

# Thermochemistry

Mr.V

# Introduction to Energy changes

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- System
- Surroundings
- Exothermic
- Endothermic
- Internal energy
- Enthalpy

# Definitions

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- System

- A specified part of the universe which is under investigation is called the system

- Surroundings

- The rest of the universe which is not a part of the system is called the surroundings

# Systems

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- Open system:
  - A system which can exchange both energy and matter with the surroundings E.g glass of water
- Closed system:
  - A system which can exchange only energy with the surroundings and not matter. E.g. Pepsi can
- Isolated system:
  - A system which can neither exchange energy or matter with the surroundings. E.g Thermos flask

# Energy and Heat

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- Gasoline contains a significant amount of chemical potential energy
- Heat - represented by “q”, is energy that transfers from one object to another, because of a temperature difference between them.
  - only *changes* can be detected!
  - flows from warmer → cooler object

# Energy changes in reactions

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## ■ Exothermic reaction

- A chemical reaction which is accompanied with evolution of heat. – Releases energy
- System to surroundings
- 'q' is -ve

## ■ Endothermic reaction

- A chemical reaction in which heat energy is absorbed. – Absorbs energy
- Surroundings to system
- 'q' is +ve

# Internal energy $\Delta E$

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- It is the total sum of the intrinsic energy possessed by a system.
- The different form of energies are
  - Translational energy
  - Vibrational energy
  - Rotational energy
  - Electronic energy
  - Nuclear energy
  - Chemical potential energy

# Change in Internal Energy $\Delta E$

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- $\Delta E = E_{\text{products}} - E_{\text{reactants}}$
- It is heat change measured at constant volume  
 $\Delta E$
- If the internal energy of the product is less than the reactants the value is negative (–ve) and the reaction is exothermic

# Determination of Internal Energy

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- Internal energy is heat change at constant volume
- Instrument used to measure it is the bomb calorimeter
- The bomb calorimeter is a closed system
- Self study - different types of calorimeters

# Calorimetry

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- Calorimetry - the accurate and precise measurement of heat change for chemical and physical processes.
- The device used to *measure* the absorption or release of heat in chemical or physical processes is called a Calorimeter

# Calorimetry

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- Foam cups are excellent heat insulators, and are commonly used as simple calorimeters
- For systems at constant pressure, the heat content is the same as a property called Enthalpy (H) of the system

# Calorimetry

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- Changes in internal energy =  $\Delta E$
- Changes in enthalpy =  $\Delta H$
- $q = \Delta H$
- Thus,  $q = \Delta H = m \times C \times \Delta T$
- $\Delta H$  is **negative** for an **exothermic** reaction
- $\Delta H$  is positive for an endothermic reaction

# Enthalpy change $\Delta H$

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- Enthalpy is heat evolved or absorbed in a chemical reaction at constant pressure and temperature  $C_p$
- Change in enthalpy is  $\Delta H$
- $\Delta H = H_{\text{products}} - H_{\text{reactants}}$
- It may also be called as heat capacity at constant pressure
- If enthalpy of the products are lesser than the reactants the value of  $\Delta H$  is -ve and the reaction is exothermic ( From first law of TD)

