

# Unit 5 Review 2

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ENTHALPY, HESS' LAW, INTRO TO ENTROPY

# Important Announcements

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## ECIS is OPEN

### electronic Course Instructor Survey (eCIS)

Welcome to the eCIS, James Wadman!

- We like: high ratings, constructive feedback.
- **I like: entertaining feedback, funny comments**

## Next Week Exam Review:

- 5-7pm Burdine 106
- First hour: conceptual review
- Second hour: only practice problems guided by your suggestions over the next week.
- If you have requests for problems to work in the second hour:

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# Goals for Today

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- There are two types of calorimetry:
  1. **Coffee cup calorimetry measures heat at constant pressure ( $q_p = \Delta H$ ) in an insulated, open-air container**

$$q_{cal} = m_{water} C_{water} \Delta T = -q_{p,sys}$$

$$q_{p,sys} = \Delta H_{sys}$$

2. **Bomb calorimetry measures heat at constant volume ( $q_v = \Delta U$ ) in a rigid, isolated container**

$$q_{cal} = C_{hardware} \Delta T + m_{water} C_{water} \Delta T = -q_{v,sys}$$

$$q_{v,sys} = \Delta U_{sys}$$

# Goals for Today

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- There are three ways of using Hess' Law to solve for enthalpy:
  1. **The first technique is the one where you algebraically rearrange multiple steps that will equal the total enthalpy change of a single reaction**

$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3 \dots + \Delta H_n$$

2. **Formation reactions take the sum of the formation enthalpy of products minus the reactants**

$$\Delta H_{rxn} = \sum n\Delta H_f^\circ(\text{prod}) - \sum n\Delta H_f^\circ(\text{react})$$

3. **Bond dissociation enthalpy is the weird one that takes the bond strength of the reactants minus the products**

$$\Delta H_{rxn} = \sum BE(\text{react}) - \sum BE(\text{prod})$$

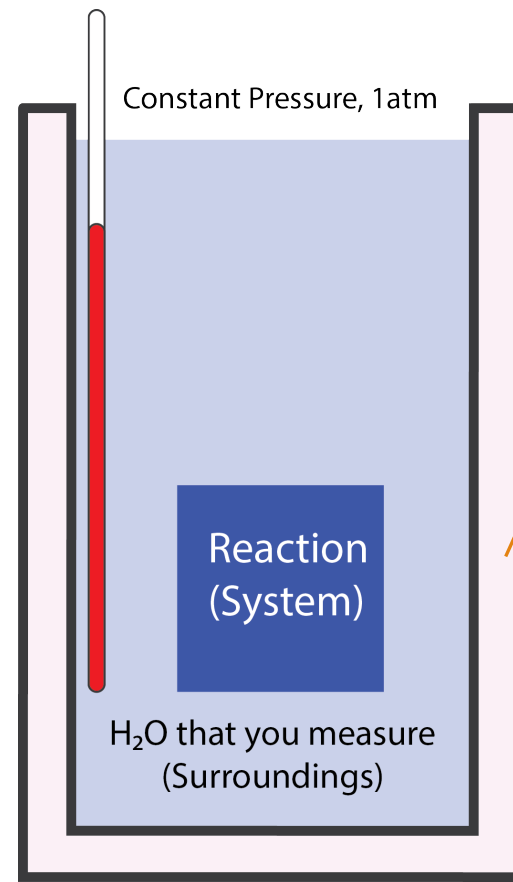
# Coffee Cup Calorimetry

Coffee Cup: the goal is to get the enthalpy change ( $\Delta H$ ) of a reaction by measuring the  $\Delta T$  of the water surrounding the reaction system

$$q_{cal} = m_{water} C_{water} \Delta T = -q_{p,sys}$$

$$q_{p,sys} = \Delta H_{sys}$$

The sign switches to get the heat flow for the system



Insulated hardware does not absorb heat, so we don't care about the  $C\Delta T$  term for the calorimeter

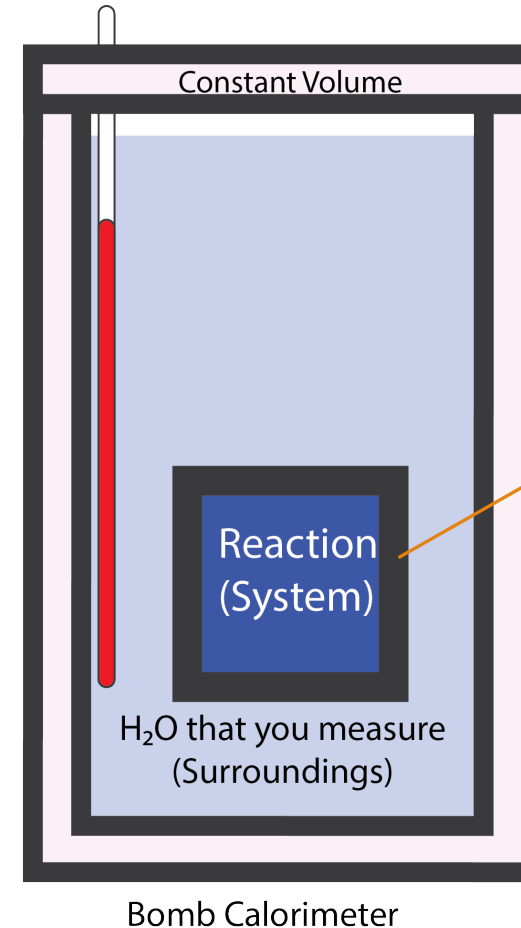
# Bomb Calorimetry

Bomb Calorimetry: the goal is to get the internal energy change ( $\Delta U$ ) of a combustion reaction by measuring the  $\Delta T$  of both the surrounding water and the hardware of the calorimeter

$$q_{cal} = C_{hardware} \Delta T + m_{water} C_{water} \Delta T = -q_{v,sys}$$

$$q_{v,sys} = \Delta U_{sys}$$

The sign switches to get the heat flow for the system



Stainless steel hardware **does** absorb heat, so we **do** care about the  $C\Delta T$  term for the calorimeter

