

Queen's **CHEM 112A**

Fall 2024, Chapter 6 Notes



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6. Thermochemistry

6.1 Introduction to Thermodynamics

6.1.1

Key Terms

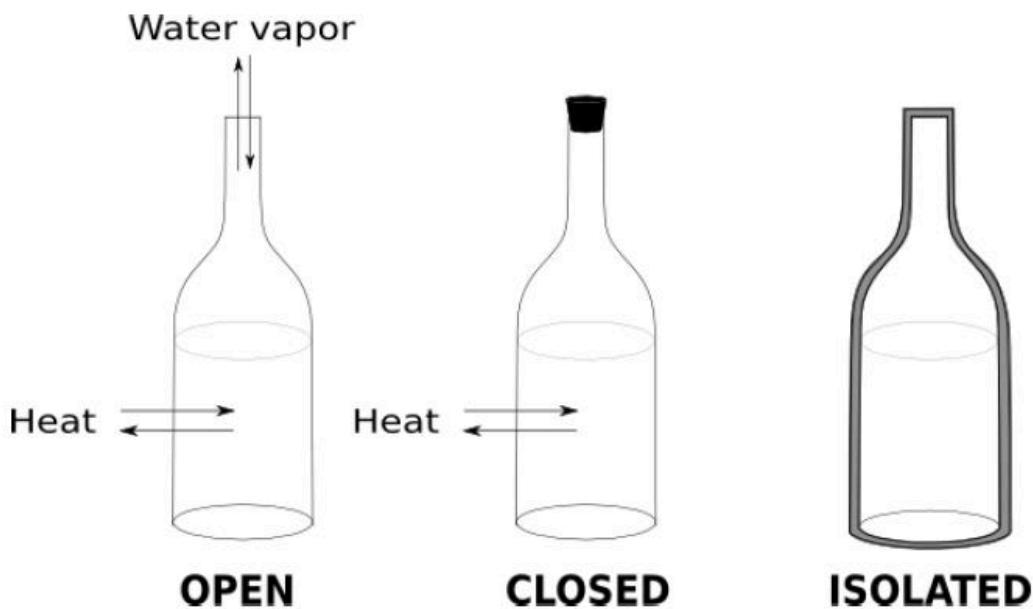
The following lesson is low yield in terms of exams. We'll just focus on **understanding**. 

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

6.2 State Variables

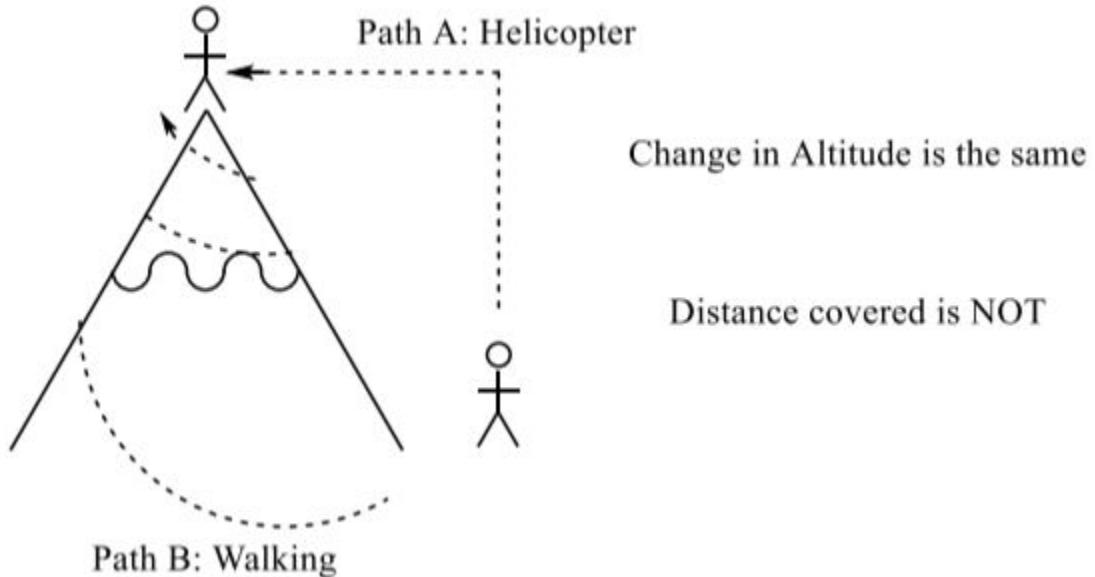
6.2.1

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

6.3

Additional Terminology

6.3.1

Additional Terminology

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

Example: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

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

Example: $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$ (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)

