WHAT DRIVES A REACTION TO BE THERMODYNAMICALLY FAVORABLE?

ENTHALPY (ΔH) – heat exchange (exothermic reactions are generally favored)
ENTROPY (ΔS) – dispersal (disorder) of the *matter and energy* of a system (more dispersal/disorder is favored) Nature tends toward chaos! Think about your room at the end of the week. Your mom knows this concept all too well.

A disordered pile of playing cards.

Thermodynamically favored processes or reactions are those that involve both a decrease in the internal energy of the components ($\Delta H° < 0$) and an increase in entropy of the components ($\Delta S° > 0$). These processes are necessarily "*thermodynamically favored*" ($\Delta G° < 0$) or negative. If you are using an older textbook, you may see these reactions referred to as "spontaneous". Avoid that language as you answer free-response questions!

Thermodynamically favored processes occur without outside intervention once the energy of activation has been reached. Thermodynamics does not predict nor take into account the rate of the reaction. That is the realm of kinetics. Some reactions are very fast (like combustion of hydrogen) other reactions are very slow (like graphite turning to diamond) but both are thermodynamically favored.

The first law of thermodynamics: Energy can never be created nor destroyed. Therefore, the energy of the universe is constant. This is simply a statement of the law of conservation of energy you've know about for quite some time.

The second law of thermodynamics: the universe is constantly increasing the dispersal of matter and energy. Rudolph Clausius "discovered" it and gave it its symbol.

The third law of thermodynamics: the entropy of a perfect crystal at 0 K is zero.
[Not a lot of perfect crystals out there so, entropy values are RARELY ever zero—even elements]
So what? This means the absolute entropy of a substance can then be determined at any temp. higher than zero K. (Handy to know if you ever need to defend *why G & H* for elements = 0. . . . BUT *S* does not!)
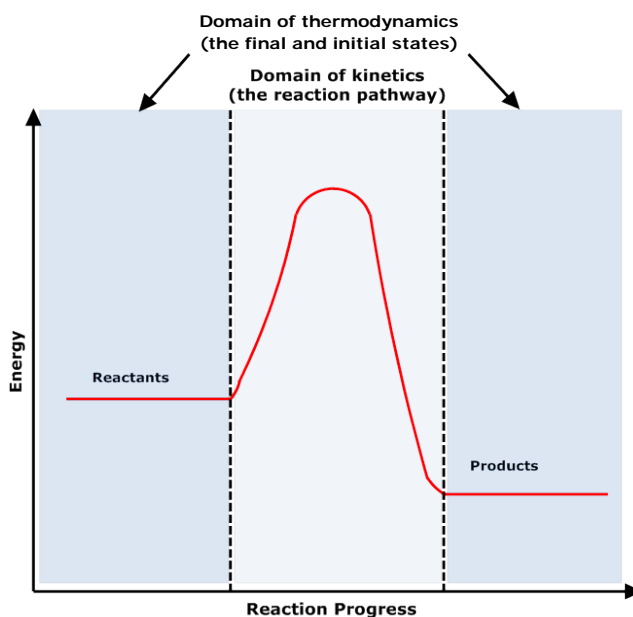
What is entropy? It's difficult to narrow this concept down to a single definition, but let's try anyway! Entropy is a thermodynamic function that describes the *number of arrangements* (positions and/or energy levels) that are *available to a system* existing in a given state. *Entropy* is closely related to probability. The key concept is that the more ways a particular state can be achieved; the greater is the likelihood (probability) of finding that state. In English…***nature spontaneously proceeds toward the states that have the highest probabilities of existing***.

Let's use a simple example, an ideal gas expanding into an evacuated bulb. WHY is this process thermodynamically favorable? Simple, the driving force is *probability*. Because there are more ways of having the gas evenly spread throughout the container than there are ways for it to be in any other possible state, the gas disperses attaining a uniform distribution. The consequences are dramatic for large numbers of molecules, as you can see at right.

