

McGill **CHEM 120**

Winter 2025, Chapter 3 Notes



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3. Thermochemistry (Ch 9)

3.1 Introduction to Thermodynamics

3.1.1

Key Terms

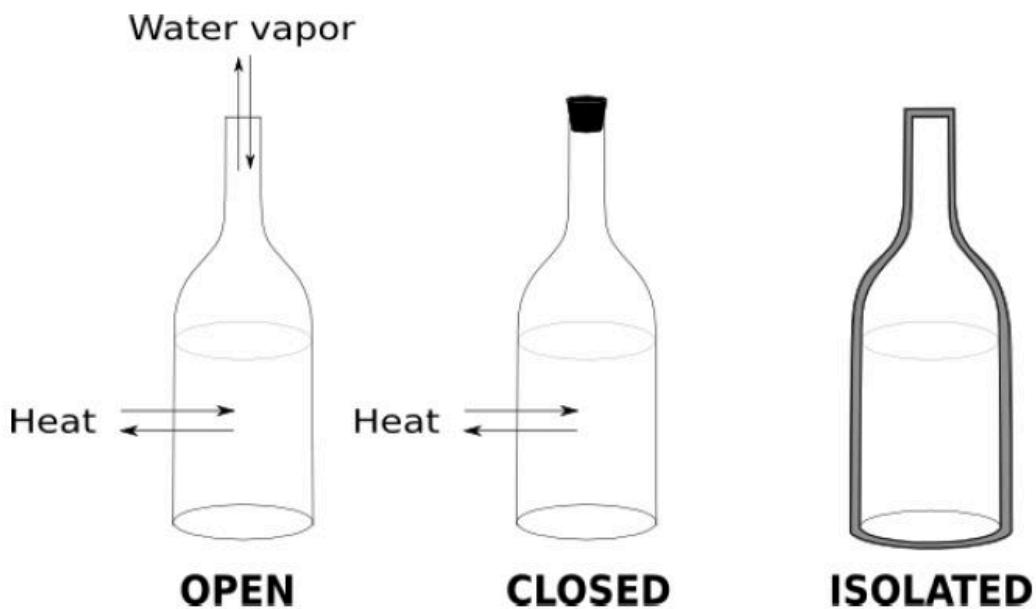
The following lesson is low yield in terms of exams. We'll just focus on **understanding**.💡

System Vs Surroundings

System-reactants and products that are part of the **chemical reaction**

Term	Definition
System	The collection of matter that is under consideration
Surroundings	Everything that is not a part of the system
Universe	System + Surroundings
Open system	Can exchange matter and energy with surroundings
Closed system	Can exchange only energy with surroundings
Isolated system	Cannot exchange matter or energy with surroundings (adiabatic, $q = 0$)

Open Vs Closed Vs Isolated Systems



Examples:

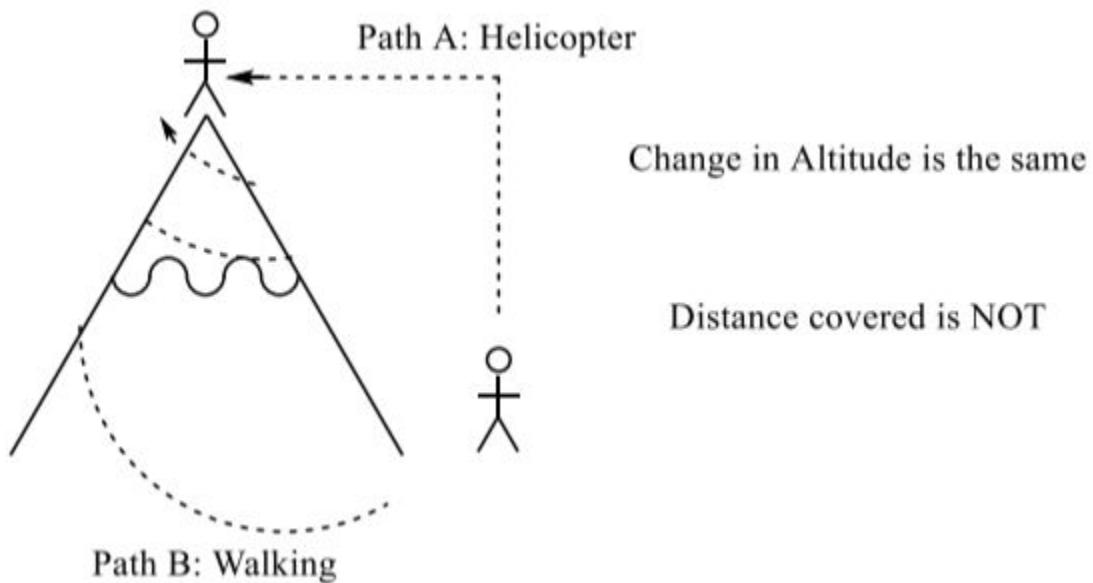
- open system → cup of coffee
- closed system → bottle of pop
- isolated system → perfect thermos

State Variables

The following lesson is low yield in terms of exams. We'll just focus on **understanding**.💡

State variable (aka state function): is a variable that depends only on the current state of a system, NOT on the path taken to that state.

