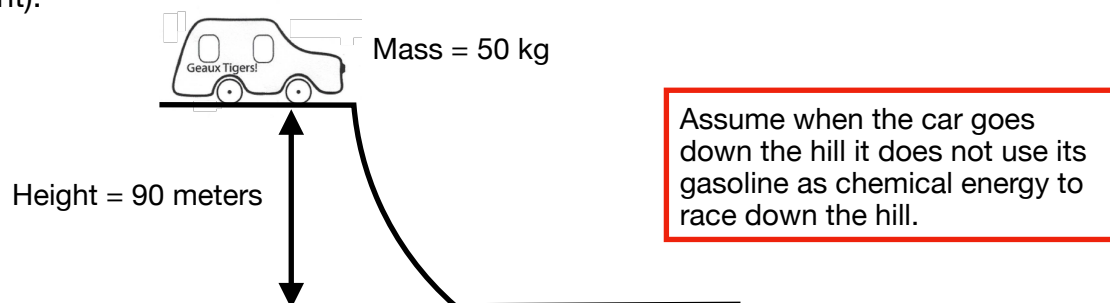


# Thermochemistry

- Thermochemistry is the study of how different forms of energy, such as heat, can influence a chemical reaction to perform some type of work and how different forms of energy are always conserved. **Energy** is defined as the ability to do work. Two types of energy that you are probably familiar with are gravitational potential energy and kinetic energy, which is the energy in motion.

## Energy is Conserved (for non-nuclear RXNs)

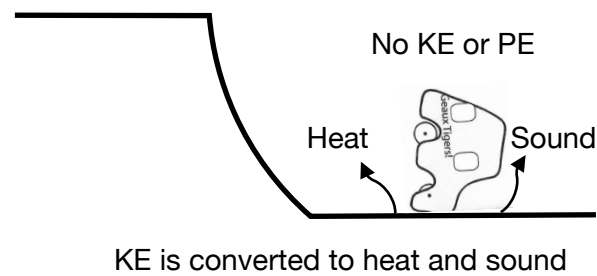
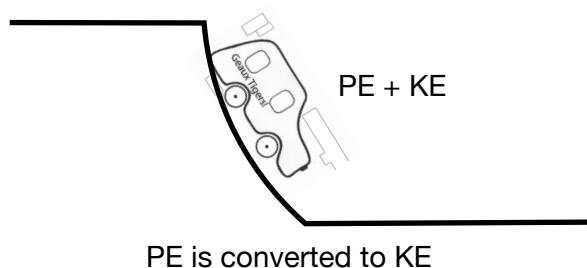
- Let's imagine that we have a car on the top of a hill. When the car is on the top of the hill it has potential energy. **Potential energy** is energy that is considered stored which can be converted to **kinetic energy** which is the energy in motion. For now just focus on how energy can be stored due to being above ground (or raised above some type of reference point).



- To calculate the potential energy you use the equation:  $PE = mgh$  where  $m$  is the mass in kg,  $g$  is the acceleration of gravity (for earth it is  $9.8 \text{ m/s}^2$ ), and  $h$  is the height in meters. The units for energy will be Joules.

$$PE = 50 \times 9.8 \times 90 = 44,100 \text{ J}$$

- When the car rolls down the hill the potential energy will be converted to kinetic energy. To calculate the kinetic energy you use the equation:  $KE = 0.5mv^2$ .
- When the car reaches the bottom of the hill all of the kinetic energy will be converted to other forms of energy like sound and heat.

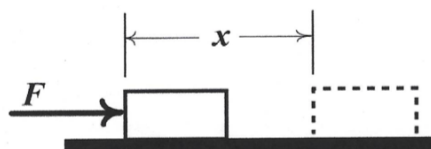


The total amount of energy does not disappear. It is just converted from one form to another.

- Thermodynamics does not divide energy into two forms of kinetic and potential energy. Instead, thermodynamics uses heat and work as the classification of energy.
- The definition of work is a force that moves through a distance.

**TIP:** When looking for work being done on an object look for something moving *against* a force.

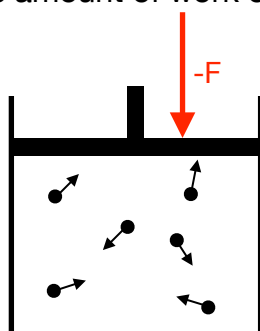
$$w = +Fx$$



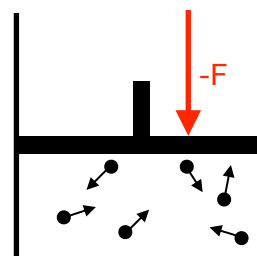
- You will use the equation more when you take physics, but for reference work is measured in Joules, Force is measure in Newtons or  $\text{kg}\cdot\text{m}/\text{s}^2$ , and x is measured in meters.

### Work as a form of energy:

- In chemistry we can refer to gas molecules as the force (due to pressure) that is pushing against a container and if parts of the container expand (or shrinks) then work is being done.
- Let's imagine we have a container with a gas. If we push down on the piston with a force (which will be negative because the force is down) we can preform some amount of work on the gas just like if we push on an object with a force we can do some amount of work on the object.



$$\begin{aligned}
 W &= -F x \\
 P &= \frac{F}{A} & P A &= F \\
 W &= -P A x \\
 W &= -P \Delta V
 \end{aligned}$$

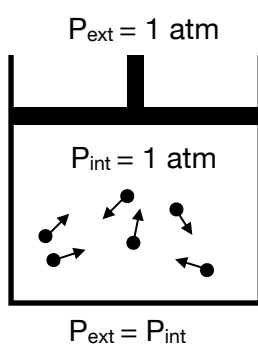


- The force that is applied to the container is the same force that is being applied to the entire surface area of the top lid. From the gas laws equations we know that pressure is equal to force divided by area and solving this equation for force gives  $F = P A$ . Now if we sub that equation into the work equation we get  $W = -P A x$ . The area of the lid times the displacement of the lid is the volume or  $\Delta V = A x$ . Therefore the equation for work is equal to  $W = -P \Delta V$ . Keep in mind that when you use the equation  $W = -P \Delta V$  the *external pressure must remain constant*. If the pressure is not constant you would need calculus to find the amount of work.

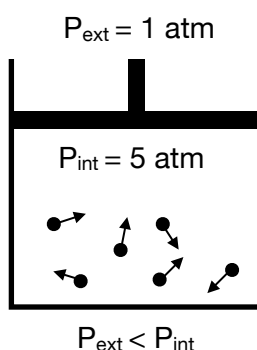
- The units for work using the equation  $W = -P \Delta V$  is an  $\text{atm} \cdot \text{L}$ . When we talk about energy it is often referred to in Joules not  $\text{atm} \cdot \text{L}$ . To convert from  $\text{atm} \cdot \text{L}$  to Joules you use the following:

$$101.3 \text{ J} = 1 \text{ atm} \cdot \text{L}$$

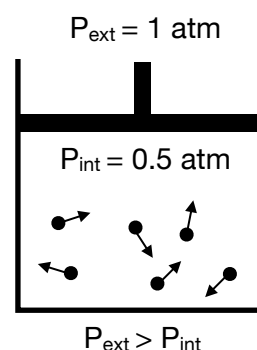
- From now on we will describe the force as pressure just to make things simpler, but know that they mean almost the same thing.
- One major difference between finding the work on an object that is being pushed vs finding the work on a container that has a gas in it is that the container with the gas is going to exert a pressure against the container in the opposite direction that we are applying the pressure to. If the piston is allowed to move freely then the container will expand or shrink if there is a pressure difference between the two. Pressure will always move from high to low.