# Bomb Calorimetry – $\Delta U$ to $\Delta H$

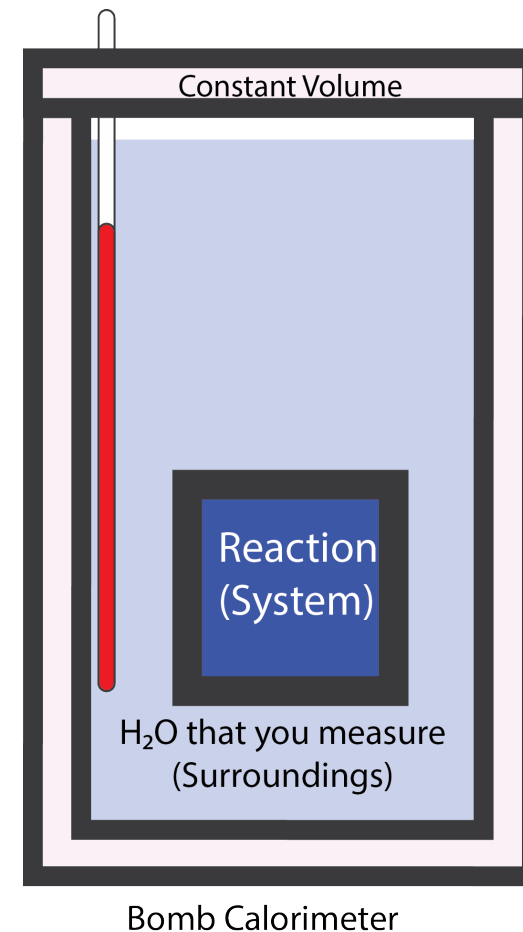
If we are interested in finding the  $\Delta H^\circ$  of the combustion reaction, two additional steps are necessary.

$\Delta U = q + w$  ; remember that at standard conditions and constant pressure:

$$q = \Delta H^\circ \text{ and } w = - \Delta nRT$$

If you can write out your balanced combustion reaction, you can easily solve for  $\Delta H^\circ$

$$\Delta U + \Delta nRT = \Delta H^\circ$$



# Coffee Cup

$$q_p = -q_{cal}, \quad \boxed{q_p = \Delta H}$$

$$q_{cal} = mC\Delta T$$

For the water

# Bomb Calorimeter

$$* q_v = -q_{cal}, \quad \boxed{q_v = \Delta U}$$

$\frac{\Delta U}{\text{moles}}$  = molar internal energy of combustion  
( $\frac{\text{kJ}}{\text{mol}}$ )

$$q_{cal} = \underbrace{mC\Delta T}_{\text{H}_2\text{O}} + \underbrace{C\Delta T}_{\text{Hardware}}$$

\* We run combustions in bomb calorimeters; expect  $q_v$  to be negative (exothermic) \*

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1st Law:

$$\Delta U = \underbrace{\Delta H}_{q_p} - \underbrace{\Delta nRT}_{w}$$

bomb      coffee cup      balanced reaction



# Definition of Enthalpy

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- **Enthalpy (H):** a state function that describes the heat content of a system, given by the equation:

$$H = U + PV$$

- **However, in chemistry we are more concerned with the change in enthalpy,  $\Delta H$ , which is simply the heat flow at constant pressure,  $q_p$**

$$\Delta H = q_p$$

PS: if you want to think of reactions in our environment as occurring at constant pressure, change in enthalpy is a great term for determining the heat flow of reactions “IRL”

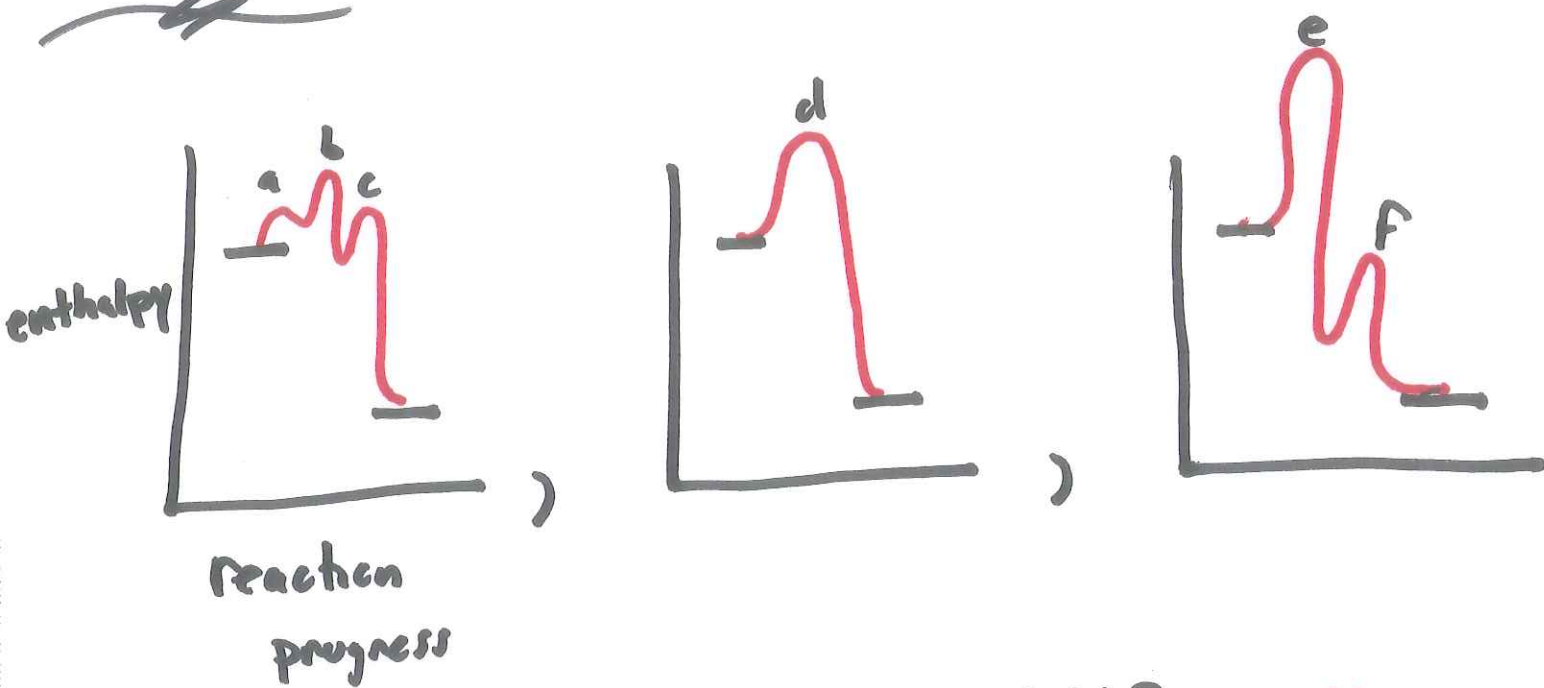
# Hess' Law – 3 Calculations

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- For any state function, the path does not matter as long as you have final and initial values.
- Suppose you have a reaction but no way to directly calculate its enthalpy. You can “create” a path for your reaction using one of three techniques:
  1. Sum of hypothetical reactions that serve as “steps” from your initial to your final
  2. The standard enthalpy of formation for your reaction (products minus reactants)
  3. The bond energies of the molecules that make up your reaction (reactants minus products)