Example:



Is the distance travelled or change in altitude a state function?

Example: State Variables

Which of the following variables are state variables? Label each as yes or no.

a) mass _____

b) temperature _____

c) work _____

d) pressure _____

e) volume _____

f) density _____

Extensive vs. Intensive Properties

The following lesson is **low yield** in terms of exams. We'll just focus on **understanding**. 

Extensive properties: depend on the **extent (or amount)** of a substance

Examples: mass, volume, amount of heat released in a combustion reaction

Intensive properties: does not depend on the amount of substance

Examples: melting point, boiling point, density

Think* no matter how much water you are boiling in a pot, water will always boil at 100°C and melt at 0°C!

When we take a ratio of 2 extensive properties what do we get?

Example: mass/volume=density

Additional Terminology

Reversible Process: The system is at equilibrium (and the reaction can go in either direction).

Example: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

Irreversible Process: The system is not at equilibrium and proceeds in one direction only. This reaction is spontaneous in the forward direction.

Example: $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$ (combustion reaction)

Spontaneous Process: An irreversible process that has a predetermined direction.

Example: An egg shell breaks during birth

Isothermal: There is no change in temperature for the system

$$\Delta T = 0$$

For Ideal Gases: $\Delta U = 0, \Delta H = 0$

Isobaric: There is no change in pressure

$$\Delta p = 0$$

Isochoric: There is no change in volume

$$\Delta V = 0$$

Adiabatic: No heat exchange (no heat enters or leaves the system)

$$q = 0$$

Exothermic: A Process in which heat is _____ (absorbed/released) to the _____
(system/surroundings)

$$q < 0$$

Endothermic: A Process in which heat is _____ (absorbed/released) into the the _____
(system/surroundings)

$$q > 0$$

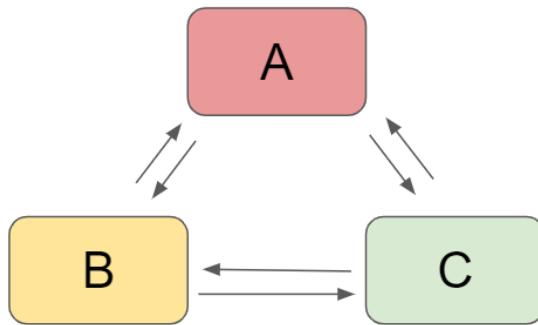
Standard Conditions: Pressure of all gases is 1 atm, all solutions have 1M concentration, and temperature is 298K (25C). This is denoted as $H^\circ S^\circ G^\circ$ etc.

3.2

0th Law of Thermodynamics

3.2.1

0th Law of Thermodynamics



- **0th law:** If a body, A, is in thermal equilibrium with a second body, B, and that body is in thermal equilibrium with a third body, C, then A and C are in **thermal equilibrium**.
- If two bodies/systems are in **thermal equilibrium** with one another, it means they are at the **same temperature!**

What is the difference between thermal equilibrium and temperature?

Thermal equilibrium: When two substances are in **physical contact** and **exchange no heat energy** with one another.

Temperature: A measure of the **average kinetic energy** of the particles in a sample of matter

Increasing the temperature means that average kinetic energy of the particles will (increase/decrease)

