

Don't forget to do my course evaluation!

electronic Course Instructor Survey (eCIS)

I thoroughly enjoy reading all feedback

Unit 5 Exam Review

THERMODYNAMICS

Spotify: "Exam Study (Ambient)"

Learning Objectives – Unit 5 (part one)

Identify the system, surroundings, and universe in order to distinguish what is changing during a chemical and/or physical process.

Define and recognize state versus process functions.

Describe the concept of the energy units, including calories, kilocalories, and kilojoule.

Distinguish between kinetic energy, potential energy, and electromagnetic energy.

Define the first law of thermodynamics in the context of internal energy, heat, and work.

Recall sign conventions associated with thermodynamic change.

Define conduction and describe the microscopic view of thermal energy transfer due to molecular collisions.

Define heat capacity, specific heat capacity, and molar heat capacity.

Calculate the heat and work associated with chemical and/or physical change.

Calculate $P\Delta V$ (expansion) work for both physical and chemical changes.

Define enthalpy, and calculate the enthalpy change for chemical and/or physical changes.

Calculate change in enthalpy for physical change – both change in temperature and phase change.

Fully interpret the heating curve of a substance.

Draw and fully interpret energy reaction diagrams.

Differentiate between the change in internal energy and enthalpy for a process, and describe how these quantities are measured (coffee cup vs. bomb calorimetry).

Calculate the change in enthalpy (ΔH) and internal energy (ΔU) based on calorimetric data.

Learning Objectives – Unit 5 (part two)

Write formation reactions for elements and compounds.

Calculate change in enthalpy based on tabulated data (e.g. Hess's law, formation data, bond enthalpy data).

Define entropy (S) and describe the second law of thermodynamics in the context of ΔS .

Differentiate between the entropy of system, surroundings, and universe.

Recognize how changes in system properties (T , V , phase, mixing, and composition) will affect the entropy of the system.

Calculate change in entropy for the system and surroundings for a physical change.

Describe entropy using a microscopic perspective of energy distribution (Boltzmann/microstates).

Calculate change in entropy for the system and surroundings for a chemical change.

Define the change in free energy.

Calculate change in free energy (ΔG) for a chemical change from change in enthalpy and change in entropy.

Use the change in free energy to determine the spontaneity of a chemical and/or physical process at a given temperature.

Calculate ΔG for a chemical change from tabulated thermodynamic data.

Link ΔG to the second law of thermodynamics and chemical equilibrium.

What to do now / tonight

- **Practice a lot**
 - McCord “Bigass” problem set
 - Canvas Extra Practice
 - You should have put a good effort into Sapling; but be done with it now
- **Download, print, and annotate the formulas**
 - Have your own understanding of each equation in order to make calculations and answer conceptual questions about them
 - The Bigass problem set has some great examples of applying calculations to purely conceptual questions
- **Use lectures, reviews to study conceptual points**
- **Get good sleep tonight, but don't go to bed unconfident**

Exam 5 Breakdown – The Mistakes

- **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_{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 ΔS_{sys} versus ΔS_{surr} or $\Delta S_{\text{universe}}$, etc.

- **Know how to use natural log (ln) on your non-graphing calculator**

- **Then there's stoichiometry...**

Internal Energy

THE SUM OF ALL POTENTIAL AND KINETIC ENERGY;

FIRST LAW: THE INTERNAL ENERGY OF THE UNIVERSE IS CONSERVED

The First Law of Thermodynamics

- 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

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

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

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

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

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

Basic First Law Calculations

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

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

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

$$q = mC_s\Delta T$$

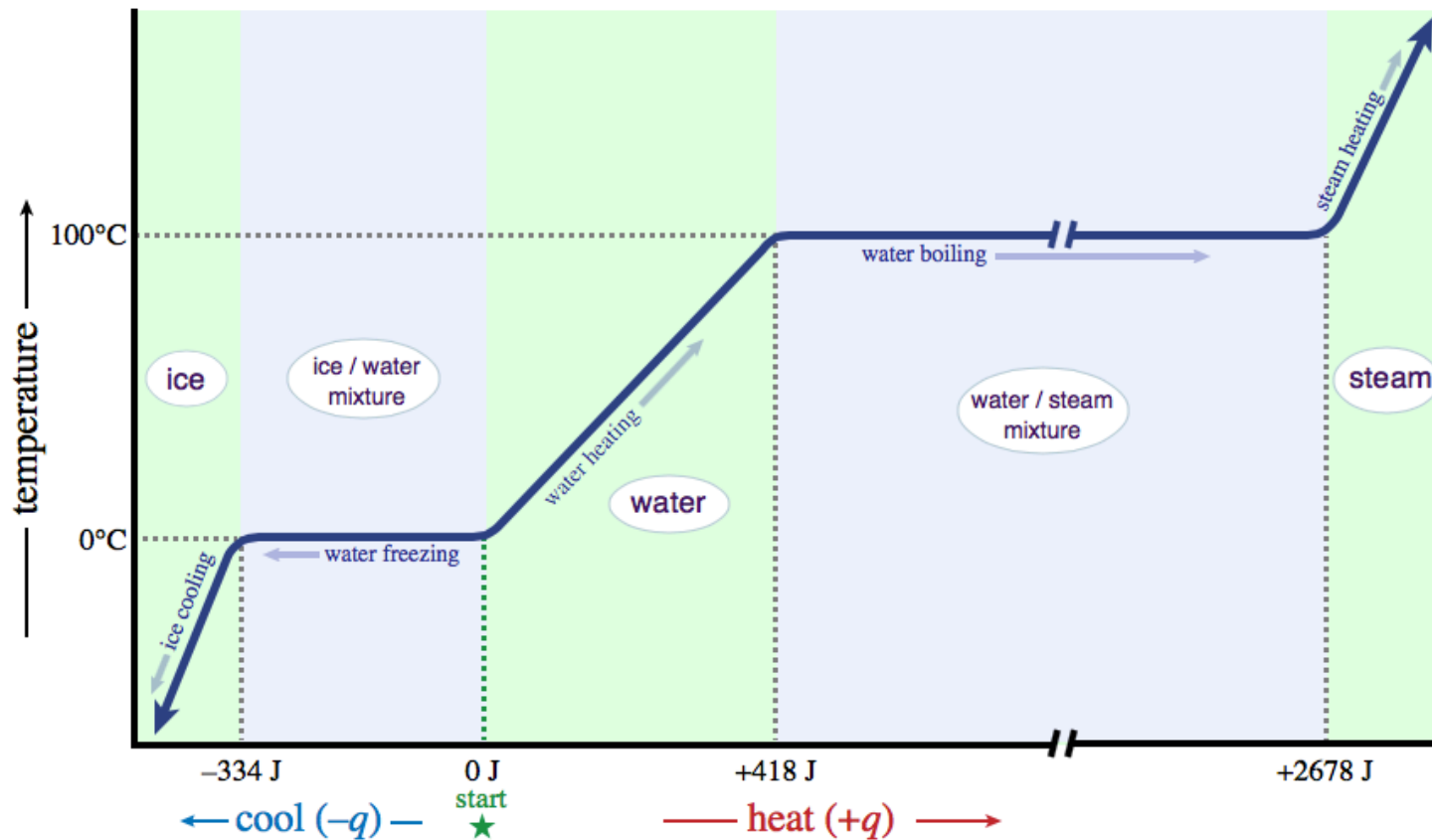
- The heat of a phase change ($\Delta T = 0$) is dependent on the mass of the substance and the enthalpy of the phase transition:

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

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)**
- **If two substances have different masses, you can't just "eye-ball" it. You must calculate heat capacity as an extensive property.**

Heat Flow: Heating Curves



Heat of a Temperature Change

$$q = mC_s\Delta T$$

Heat of a Phase Change

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

Entropy of a temperature change

$$\Delta S = mC_s \ln(T_f/T_i)$$

Entropy of a phase change

$$\Delta S = m\Delta H_{\text{trans}}/T$$

Work Calculations

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 (Δn) 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.