$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3 \dots + \Delta H_n$$

# Hess Law



Q: Which has the greatest  $\Delta H$ ? *All the same*

$$\Delta H_{\text{rxn}} = \Delta H_{a+b+c} = \Delta H_d = \Delta H_{e+f}$$

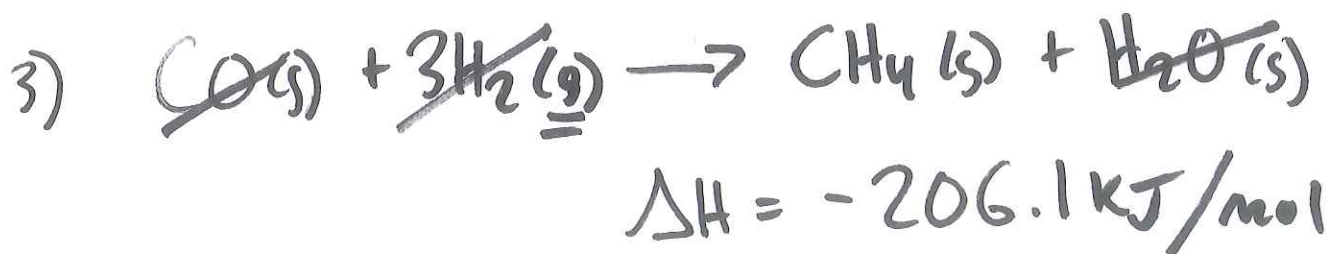
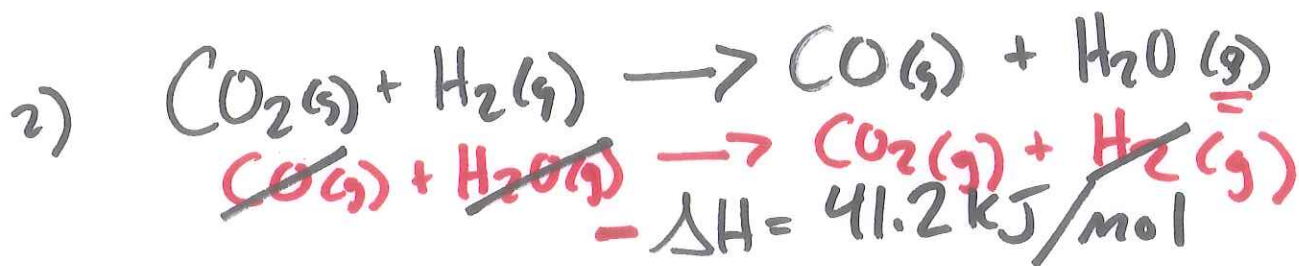
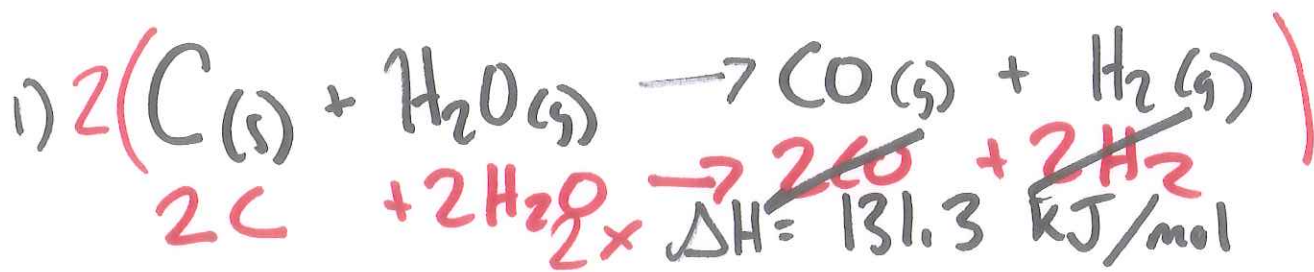
# Hess' Law – Sum of Reactions

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- **Goal: create your desired equation using a given set up hypothetical steps**

$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3 \dots + \Delta H_n$$

- What you can do to “make” your sum of reactions equal your goal reaction: multiply the entire reaction by a coefficient or fraction (including the enthalpy value associated with that step!) or reverse the entire reaction (changing the sign of the enthalpy value associated with that step).



$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

$$\boxed{15.3 \text{ kJ/mol}} = 262.6 + (-41.2) + (-206.1)$$

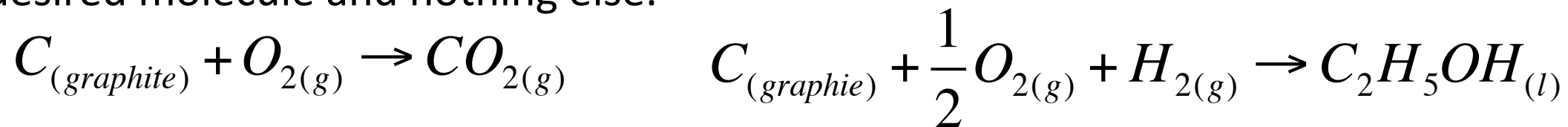
# Hess' Law – Formation Reactions

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- **Goal: determine the enthalpy of formation for your products and reactants. The enthalpy of the reaction is the difference between the products and reactants.**

$$\Delta H_{rxn} = \sum n\Delta H_f^\circ(\text{prod}) - \sum n\Delta H_f^\circ(\text{react})$$

- Phase and number of moles are important!
- Note: a formation reaction for a molecule is a balanced chemical reaction that shows the constituent elements combining to form a single mole of your desired molecule and nothing else.