Let's simplify! How many possible microstates exist for a sample of four ideal gas molecules in two bulbs of equal volume?
(Why ideal gas molecules? There are no pesky attractive forces to influence their motion.)
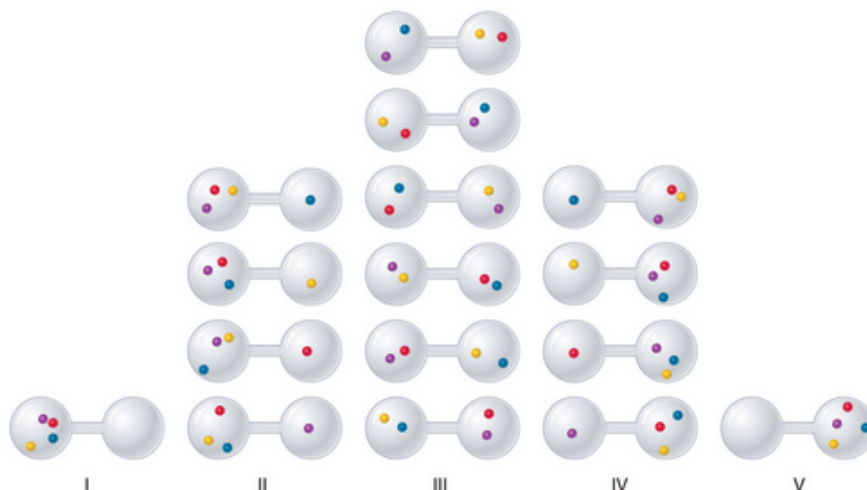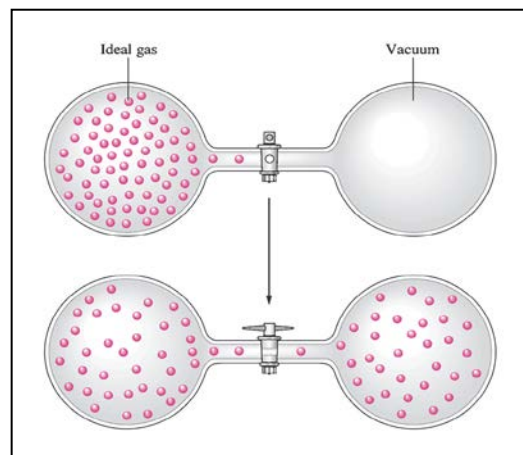
There are 16 different ways to distribute four gas molecules between the bulbs, with each distribution corresponding to a particular microstate. Arrangements I and V each produce a single microstate with a probability of 1/16. This particular arrangement is so improbable that it is likely not observed. Arrangements II and IV each produce four microstates, with a probability of 4/16. Arrangement III, with half the gas molecules in each bulb, has a probability of 6/16. It is the one encompassing the most microstates, so it is the most probable.

Predicting the entropy of a system is based on physical evidence:

- The greater the dispersal of matter and/or energy in a system, the larger the entropy.
- The entropy of a substance always increases as it changes from solid to liquid to gas.
- When a pure solid or liquid dissolves in a solvent, the entropy of the substance increases (Carbonates are an exception! Carbonates interact with water and actually bring MORE order to the system.)
- When a gas molecule escapes from a solvent, the entropy increases
- Entropy generally increases with increasing molecular complexity (crystal structure: KCl vs. $CaCl_2$) since there are more MOVING electrons!
- Reactions increasing the number of moles of particles often increase entropy.

In general, the greater the number of arrangements, the higher the entropy of the system!

Exercise 1 **Predicting Entropy Changes**

Predict the sign of the entropy change for each of the following processes. Justify your answers.

a) Solid sugar is added to water to form a solution.

b) Iodine vapor condenses on a cold surface to form crystals.

a) positive
b) negative

Calculating Entropy from tables of standard values:

(You already know how to solve problems like this, just pay close attention to the UNITS!)