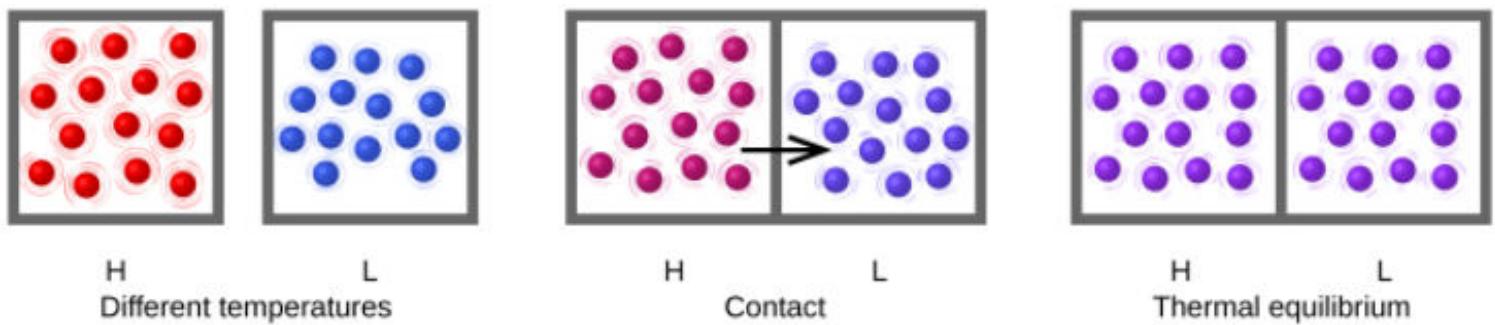


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3.3 The 1st Law of Thermodynamics and Work

3.3.1

The 1st Law of Thermodynamics

- **1st Law of Thermodynamics:** The energy of an isolated system is constant, $\Delta E = 0$.
 - Sometimes this is re-worded as "energy cannot be created or destroyed".
- E is very difficult to measure so instead we measure changes in E indirectly
- The change in energy can be considered as a sum of heat and work done on and by the system.
 ΔE is a state function, q and w are not.

$$\boxed{\Delta E = q + w}$$

ΔE is the change in Energy

q is heat (in J)

w is work (in J)

WIZE TIP

Some profs write **ΔE** and others write **ΔU** . They mean the same thing! Both are referring to the internal energy of the system!

From the 1st law of thermodynamics we can see that change in energy for system and surroundings must be equal in magnitude because the **change in internal energy of the universe must be equal to zero.**



$$\Delta E_{univ} = \Delta E_{sys} + \Delta E_{surr} = 0$$

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

Examples:

- If the system gains 5 J of energy, the surroundings (gains/loses) _____ 5 J of energy.
- If the system loses 10 J of energy, the surroundings (gains/loses) _____ 10 J of energy.

Internal Energy of Ideal Gases

The internal energy of an ideal gas is only dependent on temperature:

$$\Delta E(T)$$

So for any Isothermal process involving an ideal gas,

$$\Delta E = 0$$

Signs of Heat and Work & Calculating Work

Recall the equation for the first law of thermodynamics:

$$\Delta E = q + w$$

ΔE is the change in Energy

q is heat (in J)

w is work (in J)

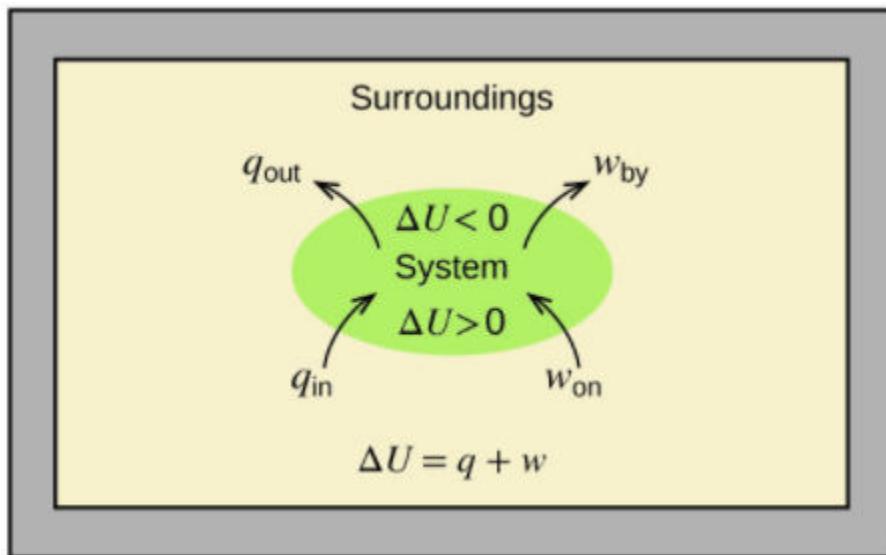


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In chemistry **everything is with respect to the system** so the following conventions exist:

WIZE CONCEPT

w > 0 if the surroundings do work on the system

w < 0 if the system does work on the surroundings

q > 0 if heat moves from the surroundings to the system

q < 0 if heat moves from the system to the surroundings

When the external pressure is constant we can **calculate work** using the following equation:

$$w = -P_{ex}\Delta V$$

w =work (J)

P_{ext} =constant external pressure (in kPa)

$\Delta V=V_f-V_i$ (in L)

Example: Work Heat and Internal Energy of an Ideal Gas

20 L of an ideal gas isothermally expands to 40 L against a constant external pressure of 1 atm. Calculate w , q , and ΔE for this process.

