That's kind of what we're seeing here. Universal entropy tends to increase is translated into systems' Helmholtz or Gibbs free energy tends to decrease.
 - **Entropy effect**
 - But this analysis adds an interesting detail both free energies involve $\Delta U - T\Delta S$: the systems could decrease free energy *either* by decreasing internal energy *or* by *increasing entropy*. For that matter, generally higher energy states have higher entropy.
 - As you'll find in problem 20, there's a temperature above which hydrogen atoms would rather be in their 1st excited state!