

# Unit 4 Exam Review

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THERMODYNAMICS

# Exam 4 Breakdown

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- **13 conceptual questions:** can you use the laws, equations, and thermodynamic relationships to come up with a non-numerical answer?
- **13 calculation questions:** can you remember the formulas, convert your units, and apply the various laws to come up with a numerical answer?

# Exam 4 Breakdown – The Mistakes

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- **Sign Convention**
  - Work done on the system ( $w$ ) is positive
  - Energy absorbed by the system ( $q$ , endothermic) is positive
  - The heat measured by the calorimeter ( $q_{\text{cal}}$ ) is equal to the heat of the surroundings; or  $q_{\text{cal}} = -q_{\text{sys}}$
- **Unit Conversion**
  - Energy is measured in J, kJ, cal, and Cal (kcal)
    - Entropy is experimentally measured in J, free energy and enthalpy are measured in kJ
  - Use the correct R-value (usually J/ K mol)
  - Celsius and Kelvin are interchangeable when taking a difference, but not when you are dividing absolute temperatures
- **Subscript Convention**
  - Understand the differences between being asked for the  $\Delta S_{\text{sys}}$  versus  $\Delta S_{\text{surr}}$  or  $\Delta S_{\text{universe}}$ , etc.
- **Know how to use natural log (ln) on your non-graphing calculator**

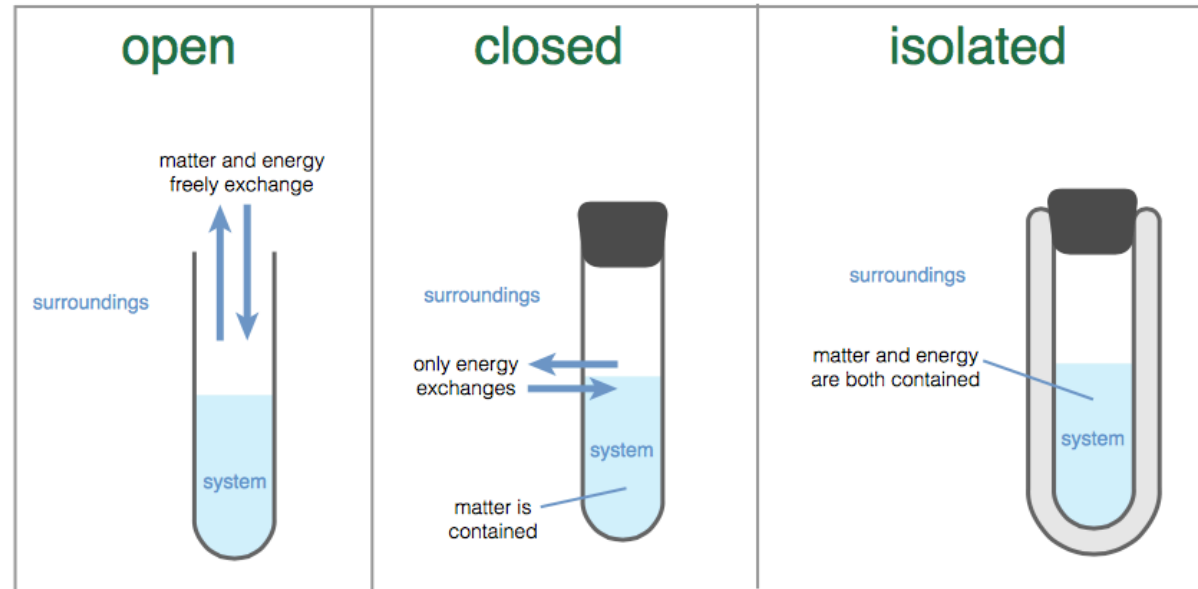
# First Law

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INTERNAL ENERGY, HEAT, AND WORK

# Types of Systems

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- **Open System:** matter and energy are exchanged between the system and the surroundings
- **Closed System:** only energy is exchanged between the system and the surroundings
- **Isolated System:** an insulated container contains matter AND energy in the system

# The First Law of Thermodynamics

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- The energy of the universe is always conserved
- The conclusions of this law are:
  1. The internal energy change of the system is the sum of the heat and work
  2. The internal energy loss of the system is the equal to energy gain of the surroundings
  3. The internal energy change of the universe is zero and there is no energy or matter leaving

$$\Delta U_{sys} = q + w$$

$$\Delta U_{sys} = -\Delta U_{surr}$$

$$\Delta U_{universe} = 0$$

$$q_{sys} = -q_{surr}$$

$$w_{sys} = -w_{surr}$$

# Basic First Law Calculations

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$$\Delta U_{sys} = q + w \longrightarrow$$

Work is the energy derived from **organized molecular motion**



Heat is the energy derived from **random molecular motion** (always travels from high T to low T)

**$q > 0$  ; endothermic (+), heat is absorbed**  
 **$q < 0$  ; exothermic (-), heat is released**

**$w > 0$  ; work energy in, work is done on the system (+), compression**

**$w < 0$  ; work energy out, work is done by the system (-), expansion**

Even though these are the simplest problems on the test, make sure to work a few more problems to practice sign convention

# Heat Calculations

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We calculate heat in three different ways (we will discuss isothermal expansion later), and it is important to understand that heat can be evolved with or without a temperature change.