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

Δn is ONLY the change in gas moles!

Work Calculations

What is the value of work when an external pressure of 2 atm compresses a piston from an initial volume of 11.2 liters to a final volume of 2 liters.

1. -18.4 kJ

2. 18.4 kJ

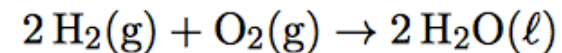
3. 1.86 kJ

4. -1.86 kJ

$$w = -P\Delta V$$

* Don't forget to convert L atm into Joules

For the reaction



find the value for the work done at 300 K.

1. 2.5 kJ

2. -7.5 kJ

3. 7.5 kJ

4. -2.5 kJ

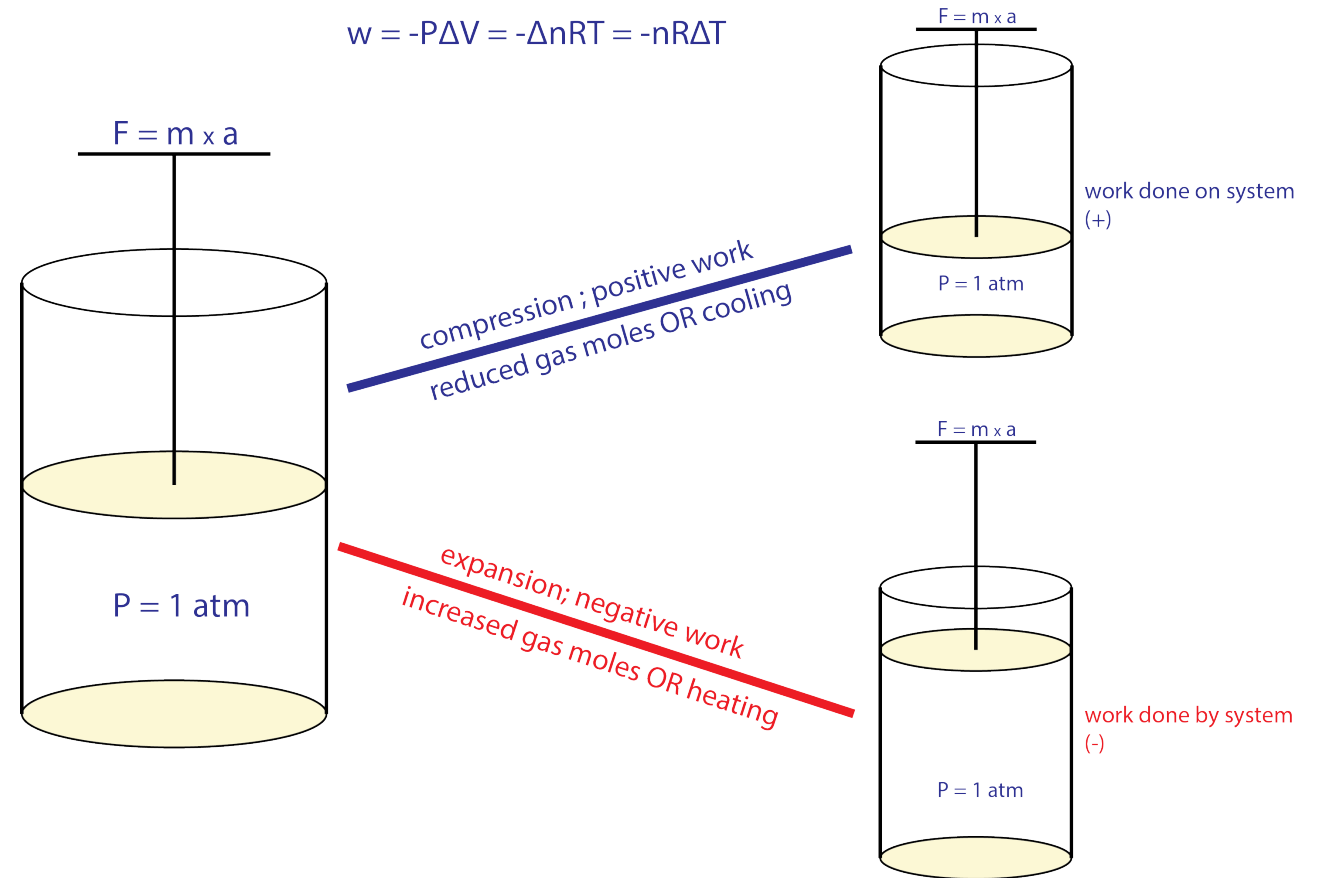
$$w = -\Delta nRT$$

Visualizing Chemical Work

- In chemistry, we focus on PV work, which involves the expansion and compression of gas moles in a chemical reaction:

$$\text{work} = -P\Delta V = -\Delta nRT$$

- We often think of experiments measuring "PV" work in the context of using a piston
- 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)



$$\Delta U = q + w$$

@ Constant Pressure: Balanced reaction

$$\Delta U = \Delta H - \overbrace{\Delta n R T}$$

↓

$$\Delta H = q_p \quad (\text{coffee cup})$$

@ Constant volume:

$$\Delta U = q_v - \cancel{P\Delta V} \quad \tau = 0$$

$$\Delta U = q_v \quad (\text{Bomb calorimeter})$$

In Both Calorimeters

$$\underbrace{q_{cal}}_{\downarrow} = - \underbrace{q_{sys}}_{\downarrow}$$

What we measure What we are interested in...

Calorimetry

COFFEE CUP: HEAT RELEASED/ABSORBED FROM THE SYSTEM GIVES YOU CHANGE IN ENTHALPY (HEAT AT CONSTANT PRESSURE)

BOMB CALORIMETER: HEAT RELEASED FROM THE SYSTEM GIVES YOU HEAT AT CONSTANT VOLUME (INTERNAL ENERGY)

Calorimetry Basics

- 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**

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

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

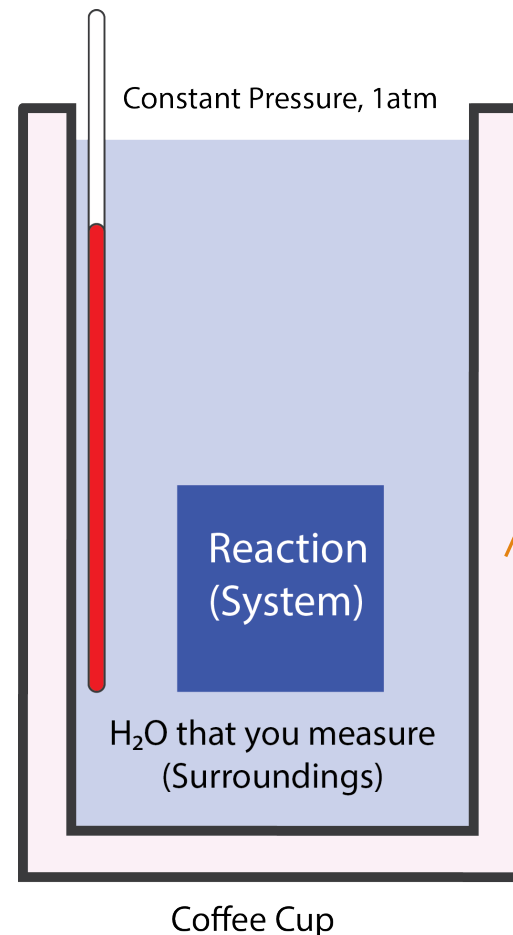
Coffee Cup Calorimetry

Coffee Cup: the goal is to get the enthalpy change (ΔH) of a reaction by measuring the ΔT 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