3.3.4

A system composed of 4.50 L of N₂ in a cylinder expands against an external pressure of 300 kPa until its volume is 6.30 L.

- a. What is the value of w for this process?
- b. What would the value of w be if the external pressure was 0 kPa?

a)

b)

3.3.5

Fill in the following blanks!

How to fill in this table:

For the first column we have ΔU . Your options are temperature is constant, temperature increases, or temperature decreases

For the second column we have q . Your options are no heat is exchanged, heat enters the gas, or heat exits the gas

For the third column we have w . Your options are the volume is constant, the gas is compressed, or the gas expands.

	ΔU (Change in Internal Energy):	q (heat):	w (work):
Is positive when...	_____	_____	_____
Is negative when...	_____	_____	_____
Is 0 when...	_____	_____	_____

3.4 Relating Work and the Ideal Gas Law

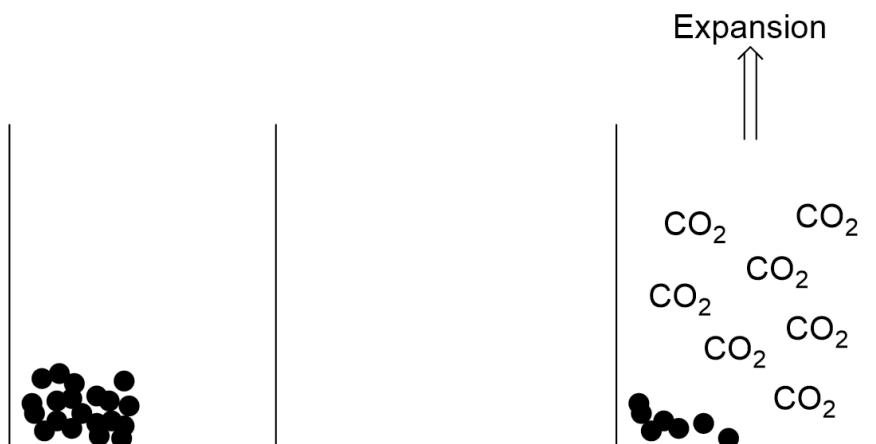
3.4.1

Expansion Due to Chemical Reaction

When a chemical reaction takes place where the number of moles of gas changes, expansion can occur. Typically this would happen with a reaction in a balloon, but this also happens for a reaction happening in an open vessel.

Example:

Calcium carbonate decomposes into calcium oxide and carbon dioxide as shown below. If 12g of calcium carbonate are placed into a vessel open to the atmosphere at room temperature and the reaction takes place, how much work is done on/by the system?



The flask is open to the atmosphere so the expansion is taking place against a constant external pressure of 1 atm, however we don't know the change in volume.

$$w = -P_{ex}\Delta V$$

Using the Ideal gas law,

$$V = \frac{nRT}{P} \quad \text{and} \quad \Delta V = \frac{\Delta nRT}{P}$$

substituting we get,

$$w = -P_{ex}\Delta V = -P_{ex} \left(\frac{\Delta nRT}{P} \right) = -\Delta nRT$$

We can find the number of moles of gas produced by the reaction, Δn , by examining the stoichiometry in the question.

Example:

Calcium carbonate decomposes into calcium oxide and carbon dioxide as shown below. If 12g of calcium carbonate are placed into a vessel open to the atmosphere at room temperature and the reaction takes place, how much work is done on/by the system?



$$n_{CaCO_3} = \frac{m}{MW} = \frac{12 \text{ g}}{100.09 \text{ g mol}^{-1}} = 0.12 \text{ mol}$$
$$n_{CO_2} = n_{CaCO_3} \times \frac{1}{1} = 0.12 \text{ mol}$$

We can now solve for the work done by this chemical reaction,

$$w = -\Delta nRT$$
$$w = -(0.12 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K}) = -297 \text{ J}$$

Example: Relating Work and the Ideal Gas Law

For the following reaction at 25°C, $\Delta H_{rxn} = -405 \text{ kJ/mol}$ what is ΔU_{rxn} ?