(The piston will not move)



(The piston will move up and the container will get larger)



(The piston will move down and the container will get smaller)

- It does not matter if the piston is moving up or down the direction of the external force is always negative so work will always be found using the equation  $W = -P \Delta V$ .
- If the piston moves up or down it will not move up or down forever. It will stop moving up or down until the internal pressure is equal to the external pressure. The way the internal pressure changes is when the volume changes, which is from Boyle's Law that says  $P_1 V_1 = P_2 V_2$ .

### Example-1:

A balloon that has a volume of 4L and a pressure of 4 atm expands against an external pressure of 2 atm. How much work in Joules is done on the balloon?

— When the balloon expands its volume changes and so does its pressure. The pressure inside the balloon is higher than the pressure outside the balloon, which is what causes the balloon to expand. The balloon will continue to expand until the external pressure is equal to the internal pressure (or the pressure in the balloon becomes 2 atm to match the external pressure). To find the final volume of the balloon we will use Boyle's Law ( $P_1V_1 = P_2V_2$ )—

$$P_1V_1 = P_2V_2$$

$$(4)(1.5) = (2)V$$

$$V = 3 \text{ L}$$

— If the final volume of the balloon is 3L and the initial volume is 1.5L then we can find the change in volume of the balloon and we know the external pressure is 2 atm then we can find the work done on the balloon.—

$$W = -P \Delta V$$

$$W = -(2)(3 - 1.5)$$

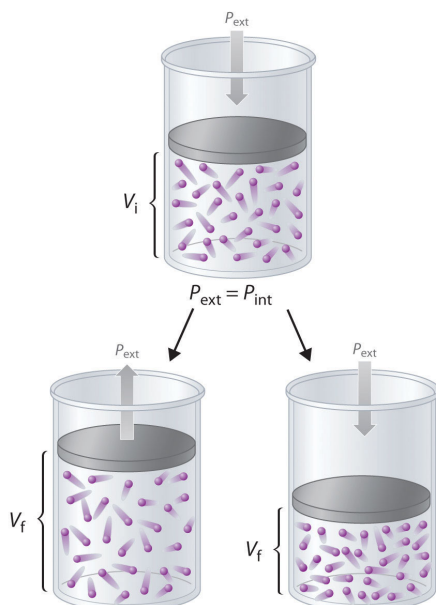
$$W = -(2)(1.5)$$

$$W = -3 \text{ atm} \cdot \text{L}$$

— Now that we know the work done on the balloon is  $-3 \text{ atm} \cdot \text{L}$  we need to convert that to Joules.—

$$-3 \text{ atm} \cdot \text{L} \left( 101.3 \text{ Joule} / 1 \text{ atm} \cdot \text{L} \right) = -303.9 \text{ J}$$

- When the work is negative the container is expanding and when the work is positive the work is positive. When work is negative it is because energy exist the system and is transferred to the surroundings.

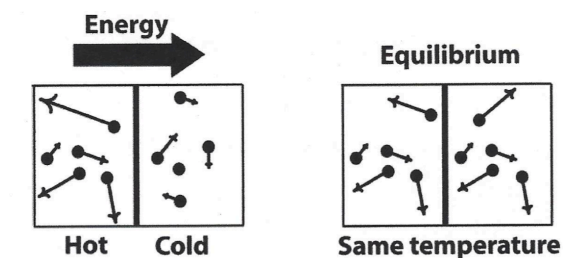


Work is negative  
Change in volume is positive  
System does work on surroundings

Work is positive  
Change in volume is negative  
Surroundings does work on system

## Heat as a form of energy:

- When we talk about heat we are referring to the amount of energy that is able to be transferred through random motions of the molecules. At every temperature (other than 0 Kelvin, which is impossible to get to) molecules are in constant motion as described in the theory of gases.
- When the temperature increases the average kinetic energy of the molecules increases.
- Heat will always travel from a higher temperature to a lower temperature distributing the motion of the molecules from the higher temperature to the lower temperature until equilibrium is established. At equilibrium all of the molecules have the same temperature and the same amount of kinetic energy.



- A system is defined as something of particular interest, such as a chemical reaction. A surroundings is defined as everything else in the universe except the system. There are two different systems you need to know about when talking about heat transferred from one location to another, which are an isolated system and a closed system.
- For an isolated system neither matter nor energy can flow between the system and surroundings. For a closed system energy can flow between the system and surroundings. A chemical reaction can take place but no atoms are gained or lost in the system.



- When heat, energy, or work is gained by the system it is considered positive and when heat, energy, or work leave the system it is considered negative.

*Example-2:*

Determine the signs for heat and work for the following reaction



— To determine the sign for heat we need to determine if heat is being put into the aluminum or if heat leaves. Because the aluminum is being heated up and represents the system, the heat is positive. —

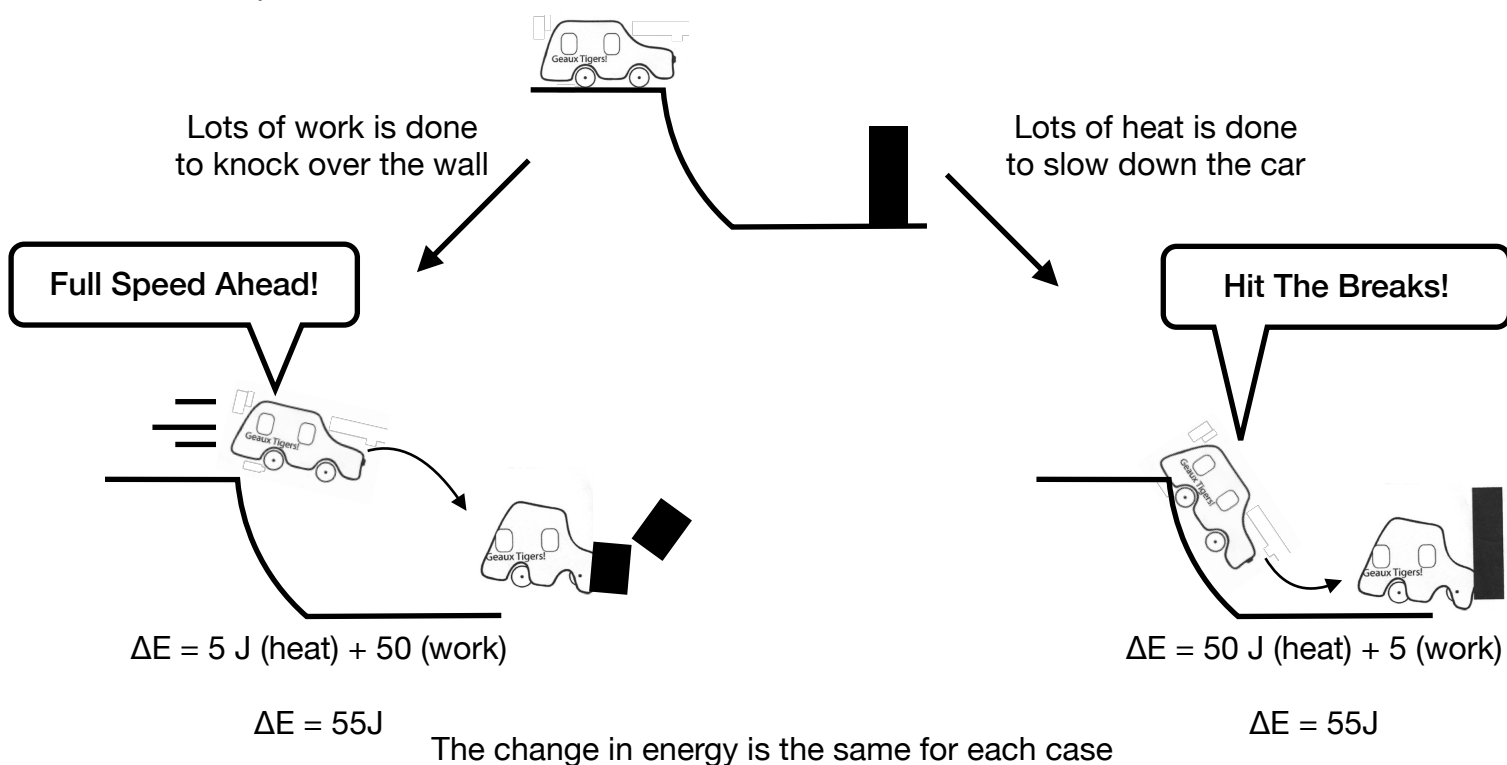
— To determine the sign of the work you need to look to know if the system is expanding or is shrinking. Because the system is expanding due to the aluminum pushing against the surroundings, the work is negative.

