Spontaneity

* Recall the 2nd law: ΔSuniv > 0
  + This is difficult to evaluate as a condition of spontaneity because the surroundings are so vast, and are of little interest. So, why should we rely on a state function that does not explicitly describe the system?
  + We need to find a way to predict spontaneity using terms that depend only on the properties of the system!
    - We also want our spontaneity condition to be based on realistic conditions like constant T or P
    - We can establish criteria for spontaneity based on U and H

eq. 4.1 (4.3) *Requirements for spontaneity*

eq. 4.2 (4.4)

* + We can see that these expressions are not practical (and virtually impossible) because both require entropy to be held constant (isentropic). However, in the case of eq 4.2, we can see that half of the requirement of spontaneity (constant pressure) is easily attained. This is why the majority of spontaneous processes are exothermic.
  + The common trend between equations 4.1 and 4.2 are that, for both conditions, the energy terms decrease.
* We define the Helmholtz Free Energy, A (T,V)

\*Here, we must expand our definition of dU. We can introduce a new term known as **chemical potential**.

* It is usually assumed that the moles of a substance remain constant during a given process. But what if we were interested in how the energetics of a process are altered by the amount of material (ex. Phase change)
  + The chemical potential of a substance, µ, is the change in free energy with respect to amount
  + In a closed system, we evaluate this change at constant T,V
    - (4.47) *Chemical Potential of closed system*
* Chemical potential is, essentially, a measure of how much a species wants to undergo a chemical change. If two or more substances exist in a system and have different chemical potentials, some process will occur to equilibrate the potentials.
  + For systems with multiple components, each component has a potential energy µi
* eq. 4.3 *Expression for dA for a reversible process*
* At constant T,V
* If dA < 0 SPONTANEOUS
* If dA > 0 NONSPONTANEOUS
* We have our first spontaneity criteria that does not directly involve entropy! T and V are considered the *natural variables* of A. Now, we can define another term, **the Gibbs Free Energy**, G (T,P). In this case, T and P are the natural variables of G.

* Here, we define the chemical potential at constant T, P:

+ eq. 4.4 *dG for a reversible process*

* At constant T,P
* If dG < 0 SPONTANEOUS
* If dG > 0 NONSPONTANEOUS

Applications of dA

* For an isothermal, reversible process occurring at constant V, Helmholtz free energy represents the maximum possible value of w. In other words, it is maximum amount of **PV work** that can be extracted from the system having volume V at temperature T. If the process is irreversible, the system can not use all of the energy that is “freely available” for work, and thus, a portion is lost to entropy.

Applications of dG

* Not all work is PV work! The most common (and important) example of non-PV work is electron transfer. We can expand our definition of dU to include non-PV work:

Applying the Clausius theorem:

* + - For a cyclical process:

(Clausius Theorem) Eq. 4.5.

* In the case of an irreversible process, the change in entropy will be greater than the value dq/T. The “equal to” term applies to reversible change only.

At constant P:

eq. 4.6a

eq. 4.6b

\*Gibbs Free energy is the maximum amount of non-PV work that can be done by a system having pressure P at temperature T.

eq. 4.7a (4.12)

eq. 4.7b (4.13)

* + In both expressions above, the term –TΔS is thermal energy that must be used to satisfy the 2nd law of thermodynamics. The remaining energy is “free” to do work.

Natural Variables

* Natural variables are those variables of a function whose differentials dictate the values of the function. Ex. dA = -SdT – PdV. The natural variables of A are T and V.
  + We can express all energy quantities in terms of natural variables P, V, T and S. Here, we are considering single component systems, so there is no chemical potential term since dn = 0.

*Natural Variable Expressions*

* + Let’s consider the total differential of U in terms of the natural variables, U (S,V)

If we set this equal to the expression for dU above:

Therefore:

eq. 4.8a (4.18)  
 eq. 4.8b (4.19)

* + These are amazing and incredibly insightful relationships between thermodynamic parameters. These types of relationships also show that we do not have to try to empirically measure these complex derivatives….we can just evaluate simple parameters like T, P and V.

eq. 4.9a (4.20)  
 eq. 4.9b (4.21)

eq. 4.10a (4.22)  
 eq. 4.10b (4.23)

eq. 4.11a (4.24)  
 eq. 4.11b (4.25)

Maxwell Relations

* If we know how any one of the energies varies in terms of its natural variables, we can construct expressions for any other energy.
  + Example. Let’s say I wanted to express U in terms of G

Such an approached can be taken to equate any energy terms.

* We know that for a function F(x,y), we can express the total differential dF. If F is a state function, and both x and y change, it does not matter which change occurs first, because the path is irrelevant.
  + This suggests that if we were to take the 2nd derivative of F, the order of differentiation is also irrelevant.
  + Any differential that satisfies the condition above is known as an exact differential.
    - \*The differentials of U, H, A and G are exact! We can establish equalities from 2nd derivatives (see pg 113)
    - From these, we can establish relationships between derivatives of non-energy terms. These are known as Maxwell’s equations.

Eq. 4.12 (4.35-37) *Maxwell’s relations*

* + These extremely useful relationship apply to all phases of matter and apply to both real and ideal systems. Most importantly, they express complex derivatives in terms of simple ones.
    - Class Example. Find for an ideal gas
    - Class example. Starting from the natural variable equation for the differential of U, develop an expression for the dependence of U on V under isothermal conditions for an ideal gas. What does your answer reveal?

More about ΔG

* The changes in U and H with respect to temperature are heat capacities. How does G change with T? From eq. 4.11a, we see that the slope of dG vs dT is the negative of the entropy of the system. The negative slope indicates that G decreases with T. Let’s consider the fraction G/T. We can calculate the differential of this term using quotient rule:

Substitute in the natural variable expression for dG

Constant P

Using changes in G and H and dividing by

Eq. 4.13 (4.44) *Gibbs Helmholtz Equation*

* + See ex. 4.12

* The relationship between G and P at constant T:

eq. 4.14 (4.46) *ΔG related to changes in pressure at constant T*

* Here, we see that an increase in pressure results in an increase in Gibbs Free energy. We know that for a given amount of a substance, the volume increases according to the following: g>> L > s (water is a notable exception), so the dependence of G on P changes with phase.
  + The system will spontaneously convert to the state of lowest Gibbs Energy at a given value of P.

Fugacity

* Chemical potential varies with pressure. For an *ideal gas*, we can show that:

Eq. 4.15 (4.55) *Change in chemical potential with pressure for an ideal gas*

* + As we know, gases are typically non-ideal and the intermolecular forces alter the pressures in the system. At moderate pressures, µ is lower than predicted due to attractive forces, whereas, at high pressures, µ is higher than predicted due to repulsive forces.
  + We must use an adjusted pressure called fugacity, f. In other words, a gas at some “real pressure” P will behave as if it has a pressure f due to non-ideal interactions. For an ideal gas, f = P.

Eq. 4.16 (4.58) *Fugacity*

* + - Where ɸ is the fugacity coefficient. We can consider f to be a measure of the non-ideality of a real gas. ɸ approaches 1 as P approaches 0. Revising eq 4.17 for a real gas:

Eq. 4.17 (4.59) *Change in µ with pressure for a real gas*

* + - Fugacity terms are indirectly calculated by comparing the actual and ideal molar volumes of a gas in order to obtain ɸ:

Eq 4.18 (4.62) *Calculation of fugacity coefficient*

Ex. Ex. 4.14 in chapter.