- With a temperature change, heat depends on the mass of your substance, its heating capacity, and the total change in temperature:

$$q = mC_s\Delta T$$

- If you reach the melting (fusion) point or boiling (vaporization) point, the temperature remains constant until your entire substance has reached the next phase. This heat is dependent on the mass of the substance and the enthalpy of the phase transition:

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

A note on heat capacity:

- Specific heat capacity ( $C_s$ ) is the amount of energy necessary to raise 1g of your substance 1K or 1°C.
- **This means a high heat capacity requires more energy and a low heat capacity heats more easily (requires less energy)**



# Work Calculations

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In chemistry we calculate work based on a change in volume at constant pressure.

- Provided a change in volume at constant pressure, the value of work is:

$$w = -P\Delta V$$

- However, if we are not provided a change in volume, we must rely on the change in gas moles of the balanced chemical reaction ( $\Delta n$ ) to solve for work:

$$w = -\Delta nRT$$

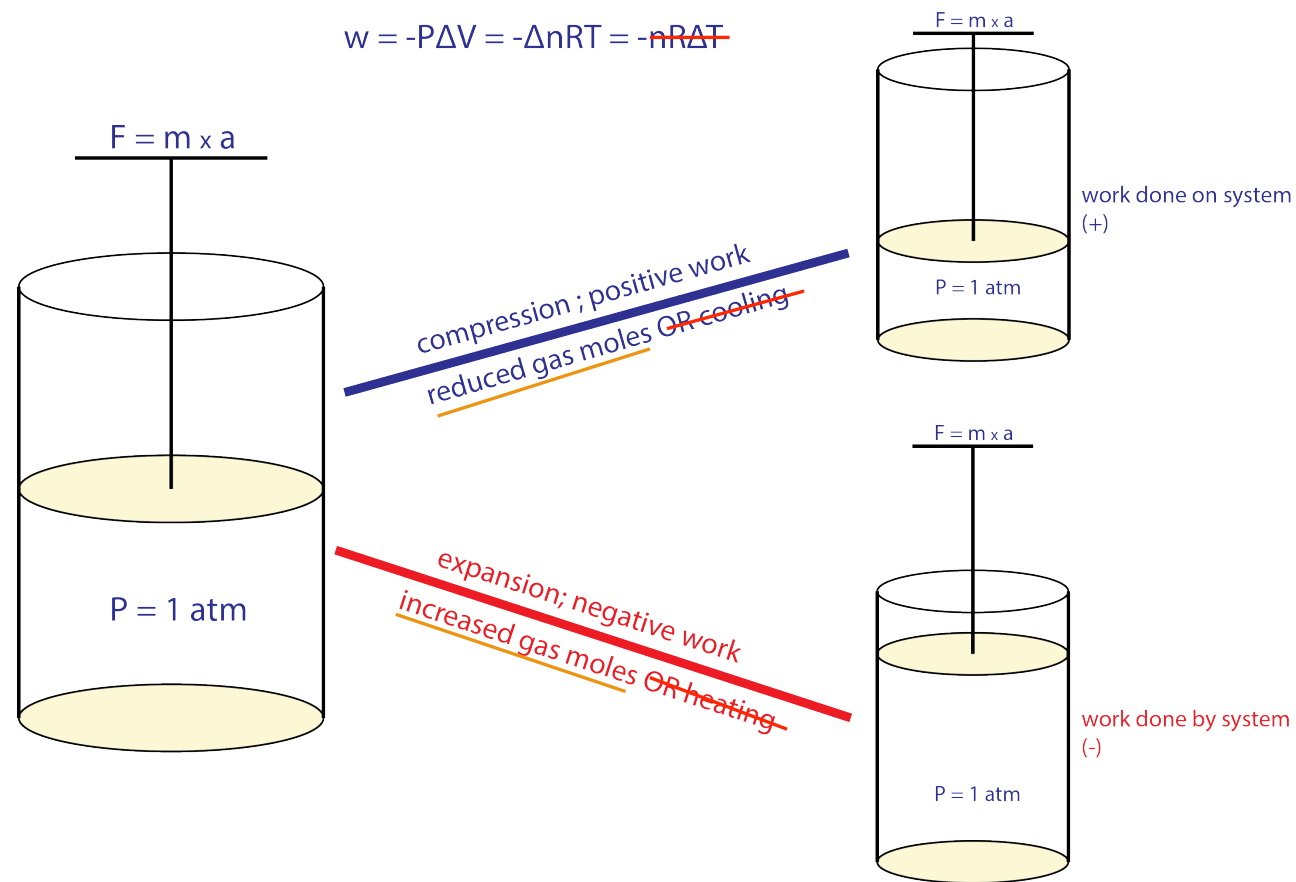
Remember from the first unit that liquids, solids, and aqueous phase compounds contribute negligible volumes to the system.