The system does work on the surroundings. —

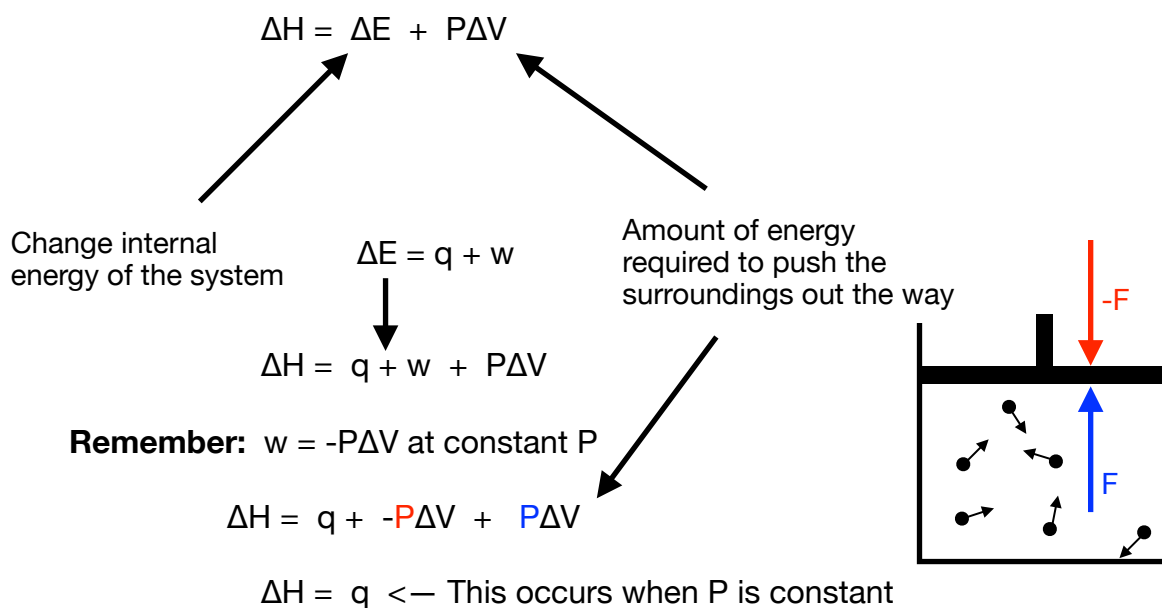
- When a system gains/loses heat and gains/loses work there is a change in energy of the system.

$$\Delta E = q + w$$

- This is the first law of thermodynamics, which states that energy must be conserved. Notice that the  $q$  and  $w$  in the equation do not have delta (change) as part of the equation. This is because both heat and work are path functions.
- Let's go back to the idea of a car being on top of a hill, but this time let's imagine that the car hits a brick wall once it gets to the bottom of the hill. If the car hits the wall once it gets to the bottom it can take one of several paths that have to do with how much heat and work will be generated during this process, but the change in energy for each path will be the same.

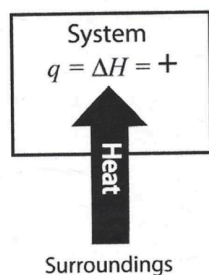


- The fact that the energy does not change regardless of the path taken is because energy is a state function. You can assume the gasoline used in both cases was the same to avoid the idea of taking into account the chemical energy being converted to mechanical energy.
- Notice that we are talking about the change in energy, which means we started with some unknown amount of energy then we added up the heat plus work and we got the change in energy for the entire process.
- When we talk about the energy from a chemical reaction we will talk about the change in energy that takes place to go from reactants to products. This is because the amount of energy that is within a single molecule is very high and impossible/not practical to calculate.
- The total amount of energy lost or gained from a chemical reaction is called enthalpy.

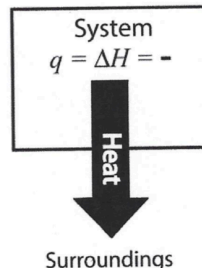


- Most of the time when you get a question about enthalpy it will be at constant pressure. What the  $\Delta H = q$  equation tells us is that if heat enters the system (positive  $q$ ) then the change in enthalpy will also be positive. We call this an endothermic reaction, which is a reaction that requires heat. If the heat is negative then the change in enthalpy will be negative and system will release heat into the surroundings.

Endothermic



Exothermic



- To show if a reaction is endothermic or exothermic you write the change in enthalpy next to the reaction. For example, consider the following reaction:



- Notice that the change in enthalpy is measured in kJ/mol. The per mole part is for one mole of  $\text{O}_2$  or two moles of  $\text{H}_2$  or two moles of  $\text{H}_2\text{O}$ . Therefore, we can use the chemical reaction to write the enthalpy a few different ways as shown below:

(-571.7 kJ/ 1 mol  $\text{O}_2$ ) or (1 mol  $\text{O}_2$  /-571.7 kJ)

(-571.7 kJ/ 2 mol  $\text{H}_2$ ) or (2 mol  $\text{H}_2$  /-571.7 kJ)

(-571.7 kJ/ 2 mol  $\text{H}_2\text{O}$ ) or (2 mol  $\text{H}_2\text{O}$  /-571.7 kJ)

#### *Example-3:*

How much heat is given off when 0.375 moles of hydrogen reacts with hydrogen to form water?



— To solve this question we need to be able to relate the change in enthalpy given in the reaction to the number of moles that we have of hydrogen gas, which is 0.375. The balanced reaction and the change in enthalpy tells us that -571.7 kJ of energy is released for every 2 moles of  $\text{H}_2$ .—

$$0.375 \text{ mole } \text{H}_2 \left( -571.7 \text{ kJ} / 2 \text{ mol } \text{H}_2 \right) = -107.2 \text{ kJ}$$

#### **Bond Energy:**

- Chemical reactions can either give off heat (exothermic) or require heat (endothermic), but where does this heat come from? The energy comes from breaking covalent bonds of the reactants and forming covalent bonds of the products.
- The energy that is stored within a bond is called bond energy and is found from a looking at a table.
- If a reaction requires more energy to break bonds of the reactants than the energy needed to form bonds the reaction will be endothermic, which means we have to put a net effect of energy into the reaction to get it to produce products.