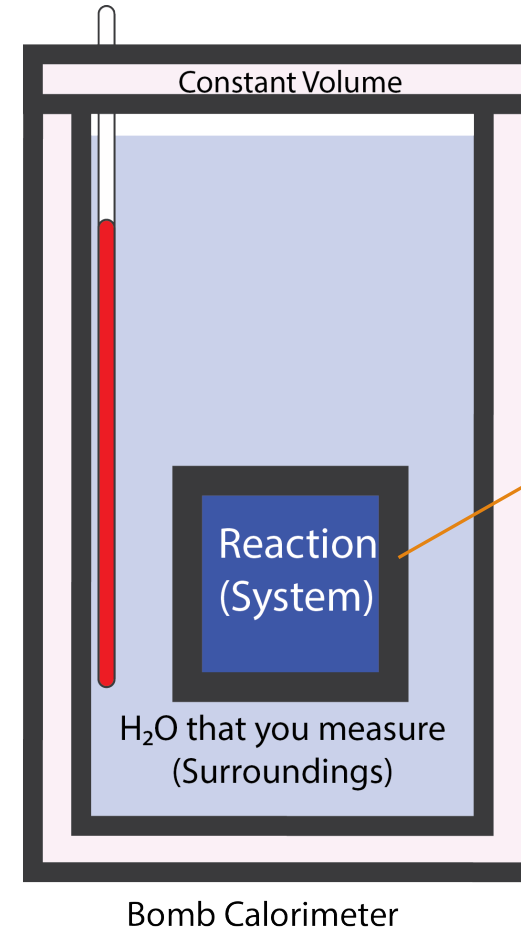
Bomb Calorimetry

Bomb Calorimetry: the goal is to get the internal energy change (ΔU) of a combustion reaction by measuring the ΔT 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



$$1) q_{\text{cal}} = \underbrace{m C_s \Delta T}_{\text{H}_2\text{O}} \overset{\text{kJ}}{+} \underbrace{C \Delta T}_{\text{hardware}}$$

$$2) \underline{q_{\text{cal}}} = -q_v, \quad q_v = \Delta U$$

→ Combustion, always exothermic

3) Final answer:

$$\boxed{\Delta U} \begin{cases} \div g \rightarrow \text{kJ/gram} \\ \div \# \text{ of moles} \rightarrow \text{kJ/mol} \end{cases}$$

Enthalpy

CHANGE IN ENTHALPY (ΔH) IS THE HEAT FLOW AT CONSTANT PRESSURE

HESS' LAW: A PATH CAN BE "CREATED" TO GIVE THE ΔH OF AN OVERALL REACTION

Hess' Law

- 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**

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

Hess' Law – Sum of Reactions

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

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

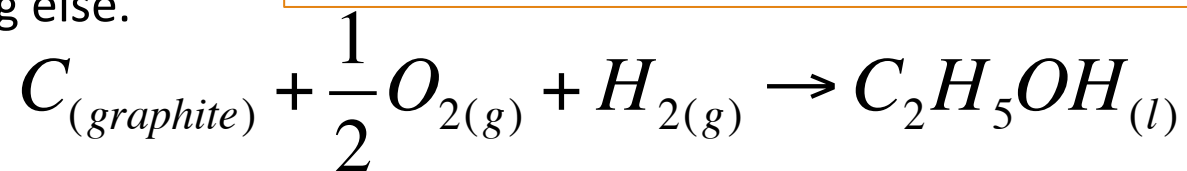
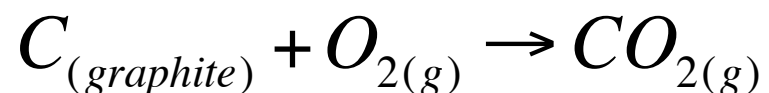
- What you can do to “make” your sum of reactions equal your goal reaction: multiply the entire reaction by a coefficient or fraction (including the enthalpy value associated with that step!) or reverse the entire reaction (changing the sign of the enthalpy value associated with that step).

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!**

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

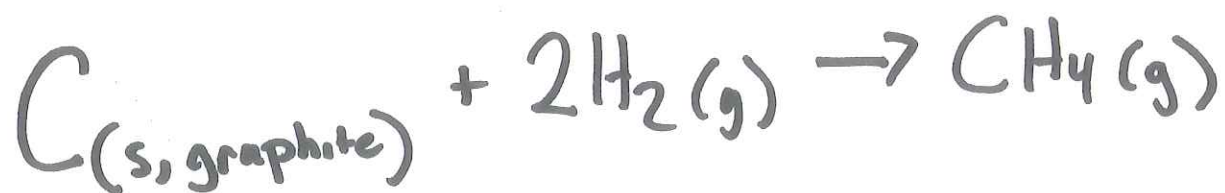
- Phase and number of moles are important!
- Note: a formation reaction for a molecule is a balanced chemical reaction that shows the constituent elements combining to form a single mole of your desired molecule and nothing else.



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

For a formation reaction, $\Delta H_{\text{rxn}}^{\circ} = \Delta H_{\text{f}}^{\circ}$



1) One Product

2) One mole product

3) Formed from elements in their std. state

Hess' Law – Bond Energy Data

- **Goal: determine the energy difference between all bonds breaking and all bonds forming. Find this data on the coversheet!**
- 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 the halogens make 1 bond

Entropy

A MEASUREMENT OF ENERGY DISPERSAL;

UNIVERSAL ENERGY INDICATES SPONTANEITY (+)

The 2nd Law of Thermodynamics

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

The second law of thermodynamics states that the entropy of the universe (total) is always increasing.

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

- This law gives us three conditions for ΔS_{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

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

$$\Delta S_{\text{universe}} = \frac{q_{\text{rev}}}{T} + \frac{-q_{\text{rev}}}{T_{\text{surr}}}$$

Phase Changes

$$(\pm) = \frac{m \Delta H_{\text{trans}}}{T_{\text{trans}}} + \frac{-m \Delta H_{\text{trans}}}{T_{\text{surr}}}$$

$\text{H}_2\text{O}_{(s)} \xrightarrow{RT} \text{H}_2\text{O}_{(l)}$

$$T_{\text{trans}} = 273\text{K} \quad T_{\text{surr}} = 298\text{K}$$

Positive because $\rightarrow T_{\text{surr}} > T_{\text{trans}}$

* Explains the opposite reaction @ -25°C , as well *

Conceptual Entropy: phases, volume, temperature

- **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)

Increasing Entropy

- **In summation, you can increase entropy based on:**
 1. Phase (going from solid to liquid to gas)
 2. Increasing volume (decreasing pressure)
 3. Increasing temperature
 4. Complexity of your molecule (a larger number of more diverse bonds)
 5. Dissolution reactions (solid to aqueous)
 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:

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

Free Energy

A MEASUREMENT OF SPONTANEITY FOR A REACTION SYSTEM (-)

Defining Spontaneity

- 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.

$$\Delta G_{\text{rxn}} < 0$$

$$\Delta S_{\text{universe}} > 0$$

- **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.**

Definition of Free Energy

- **Free Energy (G):** A state function derived to describe the stability of a system. For now, we are concerned most with the ΔG because of the conclusions we can make using its **sign** and **magnitude**.
- **The change in free energy of a reaction (ΔG) 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 inconvenient 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!