$$q > 0$$

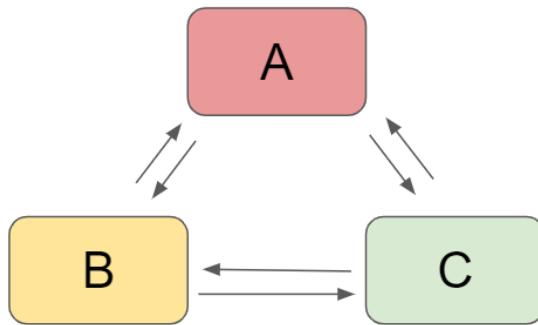
Standard Conditions: Pressure of all gases is 1 atm, all solutions have 1M concentration, and temperature is 298K (25C). This is denoted as $H^\circ S^\circ G^\circ$ etc.

6.4

0th Law of Thermodynamics

6.4.1

0th Law of Thermodynamics



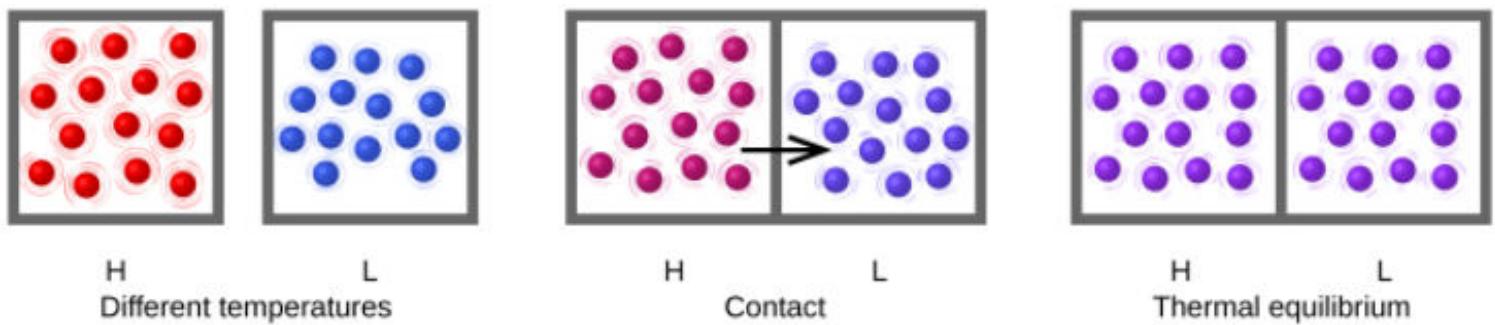
- **0th law:** If a body, A, is in thermal equilibrium with a second body, B, and that body is in thermal equilibrium with a third body, C, then A and C are in **thermal equilibrium**.
- If two bodies/systems are in **thermal equilibrium** with one another, it means they are at the **same temperature!**

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)



6.5 The 1st Law of Thermodynamics and pV work

6.5.1

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)

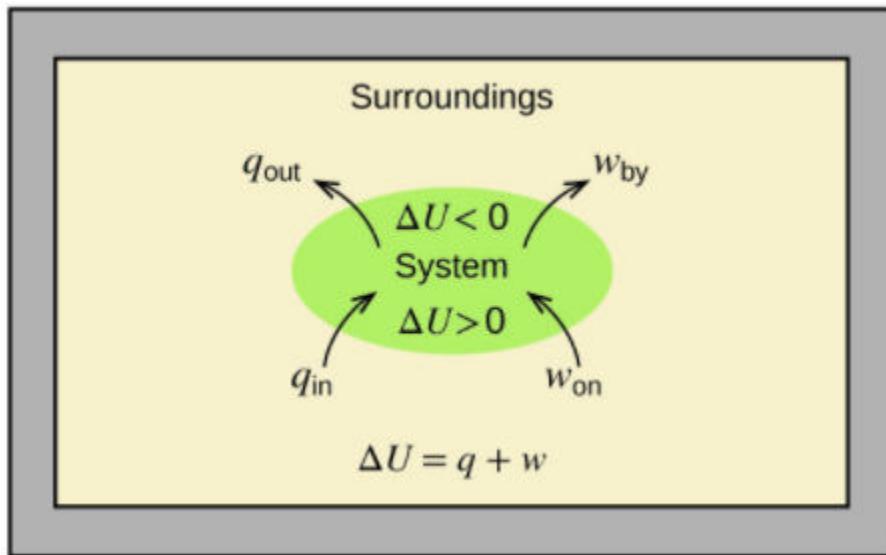


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In chemistry **everything is with respect to the system** so the following conventions exist:

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.