$$w = -P\Delta V = -\Delta nRT$$

**$\Delta n$  is ONLY the change in gas moles!**

# Visualizing Chemical Work

- Work in chemistry is most often related to what we call “PV” work, where  $w = P\Delta V$
- We often think of experiments measuring “PV” work in the context of using a piston
- Pistons exert a variable force to maintain a constant pressure. This pressure is used to determine the work done by or on the system
- When you are compressing your sample, you are doing work on the system (positive)
- When your sample expands, your system is doing work on the surroundings (the piston) to maintain the constant pressure (negative)



# Calorimetry Calculations

- We use calorimetry to measure the heat flow to the surroundings (water + calorimeter) in two different set-ups:

- Coffee cup calorimetry measures **heat at constant pressure** ( $q_p = \Delta H$ ) in an insulated, open-air container

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

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

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

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

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

Students miss calorimeter problems based on three mistakes:

- The mass in the  $mC\Delta T$  formula is for water not your reactants
- The heat you solve for in the beginning is for the surroundings, so students forget to switch the sign and end up with the correct answer but the wrong sign (remember: bomb calorimetry is used for exothermic combustion reactions)
- Your final answer should match the units of the answer choices (J, kJ, kJ/mol, etc.)

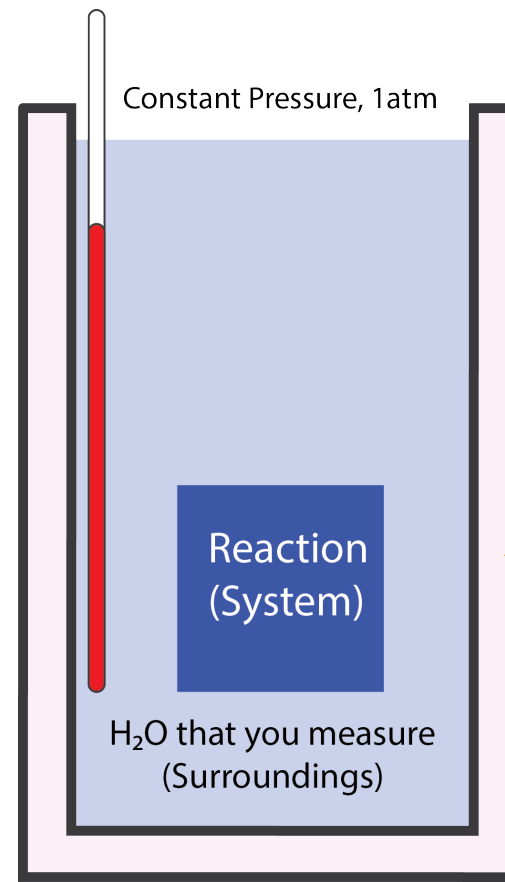
# Coffee Cup Calorimetry

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

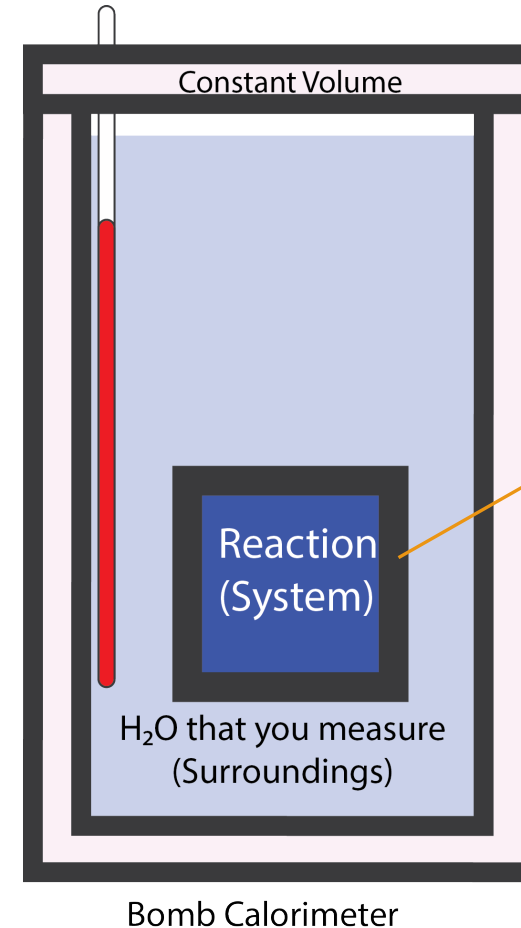
# Bomb Calorimetry

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 $\Delta H$

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Remember that bomb calorimeters are NOT at constant pressure if there is a change in gas moles. If we are interested in finding the  $\Delta H^\circ$  of the combustion reaction, two additional steps are necessary.