BIG MAMMA, verse 2: $\Delta S°_{rxn} = \Sigma \Delta S°_{(products)} - \Sigma \Delta S°_{(reactants)}$
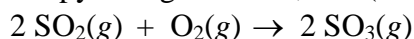
ΔS **is** + when dispersal/disorder increases (favored)
ΔS **is** – when dispersal/disorder decreases
NOTE: Units are usually J/(mol$_{rxn}$ • K) (**not** kJ!)

Exercise 2

Calculate the entropy change at 25°C, in J/(mol$_{rxn}$ • K) for:

$$2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$$

Given the following data:

|	
$SO_2(g)$	248.1 J/(mol• K)
$O_2(g)$	205.3 J/(mol• K)
$SO_3(g)$	256.6 J/(mol • K)

–188.3 J/(mol$_{rxn}$ • K)

ENTROPY CHANGES AS THEY RELATE TO REVERSIBLE PHASE CHANGES

Phase changes occur *at constant temperature* and represent a system which is also in *equilibrium* $\therefore \Delta G = 0$.

$$\Delta S^{\circ}_{surroundings} = \frac{\text{heat transferred}}{\text{temperature at which change occurs}} = \frac{q}{T} = \frac{-\Delta H}{T} \text{ expressed in } \frac{J}{\text{mol}_{rxn} \cdot K}$$

**Where the heat supplied (endothermic) ($q > 0$) or evolved (exothermic) ($q < 0$) is divided by the temperature in Kelvins

** It is important here to note if the reaction is endothermic or exothermic. The actual significance of this is really *dependent on the temperature* at which the process occurs. (i.e., If you gave a millionaire $100 it would not make much difference in his happiness; if you gave a poor college student $100 it would create a totally different expression of happiness!)

EX: water (ℓ @ 100 °C) $\rightleftarrows$ water (g @ 100°C)
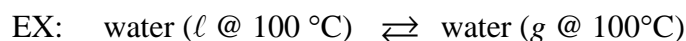
The entropy will increase for the forward reaction (vaporizing) since the reaction produces water in a less condensed state, thus the molecules are more dispersed.
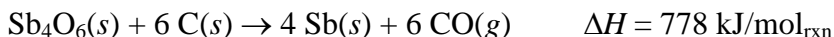

Exercise 3   **Determining ΔS_{surr}**
In the metallurgy of antimony, the pure metal is recovered via different reactions, depending on the composition of the ore. For example, iron is used to reduce antimony in sulfide ores:

$$Sb_2S_3(s) + 3\ Fe(s) \rightarrow 2\ Sb(s) + 3\ FeS(s) \qquad \Delta H = -125 \text{ kJ/mol}_{rxn}$$
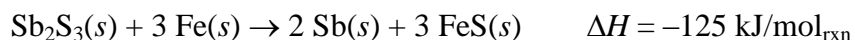
Carbon is used as the reducing agent for oxide ores:

$$Sb_4O_6(s) + 6\ C(s) \rightarrow 4\ Sb(s) + 6\ CO(g) \qquad \Delta H = 778 \text{ kJ/mol}_{rxn}$$

Calculate ΔS_{surr} for each of these reactions at 25°C and 1 atm.

419 J/K $\bullet$mol$_{rxn}$ & -2.61×10^3 J/K$\bullet$mol$_{rxn}$

Entropy & Free Energy

ENTROPY SUMMARY:

$\Delta S = +$ **MORE DISPERSAL (FAVORED CONDITION)**
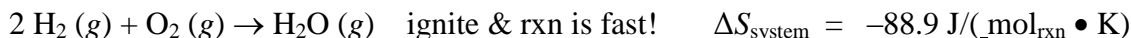$\Delta S = -$ **LESS DISPSERSAL**

Whether a reaction will occur spontaneously *may be* determined by looking at the ΔS of the universe.