6.5.4

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)

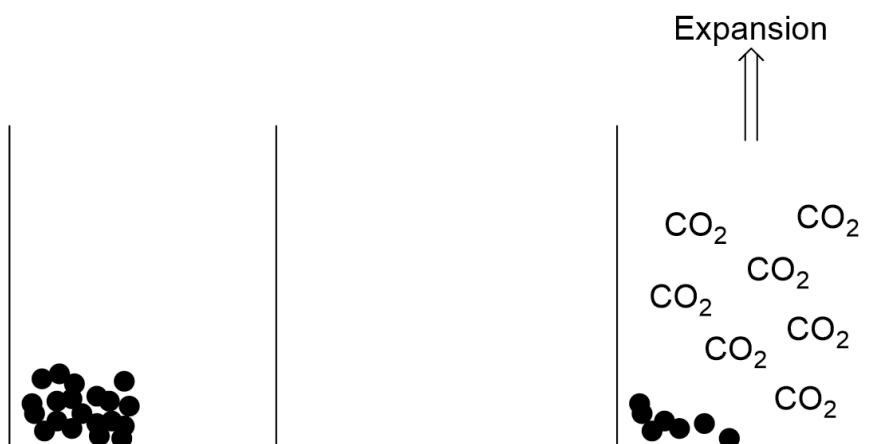
b)

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,

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

6.5.6

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.

6.6 Calorimetry

6.6.1

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 $^{\circ}C$

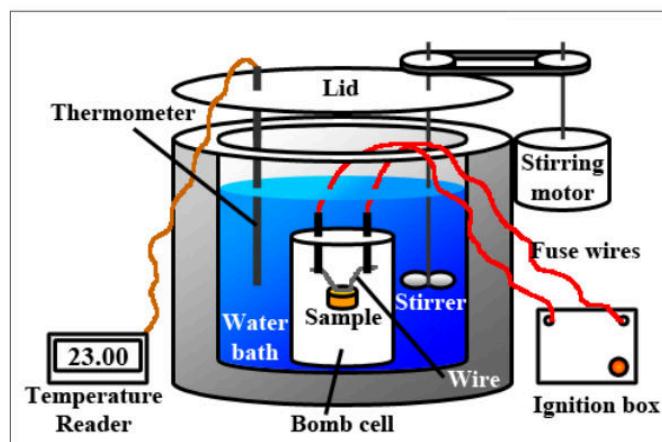
n=moles

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:

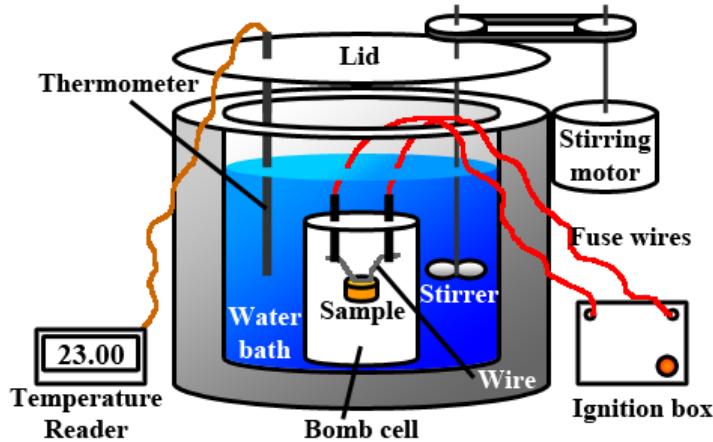
$$q_{\text{system}}(\text{sample}) = -q_{\text{surroundings}}(\text{H}_2\text{O})$$

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 ($q_{\text{total}} = q_{\text{bomb}} + q_{\text{water}}$)

i WIZE TIP

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



In general:

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

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

6.6.2

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

6.6.3

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?

5000 J

51 000 J

513 kJ

573 kJ

6.6.4

A fuel compound was burned in oxygen in a bomb calorimeter with a combined heat capacity of $56.5 \text{ kJ} / \text{K}$ (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?

6.7 Another Look at Calorimetry

6.7.1

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)
- Molar heat capacity is expressed as a function of the number of moles (C_m).

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

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

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

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

$$H = E + pV$$

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

- It can be shown that

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

6.7.2

A copper weight (**52.3 g**) is heated by a flame from room temperature ($25^{\circ} C$) to a temperature of $189^{\circ} C$. 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 pt b) with respect to the water?

6.7.3

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?

