**Ch 19 Free Energy and Thermodynamics Name:**

What is the ultimate driving force behind chemical and physical changes? How does it relate to the universe?

*18.1 Cold Coffee and Dead Universes*

What do you have to determine if you want to know if a process will occur? Why is this not always obvious?

*19.2 Spontaneous and Nonspontaneous Processes*

What does it mean when a process is spontaneous and how does it relate to the speed of the reaction? *Figure 19.2*

How can a nonspontaneous process be made to occur?

*19.3 Entropy and the Second Law of Thermodynamics*

Most spontaneous processes are \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_. What drives the endothermic processes at mentioned?

Read the formal definition of entropy (*S*). On the molecular scale entropy is more complicated than disorder, it has

more to do with the ways particles can be arranged – called \_\_\_\_\_\_states. Systems with high entropy have the greatest

\_\_\_\_\_\_\_\_\_\_\_al of energy (more possible \_\_\_\_\_\_\_\_\_\_\_\_\_\_ments).

*19.4 Entropy Changes Associated with State Changes*

Look at the example of phase changes *Figure 19.3.* List the 3 ways water molecules can disperse energy in the gas phase *(Figure 19.4):*

*Practice 19.1* a) \_\_\_ b) \_\_\_ c) \_\_\_ *CC19.3 \_\_\_*

*19.5 Heat Transfer and Changes in the Entropy of the Surroundings*

How can processes like ice freezing or water vapor condensing from the air be spontaneous if both changes result in more “order” for the water molecules (Δ*S*sys <0 entropy decreases)? *(temperature must be below 0oC for freezing)*

The freezing of water becomes \_\_\_\_spontaneous above \_\_\_\_\_ because entropy is \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ dependent.

*(The analogy of giving $1000 to a rich man vs a poor man compared to dispersing 1000J of energy into hot vs cold surroundings should be helpful.) The explanation on pg861 of* Δ*S*univ *for freezing water at low vs high temperature also helps to explain when the process is spontaneous.*

*The end of this section shows how* Δ*S*univ *can be quantified by relating it to q and ΔH for the system at a particular T.*

*CC19.4 \_\_\_\_*

*17.6 Gibbs Free Energy*

The beginning of this section shows how Gibbs free energy is defined by: enthalpy – temperature x entropy. This allows us to determine the spontaneity of a process by calculating the change in Gibbs free energy: Δ*G*

Δ*G = \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_* Δ*G = −T*Δ*S*univ (at constant \_\_ and \_\_)

Gibbs free energy is also called \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ and chemical systems tend toward

\_\_\_\_\_\_\_\_\_\_\_\_er Gibbs free energy: Δ*G* < 0corresponds to a \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ process

Δ*G* > 0 corresponds to a \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ process and Δ*G* = 0 corresponds to equilibrium.

*The Effect of ΔG, ΔS, and T on Spontaneity* *(discussions presented in this section are often used in AP questions)*

*Case 1 Example:* 2N2O(g) → 2N2(g) + O2(g) Δ*H*orxn = -163.2kJ The reaction is \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ so enthalpy

is \_\_\_\_\_\_tive (releases energy) and the entropy is \_\_\_\_\_\_tive (increase in disorder/more possible states). This leads

the reaction to be\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ at all temperatures.

(Δ*G < 0)*  Δ*G (negative at all temperatures)* = Δ*H(negative)* – TΔ*S(positive)*

*Case 2 Example:* 3O2(g) → 2O3(g) Δ*H*orxn = +285.4kJ The reaction is \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ so enthalpy

is\_\_\_\_\_\_\_\_\_\_\_\_ (heat \_\_\_\_\_\_\_\_\_\_\_\_ed) decreasing the entropy of the surroundings. The change in entropy of the

system is \_\_\_\_\_tive (entropy \_\_\_\_\_\_\_\_\_\_\_\_\_s. In this case the reaction is \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ at all

temperatures. (Δ*G < 0)* Δ*G (positive at all temperatures)* = Δ*H(positive)* – TΔ*S(negative)*

*Case 3 Example:* H2O(l) → H2O(s) Δ*H*orxn = -6.01kJ This case shows why freezing water becomes

spontaneous at low temperatures as the *T*Δ*S* term becomes small enough so that the process is spontaneous (Δ*G < 0).*

(Δ*G is − at low temps and + at high temps)* Δ*G*  = Δ*H(negative)* – TΔ*S(negative)*

*Case 4 Example:* H2O(l) → H2O(g) Δ*H*orxn = +40.7kJ(at 100oC) The reaction is \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ so

enthalpy is\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ but the entropy is also \_\_\_\_\_\_\_\_\_\_\_\_\_ which makes the process \_\_\_\_\_\_\_\_\_\_\_ture

dependent. For boiling water, the *T*Δ*S* term becomes large enough to make Δ*G < 0 (spontaneous).*

(Δ*G is + at low temps and − at high temps)* Δ*G*  = Δ*H(negative)* – TΔ*S(negative)*

*Table 19.1* nicely summarizes the effects. When Δ*H* and Δ*S* have \_\_\_\_\_\_\_\_\_\_\_\_ signs spontaneity DOES NOT

depend on \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ when they have the \_\_\_\_\_\_\_\_\_ signs spontaneity DOES depend on temperature.