How are ΔH and ΔU related?

$$\Delta H = \Delta U + \Delta(PV)$$

3.4.3

A 10.0 g piece of $Mg_{(s)}$ is deposited in a container with a vast excess of $HCl_{(aq)}$. A reaction takes place forming hydrogen gas and Magnesium Chloride.

- a) Write a balanced chemical reaction for the transformation
- b) Calculate the work done by the system as a consequence of the reaction, if $P_{ex} = 1.1 \text{ atm}$ and $T = 298.15 \text{ K}$. You may assume ideal behaviour.

3.5

Relating Calorimetry to the 1st Law

3.5.1

Calorimetry

- We use calorimetry to measure the heat flow of a system. The following equation can be used to calculate heat flow using given that C is the **heat capacity** of the calorimeter

$$q = C\Delta T$$

- Heat capacity, C , is dependent on the substance and is different depending on whether the calorimetry is performed at constant volume, C_V or constant pressure, C_P
- Specific heat capacity is expressed as a function of mass (C_s or c)
- Molar heat capacity is expressed as a function of the number of moles (C_m).

Case 1: Constant Volume Process, $\Delta V = 0$

$$\Delta V = 0 \therefore w = 0 \therefore \Delta U = q_v$$

$$\Delta U = q_v = \int_{T_1}^{T_2} nC_{V,m} dT = nC_{V,m}(T_f - T_i)$$

Note that we can use the exact same equations if we are told there is free expansion into a vacuum:

- When expanding freely into a vacuum there is **no external pressure**
- Since $w=-P\Delta V$ and $P=0$, then $w=0$

$$p_{ex} = 0 \therefore w = 0$$

$$\Delta U = q + w \therefore \Delta U = q_v$$

Case 2: Constant Pressure Calorimetry, $\Delta p = 0$

We need to define a new state function to keep track of heat exchange at constant p

$$H = U + pV$$

$$\Delta H = q_p = \int_{T_1}^{T_2} nC_{p,m}dT = nC_{p,m}(T_f - T_i)$$

It can be shown that

$$C_{p,m} = C_{V,m} + R$$

Case 3: Isothermal Conditions

Under isothermal conditions (constant temperature), $\Delta T=0$

 WIZE TIP

ΔU in the equation: $\Delta U = q + w$, depends only on temperature!

So when there is no temperature change under isothermal conditions, there is no change in U ($\Delta U=0$)

Note: because it's isothermal, $\Delta U=0$

$$\Delta U = q + w = 0 \therefore q = -w$$

Heat Capacity of Ideal Gases

- It can be shown that

$$C_{p,m} = C_{V,m} + R$$

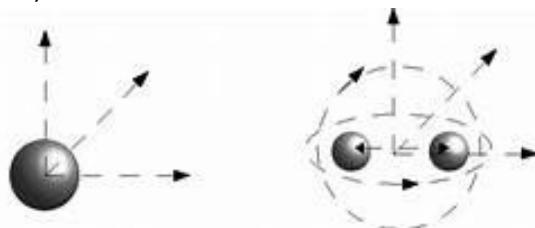
- For an ideal monoatomic gas

$$C_{V,m} = \frac{3}{2}R \quad C_{p,m} = \frac{5}{2}R$$

- For an ideal diatomic gas

$$C_{V,m} = \frac{5}{2}R \quad C_{p,m} = \frac{7}{2}R$$

The following is **low yield** info that can help you memorize these equations (but they will most likely be provided to you on a formula sheet).



Monatomic: only translational degrees of freedom.

Diatom: translational, rotational, and vibrational degrees of freedom.

- Monoatomic gases have 3 degrees of freedom (they are able to move in 3 directions)
- While diatomic gases have 5 degrees of freedom (they are able to move in 5 directions)
 - The degrees of freedom matches the numerator of the Cv equation for each!

3.5.3

The enthalpy of combustion for ethanol C_2H_5OH is -1370.7 kJ/mol. Calculate q and ΔH when 45 g of ethanol are burned at 1 atm and 298 K.

- a. q (kJ)
- b. ΔH (kJ)

(Don't include units in your answer and round to the nearest whole number)

a.

b.

3.5.4

Practice: Isothermal Expansion

4 moles of neon was confined to a 8L flask initially at room temperature underwent an isothermal expansion into a vacuum at 348K. Calculate ΔU , ΔH , and q for this process.