**BEWARE:** All reactions require energy to be put into them to produce product. The difference between a reaction that is endothermic or exothermic is the net effect of how much energy we put in.



$$\Delta H_{\text{rxn}} = \sum (\text{bond energy}_{\text{reactants}}) - \sum (\text{bond energy}_{\text{products}})$$

- Given the following table of bond energy determine the change in enthalpy for the following reaction:

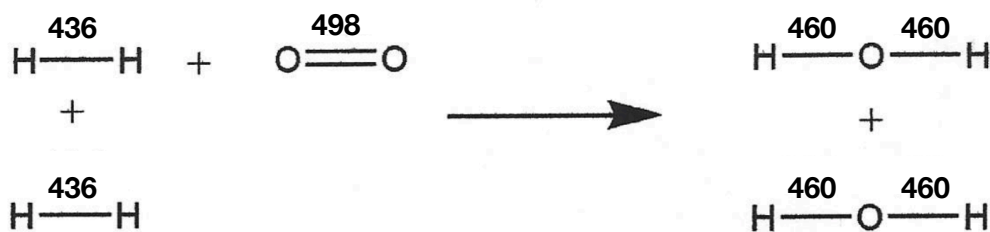


### Bond Energies Chart

H—H	436 <sup>a</sup>	C—H	410	N—H	390	O—H	460	F—F	159 <sup>a</sup>
H—C	410	C—C	350	N—C	300	O—C	350	Cl—Cl	243 <sup>a</sup>
H—F	570 <sup>a</sup>	C—F	450	N—F	270	O—F	180	Br—Br	193 <sup>a</sup>
H—Cl	432 <sup>a</sup>	C—Cl	330	N—Cl	200	O—Cl	200	I—I	151 <sup>a</sup>
H—Br	366 <sup>a</sup>	C—Br	270	N—Br	240	O—Br	210	S—F	310
H—I	298 <sup>a</sup>	C—I	240	N—I	—	O—I	220	S—Cl	250
H—N	390	C—N	300	N—N	240	O—N	200	S—Br	210
H—O	460	C—O	350	N—O	200	O—O	180	S—S	225
H—S	340	C—S	260	N—S	—	O—S	—		
<b>Multiple covalent bonds<sup>b</sup></b>									
C=C	611	C≡C	835	C=O	732	O=O	498 <sup>a</sup>	N≡N	945 <sup>a</sup>

The following chart are estimates only

- To determine the change in enthalpy for the reaction given the bond energies we must first draw out the lewis structure of each chemical involved in the reaction. Keep in mind we must draw out H<sub>2</sub> twice because the balanced chemical reaction tells us that two moles of hydrogen are required to react with one mole of oxygen to produce two moles of water.
- The next step is to write out the bond energies above each bond.



- The bond energy of each bond represents the amount of energy that is stored within a bond. To find the energy released or required by this reaction we will first see how much energy is required to break each of the bonds that are part of the reactants.

$$\sum (\text{bond energy}_{\text{reactants}}) = 436 + 436 + 498 = 1,370 \text{ kJ}$$

- Now we need to find the bond energy that will be released when the covalent bonds between products form.

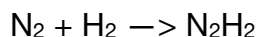
$$\sum (\text{bond energy}_{\text{products}}) = 460 + 460 + 460 + 460 = 1,840 \text{ kJ}$$

$$\Delta H_{\text{rxn}} = \sum (\text{bond energy}_{\text{reactants}}) - \sum (\text{bond energy}_{\text{products}}) = 1,370 - 1,840 = -470 \text{ kJ}$$

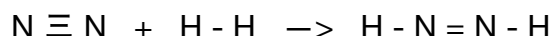
- Because the change in enthalpy is negative it means that less energy was required to break bonds than form bonds and therefore energy will be given off as part of the reaction.

*Example - 4:*

Determine the change in enthalpy for the following reaction given the different bond energies.



— The first thing you want is make sure the reaction is balanced. The next thing you want to do is draw out the lewis structure for each chemical. —

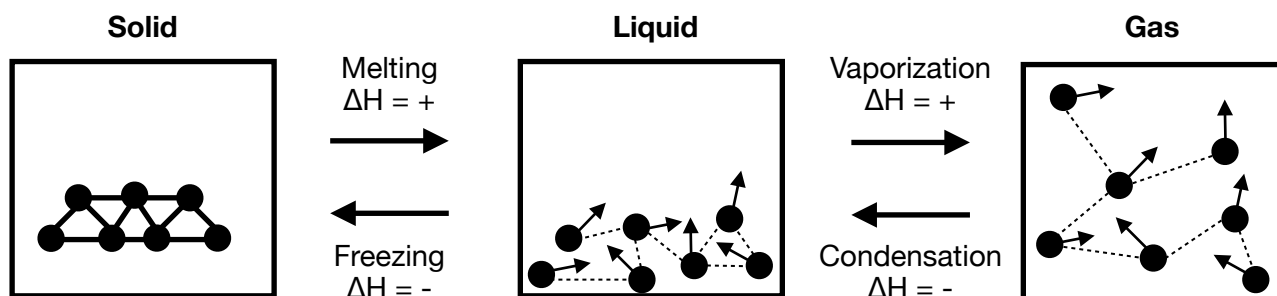


— Now from looking at the bond energy chart write the bond strength above each bond and do the reactants minus products. —

$$[ 945 + 436 ] - [ 390 + 418 + 390 ] = 1,381 - 1,198 = 183$$

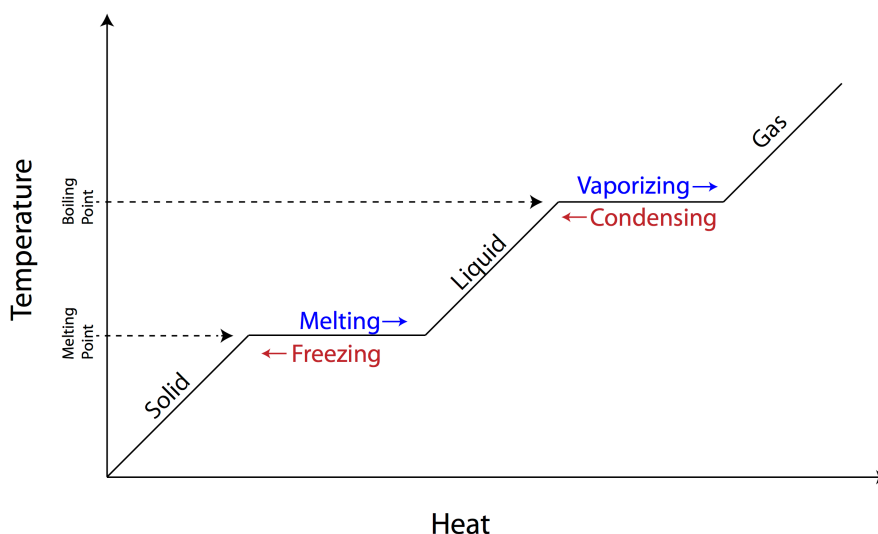
— Notice that the N to N triple bond requires more energy than the N to N double bond. As the bond number increases (the double of bonds between two atoms) the amount of energy stored in that bond also increase. As the bond number increase the length of the bond decreases because the bond is pulled tighter together. —

- When heat is put into a chemical it does not always break covalent bonds, instead sometimes the heat breaks intermolecular bonds (london dispersion, dipole-dipole, H-bonds). Once a significant amount of intermolecular molecular bonds are broken it will cause a phase change. The following illustration shows the signs of the change in enthalpy for different phase transitions.



- Phase transitions that release energy have negative values of  $\Delta H$ .

- There is a relationship between heat and temperature. Temperature is related to the average amount of kinetic energy stored within a chemical. If we make a graph of temperature vs heat we will get the following:



- Notice that when a phase transition happens the amount of energy in the form of heat increases, but the temperature does not increase (where the line is flat). This heat energy goes into breaking the intermolecular bonds.