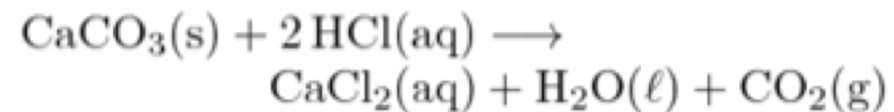
# Hess' Law – Formation Reactions Example

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- **Goal: determine the enthalpy of formation for your products and reactants. The enthalpy of the reaction is the difference between the products and reactants.**
- Number of moles are important!

$$\Delta H_{rxn} = \sum n\Delta H_f^\circ(\text{prod}) - \sum n\Delta H_f^\circ(\text{react})$$

Calculate the standard reaction enthalpy for the reaction of calcite with hydrochloric acid



The standard enthalpies of formation are:

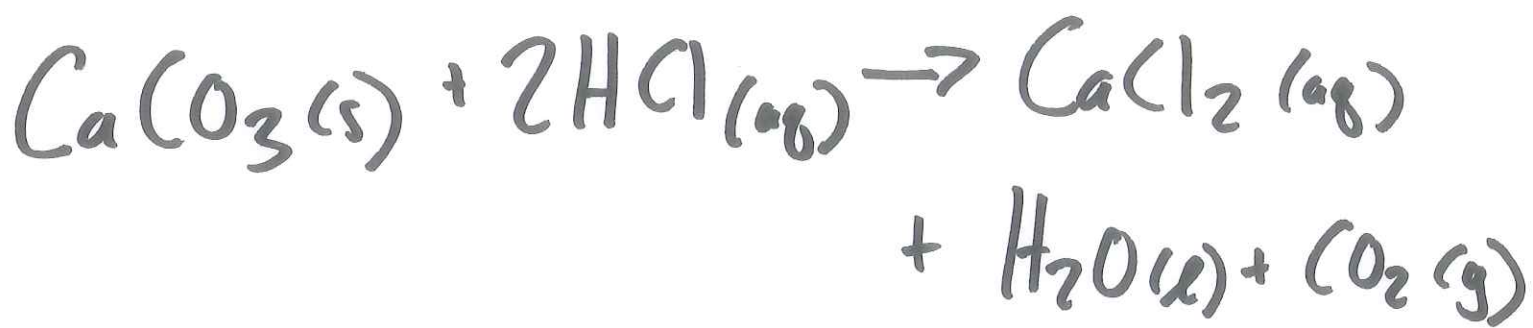
for  $\text{CaCl}_2(\text{aq})$  :  $-877.1$  kJ/mol;

for  $\text{H}_2\text{O}(\ell)$  :  $-285.83$  kJ/mol;

for  $\text{CO}_2(\text{g})$  :  $-393.51$  kJ/mol;

for  $\text{CaCO}_3(\text{s})$  :  $-1206.9$  kJ/mol;

and for  $\text{HCl}(\text{aq})$  :  $-167.16$  kJ/mol.



$$\Delta H_{\text{rxn}} = \text{Products} - \text{Reactants}$$

Products

$$(-877.1) + (-285.83) + (-393.51)$$

Reactants

$$- (-1206.9 + 2(-167.16))$$

$$= -15.22 \text{ kJ/mol}$$



# Hess' Law – Bond Energy Data

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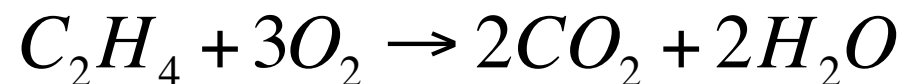
- **Goal: determine the energy difference between all bonds breaking and all bonds forming**
- You must draw a proper Lewis structure, determine what kind of bonds are breaking (reactants) and what kind of bonds are forming (products), and take the difference.

$$\Delta H_{rxn} = \sum BE(react) - \sum BE(prod)$$

- Hint: you will only be drawing very simple Lewis Structures that follow these rules:
  - Carbon makes 4 bonds
  - Nitrogen makes 3 bonds
  - Oxygen makes 2 bonds
  - Hydrogen and halogens make 1 bond

# Hess' Law – Bond Energy Data Example

- What is the standard enthalpy for the combustion of ethylene given the following data?



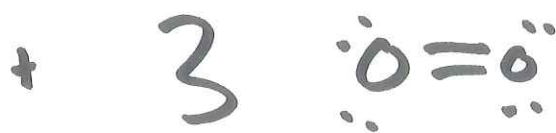
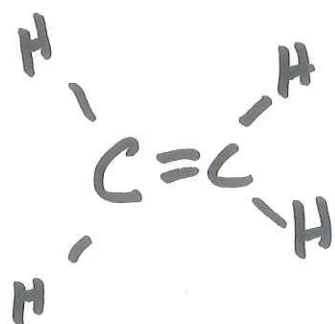
hydrogen	
H-H	432
H-C	413
H-N	391
H-O	467
H-F	565
H-Cl	427
H-Br	363
H-I	295
H-S	347
H-Si	393

carbon	
C-H	413
C-C	347
C-N	305
C-O	358
C-F	485
C-Cl	339
C-Br	276
C-I	240
C-Si	360
C-S	259

oxygen	
O-H	467
O-O	146
O-C	358
O-N	201
O-F	190
O-Cl	203
O-I	234
O-Si	452

multiple-bond	
C=C	614
C≡C	839
O=O	495
C=O	745
C=O (CO <sub>2</sub> )	799
C≡O	1072
C=S (CS <sub>2</sub> )	577
N=O	607
N=N	418
N≡N	941
C=N	615
C≡N	891

Note: I used C=O as 745kJ instead of the 799kJ on this table



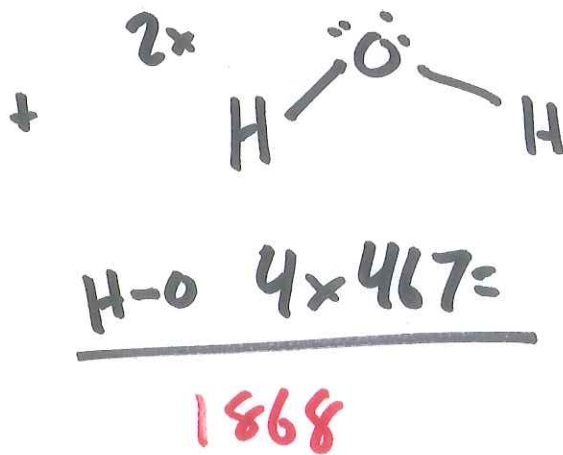
Bonds Breaking  
3751 kJ

$$\begin{array}{l} \text{C-H } 4 \times 413 \\ \text{C=C } 1 \times 614 \\ \hline 1652 + 614 \end{array}$$

$$\begin{array}{l} 3 \text{ O=O: } 3 \times 495 \\ \hline 1485 \end{array}$$



$$\begin{array}{l} 2 \times \\ \cdot\cdot \quad \text{O} = \text{C} = \text{O} \quad \cdot\cdot \\ \hline \text{C=O } 4 \times 745 \\ 2980 \end{array}$$



Bonds Forming  
4848 kJ

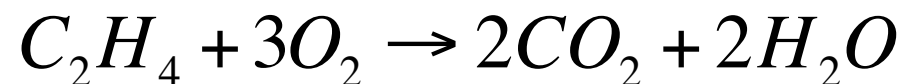
$$\Delta H = \text{reactants} - \text{products}$$