Calculating Free Energy

- 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:

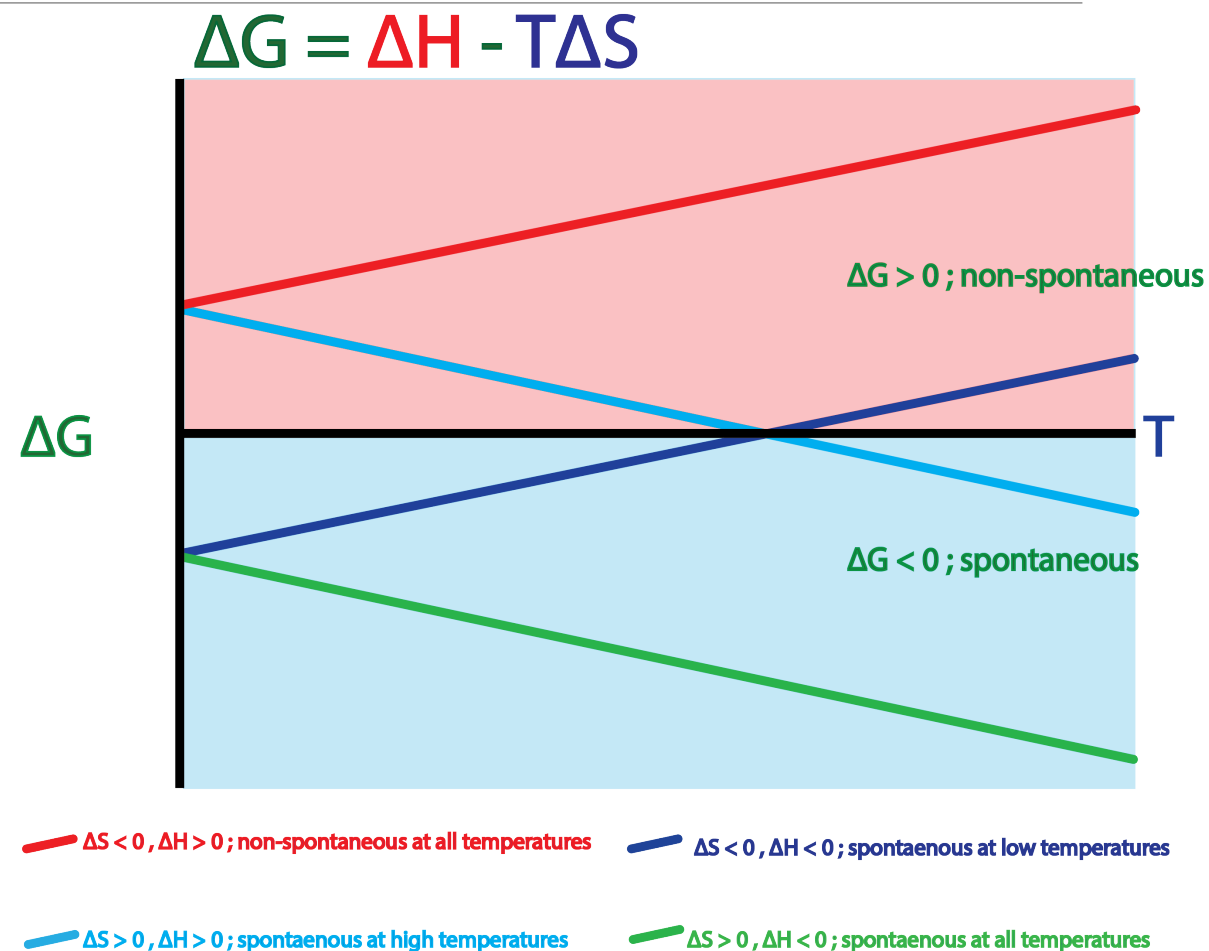
$$\Delta G_{rxn} = \sum n \Delta G_f^\circ(\text{prod}) - \sum n \Delta G_f^\circ(\text{react})$$

Free Energy Conclusions

- **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 ΔG :
 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: All Conditions Summary

ΔH	ΔS	Temperature Dependent?	Spontaneous?
-	+	No	Always
+	-	No	Never
-	-	Yes	Low T
+	+	Yes	High T

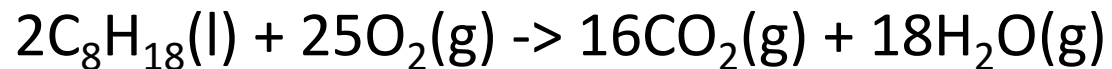


Free Energy: $-\Delta H$, $+\Delta S$

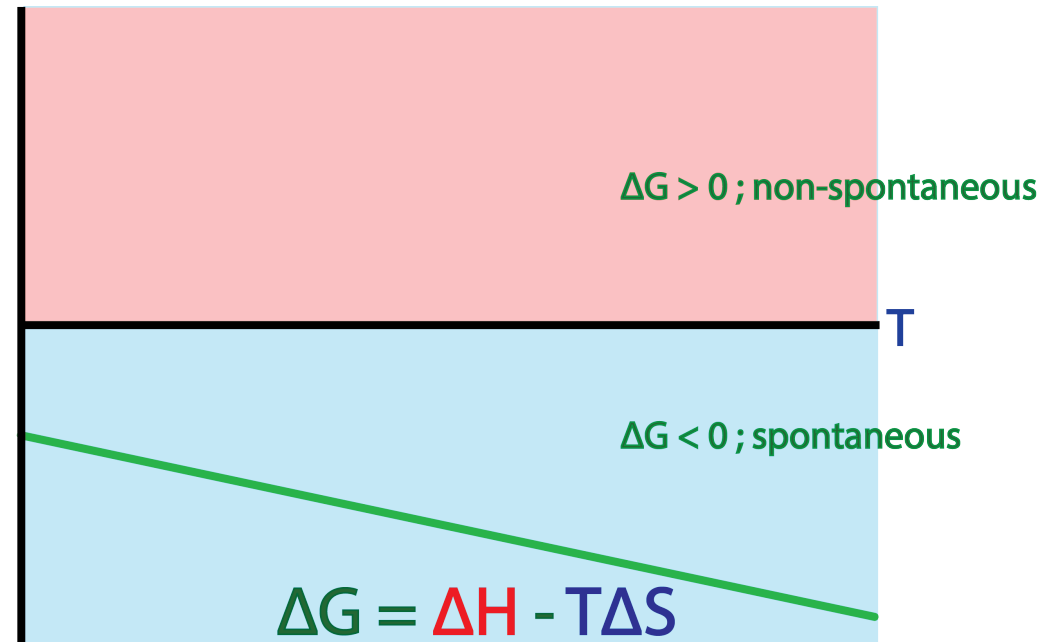
In this case, our enthalpy and entropy are “favorable” for a spontaneous reaction.