*Example - 5:*

Determine how much energy is required to transform 12 grams of ice to water at 0 degrees Celsius and 1 atm.  $\Delta H_{\text{fus}} = +6.01 \text{ kJ/mol}$

— The change in enthalpy represents the amount of energy that is needed to transform a solid to a liquid. Notice that the units for the enthalpy are in kJ per mole and we have grams. Therefore, you need to convert 12 grams of  $\text{H}_2\text{O}$  to moles of  $\text{H}_2\text{O}$ .—

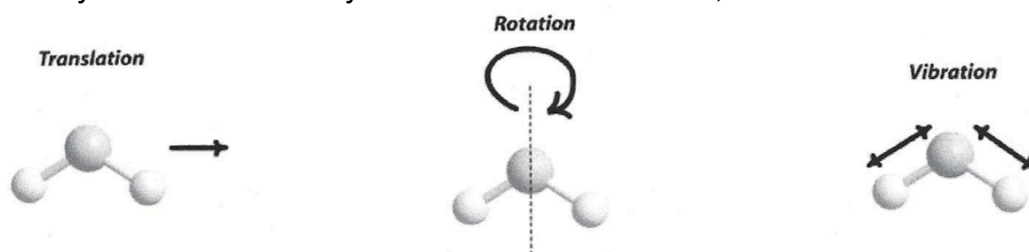
$$(12 / 18) = 0.66 \text{ moles } \text{H}_2\text{O}$$

$$(0.66 \text{ moles } \text{H}_2\text{O}) (6.01 \text{ kJ} / \text{mol}) = 3.96 \text{ kJ}$$

- Notice that the graph of heat vs temperature has two types of lines. The places where the line has a positive slope represents warming or cooling. The equation for this is  $q = m(\text{grams})C_s\Delta T$  or  $q = n(\text{moles})C_m\Delta T$  or  $q = C_s\Delta T$  where  $q$  is the heat,  $C$  is a constant that depends on if the amount is grams or moles,  $m$  is the mass, and  $\Delta T$  is the change in temperature.

Quantity	Description	Units
$C_s$	Specific heat capacity	J / g K
$C_m$	molar heat capacity	J / mol K
$C$	total heat capacity	J / K

- This equation shows how much energy is stored in a chemical as the temperature increases. The higher the temperature, the more energy can be stored, and the more movement the molecules will have. Molecules can store this type of energy in one of three ways. These three ways are translation, rotation, and vibration.



**BEWARE:** Do not confuse the energy that is stored as a result of the temperature increasing with the energy that is stored within a chemical bond.

*Example - 6:*

How much heat is required to raise the temperature of 50g of water from 20C to 30C if  $C_s = 4.184 \text{ J/gK}$

— This question is very simple if you know the correct equation to use. The equation you use is  $q = mC\Delta T$ . —

$$q = mC\Delta T = (50)(4.184)(30 - 20) = 2,092 \text{ J}$$

— Notice that the sign of the heat is positive. This is because in order to raise the temperature of water it will require energy and energy will be put into the system. —

*Example - 7:*

How much heat is required to transform 36g of ice at -10C to water at 40C?

$$\Delta H_{\text{fus}} = +6.01 \text{ kJ/mol}$$

$$C_{s \text{ water}} = 4.184 \text{ J/gK}$$

$$C_{s \text{ ice}} = 2.09 \text{ kJ/gK}$$

— This question can be broken into three parts. The first part involves adding heat to warm the ice to the 0C or warming the ice to the melting point. Then adding heat to break the intermolecular bonds and last to warm the water from 0C to 40C. First lets find the heat required to warm the ice to the melting point. —

$$q = (m)(C_{s \text{ ice}})(\Delta T) = (36)(2.09)(0 - (-10)) = 752.4 \text{ kJ}$$

— We used ( 0 - -10) because the melting point of ice is 0C. We had to warm the ice to get it to the melting point before intermolecular bonds could be broken to cause a phase change. Now lets find how much energy is required to break the intermolecular bonds and melt the ice.—

$$q = ( \Delta H_{\text{fus}} ) ( \text{moles} ) = ( 6.01 ) ( 36 / 18 ) = 12.02 \text{ kJ}$$

**BEWARE:** When you do these types of questions watch your units. The units are determined from the constant that you are using. Sometimes it will requires moles and other times it will require grams. Sometimes the energy will come out in J and other times it will come out in kJ.

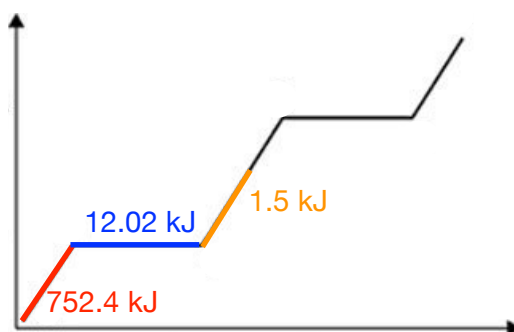
— Now lets find out how much energy is required to warm the water to 40C.—

$$q = ( m ) ( C_{\text{s water}} ) ( \Delta T ) = ( 36 ) ( 4.184 ) ( 0 - -10 ) = 1506.24 \text{ J}$$

$$( 15505.16 \text{ J} ) * ( 1 \text{ kJ} / 1000 \text{ J} ) = 1.5 \text{ kJ}$$

— Now to find the energy needed to take ice at -10 to water at 40C you add all the energies up.—

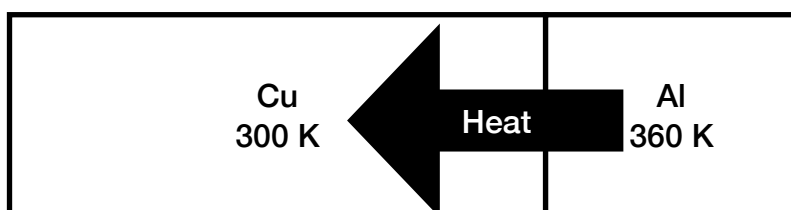
$$\text{Total energy} = 752.4 \text{ kJ} + 12.02 \text{ kJ} + 1.5 \text{ kJ} = 765.92 \text{ kJ}$$



*Example - 8:*

A 10 gram piece of solid copper at 300 K is placed in thermal contact with a 9 gram piece of solid aluminum at 360 K. What is the final temperature of these materials after thermal equilibrium is established?  $C_{\text{Cu}} = 0.387 \text{ J / g K}$   $C_{\text{Al}} = 0.9 \text{ J / g K}$

— This problem has two different metals each at different temperatures and neither metal goes through a phase transition. Therefore, heat will travel from the hotter metal to the colder metal (as we went over on page 5). Because the aluminum is at the higher temperature it will get colder as the copper gets hotter and heat will travel from the aluminum to the copper.—



$$q_{\text{Cu}} = - q_{\text{Al}}$$

$$( m_{\text{Cu}} ) ( C_{\text{Cu}} ) ( \Delta T_{\text{Cu}} ) = - ( m_{\text{Al}} ) ( C_{\text{Al}} ) ( \Delta T_{\text{Al}} )$$

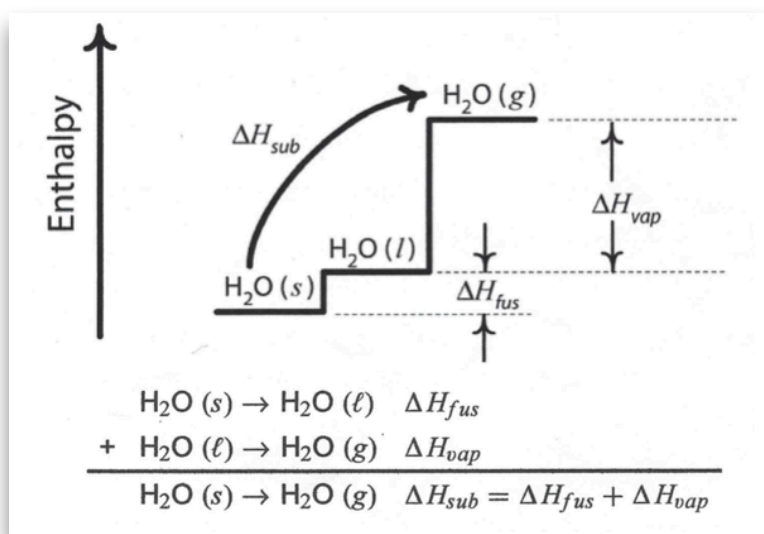
— Each of the metals share the same final temperature so you should get the following equation to solve for T final. —

$$T_f = [ ( 3.87 ) ( 300 ) + ( 8.1 ) ( 360 ) ] / [ ( 8.1 + 3.87 ) ] = 340.6 \text{ K}$$

**BEWARE:** When you do these types of questions watch the negative sign, which indicates if heat is entering or existing the metal. The amount of heat gained by one metals will be acquired by the other metal, therefore the sign of heat will be opposite for each metal.