Bonds Breaking - Bonds Forming

$$\begin{array}{l} 3751 - 4848 \\ = -1097 \text{ kJ/mol} \end{array}$$

# Hess' Law – Bond Energy Data Example

- What is the standard enthalpy for the combustion of ethylene given the following data? Ans:  $3751\text{kJ} - 4848\text{kJ} = -1097\text{kJ}$



hydrogen	
H-H	432
H-C	413
H-N	391
H-O	467
H-F	565
H-Cl	427
H-Br	363
H-I	295
H-S	347
H-Si	393

carbon	
C-H	413
C-C	347
C-N	305
C-O	358
C-F	485
C-Cl	339
C-Br	276
C-I	240
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oxygen	
O-H	467
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multiple-bond	
C=C	614
C≡C	839
O=O	495
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C=O (CO <sub>2</sub> )	799
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C=S (CS <sub>2</sub> )	577
N=O	607
N=N	418
N≡N	941
C=N	615
C≡N	891

# The 2<sup>nd</sup> Law of Thermodynamics

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Entropy is a measurement of energy dispersal in a system. The second law of thermodynamics states that energy in the universal tends to become more and more dispersed through spontaneous processes

- The second law of thermodynamics states that the entropy of the universe is always increasing.

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

- This law gives us three conditions for  $\Delta S_{total}$ :
  1.  $\Delta S < 0$  (negative) ; your reaction is nonspontaneous
  2.  $\Delta S = 0$  (zero) ; your reaction is at equilibrium / reversible
  3.  $\Delta S > 0$  (positive) ; your reaction is spontaneous

# Entropy

thermo  
heat flow

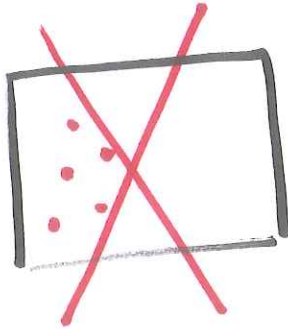
Statistical  
Micro states

Orientation  
# of particles

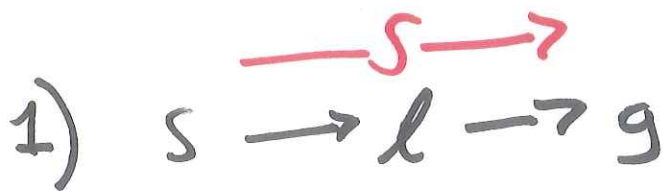
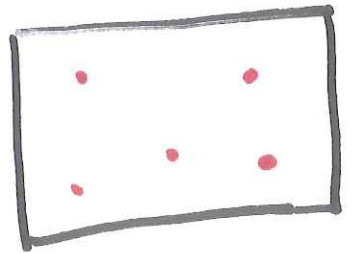
$$\Delta S = \frac{q_{rev}}{T} \quad \boxed{\frac{J}{K}}$$

$$S = k \ln X^i$$

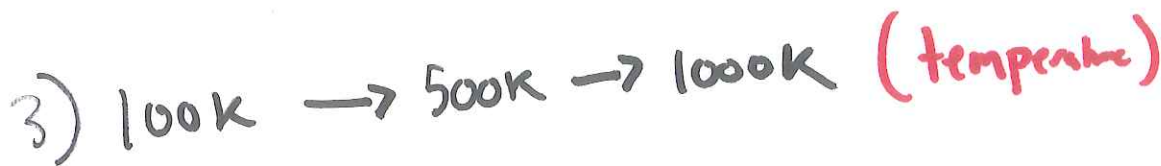
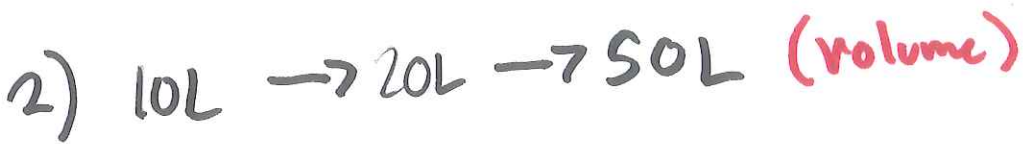
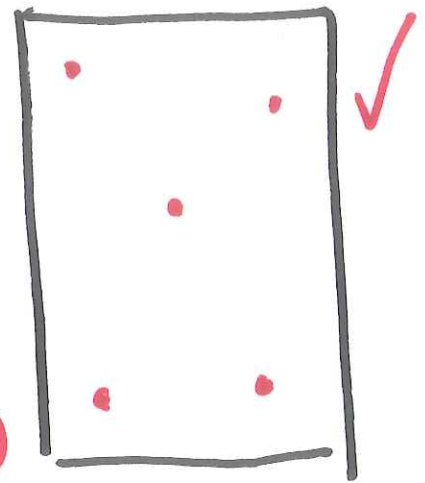
Disorder:



vs



(Phase) vs



Thermodynamic <sup>Change in</sup> Entropy ( $\Delta S$ )

↓

$$\frac{q_{\text{rev}}}{T} \Rightarrow \frac{\text{J}}{\text{K}}$$

must be  
Kelvin  
↑

Calculating heat...

$$q = m C \Delta T \rightarrow \Delta S = m C \ln\left(\frac{T_f}{T_i}\right)$$

$$q = m \Delta H_{\text{trans}} \rightarrow \Delta S = \frac{m \Delta H_{\text{trans}}}{T_{\text{trans}}}$$



# Conceptual Entropy: phases, volume, temperature

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- **Qualifying Entropy:** although not quite accurate scientifically, we tend to think of entropy as disorder. More disordered phases of matter are higher in entropy.
- **We can easily see that the change in entropy correlates with the change in phase:**  
Solids (low entropy) < Liquids < Gases (high entropy)
- **Or with volume** (consider 1 mole of gas at room temperature)  
10L gas (lowest entropy) < 20L gas < 50L gas (highest entropy)
- **Or with temperature**  
Gas at 100K (lowest entropy) < gas at 500K < gas at 1000K (highest entropy)



# Conceptual Entropy: Microview

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- The relationship between entropy and microstates is given by the formulas:

$$S = k \ln \Omega$$

$$S = k \ln x^i$$

Understand these  
conceptually

- Entropy depends on the **“complexity” of the molecule**, represented by the orientations possible (x)
  - Larger molecules with diverse sets of bonds are more complex (higher entropy)
- Entropy depends on the total number of particles, represented by **“i”**
  - Having more particles (or more moles) leads to a higher entropy