$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \Delta S_{\text{universe}}$

IF $\Delta S_{\text{universe}}$ is +, then reaction is thermodynamically favorable

IF $\Delta S_{\text{universe}}$ is −, then reaction is NOT thermodynamically favorable

Consider

$2 H_2 (g) + O_2 (g) \rightarrow H_2O (g)$ ignite & rxn is fast! $\Delta S_{\text{system}} = -88.9 \text{ J/(\_mol}_{\text{rxn}} \bullet K)$

Therefore, the entropy declines mainly due to 3 moles of gas $\rightarrow$ 2 moles of gas which is a more condensed or less dispersed state!

To confirm we need to know entropy of surroundings!

$\Delta S_{\text{surroundings}} = \dfrac{q_{\text{surroundings}}}{T}$

$\Delta H_{\text{system}} = -483.6 \text{ kJ/mol}$

The First Law of Thermodynamics demands that this energy is transferred ***from*** the system ***to*** the surroundings so...

…Note that the change (increase or decrease) in the entropy of the surroundings is the result of energy flow into or from the surroundings as a function of temperature, such that,

$\Delta S_{\text{surroundings}} = \dfrac{\Delta H_{\text{surrounings}}}{T} = \dfrac{-\Delta H_{\text{system}}}{T}$;

$\therefore -\Delta H_{\text{system}} = \Delta H_{\text{surroundings}}$ OR $-(-483.6 \text{ kJ}) = +483.6 \text{ kJ}$

Now, $\Delta S_{\text{surroundings}} = \dfrac{\Delta H_{\text{surroundings}}}{T} = \dfrac{+483.6 \text{ kJ/mol}_{\text{rxn}}}{298 \text{ K}} = 1{,}620 \text{ J/(\_mol}_{\text{rxn}} \bullet K)$

Now we can find $\Delta S_{\text{universe}}$

$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \Delta S_{\text{universe}}$

$-88.9 \dfrac{J}{(\text{mol}_{\text{rxn}} \bullet K)} + 1620 \dfrac{J}{(\text{mol}_{\text{rxn}} \bullet K)} = 1530 \dfrac{J}{(\text{mol}_{\text{rxn}} \bullet K)}$

Even though the entropy of the system declines, the entropy change for the surroundings is SO VERY large that the overall change for the universe is positive.

Bottom line: A process is thermodynamically favorable in spite of a negative entropy change as long as it is **EXTREMELY** exothermic. In other words, ***sufficient exothermicity offsets system ordering.***

What is FREE ENERGY?

The calculation of *Gibbs free energy,* ΔG is what **ultimately** decides whether a reaction is thermodynamically favored or not. A *NEGATIVE* sign on ΔG indicates the reaction is thermodynamically favored.

ΔG can be calculated several ways and links thermochemistry, entropy, equilibrium and electrochem together!

1. **"Big Mamma" Equation, verse 3:** $\Delta G^\circ_{rxn} = \Sigma \Delta G^\circ_{(products)} - \Sigma \Delta G^\circ_{(reactants)}$

   You already know how to calculate enthalpy and entropy, just substitute free energy values using tables of standard values! So, calculating the standard molar free energy of formation is simply the same song, 3rd verse. BOTH ΔH_f° and $\Delta G_f^\circ = 0$ for elements in their standard state and both bear units of kJ/mol$_{rxn}$. You have no idea how handy this is going to be with regard to solving homework problems and acing quizzes & exams! The Big Mamma equations are simply different versions of Hess's Law.

   But, aw shucks! You've got to stop and look up S° values rather them being zero as well. (Note the lack of a "delta". That's not a typo!) Only a perfect diamond at absolute zero has a S° value = 0.