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

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


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

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

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

# Isothermal Expansion

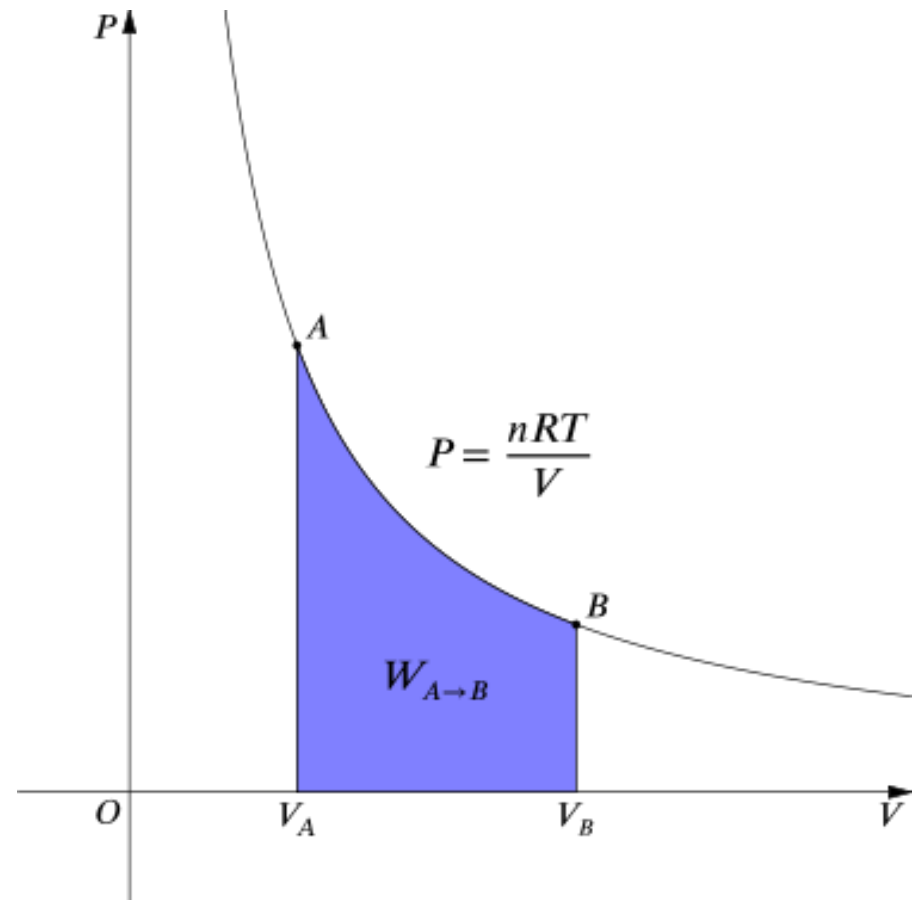
Isothermal expansion/compressions are recognized by one major condition:

Temperature is constant,  $\Delta U = 0$   
which means that:  
 $q = -w$

This gives us the final method of calculating heat and work:

$$q = nRT \ln(V_2 / V_1)$$

$$w = -nRT \ln(V_2 / V_1)$$



# Enthalpy: Hess' Law

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SUM OF REACTIONS, FORMATION REACTIONS, BOND ENTHALPY



# 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 – Sum of Reactions

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

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

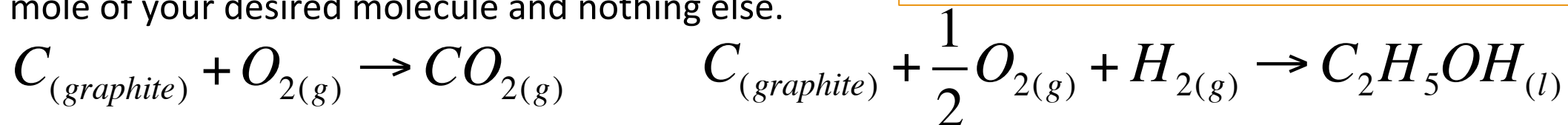
- What you can do to “make” your sum of reactions equal your goal reaction: multiply the entire reaction by a coefficient or fraction (including the enthalpy value associated with that step!) or reverse the entire reaction (changing the sign of the enthalpy value associated with that step).

# Hess' Law – Formation Reactions

- **Goal: determine the enthalpy of formation for your products and reactants. The enthalpy of the reaction is the difference between the products and reactants. Find this data on the coversheet!**

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

- 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.



Students miss these types of questions because they forget what constitutes a formation reaction:

- The elements must be in their standard state (hints: there are only two liquids on the periodic table, carbon is always graphite, and diatomics should be written properly)
- There should only be 1 product
- There should only be 1 mole of that 1 product
- Fractional coefficients of reactants are OK
- The value for the enthalpy of formation for elements (including diatomics) in their standard state is zero.
  - This is also true for free energy but NOT for absolute entropy

# 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 makes 1 bond

# Second and Third Laws; Free Energy

SPONTANEITY, ENTROPY AND FREE ENERGY

# Conceptual Entropy: phases, volume, temperature

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Entropy is a popular topic for conceptual questions. However, there are also a few ways we can calculate it directly.