# Increasing Entropy

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- **In summation, you can increase entropy based on:**
  1. Phase (going from solid to liquid [to aqueous] to gas)
  2. Increasing volume (decreasing pressure)
  3. Increasing temperature
  4. Complexity of your molecule (a larger number of more diverse bonds)
  5. Complexity of your solution \*we don't really talk about this
  6. Increasing the number of particles

# Entropy: Quantifying Entropy

$$\Delta S = \frac{q_{rev}}{T}$$

- **Quantifying Entropy:** lastly, we must understand how to calculate entropy changes in different experimental conditions.
  - The trick to understanding how to quantify entropy is understanding the equations from which it is derived. **The key here is understanding the units of entropy: J/K**
  - **Entropy of a temperature change**

$$q = mC_s \Delta T$$

If we integrate with respect to T to get entropy:

$$\Delta S = mC_s \ln \frac{T_f}{T_i}$$

- **Entropy of a phase change**

$$q = \Delta H_{trans}$$

If we divide by the temperature we get:

$$\Delta S_{trans} = \frac{\Delta H_{trans}}{T_{trans}}$$

- **Entropy of isothermal expansion**

$$q = nRT \ln \frac{V_f}{V_i}$$

If we divide by the temperature we get:

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

Note: you don't need to know isothermal expansion for the exam

# Unit 5 Review End

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ENTHALPY, HESS' LAW, INTRO TO ENTROPY

# Definition of Free Energy

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- **Free Energy (G):** another “mythological” state function that describes the stability of a system. Like enthalpy, we are concerned most with the  $\Delta G$  because of the conclusions we can make using its **sign** and **magnitude**.
- **The change in free energy of a reaction ( $\Delta G$ ) is related to the enthalpy, entropy, and temperature of the system.**

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

$$\Delta G_{rxn} = \Delta H_{sys} - T \Delta S_{sys}$$

Remember: something strange you might notice is that entropy is often provided in tables as J. Enthalpy is provided in tables as kJ. Make sure to adjust your units if you use the two state functions together! (stated again for emphasis)

# Calculating Free Energy

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- You should be very familiar with the formula:

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

- However, remember that free energy is still a state function. So we can also use the formula:

$$\Delta G_{rxn} = \sum n \Delta G_f^\circ(\text{prod}) - \sum n \Delta G_f^\circ(\text{react})$$

# Free Energy Conclusions

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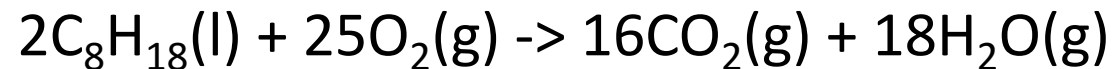
- **The final and most important lesson in thermodynamics is that there is a finite amount of “Free Energy” in the universe and that spontaneous reactions lower the free energy.**
- This point gives us three conditions for  $\Delta G$ :
  1.  $\Delta G < 0$  (negative) ; your reaction is spontaneous
  2.  $\Delta G = 0$  (zero) ; your reaction is at equilibrium
  3.  $\Delta G > 0$  (positive) ; your reaction is nonspontaneous
- We understand these ideas conceptually with a few familiar terms:
  - **Lower energy products** will be more **stable** (a reaction will tend to be spontaneous and form these products)
  - We can set up conditions that are “**favorable**” or “**unfavorable**” for a reaction, meaning they are conducive to lowering the free energy

# Free Energy: $-\Delta H$ , $+\Delta S$

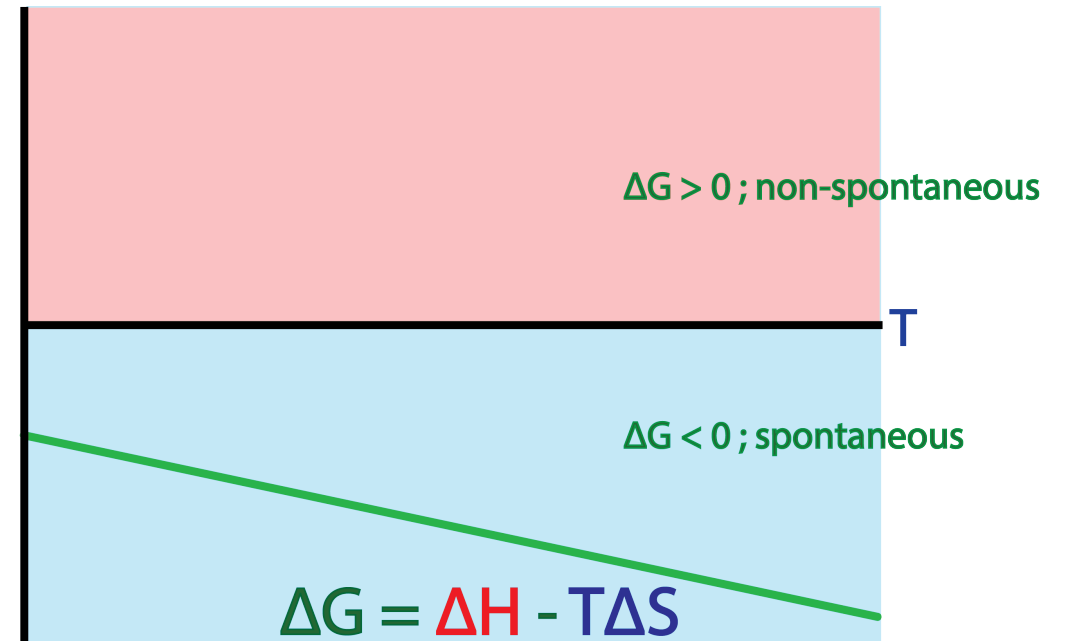
In this case, our enthalpy and entropy are “favorable” for a spontaneous reaction.

Therefore, this reaction will be **spontaneous** at all temperatures.