2. **"Granddaddy Equation" for calculating Gibbs Free Energy for a system at constant temperature :** $\Delta G = \Delta H - T\Delta S$

   By far, one of the most beneficial equations to learn for the AP exam! Case in point, taking favored equilibrium conditions where $\Delta G = 0$, into consideration, the equation rearranges rather quickly to allow you to determine the absolute temperature at which a process becomes thermodynamically favorable. Shall we? (At least indulge me!)

   $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

   $\therefore 0 = \Delta H^\circ - T\Delta S^\circ$ at equilibrium

   $-\Delta H^\circ = -T\Delta S^\circ$ (negative signs cancel)

   $\therefore T\Delta S^\circ = \Delta H^\circ$

   $\therefore T = \dfrac{\Delta H^\circ}{\Delta S^\circ}$

3. **Hess's Law of Summation** for a "new" reaction when given a *series of chemical reactions and the* ΔG° for *each reaction*. Hess's Law of Summation works exactly the same as in the enthalpy calculations; arrange a series of chemical equations for which you know the ΔG°_{rxn} to obtain the "goal equation". If you need to reverse an equation, then you change the sign of ΔG°_{rxn} and cross off common moles of substances as you sum the equations to deliver the goal equation. If you double an equation to obtain the goal, double the value of $\Delta G^\circ_{rxn,}$ if you halve a reaction halve the value of ΔG°_{rxn} for that reaction, etc.

4. **"Rat Link" equation for calculating** ΔG $^\circ$ *at standard conditions* **using the given temperature and equilibrium constant,** K**:** $\Delta G^\circ = -RT\ln K$

   Be sure to use the "energy R" 8.3145 J/mol•K
   (I predict you'll use this one the most!) In this case, the system is at equilibrium, so $\Delta G^\circ = 0$ and K represents the equilibrium constant under standard conditions.

$$K_p = \frac{P_{reactants}}{P_{products}} \quad \text{still raised to power of coefficients}$$

Knowing that $K_P = K_c (RT)^{\Delta n}$, where Δn is equal to the *change in the number of moles of gas* for the reaction.

5. **Solving for $\Delta G °$ using the "minus nunfe" equation given the standard cell potential, Faraday's constant and the number of moles of electrons involved.** Sounds far scarier than it is!
$\Delta G° = - nFE°$ where n = number of moles of electrons transferred in a balanced redox reaction, F is Faraday's constant 96,485 Coulombs/mole e^- and $E°$ is the standard cell potential for the electrochemical process. It's also handy to know that 1 volt = 1 joule/coulomb so you're units work out as they should.
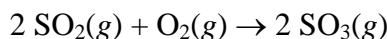

Exercise 4

$$2 \, H_2O(\ell) + O_2(g) \rightarrow 2 \, H_2O_2(\ell)$$
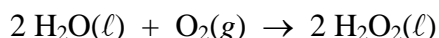
Calculate the free energy of formation for the oxidation of water to produce hydrogen peroxide given the following information $\Delta G°_f$ values:

$H_2O(\ell)$	−56.7 kcal/mol$_{rxn}$
$O_2(g)$	0 kcal/mol$_{rxn}$
$H_2O_2(\ell)$	−27.2 kcal/mol$_{rxn}$

59.0 kcal/mol$_{rxn}$

Exercise 5

$$2 \, SO_2(g) + O_2(g) \rightarrow 2 \, SO_3(g)$$

The reaction above was carried out at 25°C and 1 atm. Calculate $\Delta H°$, $\Delta S°$, and $\Delta G°$ using the following data:

Substance	ΔH_f^o (kJ/mol)	$S°$ (J/K · mol)
$SO_2(g)$	−297	248
$SO_3(g)$	−396	257
$O_2(g)$	0	205

$\Delta H° = -198$ kJ/mol$_{rxn}$; $\Delta S° = -187$ J/K•mol$_{rxn}$; $\Delta G° = -142$ kJ/mol$_{rxn}$