# Enthalpy of formation $\Delta H_f^\circ$

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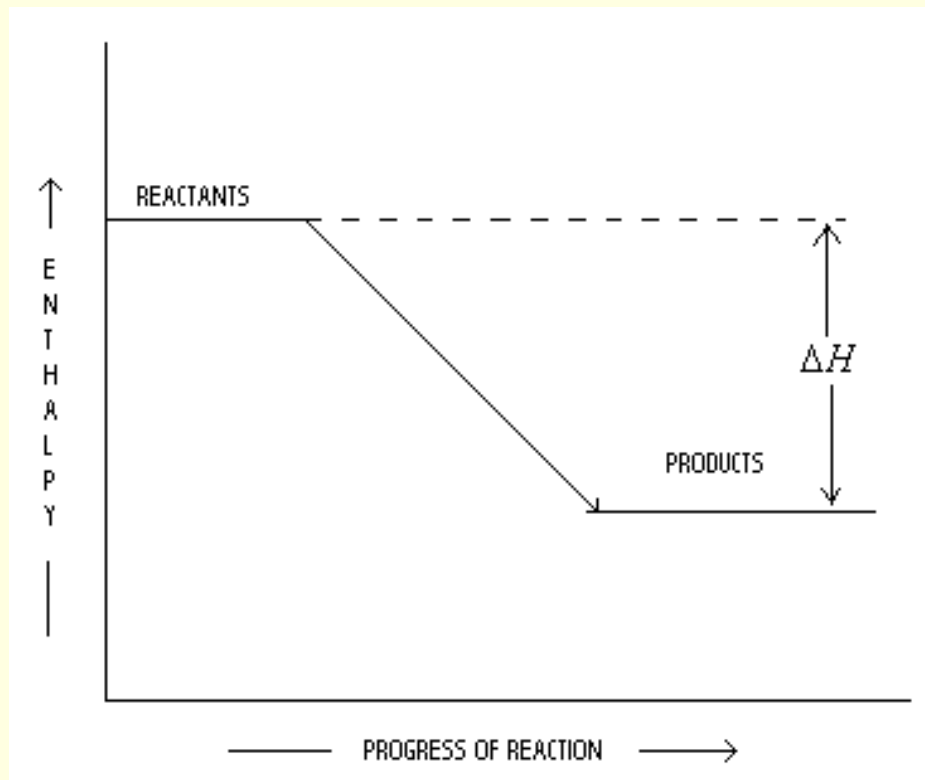
- The heat evolved or absorbed when one mole of substance is formed from its elements in the standard state.
- Standard state 25°C and 1 atmosphere
- Or 298K and 100kPa