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

Example: many combustion reactions



ΔG

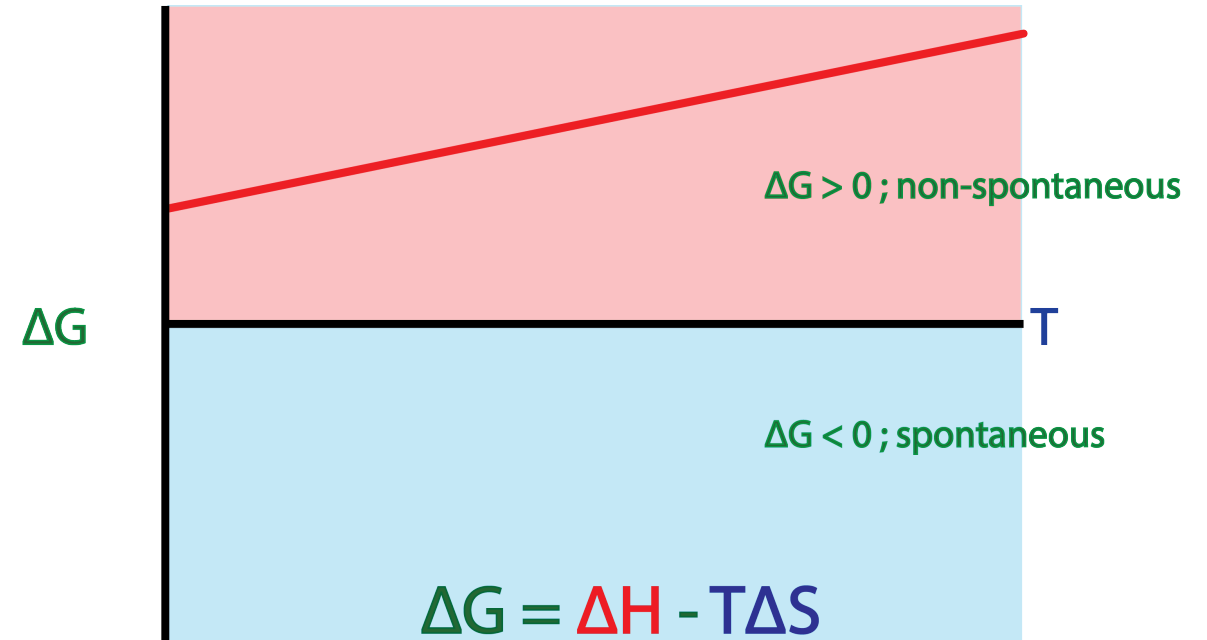


$\Delta S > 0$, $\Delta H < 0$; spontaenous at all temperatures

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 ΔG does not mean that a reaction can't happen. It means that it doesn't happen without the continuous input of energy.

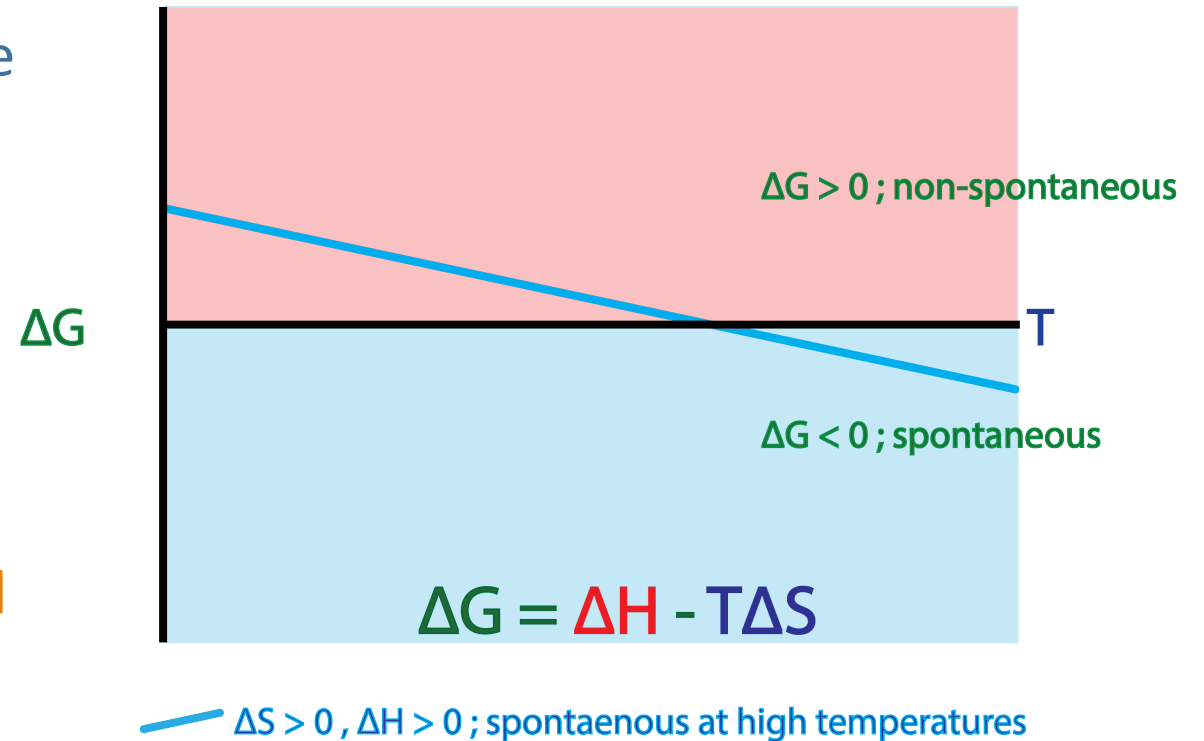
Free Energy: $+\Delta H$, $+\Delta S$

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 ΔH term in order for our ΔG to be negative.

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

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



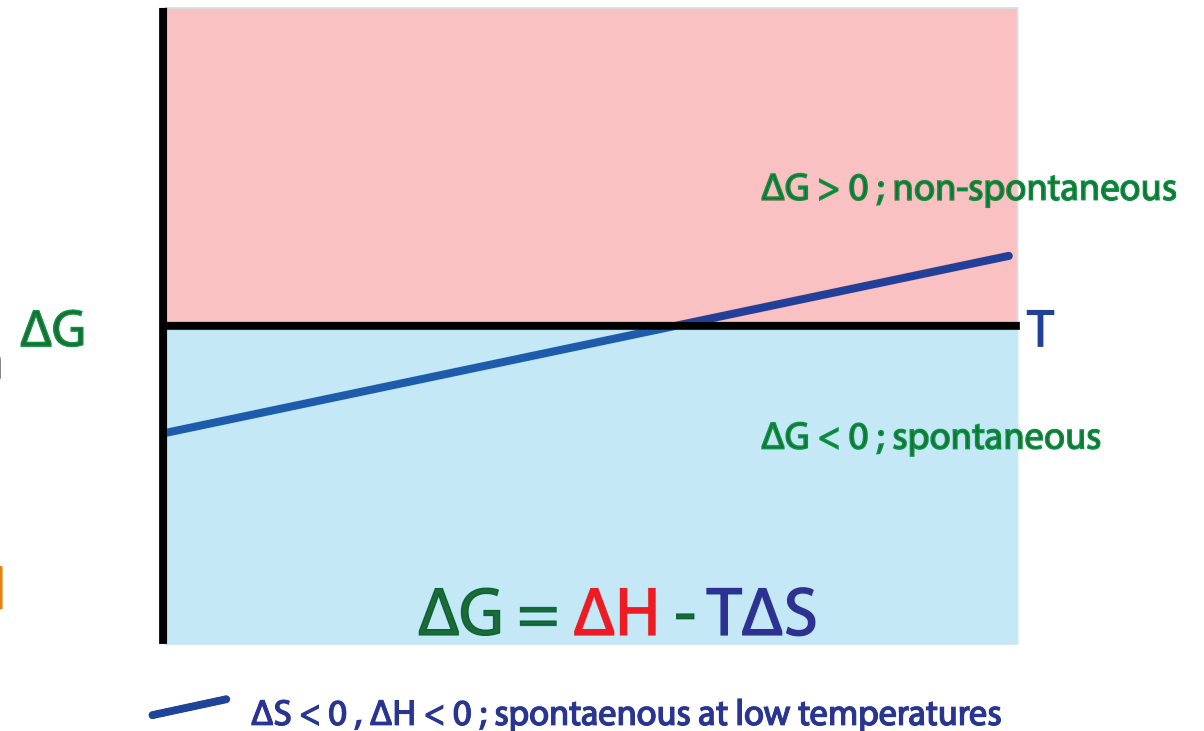
Free Energy: $-\Delta H$, $-\Delta S$

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 ΔH term in order for our ΔG to be negative.