- **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)

# Entropy: Defining Entropy

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- **Defining Entropy:** it is more appropriate to think of entropy as energy dispersal. This correlates specifically to the total number number of microstates in a system at a given temperature. This is given by the formula:

$$S = k \ln \Omega$$

Or one step further...  $S = k \ln x^i$

- In the first equation, the omega term ( $\Omega$ ) is equal to the total number of microstates. The second equation clarifies this term by representing the omega variable as permutations ( $x^i$ ). This means microstates are equal to the **number of orientations possible for a molecule** ( $x$ ) raised to the power of the **total number of molecules** ( $i$ ).
- Ps: the third law of thermodynamics states that a pure crystal solid at 0K has an entropy value equal to 0. The idea of residual entropy suggests that a crystal solid is non-zero as temperature approaches 0 based on the complexity and number of molecules (as stated above)

# 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
  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

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

- 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:


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

# Entropy: Quantifying Entropy

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- **Remember: entropy is a state function, so it is path independent. If you have absolute entropy data, you can use your reliable “products minus reactants” formula.**

$$\Delta S_{rxn} = \sum nS^{\circ}(\textit{products}) - \sum nS^{\circ}(\textit{reactants})$$



These values come from a table.  
Even elements in their standard  
state have non-zero values (based  
on the third law)

# Entropy: Quantifying Entropy (surroundings)

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- All of the previous calculations will tell you the change in entropy of the surroundings. However, if we define that  $q_{\text{sys}} = -q_{\text{surr}}$  we can apply one last equation:

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T_{\text{surr}}}$$

$$q = mC_s\Delta T$$

and/or

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

then flip the sign

# Defining Spontaneity

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- A spontaneous process is a reaction that freely proceeds without the continual input of energy.
- **Spontaneous reactions happen. Non-spontaneous reactions don't.** There is an additional energy required (the activation energy) but we aren't worried about that just yet.
- **However, we can do non-spontaneous reactions in a variety of ways (inputting energy, electricity, reaction coupling, etc.); they just don't happen on their own.**

# Spontaneity: Entropy and Free Energy

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- 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

- The equation for the second law can be rewritten for free energy

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

- This law gives us three conditions for  $\Delta G_{rxn}$ :
  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

# Calculating Free Energy

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- You should be very familiar with the formula:

$$\Delta G = \Delta H - T\Delta S \quad \text{or...} \quad \Delta G_{rxn} = \Delta H_{sys} - T\Delta S_{sys}$$

- For these equations you may be responsible for solving for each component of the reaction ( $\Delta H$  and  $\Delta S$ ).
- However, remember that free energy is still a state function. So we can also use the more direct formula when provided with the necessary data:

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

# Free Energy: Equilibrium

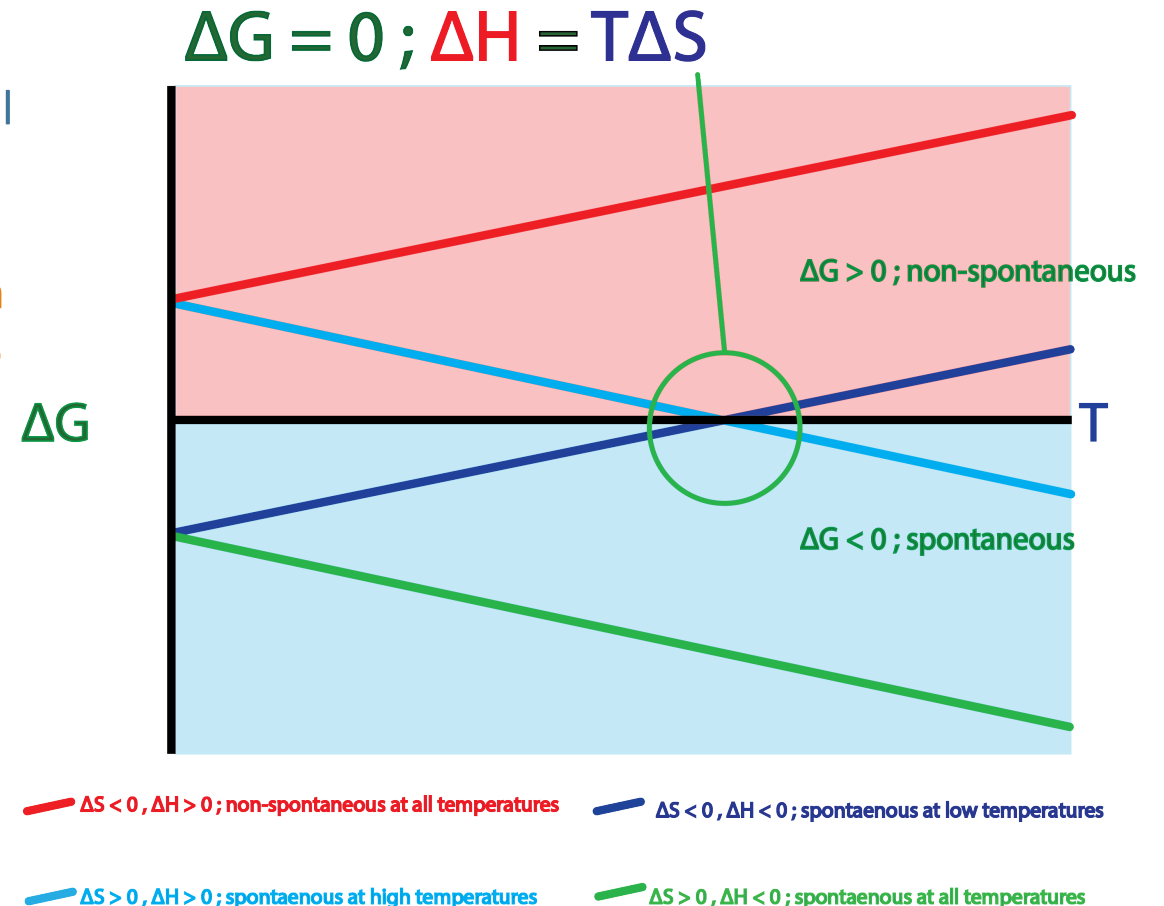
For the conditions that are temperature dependent, it is possible to have a  $\Delta G$  value equal to 0. This is, by definition, equilibrium.