6.8

Enthalpy of Phase Change

6.8.1

Enthalpy of Phase Change

- The enthalpy of a phase change is equal to the latent heat for that phase change. That is the amount of heat required to move from one phase to another at constant pressure.
- During these processes there is no change in temperature,
 - if heat is added to the system the energy goes into breaking up the molecules, overcoming the intermolecular forces
 - if heat is removed from the system the kinetic energy is lost so the intermolecular forces begin to dominate resulting in a phase change.
- The enthalpy change can be calculated using standard heats of phase change,

$$q_p = n\Delta H_{phase\ change}$$

- Enthalpy is a state function, so opposing phase changes will have equal but opposite enthalpy values.
- Eg.
 - $\Delta H_{vapourization} = -\Delta H_{condensation}$
 - $\Delta H_{melting} = -\Delta H_{fusion}$
 - $\Delta H_{sublimation} = -\Delta H_{deposition}$

6.9

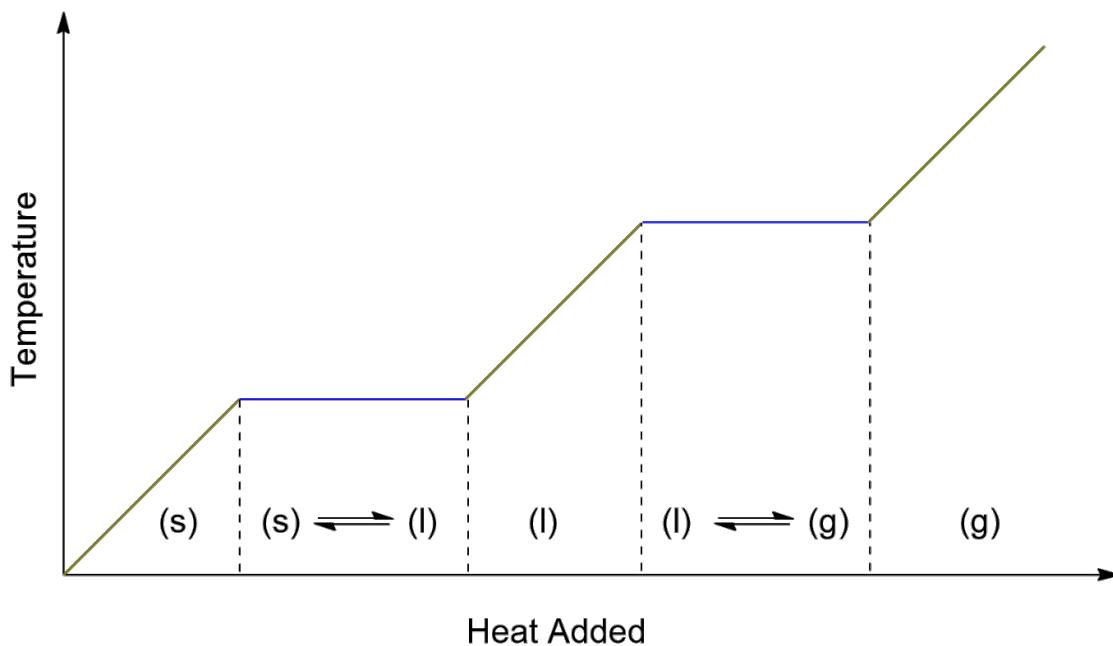
Heat and Cooling Curves

6.9.1

Heating and Cooling Curves

- A heating or cooling curve shows the change in temperature and phase as heat is added or removed from a system. They are really the same graph plotted in a different direction of heat flow

Example of a Heating Curve:



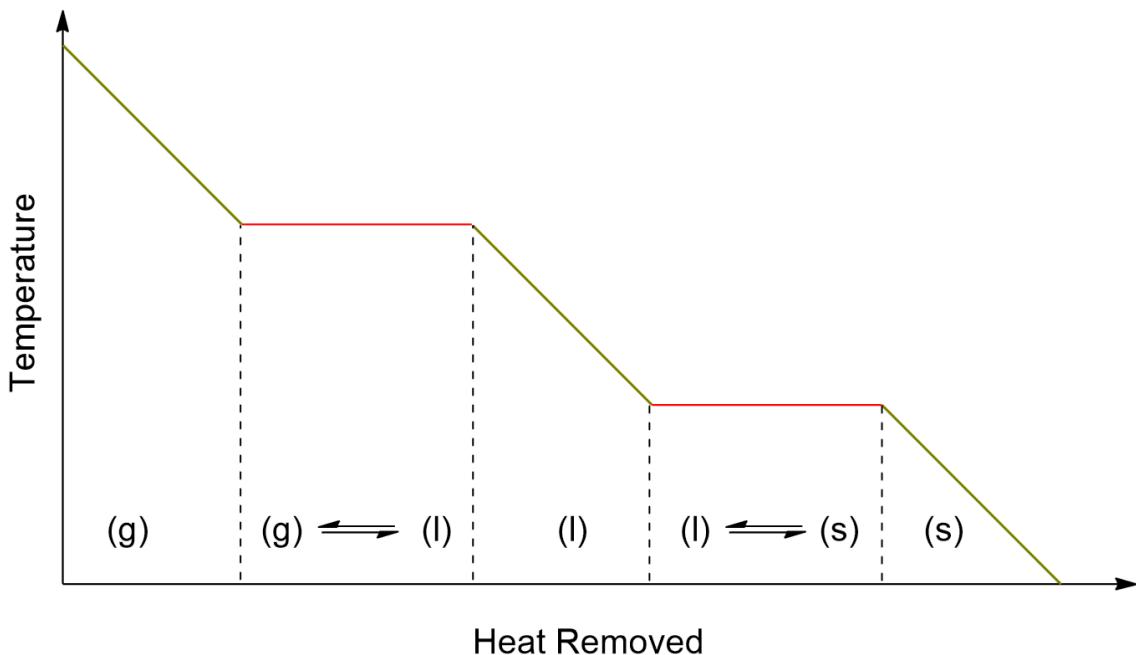
- There are two types of phases, one where a single phase is absorbing heat and increasing in temperature (shown in Olive) and another where the substance is undergoing a change in phase at a given temperature (shown in Blue)
- To calculate the Olive sections we use one of the calorimetry equations

$$q = nC_m\Delta T \quad OR \quad q = mC_s\Delta T$$

- To calculate the blue section we use the molar enthalpy for that phase change

$$q = n \Delta H_{fus} \qquad and \qquad q = n \Delta H_{vap}$$

Example of a Cooling Curve:



- There are two types of phases, one where a single phase is absorbing heat and increasing in temperature (shown in Olive) and another where the substance is undergoing a change in phase at a given temperature (shown in Red)
- To calculate the olive sections we use one of the calorimetry equations

$$q = nC_m\Delta T \quad OR \quad q = mC_s\Delta T$$

- To calculate the red section we use the molar enthalpy for that phase change

$$q = n\Delta H_{condensation} \quad and \quad q = n\Delta H_{freezing}$$

6.9.2

Find the heat required to bring 1 mol of solid ice from -20.0 °C up to 120 °C as steam. The heat capacity of solid ice is 2.06 J/ g K, the heat capacity of liquid water is 4.184 J/ g K, and the heat capacity of water vapour is 1.87 J/ g K. Enthalpy of melting is 6.01 kJ/mol and enthalpy of vaporization is 40.7 kJ/mol.

6.9.3

The enthalpy of vaporization for water, $\Delta H^{\circ}_{\text{vaporization}} = 40.7 \text{ kJ/mol}$. Determine the enthalpy change (in kJ) when 54.0 mL of water is condensed from steam at 100°C.

-122



122



-40.7



40.7



57.7



6.10 Introduction to Enthalpy Calculations

6.10.1

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

6.10.2



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?

6.11 Heats of Formation Method

6.11.1

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)

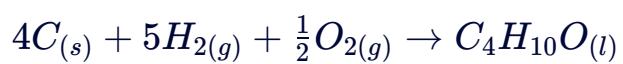
Examples:

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 $C_4H_{10}O(l)$ 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**

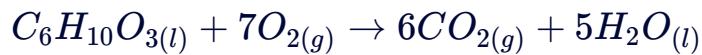
6.11.2

Practice: Formation Reaction

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

6.11.3

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 |

6.12 Hess' Law Method

6.12.1

Hess' Law

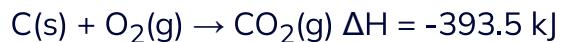
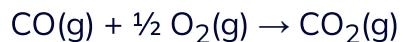
If a reaction is carried out in a series of steps, ΔH for the overall reaction can be found from the sum of the enthalpy changes of the individual steps.

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?





WIZE CONCEPT

The two things you need to remember for this method are:

- 1) Whenever we want to look at a **reaction in reverse**, we must **multiply ΔH by -1**
- 2) Whenever we want to **multiply a reaction by a coefficient**, we must **multiply the ΔH of that step by that same coefficient!**

6.12.2

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

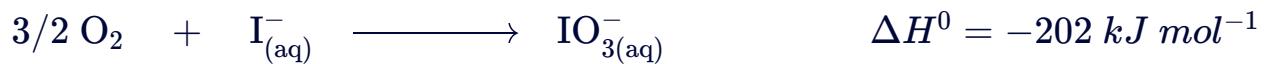


1400 kJ



6.12.3

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