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

Example: cooling processes

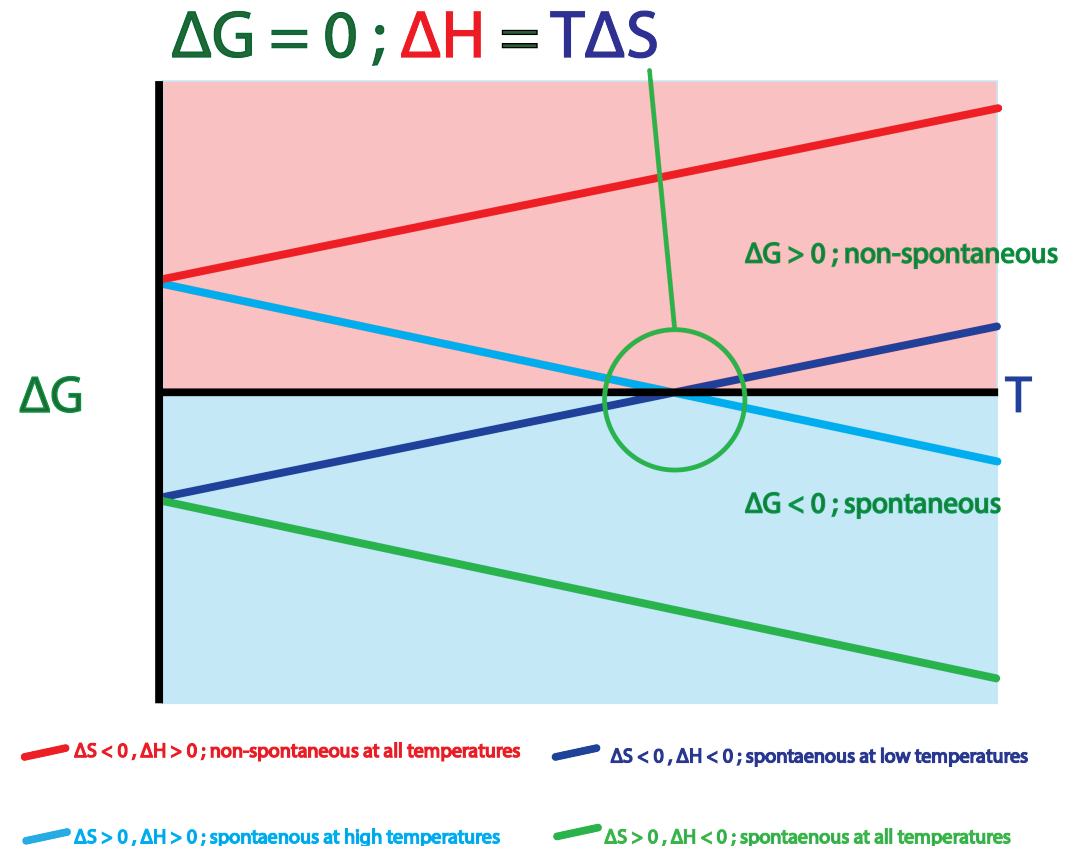


Free Energy: Equilibrium

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

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

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



Spontaneity: Entropy and Free Energy

- 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 ΔS_{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 ΔG_{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

Practice Problems

THERMODYNAMICS

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

↑ J

extensive

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

↑ J/g

intensive

Extensive: dependent on mass

Intensive: independent on mass

$$C_s \frac{J}{g \cdot ^\circ C}$$

Comparing two
substances same
mass

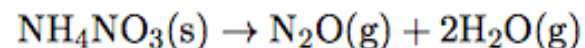
$$C_s \frac{J}{^\circ C}$$

compare two
substances w/
different masses

$$q = m C \Delta T$$

Practice Problems: Free Energy Wrap-Up

Calculate ΔG° for the following reaction at 298 K.



1. +169 kJ
2. -1.33×10^5 kJ
3. -130 kJ
4. +97.2 kJ
5. -169 kJ
6. +130 kJ
7. -113 kJ

Additional question: is this reaction spontaneous or non-spontaneous?
Is the spontaneity of this reaction dependent on temperature?
If so, at which temperature does it become spontaneous?

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



$$\sum n \Delta H_f^\circ (\text{products}) - \sum n \Delta H_f^\circ (\text{reactants})$$

$$- T \times \left(\sum n S^\circ (\text{products}) - \sum n S^\circ (\text{reactants}) \right)$$

$$\Delta H = \left(\overset{\text{N}_2\text{O}}{1 \times 82} + \overset{2 \text{H}_2\text{O}(\text{g})}{2 \times -242} \right) - \left(\overset{\text{NH}_4\text{NO}_3}{-366} \right) = -36 \text{ kJ}$$

$$\Delta S = \left(\overset{\text{N}_2\text{O}}{1 \times 220} + \overset{2 \times \text{H}_2\text{O}}{2 \times 189} \right) - \left(-151 \right) = 447 \text{ J}$$

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

$$(-36 \text{ kJ}) - 298 \text{ K} \left(\frac{447}{1000} \right)$$

$$= -169 \text{ kJ/mol}$$

Practice Problems: First Law Conceptual

Consider a thermodynamic system that is simultaneously releasing heat and doing work. The internal energy of this system will:

1. Increase, decrease, or stay the same depending on the magnitudes of heat and work
2. Decrease
3. Stay exactly the same.
4. Increase

Decrease

$$\Delta U = q + w$$

$q \rightarrow$ releasing (-)
absorbing (+)

$w \rightarrow$ on sys (+)
by sys (-)

$$\Delta U = (-) + (-)$$

U goes down ($\Delta U < 0$)

Practice Problems: First Law Gases

The standard molar enthalpy of formation of $\text{NH}_3(\text{g})$ is -46.11 kJ/mol . What is the standard molar internal energy of formation of $\text{NH}_3(\text{g})$?