**It might be useful to remember that equilibrium can only occur when entropy and enthalpy have the same sign (both positive or both negative).**

The red and green lines cannot ever be in equilibrium.

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

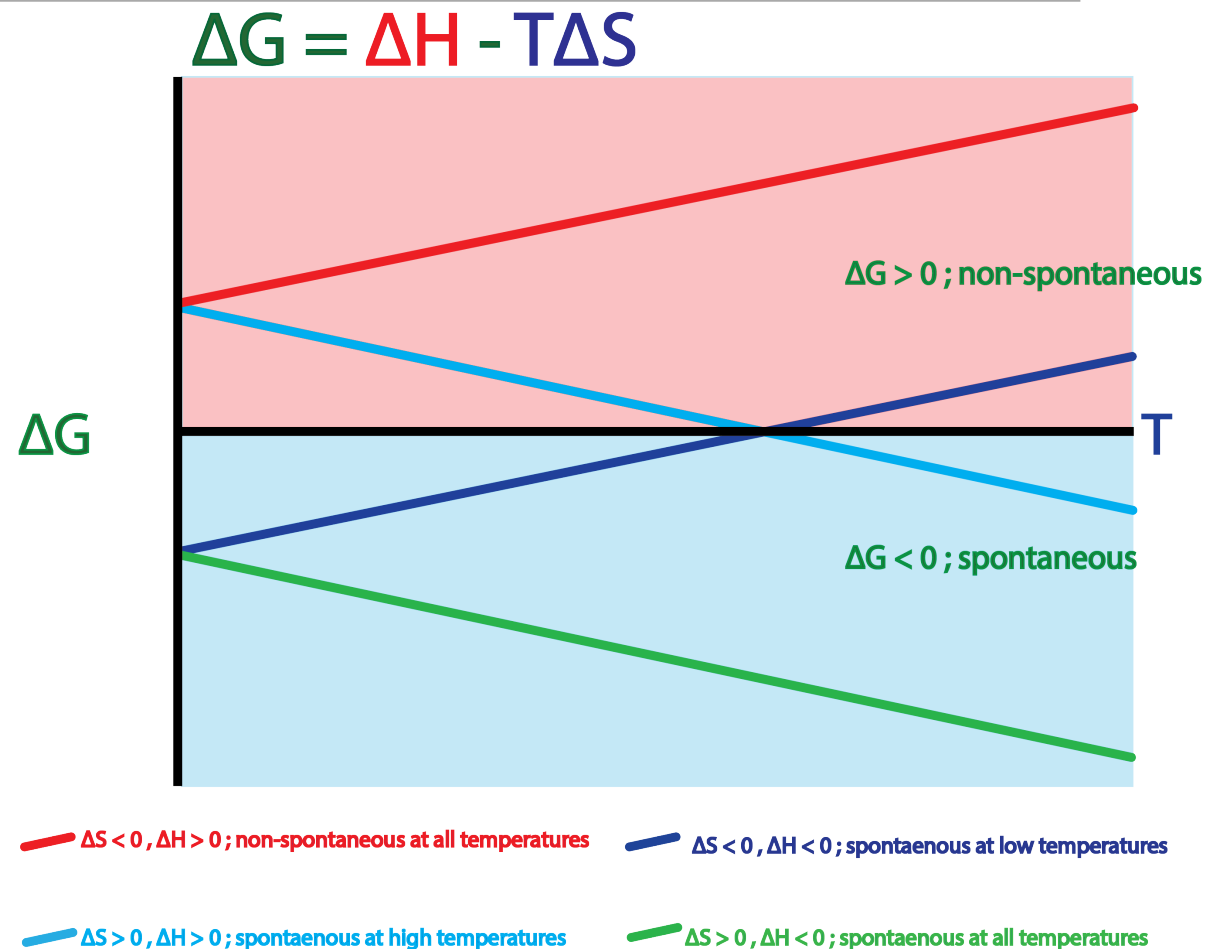
$$T_{trans} = \frac{\Delta H_{rxn}}{\Delta S_{rxn}}$$