3.6 Calorimetry

3.6.1

Heat Capacity and Calorimetry

- **Heat capacity (C):** has units of $J/^{\circ}K$ or $J/^{\circ}C$ and describes the amount of heat needed to heat up the substance or object by one degree
- **Specific heat capacity (c):** has units of $J/g^{\circ}K$ or $J/g^{\circ}C$ and described the amount of heat required to heat up 1g of a substance by one degree.
- We also have a **molar heat capacity** (units $J/Kmol$, or $J/Cmol$), which is the amount of heat required to heat up 1 mol of a substance by one degree).

$$q = C (\Delta T) \text{ or } q = mc (\Delta T) \text{ or } q = nC (\Delta T)$$

q is heat (in J)

C is the heat capacity ($J/^{\circ}K$ or $J/^{\circ}C$)

c is the specific heat capacity ($J/g^{\circ}K$ or $J/g^{\circ}C$)

m=mass (in g)

ΔT=change in temperature (T_2-T_1) in $^{\circ}K$ or $^{\circ}C$

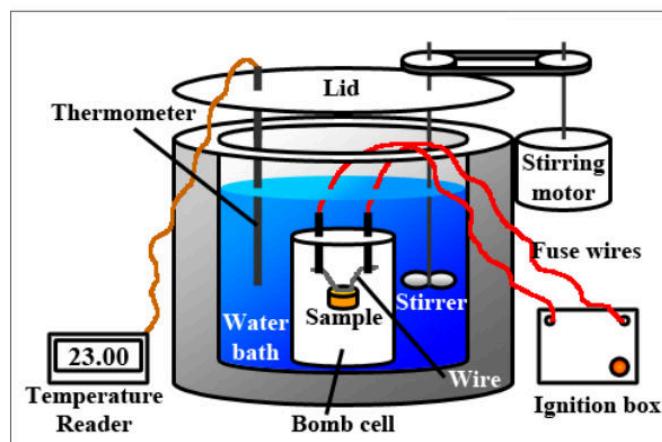
n=moles

Note: $mc=C$

General Introduction to Calorimeters

Calorimeters come in two general varieties:

- Simple "coffee cup" calorimeters
- And bomb calorimeters



Left Photo by Community College Consortium for Bioscience Credentials / CC BY, right photo by Lisdavid89 / CC BY

What is a calorimeter?

- A calorimeter is just a container that is insulated. It holds a liquid that is usually water inside of it and you can have reactions happening inside of it as well.
- For a calorimeter, the **water is the surroundings and the reaction is the system**.
- A thermometer will be able to read the temperature changes of the water.
 - If the thermometer measures an increase in temperature, that means the water went up in temperature.
 - If the water went up in temperature then that means it gained all of the heat from the system (or the reaction taking place inside the calorimeter). It didn't gain the heat from anywhere else because the calorimeter is insulated!
 - This means the system/reaction lost heat and is endothermic/exothermic: _____



WIZE CONCEPT

In general:

$$q_{\text{water}} = -q_{\text{rxn}} \text{ where } q = mc\Delta T$$

Coffee Cup Calorimeters

Essentially it's an open styrofoam cup with a thermometer.



These are most frequently used to measure the temperature change of an aqueous reaction under constant _____ conditions.

$$\Delta H = \Delta E + P\Delta V$$

$$\Delta H = q + w - w$$

$$\Delta H = q_p \text{ (under constant pressure conditions)}$$

WIZE CONCEPT

In general:

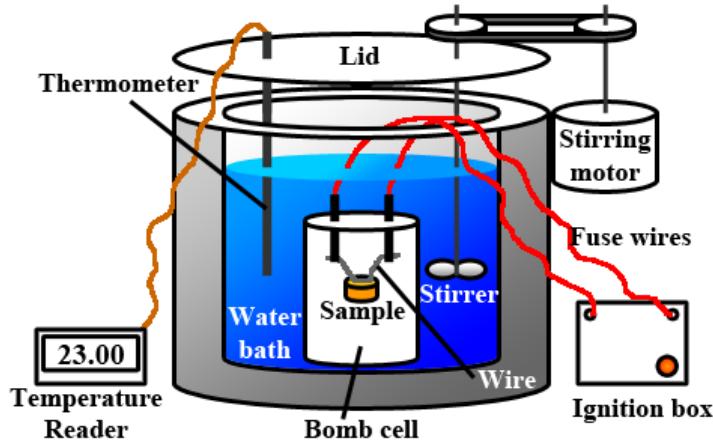
$$q_{\text{system}}(\text{sample}) = -q_{\text{surroundings}}(\text{H}_2\text{O})$$

using $q = mc\Delta T$:

$$(\text{mass of sample})(c \text{ of sample})(\Delta T \text{ of sample}) = -(\text{mass of H}_2\text{O})(c \text{ of H}_2\text{O})(\Delta T \text{ of water})$$

Bomb Calorimeters

Typically these consist of a sealed reaction vessel loaded with a combustible material and filled with oxygen placed in a surrounding water bath.