- $\text{C}_{(\text{solid})} + \text{O}_{2(\text{gas})} \rightarrow \text{CO}_{2(\text{gas})}$ ,  $\Delta H_f^\circ = -393.5\text{kJ}$
- Standard  $\Delta H_f^\circ$  for elements is zero

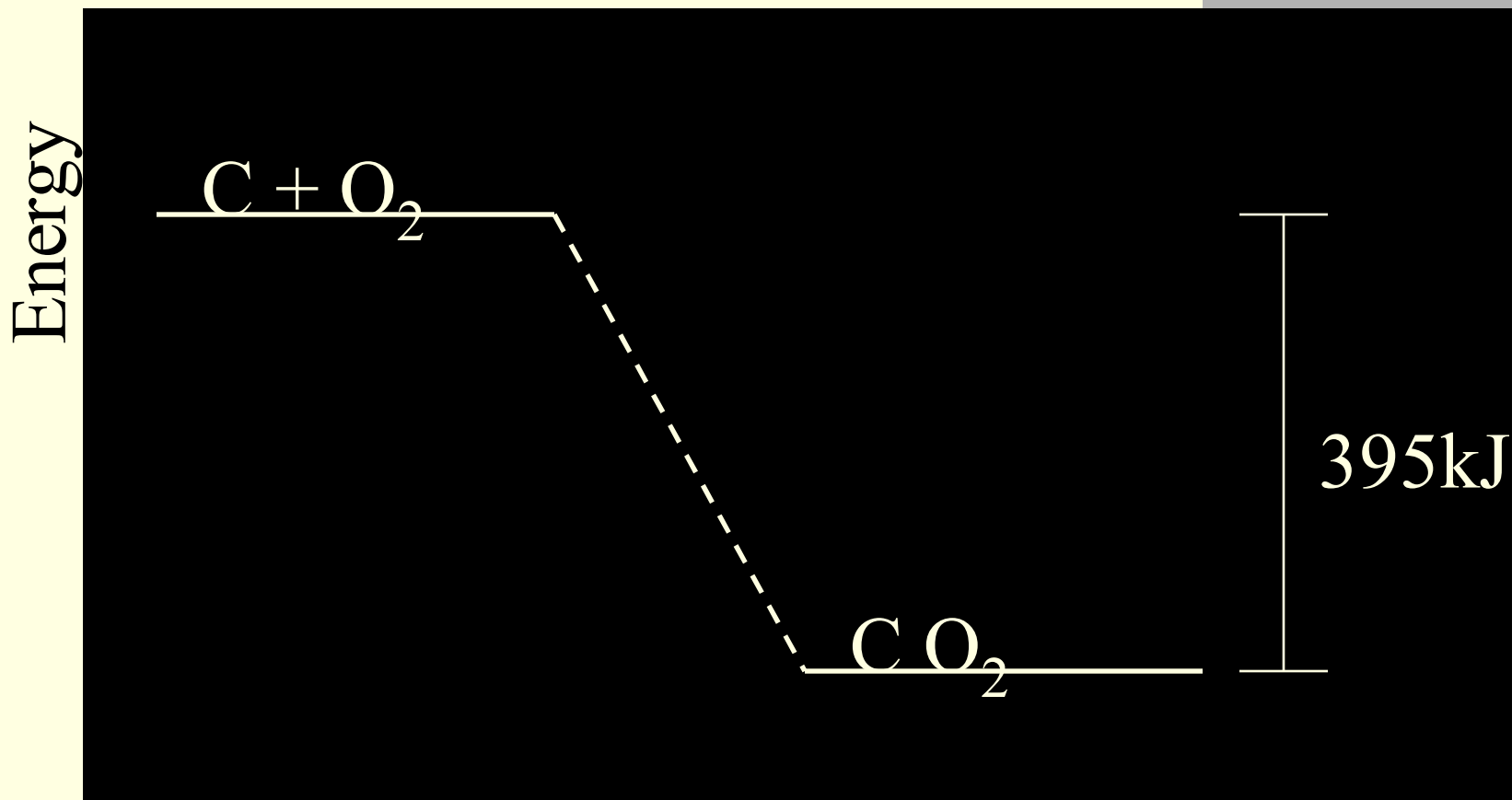
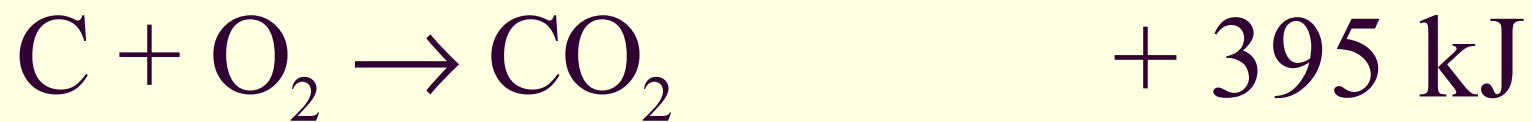
# Enthalpy of reaction, $\Delta H_{\text{reaction}}$