# Free Energy: All Conditions Summary

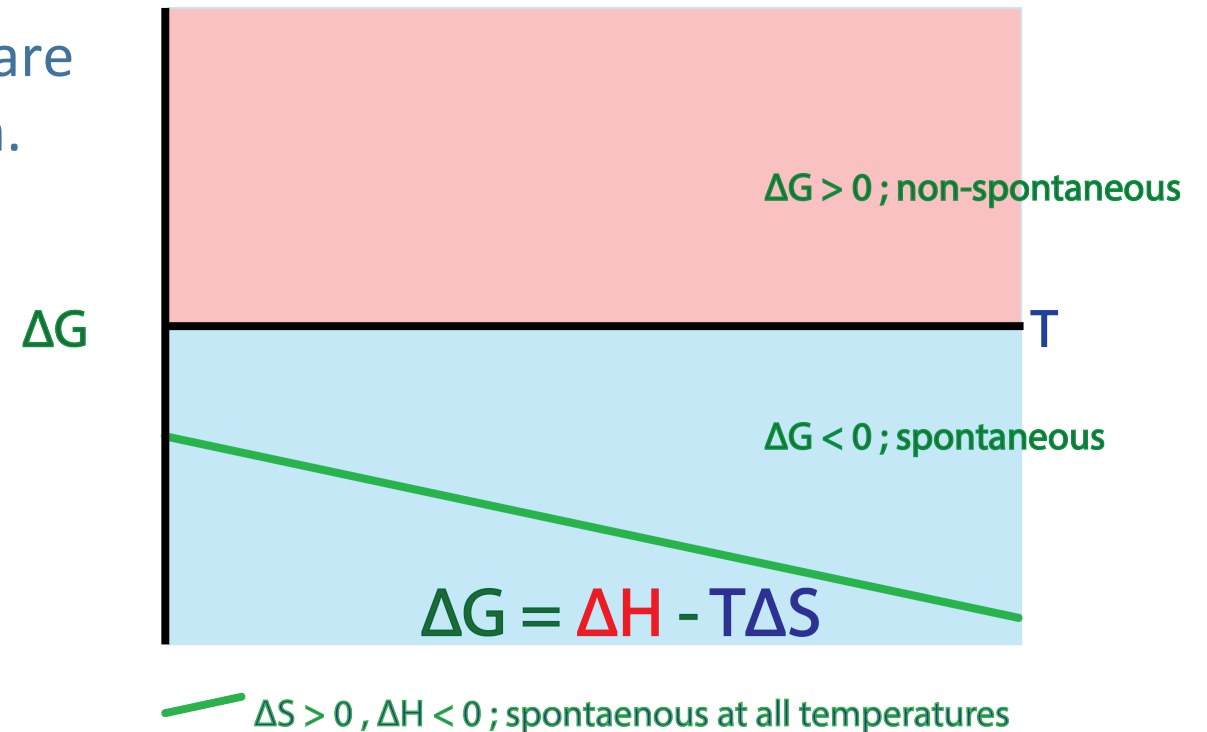
$\Delta H$	$\Delta S$	Temperature Dependent?	Spontaneous?
-	+	No	Always
+	-	No	Never
-	-	Yes	Low T
+	+	Yes	High T