A combustion reaction is performed under constant _____ conditions and the resulting change in temperature of the water bath is measured.

$$\Delta E = q_v + w$$

$$\Delta E = q_v - P\Delta V$$

$(\Delta V=0)$ so $w=0$

$$\Delta E = q_v$$

For bomb calorimeters, we will see two types of problems:

- 1) Sometimes we evaluate the heat capacity for the entire calorimeter (the q of the calorimeter represents bomb and the water bath)
- 2) Sometimes we evaluate the heat capacity of the bomb and water separately ($q_{\text{total}} = q_{\text{bomb}} + q_{\text{water bath}}$)

i WIZE TIP

Read the question carefully to figure out which one of these types of problems we are looking at!



WIZE CONCEPT

In general:

$$q_{rxn} = -q_{calorimeter}$$

Can usually use $q=C\Delta T$ for the bomb calorimeter

Example: Copper Weight Calorimetry

A copper weight (52.3 g) is heated by a flame from room temperature (25° C) to a temperature of 189° C . The specific heat capacity of copper is $0.385\text{ J g}^{-1}\text{K}^{-1}$

a) What is ΔH for this process?

b) The block is then allowed to cool in some water until the temperature of the block is $75^{\circ} C$, what is ΔH for this process?

c) What is the ΔH from part b) with respect to the water ?

Example: Calorimetry

A block of 20 g lead cube ($c_p = 0.128 \text{ J g}^{-1}\text{K}^{-1}$) is heated to 145° C . The cube is then submerged into a Styrofoam cup containing 500 g of water at room temperature ($c_p = 4.18 \text{ J g}^{-1}\text{K}^{-1}$). After the water and the lead cube come to thermal equilibrium, what is the final temperature of the water?

3.6.4

The temperature of a 12.58 g sample of calcium carbonate ($\text{CaCO}_3(s)$) increases from 23.6°C to 38.2°C . If the specific heat capacity of calcium carbonate is 0.82 J/g K. How many joules of heat are absorbed?

151 J

5.0 J

7.5 J

410 J

0.82 J

3.6.5

The ΔH_{soln} for the process when solid sodium hydroxide (NaOH) dissolves in water is 44 kJ/mol. When a 10.0 g sample of NaOH dissolves in 250.0 g of water in a coffee-cup calorimeter, the temperature increases from 23.0°C to _____ $^{\circ}\text{C}$. Assume that the solution has the same specific heat as liquid water, i.e. 4.18 J/gK.

35.2



24.0



33.5



40.2



Example: Bomb Calorimetry

When 2g of rocket fuel, N_2H_4 is burned inside of a bomb-calorimeter, the temperature of the water rises from 22°C to 29°C . If there is 0.9kg of water and the heat capacity for the bomb is $822\text{J}/^\circ\text{C}$, what is the heat of the combustion for one mole of N_2H_4 in the bomb calorimeter?

- a) 5000 J
- b) -51 000 J
- c) -513 kJ
- d) -573 kJ

Practice: Bomb Calorimetry

A fuel compound was burned in oxygen in a bomb calorimeter with a combined heat capacity of 56.5 kJ/K (Bomb assembly and water). The temperature of the surrounding water bath increased from 23.5 to 34.6 °C as a result. What was the value of q_{sys} for this process?

A) +333 kJ

B) -333 kJ

C) +627 kJ

D) -627 kJ

3.7 Introduction to Enthalpy Calculations

3.7.1

Enthalpy of Reaction (ΔH°_{rxn})

Enthalpy (H): is a measure of the energy associated with breaking or forming bonds

- Breaking bonds (requires/releases) _____ energy
 - Therefore, this is (endothermic/exothermic) _____
 - *Think: you need to be strong to break bonds!
- Forming bonds (requires/releases) _____ energy
 - Therefore, this is (endothermic/exothermic) _____
 - *Think: bonds want to form if they are stable and lower in energy!

WIZE CONCEPT

In summary: breaking bonds requires energy & forming bonds releases energy!

We will soon look at the different ways to calculate ΔH°_{rxn} :

The Heats of Formation Method (ΔH°_f)

Average Bond Enthalpy Method (BDE)

Hess' Law of Formation Method

Example: Calculating Enthalpy of a Reaction



1. How much heat is produced when 72g of water gas is produced?

2. Is the reaction endothermic or exothermic?



3. We are told that $\text{O}_2(\text{g})$ is the limiting reagent of this reaction. How many moles of $\text{O}_2(\text{g})$ are used if the reaction releases 286kJ of heat?