### Hess's Law:

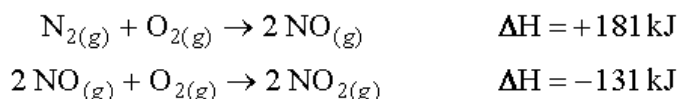
- We know from the gas notes that a phase transition can occur from a solid to a gas and skip the liquid phase if the pressure and temperature are just right.
- If we know the amount of energy needed to break intermolecular bonds in a solid phase to go to a liquid phase and we know how much energy is needed to break the intermolecular bonds in a liquid phase to go to a gas phase then we can find the energy needed to break the intermolecular bonds of the solid phase to go to the gas phase.



- If two chemicals are on opposite sides they will cancel out and if two chemical are on the same side (both reactants or both products) they will add.
- If we need to change the number of stoichiometry in a reaction we can multiple the entire reaction by some multiple which includes the enthalpy. If we want to increase the stoichiometry then you would multiple by a whole number ( 2, 3, 4 etc..) and if you want to decrease the stoichiometry you would multiple by a fraction ( 1/2, 1/3, 1/4 ect..)
- If you want to reverse the reaction you change the sign of the change in enthalpy.

*Example - 9:*

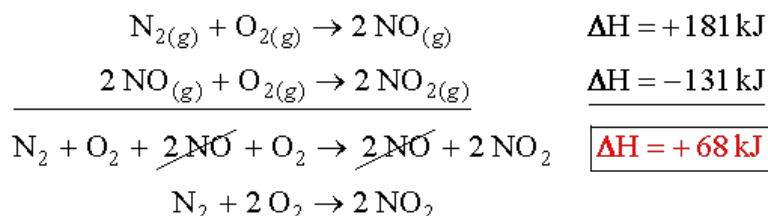
Find the change in enthalpy of  $\text{N}_2 + 2\text{O}_2 \rightarrow 2\text{NO}_2$  given the following information:



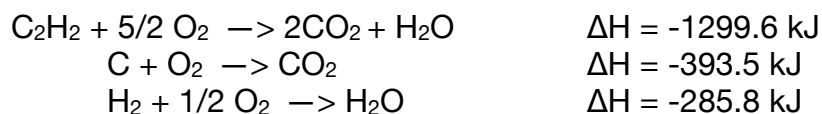
— If you look at the reaction we are trying to find the change in enthalpy for there is no NO molecule. So if we are given the two reaction that have NO we need to make sure the two NO's are on opposite sides of each reaction so they cancel out. —

— Because the reaction we are trying to make has two oxygens and the reactions we are given each have one oxygen we need to make sure those are on the same side so those will add and on the reactant side of the reaction. —

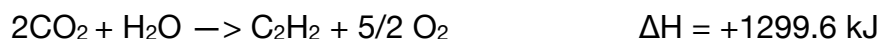
— Once we get everything the way we want it we just add the change in enthalpy together. —

*Example - 10:*

Find the change in enthalpy of  $2\text{C} + \text{H}_2 \rightarrow \text{C}_2\text{H}_2$  given the following information:



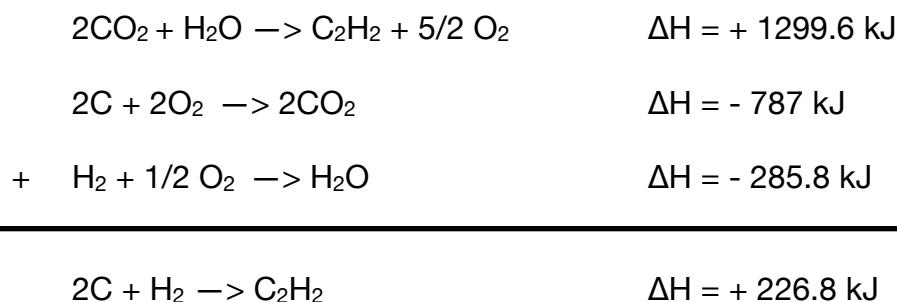
— If you look at the product we are trying to make (  $\text{C}_2\text{H}_2$  ) and if you look at the given reactions we have to work with  $\text{C}_2\text{H}_2$  is in the first reaction and is a reactant so we need to reverse the reaction to make  $\text{C}_2\text{H}_2$  a product. —



— If you look the reactants we are trying to make we need 2 carbons and if you look at the given reaction we have to work with you will notice in the second reaction we only have 1 carbon. So we need to multiply the second reaction by 2. —

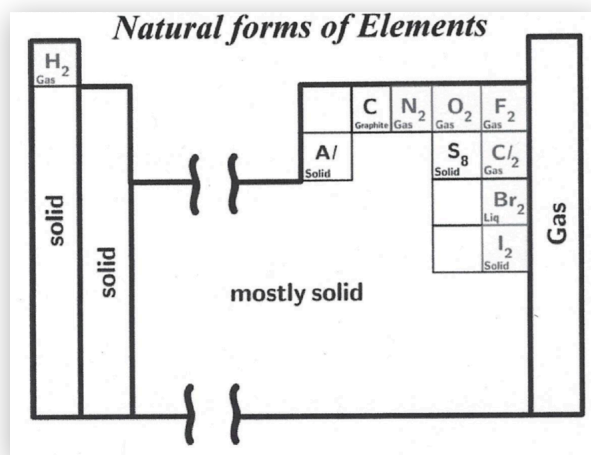


— Now all we need to do is add up the change in enthalpy for each reaction. —

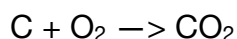


### Heat of Formation:

- Formation reaction are chemical reactions that are written to show how a single molecule is put together from individual atoms in their natural form (including their phase).
- Natural form atoms include all the diatomic elements such as N, H, F, O, I, Cl, Br. Other elements in their natural form include  $\text{S}_8$ ,  $\text{P}_4$ , and Carbon has a natural form of solid graphite over solid diamond. The difference between graphite and diamond is the way the lattice energy is structured. Turning graphite into diamond required a tremendous amount of pressure.



- If you want to write out the formation reaction for  $\text{CO}_2$  you would write  $\text{CO}_2$  as a product then separate each atom (including polyatomic ions if there are any). Next make sure that only mole of a product is formed. For a formation reaction you can have fractions for the stoichiometry of reactants.

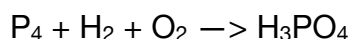




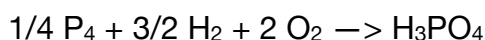
**Example - 11:**

Write the formation reaction for  $\text{H}_3\text{PO}_4$ .

— The first thing we will do is separate each element out and place those on the reactant side and put  $\text{H}_3\text{PO}_4$  on the product side. Remember that hydrogen and oxygen are diatomic. —



— The next step is to balance the reaction making sure that the product only has a one for the stoichiometry. —



- If you are given a set of formation reactions with their change in enthalpy you can find the change in enthalpy for a reaction by doing the change in enthalpy of the products minus the change in enthalpy of the reactants multiplied by the power of the stoichiometry.

$$\Delta H_{\text{rxn}} = \sum (n \Delta H_{\text{f}}^{\circ} \text{ products}) - \sum (n \Delta H_{\text{f}}^{\circ} \text{ reactants})$$

- The “o” symbol stands for “standard conditions,” which is 1 atm for pressure and 25 degrees C or 298K.