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

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

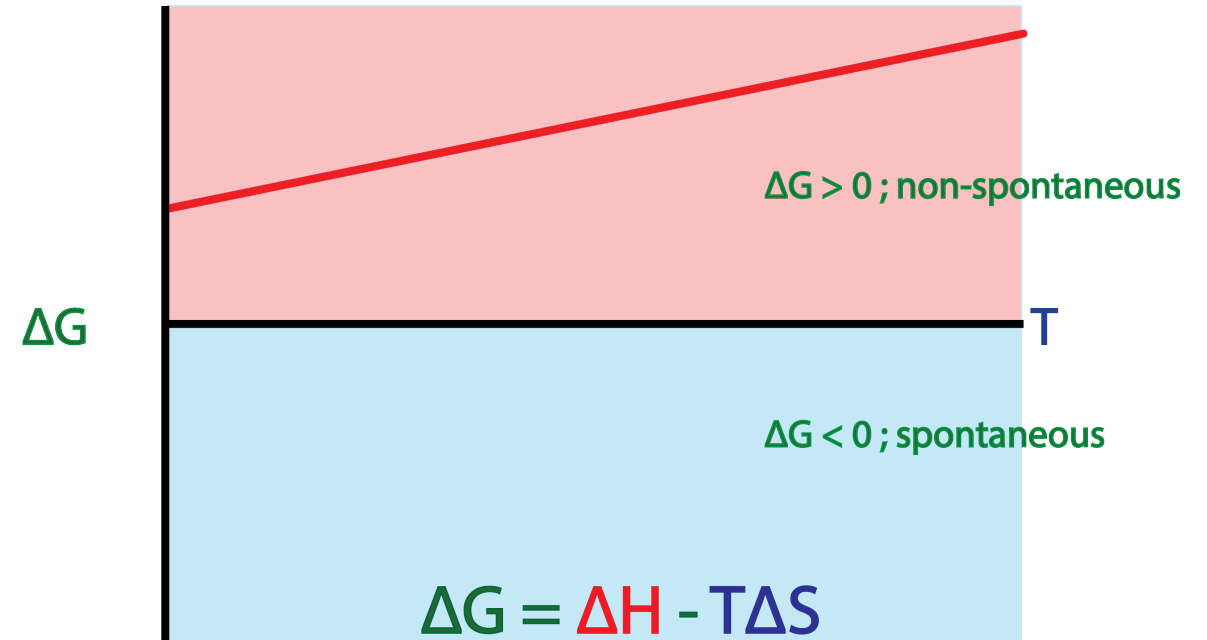
Therefore, this reaction will be **spontaneous** at all temperatures.



# 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.

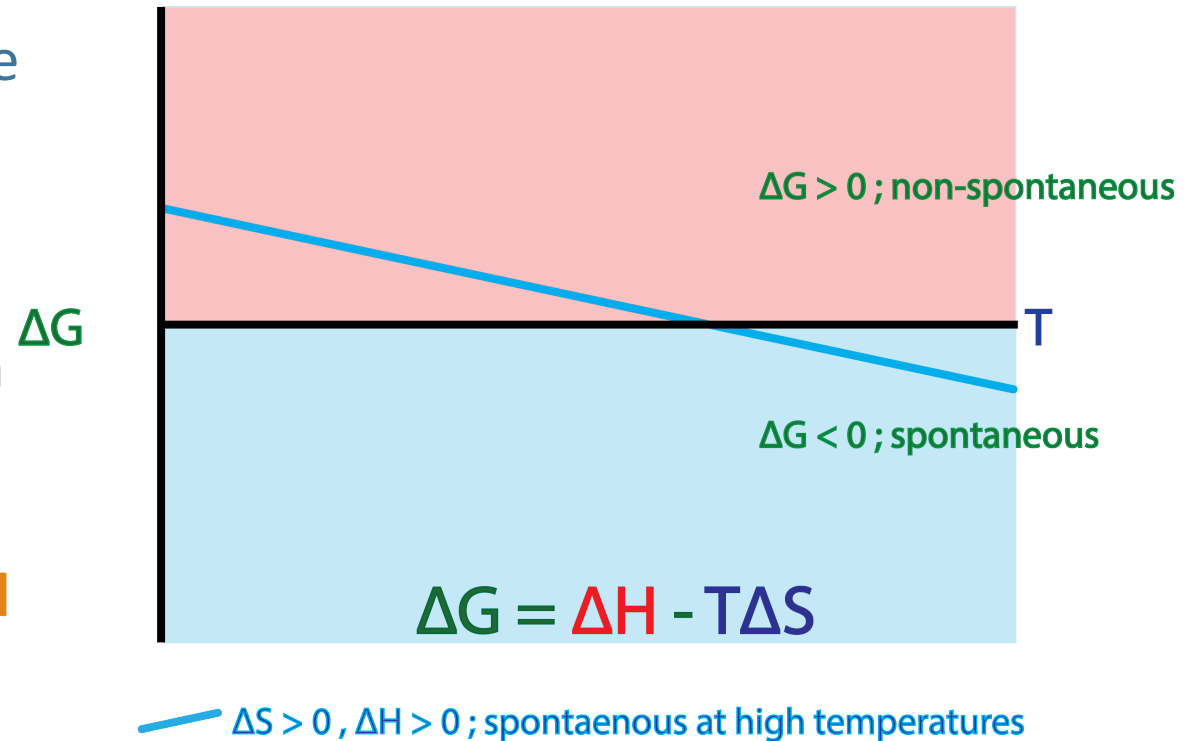
# Free Energy: $+\Delta H$ , $+\Delta S$

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)  
 $\text{NaCl}(s) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq)$



# 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.**