Example: most combustion reactions



$\Delta G$



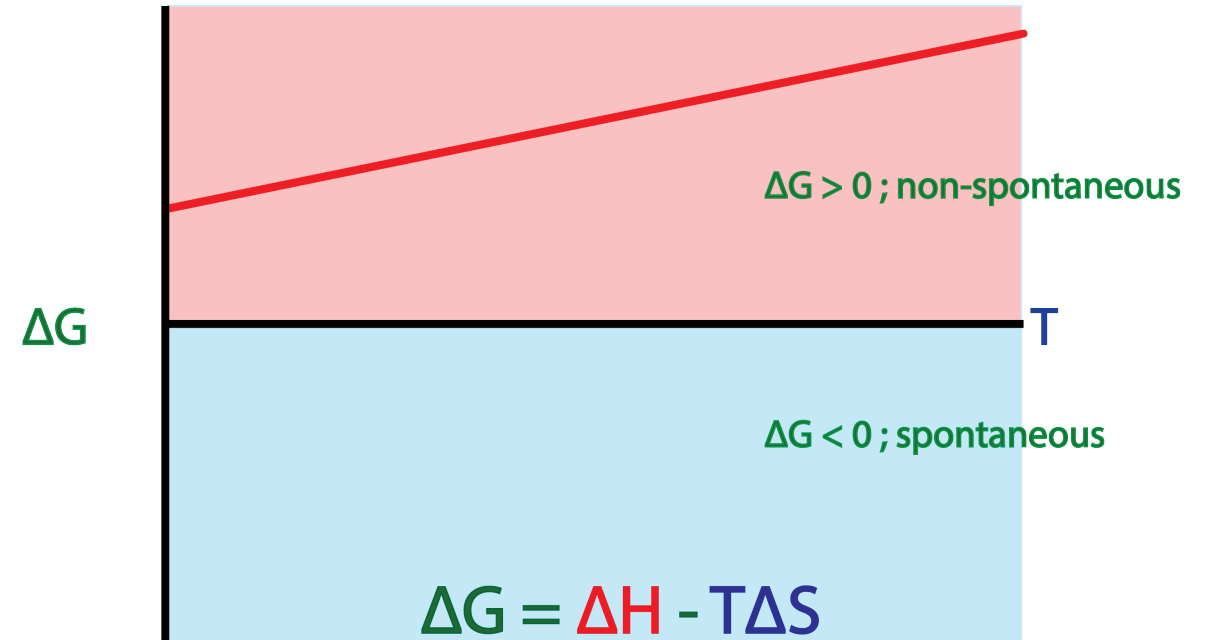
$\Delta S > 0$  ,  $\Delta H < 0$  ; spontaenous at all temperatures



# Free Energy: $+\Delta H$ , $-\Delta S$

In this case, our enthalpy and entropy are “unfavorable” for a spontaneous reaction.

Therefore, this reaction will be **nonspontaneous** at all temperatures.



$\Delta S < 0$  ,  $\Delta H > 0$  ; non-spontaneous at all temperatures

Note on spontaneity: a positive  $\Delta G$  does not mean that a reaction can't happen. It means that it doesn't happen without the continuous input of energy.

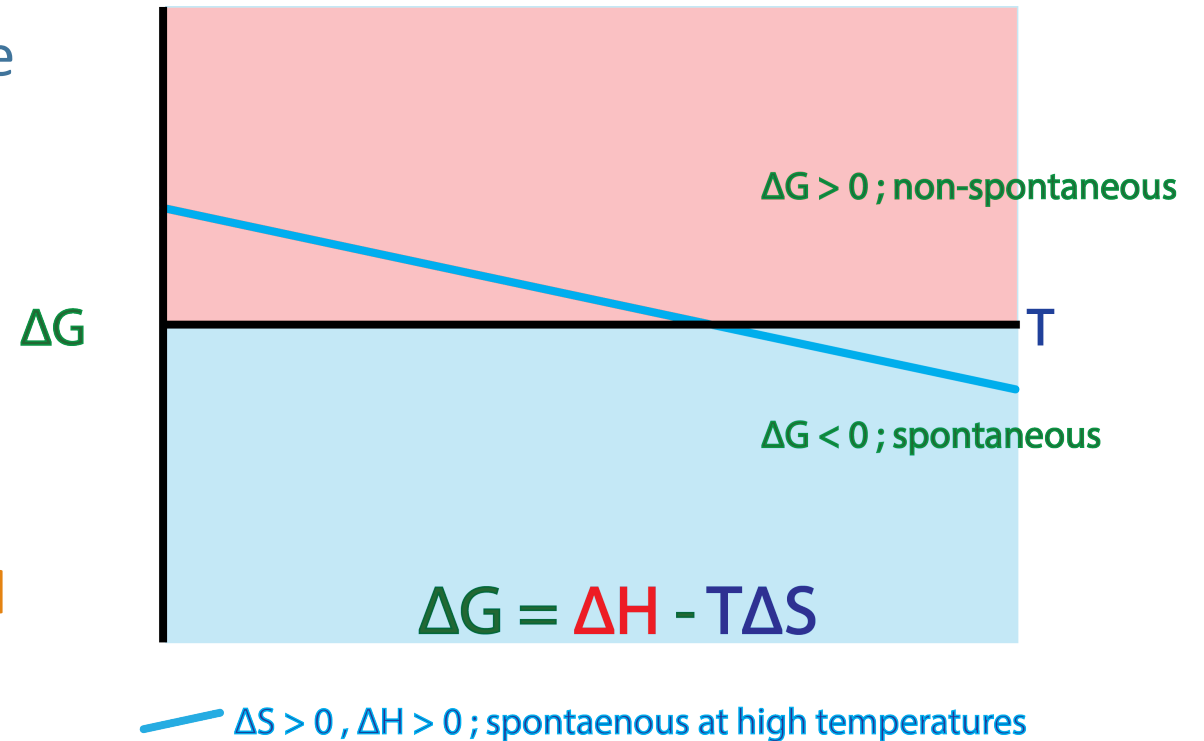
# Free Energy: $+\Delta H$ , $+\Delta S$

In this case, our enthalpy is unfavorable and our entropy is favorable.

This means that our  $T\Delta S$  term must be greater in magnitude than our  $\Delta H$  term in order for our  $\Delta G$  to be negative.

**In other words, our reaction is favored only at high enough temperatures.**

Example: dissolution (favored at High T)  
 $\text{NaCl(s)} \rightarrow \text{Na}^{\text{+}}(\text{aq}) + \text{Cl}^{-}(\text{aq})$