**BEWARE:** This equation has products minus reactants. The bond energy equation has reactants minus products.

**Formation Enthalpy**

$\text{C}_2\text{H}_6(\text{g})$	-26.7	$\text{HCl}(\text{g})$	-92.30
$\text{NH}_3(\text{g})$	-46.19	$\text{HF}(\text{g})$	-268.6
$\text{C}_6\text{H}_6(\text{l})$	49.04	$\text{HI}(\text{g})$	25.9
$\text{CaCO}_3(\text{s})$	-1207.1	$\text{CH}_4(\text{g})$	-74.85
$\text{CaO}(\text{s})$	-635.5	$\text{CH}_3\text{OH}(\text{l})$	-238.6
$\text{CO}_2(\text{g})$	-393.5	$\text{C}_3\text{H}_8(\text{g})$	-103.85
$\text{CO}(\text{g})$	-110.5	$\text{AgCl}(\text{s})$	-127.0
$\text{C}(\text{s})$	1.88	$\text{NaHCO}_3(\text{s})$	-947.7
$\text{C}_2\text{H}_2(\text{g})$	-84.68	$\text{Na}_2\text{CO}_3(\text{s})$	-1130.9
$\text{C}_2\text{H}_5\text{OH}(\text{l})$	-277.7	$\text{NaCl}(\text{s})$	-411.0
$\text{C}_2\text{H}_4(\text{g})$	52.30	$\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$	-2221
$\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	-1260	$\text{H}_2\text{O}(\text{l})$	-285.8
$\text{HBr}(\text{g})$	236.23	$\text{H}_2\text{O}(\text{g})$	-241.8

- Lets find the change in enthalpy for the reaction  $2 \text{B}_5\text{H}_9 + 12 \text{O}_2 \rightarrow 5 \text{B}_2\text{O}_3 + 9 \text{H}_2\text{O}$
- First we need to look up the enthalpy formation values for each of the compounds. These are shown in the following table:

Compound	$\Delta H_{\text{f}}^{\circ}$ (kJ/mol)
$\text{B}_5\text{H}_9(\text{g})$	73.2
$\text{B}_2\text{O}_3(\text{g})$	-1272.77
$\text{O}_2(\text{g})$	0
$\text{H}_2\text{O}(\text{g})$	-241.82

$$\Delta H^{\circ} = \sum n \Delta H_{\text{f}}^{\circ} \text{ products} - \sum m \Delta H_{\text{f}}^{\circ} \text{ reactants}$$

$$\Delta H^{\circ} = \left[ \left( 5 \text{ mol } \text{B}_2\text{O}_3 \times \frac{-1272.77 \text{ kJ}}{\text{mol}} \right) + \left( 9 \text{ mol } \text{H}_2\text{O} \times \frac{-241.82 \text{ kJ}}{\text{mol}} \right) \right] - \left[ \left( 2 \text{ mol } \text{B}_5\text{H}_9 \times \frac{73.2 \text{ kJ}}{\text{mol}} \right) + \left( 12 \text{ mol } \text{O}_2 \times \frac{0 \text{ kJ}}{\text{mol}} \right) \right]$$

$$\Delta H^{\circ} = (-6363.85 + -2176.38) - 146.4$$

$$\Delta H^{\circ} = -8686.6 \text{ kJ}$$

- The change in enthalpy for the formation of an element in its natural form will always be zero because the reactant will be the same as the product. For example, the formation of  $O_2$  is the following:

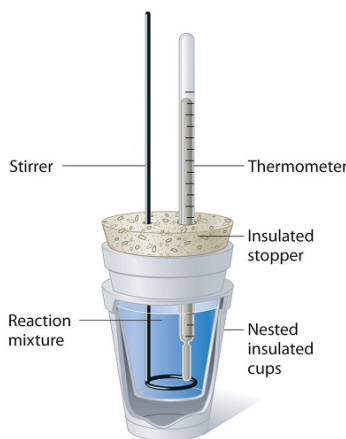


### Coffee Cup Calorimeter (constant pressure):

- If we want to determine the amount of heat that a reaction releases or absorbs we can use a lab technique called coffee cup calorimeter. The idea behind a coffee cup calorimeter combines the idea that chemical reaction either release energy or absorb energy and the idea that water (typically water is used but can be another liquid) can release or absorb energy.
- This experiment uses a coffee cup because a styrofoam coffee cup is a good insulator of heat. If a chemical reaction releases heat that same amount of heat will be absorbed by the water or if a chemical reaction absorbs heat that same amount of heat will be released from the water. Because of this the sign of heat for the reaction and the water will have opposite signs.

$$q_{\text{rxn}} = -q_{\text{water}}$$

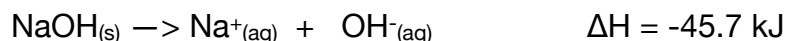
- If you look back at example-3 we covered how to find how to calculate how much heat a reaction would release and as long as the water in the calorimeter does not go through a phase transition you can use the warming/cooling equation for the water, which is  $q = mC\Delta T$ . However, if you look back at example-3 we made one assumption to find the heat of a reaction, we assumed the reaction occurred at constant pressure. This allowed us to set the heat equal to  $\Delta H$ .
- A coffee cup calorimeter occurs at constant pressure because the lid on the container is not sealed tight. The following is a picture of what a coffee cup calorimeter looks like:



- A common reaction mixture that we could use a coffee cup calorimeter for is when NaOH dissolves in water. When NaOH dissolves in water it will release heat and if we use a coffee cup calorimeter that heat will be equal to  $\Delta H$  for the reaction.

*Example - 12:*

9 grams of NaOH is dissolved in 100 grams of water at 25C and 1 atm in a coffee cup calorimeter. What is the final temperature of the solution?  $C_{\text{soln}} = 4.184 \text{ J/gC}$



— When doing a calorimeter question first figure out what is releasing heat and what is absorbing heat. From looking at the reaction the change in enthalpy is negative so it will release energy into the calorimeter. —

$$q_{\text{rxn}} = -q_{\text{cal}}$$

— Now we need to figure out how much heat is being released by the reaction. This is very similar to Example-3. —

$$q_{\text{rxn}} = (\Delta H) (n) = (-45.7 / 1 \text{ mole NaOH}) (9 \text{ grams NaOH} / 40) = -10.28 \text{ kJ}$$

— Now we need to figure out how much heat will be absorbed by the calorimeter. This part of the question is similar to example-6. —

$$q_{\text{cal}} = (m) (C_{\text{soln}}) (\Delta T) = (109) (4.184) (\Delta T) = 456 \Delta T \text{ J or } 0.456 \Delta T \text{ kJ}$$

— For a coffee cup calorimeter the water is not separate from the reaction. So the mass of the calorimeter is equal to the mass of the water plus the mass of NaOH that we put into the cup. The reason the heat capacity of the solution is the same as that of water is because the majority of the solution is water, so we can assume the heat capacity of the solution and the heat capacity of water is the same. Now we need to set the two equations equal to each other. —

$$q_{\text{rxn}} = -q_{\text{cal}}$$

$$-10.28 \text{ kJ} = -0.456 \Delta T \text{ kJ}$$

— Solving this equation for  $\Delta T$  gives 21.15C for the change in temperature of the solution. If the initial temperature is 25 C and the change in temperature is 21.15C then we can find the final temperature of the solution. —