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- The amount of heat evolved or absorbed in a reaction when the number of moles of reactants react completely to give products as given by the balanced chemical equation
- $\text{CH}_{4(g)} + 2\text{O}_{2(g)} \rightarrow \text{CO}_{2(g)} + 2\text{H}_2\text{O}_{(g)}$ ,  $\Delta H$  890.3 kJ

# Exothermic Reaction



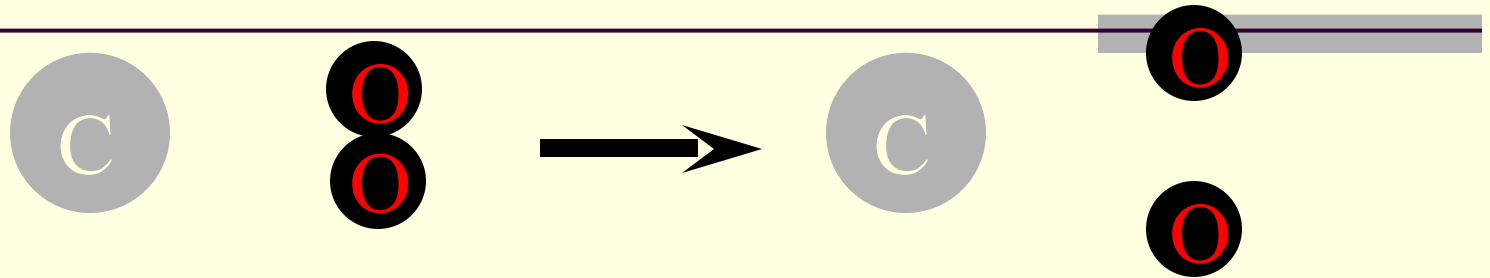


Reactants

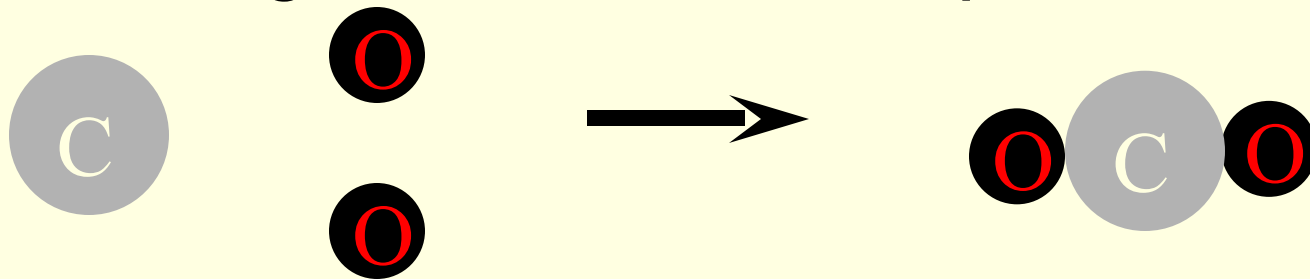


Products

# In terms of bonds

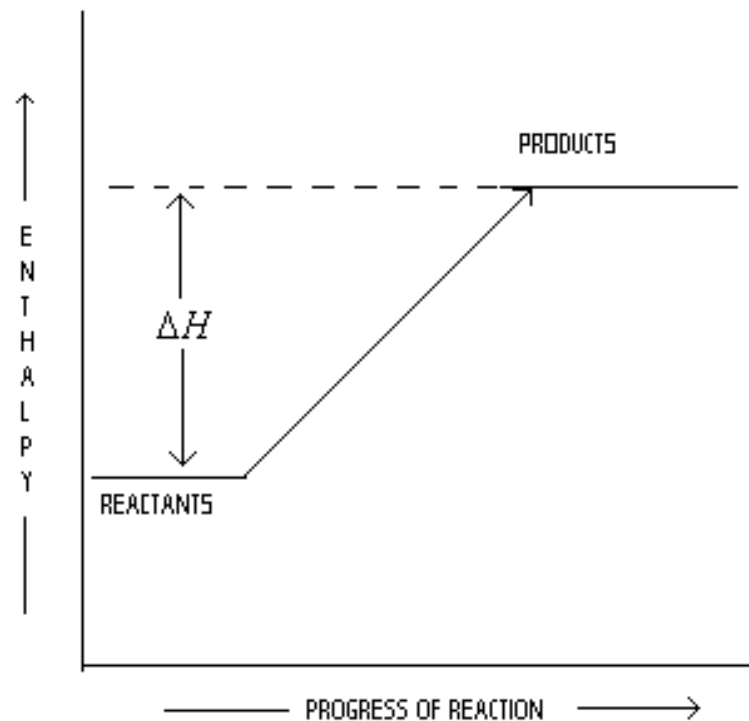


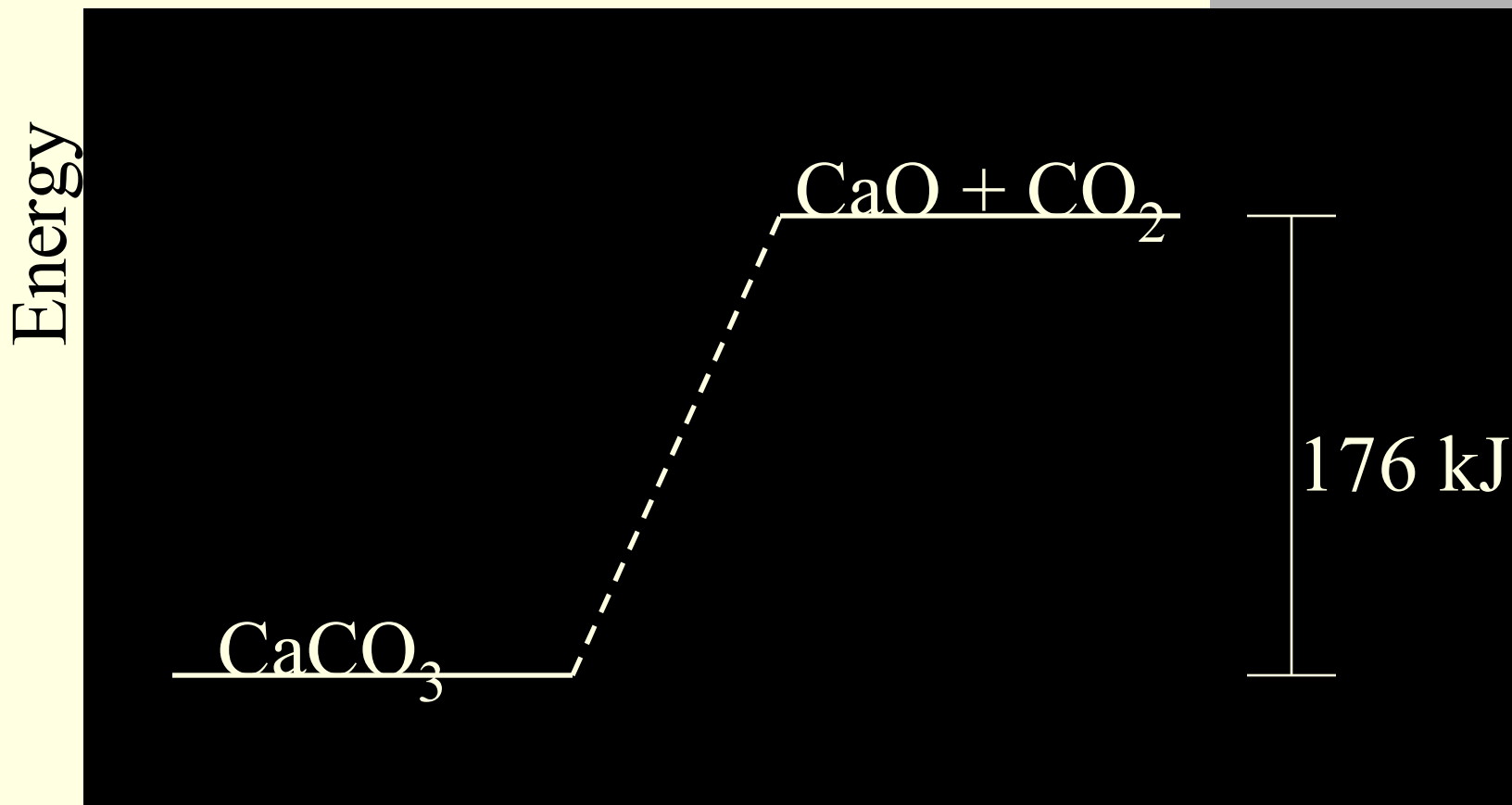
Breaking this bond will require energy.



Making these bonds gives you energy.  
In this case making the bonds gives you more energy than breaking them.

# Endothermic Reaction





Reactants



Products

# Chemistry Happens in

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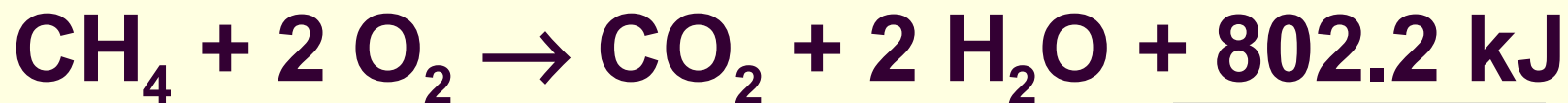
## MOLES

- An equation that includes energy is called a thermochemical equation