3.8 Heats of Formation Method

3.8.1

Heats of Formation

Heat of formation is the amount of heat that is required to **form 1 mole of a compound from its constituent elements in their natural/standard state** (the state they are in under standard conditions):

P= _____ atm, T= _____ °C, _____ M concentration, pH _____.

WIZE CONCEPT

The $\Delta H^{\circ f}$ =0 for an element in standard state.

WIZE TIP

**The following elements in their standard state should be memorized and the phase they are in is important too!

C(s) as graphite is in standard state.

I₂(s)

Br₂(l)

Hg(l)

Diatomc molecules (BrINCIHOF)

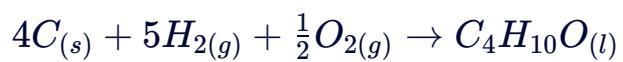
Examples:

Cl₂(g), H₂(g), O₂(g)

WATCH OUT!

If you are shown O(g) on your exam, this is NOT oxygen in its standard state. Remember oxygen in its standard state has to be gaseous AND diatomic! O₂(g) would be in standard state.

Example: The **formation reaction** for C₄H₁₀O_(l) would be:



The enthalpy of formation for this compound is -327kJ/mol.

Calculating the Enthalpy of Reaction Using Heats of Formations

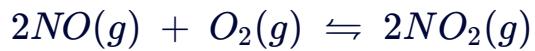
If you know the enthalpies of formation for each reactant and product in any chemical equation, you can find the enthalpy change for that reaction:

$$\Delta H^o_{rxn} = \left[\left(\sum n \Delta H^o f_{products} \right) - \left(\sum n \Delta H^o f_{reactants} \right) \right]$$

In other words, **Δ= Final - Initial**

Example: Calculating the Enthalpy of a Reaction

Calculate ΔH°_{rxn} for the following reaction:



$$\Delta H^\circ_f(NO(g)) = 90.75 \text{ kJ/mol}$$

$$\Delta H^\circ_f(NO_2(g)) = 33.18 \text{ kJ/mol}$$

$$\Delta H^\circ_f(O_2(g)) = \underline{\hspace{2cm}}$$

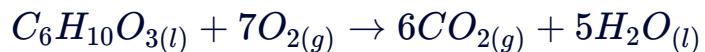
3.8.3

Practice: Formation Reaction

Write a reaction for the heat of formation for dimethylaminopyridine, $(\text{CH}_3)_2\text{NC}_5\text{H}_4\text{N}$.

Practice: Calculate the Enthalpy of the Reaction

Find ΔH°_{rxn} for the following reaction at 25°C:



Given the following data:

Species	$\Delta^\circ H_f$
$C_6H_{10}O_{3(l)}$	-640.4 kJ/mol
$CO_{2(g)}$	-393.5 kJ/mol
$H_2O_{(l)}$	-285.8 kJ/mol

A) -4220 kJ

B) -3150 kJ

C) -2250 kJ

D) +1220 kJ

3.9 Hess' Law Method

3.9.1

Hess' Law

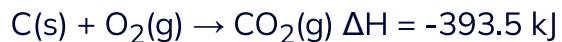
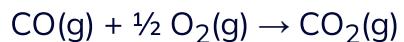
If a reaction is carried out in a series of steps, ΔH for the overall reaction can be found from the sum of the enthalpy changes of the individual steps.

This is because enthalpy (H) is a state function and when it changes, it does not depend on the pathway taken!

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

Example:

What is the ΔH for the reaction?



Practice: Calculating the Enthalpy of a Reaction Using Hess' Law

What is the ΔH_{rxn} for the following reaction?



-3200 kJ



-3000 kJ



-1800 kJ

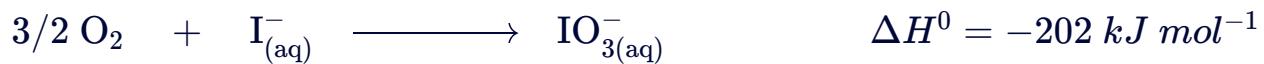


1400 kJ



3.9.3

Given that the $\Delta_f H^0$ of ozone $O_{3(g)}$ is $142.67 \text{ kJ mol}^{-1}$ and the reaction shown below, calculate the enthalpy for the unknown reaction



106 kJ/mol

196 kJ/mol

344 kJ/mol

426 kJ/mol