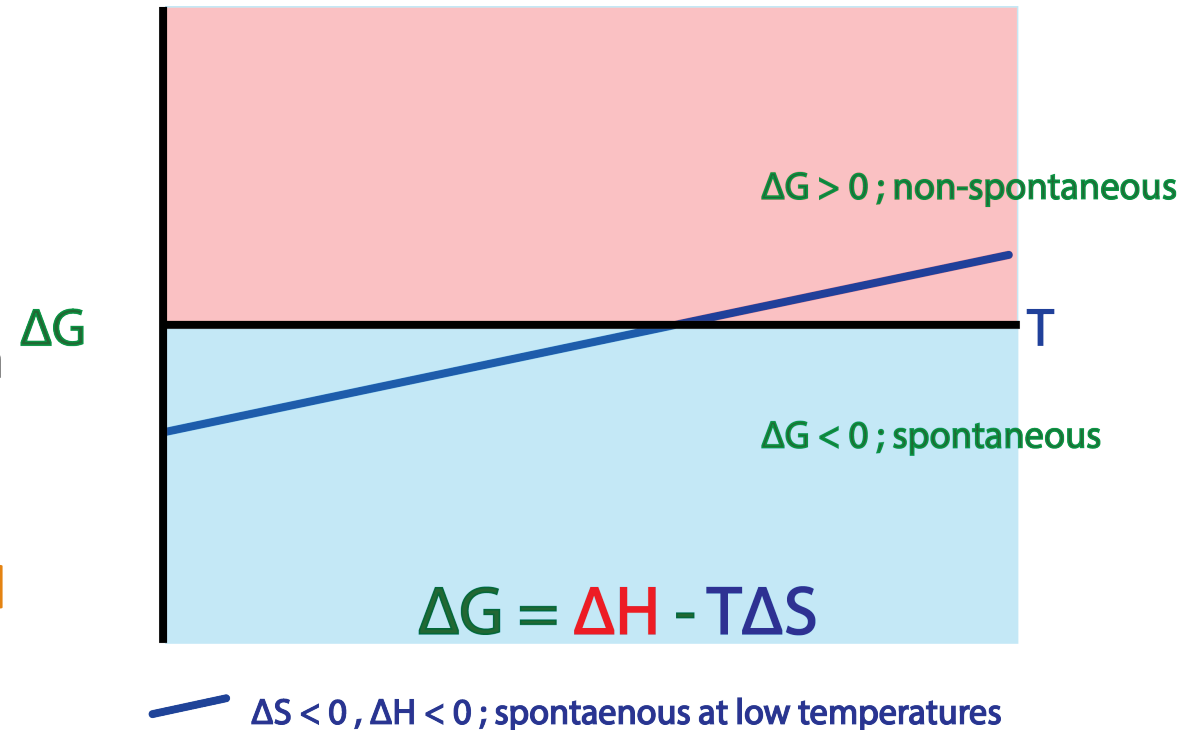


# Free Energy: $-\Delta H$ , $-\Delta S$

In this case, our entropy is unfavorable and our enthalpy is favorable.

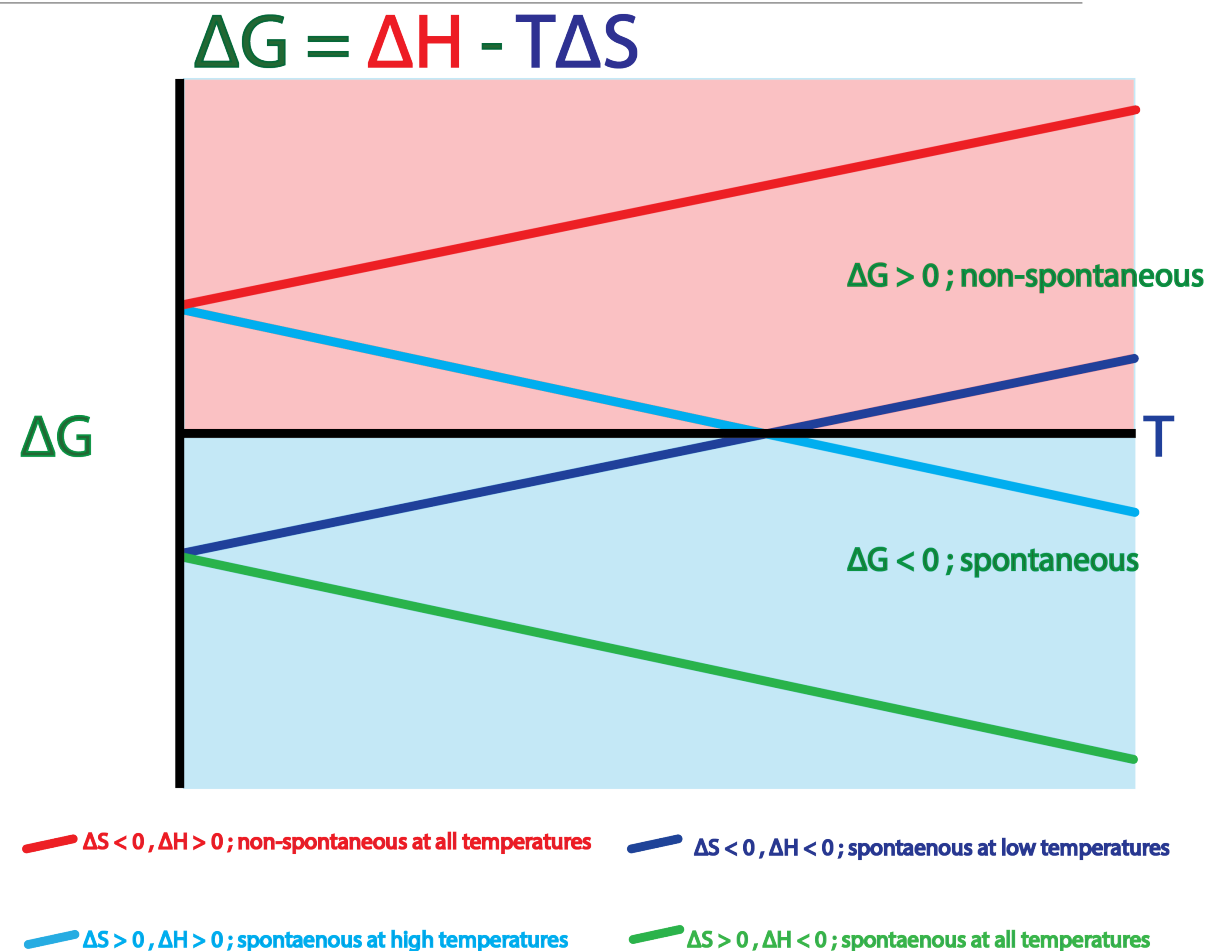
This means that our  $T\Delta S$  term must be smaller in magnitude than our  $\Delta H$  term in order for our  $\Delta G$  to be negative.

**In other words, our reaction is favored only at low enough temperatures.**



# Free Energy: All Conditions Summary

$\Delta H$	$\Delta S$	Temperature Dependent?	Spontaneous?
-	+	No	Always
+	-	No	Never
-	-	Yes	Low T
+	+	Yes	High T



# Free Energy: Equilibrium

For the conditions that are temperature dependent, it is possible to have a  $\Delta G$  value equal to 0. This is, by definition, equilibrium.

In this class we are focused on one main equilibrium condition: phase change.

$$T_{trans} = \frac{\Delta H_{rxn}}{\Delta S_{rxn}}$$