- $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 802.2 \text{ kJ}$
- 1 mole of  $\text{CH}_4$  releases 802.2 kJ of energy.
- When you make 802.2 kJ you also make 2 moles of water

# Thermochemical Equations

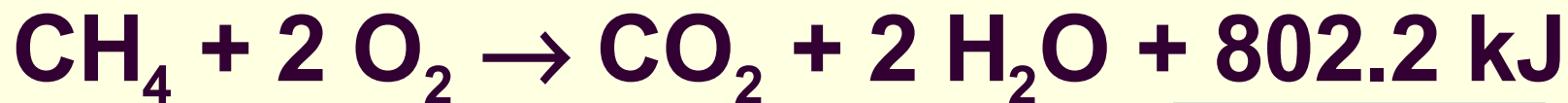
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- The heat of reaction is the heat change for the equation, exactly as written
  - The physical state of reactants and products must also be given.
  - Standard conditions for the reaction is 101.325 kPa (1 atm.) and 25 °C



- If 10.3 grams of  $\text{CH}_4$  are burned completely, how much heat will be produced?

$$10.3 \text{ g CH}_4 \left( \frac{1 \text{ mol CH}_4}{16.05 \text{ g CH}_4} \right) \left( \frac{802.2 \text{ kJ}}{1 \text{ mol CH}_4} \right) = 514 \text{ kJ}$$



- How many liters of O<sub>2</sub> at STP would be required to produce 23 kJ of heat?
- How many grams of water would be produced with 506 kJ of heat?