Entropy & Free Energy

Exercise 6

$$C_{diamond}(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta G° = -397 \text{ kJ}$$
$$C_{graphite}(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta G° = -394 \text{ kJ}$$
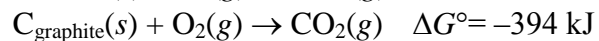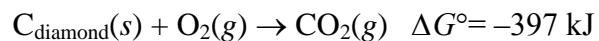
Calculate $\Delta G°$ for the reaction

$$C_{diamond}(s) \rightarrow C_{graphite}(s)$$
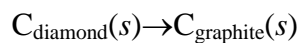
$$+3 \text{ kJ/mol}_{rxn}$$

Exercise 7

The overall reaction for the corrosion (rusting) of iron by oxygen is

$$4 \text{ Fe}(s) + 3 \text{ O}_2(g) \rightarrow 2 \text{ Fe}_2\text{O}_3(s)$$
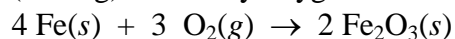
Using the following data, calculate the equilibrium constant for this reaction at 25°C.

Substance	$\Delta H_f°$ (kJ/mol)	$S°$ (J/K · mol)
$Fe_2O_3(s)$	−826	90
$Fe(s)$	0	27
$O_2(g)$	0	205

$$K = 10^{261}$$

The Gibbs equation can also be used to calculate the phase change temperature of a substance. During the phase change, the system is in *equilibrium*, thus the value of $\Delta G°$ is zero.

8

Entropy & Free Energy

Exercise 8

Calculate the thermodynamic boiling point of $H_2O(\ell) \rightarrow H_2O(g)$ given the following information:

$\Delta H_{vap} = +44$ kJ/mol$_{rxn}$ $\qquad$ $\Delta S_{vap} = 118.8$ J/(K•mol$_{rxn}$)

370 K

Exercise 9

For the reaction $2\ CO(g) + O_2(g) \rightarrow 2\ CO_2(g)$, the $\Delta G°$ for the reaction is -257.2 kJ/mol$_{rxn}$. Calculate the equilibrium constant at 25°C.

1.27×10^{45}

SUMMARY:

- If ΔG **is NEGATIVE**, the reaction is *thermodynamically favorable* and E_{cell} **would be POSITIVE**

- If ΔG **is ZERO**, the reaction is *at equilibrium* and E_{cell} **would also be ZERO**

- If ΔG **is POSITIVE**, the reaction is *NOT thermodynamically favorable* and E_{cell} **would be NEGATIVE**

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Entropy & Free Energy

Conditions of ∆*G*:

∆*H*	∆*S*	Result
negative	positive	thermodynamically favorable at all temperatures
positive	positive	thermodynamically favorable at high temperatures
negative	negative	thermodynamically favorable at low temperatures
positive	negative	NOT thermodynamically favorable, EVER

Relationship of ∆*G* to K and E:

∆G	*K*	*E*
0	at equilibrium; $K = 1$	0
negative	>1, products favored	positive
positive	<1, reactants favored	negative

COMMON MISCONCEPTIONS ABOUT THERMODYNAMIC FAVORIBILITY

"IF ∆*G* > 0 (positive thus NOT thermodynamically), the process cannot occur" Not true! External sources of energy can be used to drive change in these cases.

Consider the following:

1. Electric current is applied to charge a battery. You probably describe the equilibrium condition for a battery as "dead". It's not dead, it just reached equilibrium (and you can recharge it, but never to full capacity again).
2. Light and photon absorption in the photosystems of a chloroplast causing photoionization during photosynthesis.
3. Coupling a thermodynamically *un*favorable reaction with one that is favorable as in the conversion of ATP to ADP in biological systems.

"IF ∆*G* is large and negative, the process must proceed at a measurable rate. Not true!

Consider the following:

There are kinetic controls related to high activation energies such as

1. reactant molecules being held together by strong covalent bonds or strong IMFs
2. a required collision orientation
3. a required energy associated with collisions correctly oriented