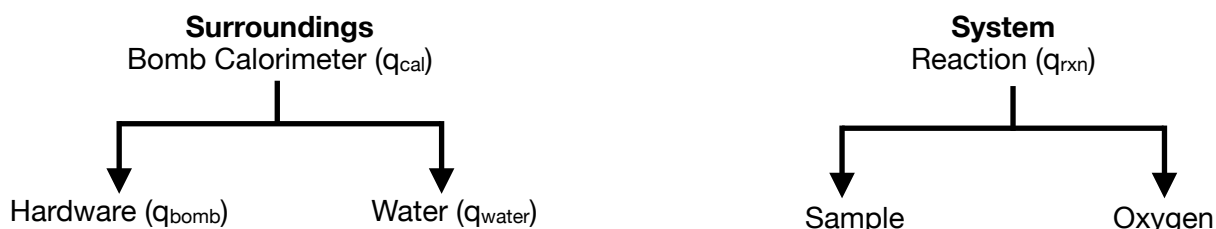
$$\Delta T = T_{\text{final}} - T_{\text{initial}}$$

$$22.54 = T_{\text{final}} - 25$$

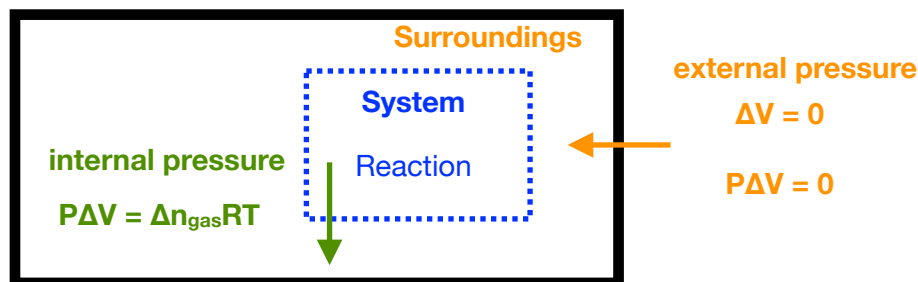
$$T_{\text{final}} = 47.54 \text{ C}$$

### Bomb Calorimeter (constant volume):

- A bomb calorimeter is another type of calorimeter lab technique but it occurs in a sealed container so the external pressure is not the same as the internal pressure. For a coffee cup calorimeter the surroundings includes everything outside the calorimeter, but for a bomb calorimeter the surroundings includes everything inside the calorimeter (the water and hardware) except the reaction. The system for a bomb calorimeter is the reaction that takes place inside the calorimeter, which includes the sample and usually oxygen because the reaction that takes place inside a bomb calorimeter is usually a combustion reaction.



- Because the calorimeter is sealed the volume can not change so the work done on the calorimeter is equal to zero and the only heat that can enter or exist the calorimeter comes from the chemical reaction.
- When we talk about the internal energy of the reaction that takes place inside the bomb calorimeter we are not talking about the internal energy of the calorimeter.



- We can set up an equation to find the change in enthalpy for the reaction by using the following equation

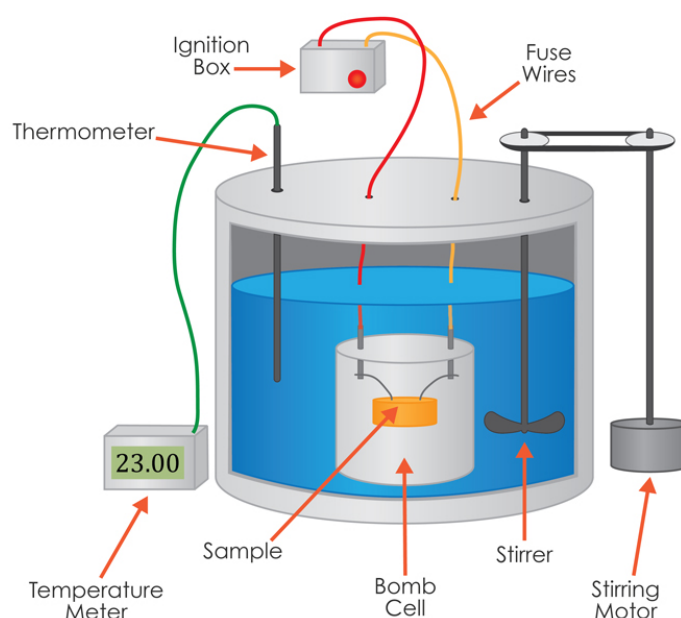
$$\begin{aligned}\Delta H &= \Delta E + P\Delta V & \Delta H &= q_{\text{rxn}} + w + P\Delta V \\ \Delta H &= q_{\text{rxn}} + -P\Delta V + P\Delta V \\ \Delta E &= q_{\text{rxn}} + -P\Delta V & \text{For a bomb cal these are zero.} \\ \Delta H &= q_{\text{rxn}} + P\Delta V\end{aligned}$$

$$\begin{aligned}\Delta E &= q_{\text{rxn}} \\ \Delta H &= q_{\text{rxn}} + \Delta nRT\end{aligned}$$

- Because the volume can not change inside a bomb calorimeter the pressure that builds up from the chemical reaction can produce a lot of pressure and the change in volume for the reaction is the result of create more moles of gas.

**BEWARE:** When we talk about a constant volume calorimeter or a bomb calorimeter we are talking about the container having a constant volume not the volume of the reaction being constant. When we talk about a coffee cup calorimeter we are talking about the internal and external pressuring being constant.

- So if a bomb calorimeter is completely closed off how do we get supply the energy necessary to get the reaction to start? We use an ignition box that has wires that run into the sample. A picture of a bomb calorimeter is show below.



**TIP:** The good thing is that most questions about calorimeters are straight forward. If you are given a calorimeter question keep track of where the heating is flowing. It should look something like this:

$$q_{\text{cal}} = -q_{\text{rxn}}$$

If you are given a bomb calorimeter you will likely not add the masses together like you would for a coffee cup calorimeter. The heat generated from a reaction for a bomb calorimeter will be equal to the change in internal energy and the heat generated from a coffee cup calorimeter will be equal to the change in enthalpy. You can still find the change in enthalpy for a bomb calorimeter you just need the change in moles of gas from the reaction.

#### For a Bomb Calorimeter

$$\Delta E = q_{\text{rxn}}$$

$$\Delta H = q_{\text{rxn}} + \Delta n_{\text{gas}}RT \quad (R = 8.314)$$

#### For a Coffee Cup Calorimeter

$$\Delta H = q_{\text{rxn}}$$

**Example - 13:**

1.5 grams of  $C_6H_6$  undergoes combustion in a constant volume calorimeter. The temperature rise of the calorimeter is  $2.7^\circ C$  and the total heat capacity of the calorimeter is  $23.24 \text{ kJ/C}$ . Calculate the molar energy of reaction.

— When the question says a calorimeter has a constant volume it is a bomb calorimeter so the change in energy of the reaction will be equal to the heat of the reaction. —

$$q_{\text{rxn}} = -q_{\text{cal}}$$

$$q_{\text{rxn}} = \Delta E_{\text{rxn}} \qquad q_{\text{cal}} = C\Delta T$$

$$\Delta E_{\text{rxn}} = -C\Delta T$$

— Because we are looking for the molar energy we need the amount of energy to come out in kJ per mole, so we need to multiple the change in energy by the moles of the reaction. Next we just need to plug in the numbers the question gives us and solve for the change in energy. —

$$\Delta E_{\text{rxn}} n = -C\Delta T$$

$$(\Delta E_{\text{rxn}}) (1.5 / 78) = - (23.24) (2.7)$$

$$\Delta E_{\text{rxn}} = 3,302 \text{ kJ/mol}$$

**Path and State Functions:**

- The value of a path functions depends on how the process is carried out. The other type of function is a state function.
- At the beginning of the section we went over the difference between potential energy, kinetic energy, heat, and work. Remember that it didn't matter the path a system took the change in the amount of energy stayed the same, but the heat and work could change. This is because heat and work are path functions and the change in energy is a state function. Time is another example of a path function.
- Other state functions include the change in enthalpy, temperature, pressure, volume, mass, gibbs free energy (discussed later), change in entropy of the system (discussed later).