*Practice 19.3 CC 19.5 \_\_\_\_*

*19.7 Entropy Changes in Chemical Reactions: Calculating* Δ*Sorxn*

How is Δ*Sorxn* defined?

Standard molar enthalpies have been defined in a similar manner to standard molar enthalpies (Δ*Hf o*). How is zero enthalpy defined?

*Table 19.2* shows standard enthalpies for selected substances at standard states (298K or \_\_\_oC, \_\_atm) in units of

\_\_\_\_\_\_\_\_\_. Standard enthalpies: gas > \_\_\_\_\_\_\_\_\_> \_\_\_\_\_\_\_\_ ; higher for atoms with a \_\_\_\_\_\_er

molar \_\_\_\_\_\_; different for \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ of the same element (graphite > \_\_\_\_\_\_\_\_\_\_\_\_); \_\_\_\_\_\_\_\_\_er for

more \_\_\_\_\_plex molecules; dissolution of a crystalline into solution ***usually*** results in an \_\_\_\_\_\_\_\_\_\_\_\_\_ in entropy.

*CC19.6 \_\_\_\_ (explain your ranking)*

Write the equation for calculating Δ*Sorxn*:

*This should look familiar (Hess’s Law) remember unlike \_\_\_\_\_\_\_\_\_\_\_\_ of formation which are \_\_\_\_\_ for elements*

*in their \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ states, standard enthalpies are always non\_\_\_\_\_\_\_ at 25oC.*

*Practice 19.5 (Use Appendix IIB)*

*19.8 Free Energy Changes in Chemical Reactions: Calculating* Δ*Gorxn*

Why is calculating Δ*Gorxn* extremely useful? And what does a more negative Δ*Gorxn* mean?

*Practice 19.6*

*Practice 19.7*

Δ*Gorxn* can also be calculated from standard free energies by:

*By definition elements have standard free energies of \_\_\_\_\_\_ and most compounds have \_\_\_\_\_\_\_\_\_\_ values (Why?)*

Why would compounds with positive values be less common?

*Practice 19.8 & More Practice 19.8 (you must use App IIB to calculate* Δ*Horxn* *and* Δ*Sorxn*  *to use the Gibbs eqn*)

Read *Chemistry in Your Day: Making a Nonspontaneous Process Spontaneous* (The explanation of producing H2 fuel from water is oversimplified. Do you see a problem with the other product? Find a way to produce H2 cleanly and efficiently and you will be a billionaire.)

Example *and Practice 19.9* (Shows how Hess’s law of adding reactions works for Δ*Gorxn*.)

The change in free energy of a reaction is the maximum amount of \_\_\_\_\_\_\_\_\_\_\_ available or “\_\_\_\_\_\_\_\_” to do work

(if Δ*Gorxn* is \_\_\_\_\_\_\_\_\_\_\_\_). The amount of energy available to do work is what remains after accounting for \_\_\_\_\_\_\_\_ lost. Why does recharging a battery always require more energy than was obtained as work from the battery?

If Δ*Gorxn* is \_\_\_\_\_\_\_\_\_\_\_\_\_ it represents the minimum amount of energy needed to make the reaction \_\_\_\_\_\_\_\_\_\_\_\_\_.

*19.9 Free Energy Changes for Nonstandard States: The Relationship between* Δ*Gorxn* *and* Δ*Grxn*

What is the key reason why water exposed to open air will evaporate? (even if the temperature is 25oC)

Write the eqn for calculating Δ*Grxn* = \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ (nonstandard condition)

*In the example for evaporation of water when Q = \_\_\_\_\_\_ then* Δ*Gorxn* *=* Δ*Grxn since ln(1) =\_\_\_\_. Since* Δ*Gorxn* *>0*

*(positive) the reverse reaction is \_\_\_\_\_\_\_\_\_\_\_\_\_\_ (under standard conditions water vapor will \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_.*

*When Q = K*p *then* Δ*Grxn = \_\_\_ because RTlnQ will be equal in \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ but opposite in \_\_\_\_\_\_\_\_ to* Δ*Gorxn*,

*therefore the reaction is not \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ in either direction, as it is at \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_.*

*Practice 17.9*

*19.10 Free Energy and Equilibrium: Relating* Δ*Gorxn* *to the Equilibrium Constant*

*K* determines how far a reaction goes towards \_\_\_\_\_\_\_\_\_\_\_\_\_, a measure of \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_. As *K* becomes

larger Δ*Gorxn* becomes more \_\_\_\_\_\_\_\_\_\_\_ (and vise versa). Δ*Gorxn* = \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ [19.14]

Review the bullet point summaries and *Figure 17.14.*

*Review Example 19.11 to see how K can be calculated from* Δ*Gorxn* *(note the inv of ln x is ex) Practice 19.11*

*CC19.8 \_\_\_\_ CC19.9 ­­­\_\_\_\_*

*Exercises* (pgs 888-890) #27, 28, 35, 39a, 43, 45, 49, 50, 51(a,b,c,f), 55(a,d), 59, 61(d), 63d, 73