2433 kJ/mol

-2525 kJ/mol

-48.59 kJ/mol

-43.63 kJ/mol

$$\Delta H_f^\circ \text{ NH}_3 = -46.11 \text{ kJ/mol}$$

$$\Delta U?$$

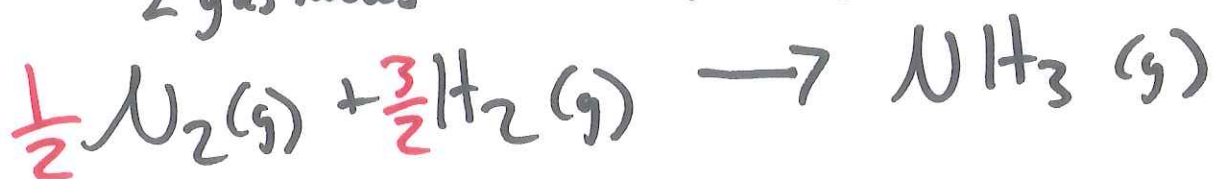
balanced reaction

$$\Delta U = \Delta H - \Delta n R T$$

$$\downarrow$$
$$-46.11$$

2 gas moles

→ 1 gas moles



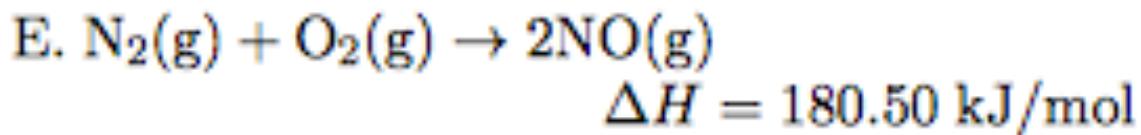
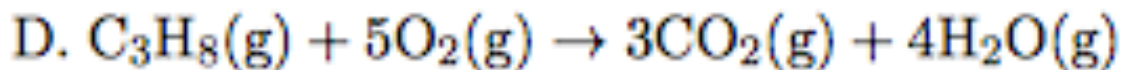
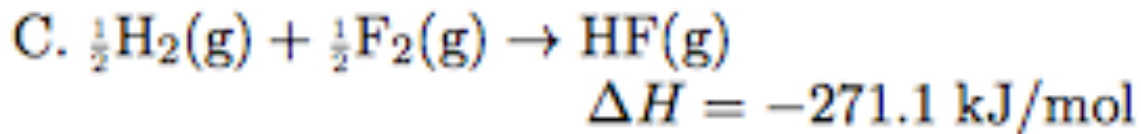
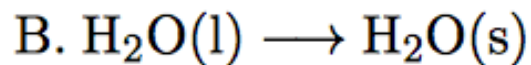
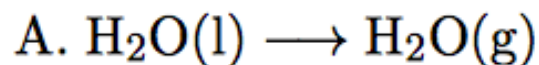
$$\Delta n = 1 - 2 = -1$$

$$\Delta U = \Delta H - \Delta n R T$$
$$-46.11 \text{ kJ/mol} - (-1)(0.008314)(298)$$

$$\boxed{= \Delta U = -43.63 \text{ kJ/mol}}$$

Practice Problems: Thermo Conceptual

Consider the following chemical and physical changes:



Which change(s) are endothermic?

1. C and D only

2. B and E only

3. C only

4. A, D, and E only

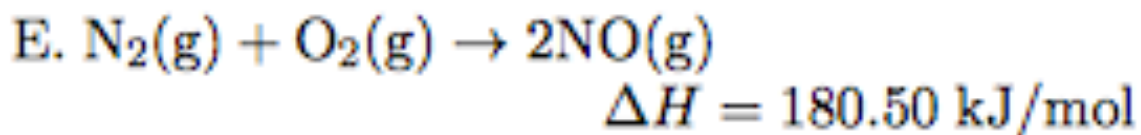
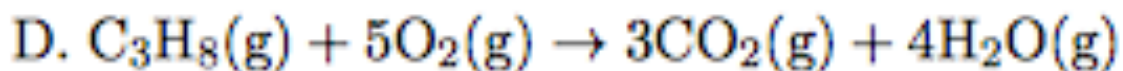
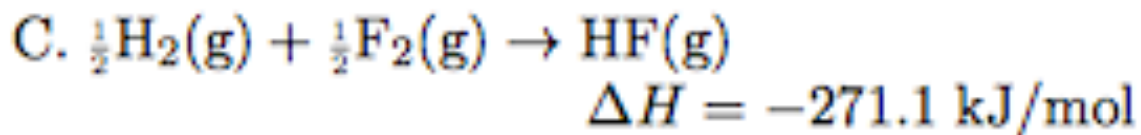
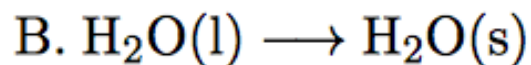
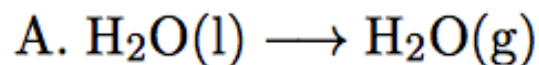
5. A, C, and D only

6. A and E only

A, E only

Thermo Conceptual II

Consider the following chemical and physical changes:



028 (part 2 of 3) 10.0 points

For which change(s) would $\Delta H = \Delta U$?

1. B and E only

2. C and D only

3. A and B only

4. A and D only

5. B, C, and E only

B, C, E

029 (part 3 of 3) 10.0 points

For which change(s) would $\Delta H_{\text{rxn}} = \Delta H_f$ of the product?

1. A, B, and C only

2. C only

3. A and C only

4. A, B, C, and E only

5. C and E only

C only

Practice Problems: Bomb Calorimeter

Methyl tert-butyl ether or MTBE is an octane booster for gasoline. The combustion of 0.9211 grams of MTBE ($\text{C}_5\text{H}_{12}\text{O}(\ell)$, 88.15 g/mol) is carried out in a bomb calorimeter. The calorimeter's hardware has a heat capacity of 1.540 kJ/ $^\circ\text{C}$ and is filled with exactly 2.022 L of water. The initial temperature was 26.336 $^\circ\text{C}$. After the combustion, the temperature was 29.849 $^\circ\text{C}$. Analyze this calorimeter data and determine the molar internal energy of combustion (ΔU) for this octane booster.

0.9211g MTBE, MW = 88.15 g/mol

2.022 L H₂O \Rightarrow 2022 g H₂O

$C_{\text{hardware}} = 1.54 \frac{\text{kJ}}{\text{g}}$, $C_{\text{S, H}_2\text{O}} = 4.184 \frac{\text{J}}{\text{g}^\circ\text{C}}$

$$\Delta T = 29.849^\circ\text{C} - 26.336^\circ\text{C} = 3.513^\circ\text{C}$$

$$1) \quad q_{\text{cal}} = \underbrace{m C_s \Delta T}_{\text{H}_2\text{O}} + \underbrace{C \Delta T}_{\text{calorimeter hardware}} \quad \left. \vphantom{q_{\text{cal}}} \right\} \text{sur.}$$

$$(2,022 \text{ g}) \left(0.004184 \frac{\text{kJ}}{\text{g}^\circ\text{C}} \right) (3.513^\circ\text{C})$$

$$+ (1.54 \frac{\text{kJ}}{\text{g}^\circ\text{C}}) (3.513^\circ\text{C})$$

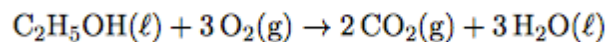
$$= 35.130 \text{ kJ} \Rightarrow \underline{\underline{-35.130 \text{ kJ}}}$$

ΔU per 0.9211g

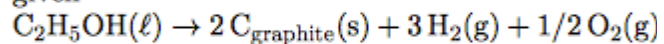
$$3) \quad \frac{-35.130 \text{ kJ}}{\# \text{ moles } 0.01045 \text{ moles}} = \underline{\underline{-3362 \frac{\text{kJ}}{\text{mol}}}}$$

Practice Problems: Hess' Law

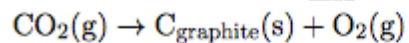
Calculate the standard reaction enthalpy for the reaction



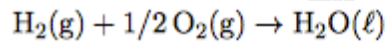
given



$$\Delta H^\circ = 228 \text{ kJ} \cdot \text{mol}^{-1}$$



$$\Delta H^\circ = 394 \text{ kJ} \cdot \text{mol}^{-1}$$



$$\Delta H^\circ = -286 \text{ kJ} \cdot \text{mol}^{-1}$$

1. $-452 \text{ kJ} \cdot \text{mol}^{-1}$
2. $336 \text{ kJ} \cdot \text{mol}^{-1}$
3. $-1,418 \text{ kJ} \cdot \text{mol}^{-1}$
4. $-846 \text{ kJ} \cdot \text{mol}^{-1}$
5. $730 \text{ kJ} \cdot \text{mol}^{-1}$

Practice Problems: Entropy Conceptual

The absolute entropy of a system (S measured in J/K) is related to the number of microstates in that system. Consider the three processes listed below. Which one(s) will result in an increase in the number of microstates in the system?

- I) The temperature of a gas is raised by 3°C .
- II) A fixed amount of gas is allowed to expand to a slightly larger volume.
- III) The total number of gas molecules in a system is reduced to a smaller number.

Practice Problems: Entropy Conceptual

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- I) The temperature of a gas is raised by 3°C .
- II) A fixed amount of gas is allowed to expand to a slightly larger volume.
- III) The total number of gas molecules in a system is reduced to a smaller number.

I and II only

Practice Problems: Entropy Conceptual

When water condenses, what are the signs for q , w , and ΔS_{sys} , respectively?

1. +, +, -
2. -, +, -
3. +, -, +
4. +, -, -
5. +, +, +
6. -, +, +

Practice Problems: Entropy Conceptual

A particular protein folds spontaneously at 25 °C and 1 atm. During this folding, the protein changes conformation from a higher entropy unfolded state to a lower entropy folded state. For this process, ΔH is

1. No way to know
2. $\Delta H < 0$
3. $\Delta H = 0$
4. $\Delta H > 0$

Negative. At least one term has to be “favorable” if spontaneous.
This means $\Delta H < 0$, 2.

Practice Problems: Entropy Conceptual

The conditions for a specific exothermic reaction are such that it is currently non-spontaneous. Which of the following changes to the conditions will likely make the reaction spontaneous?

If it is exothermic and non-spontaneous, ΔS must be negative as well.
This will be spontaneous at low temperatures

Practice Problems: Entropy Calculation

What is the change in entropy (ΔS) for the heating of 20.0 grams of methanol (CH_3OH , liquid) from 34°C to 62°C ?

1. 168.81 J/K
2. 30.42 J/K
3. -30.42 J/K
4. 0 J/K
5. 4.42 J/K
6. 0.22 J/K
7. 1418 J/K

Additional question: what is the heat evolved through this process?

Practice Problems: Entropy of Surroundings

Calculate the ΔS_{surr} for the following reaction at 25°C and 1 atm.



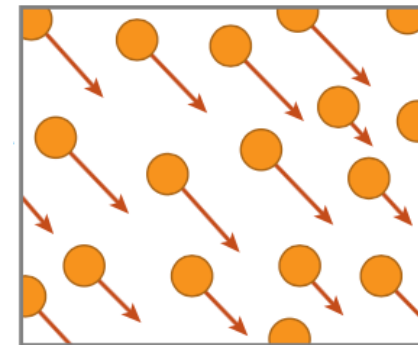
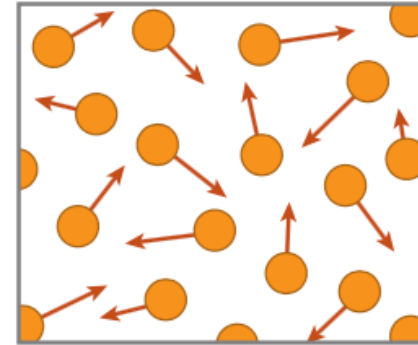
1. -93 J/K
2. +104 J/K
3. -104 J/K
4. +124 J/K
5. +93 J/K
6. -124 J/K

Extra Slides

THERMODYNAMICS

Thermodynamics Basic Definitions

- **Heat (q):** energy derived from random molecular motion (always travels from high T to low T)
- **Work (w):** the energy derived from organized molecular motion (in chemistry, mostly as a result of compression or expansion at constant pressure)
- **Internal Energy (U):** the total energy (potential and kinetic) of a system, the surroundings, or the universe
- **Enthalpy (H):** the heat content of a system (seen most frequently as ΔH ; heat flow at constant pressure, q_p)



Heat Flow: System vs. Surroundings

- We define our environment in thermodynamics as the system and the surroundings. The system is the direct environment of the reaction and the surroundings is everything outside of this.

$q > 0$; endothermic (+), heat is absorbed

$q < 0$; exothermic (-), heat is released

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

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

- Important: we often measure chemical reactions from the perspective of the surroundings. Therefore, when a reaction produces heat, we are actually measuring the change in temperature of the surroundings – not the system

Hess' Law – 3 Calculations

- For any state function, the path does not matter as long as you have final and initial values.
- Therefore, 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)

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

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

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

Hess' Law – Sum of Reactions

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

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

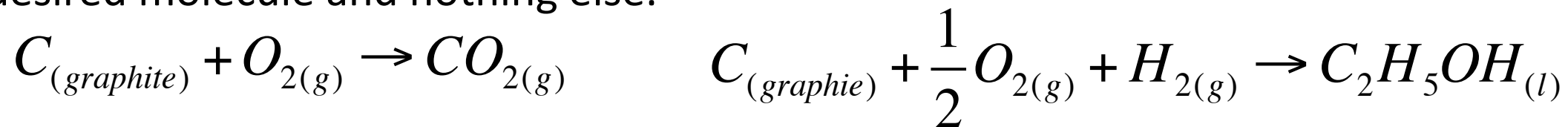
- What you can do to “make” your sum of reactions equal your goal reaction: multiply the entire reaction by a coefficient or fraction (including the enthalpy value associated with that step!) or reverse the entire reaction (changing the sign of the enthalpy value associated with that step).

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.**

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

- 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.

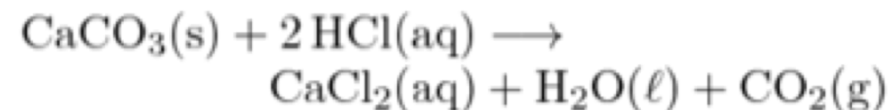


Hess' Law – Formation Reactions Example

- **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.

Hess' Law – Bond Energy Data

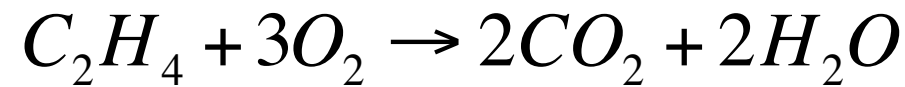
- **Goal: determine the energy difference between all bonds breaking and all bonds forming**
- You must draw a proper Lewis structure, determine what kind of bonds are breaking (reactants) and what kind of bonds are forming (products), and take the difference.

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

- 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

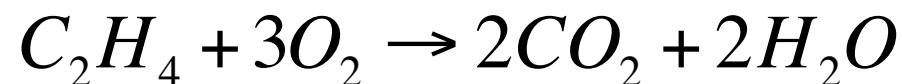
oxygen	
O-H	467
O-O	146
O-C	358
O-N	201
O-F	190
O-Cl	203
O-I	234
O-Si	452

multiple-bond	
C=C	614
C≡C	839
O=O	495
C=O	745
C=O (CO ₂)	799
C≡O	1072
C=S (CS ₂)	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

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
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
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O-Si	452

multiple-bond	
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Conceptual Entropy: Microview

- 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