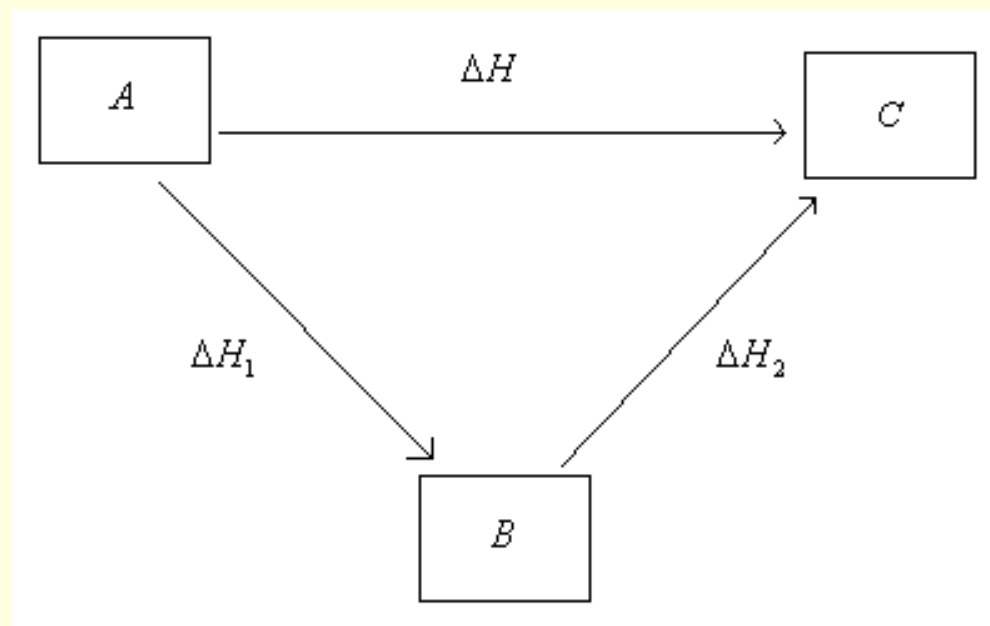
# Hess's Law

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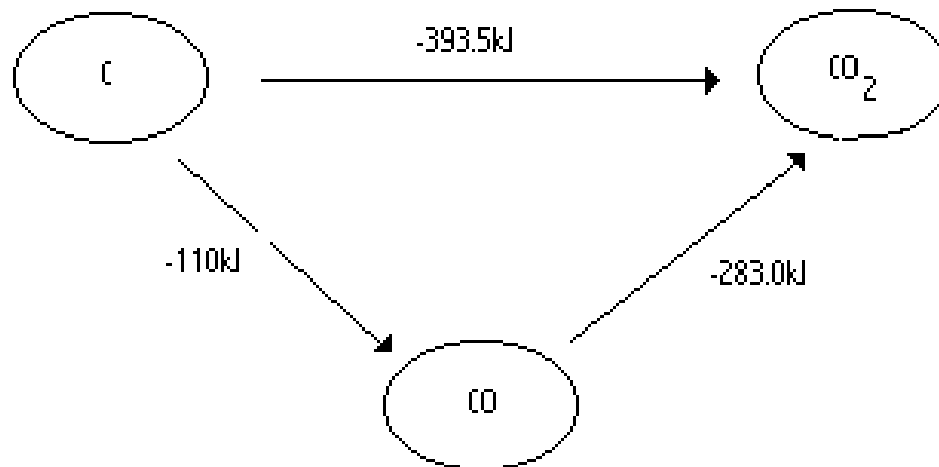
- The heat change (evolved or absorbed ) in a particular reaction is the same whether the reaction takes place in one step or in a number of steps

# Hess's Law

$$\Delta H = \Delta H_1 + \Delta H_2$$



# Hess's Law



# Problem

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- If the standard enthalpy of formation of  $\text{CO}_2$  from its elements is  $-393.5\text{kJ}$  what will be the standard enthalpy of formation for
  - 2 moles of  $\text{CO}_2$
  - 0.5 moles of  $\text{CO}_2$
  - 10 moles of  $\text{CO}_2$

# Solution

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- Standard enthalpy of formation as given in the problem and the appendix III the value for the formation of one mole is  $-393.5 \text{ kJ}$
- $\therefore$  for the formation of 2 mole =  $2 \times -393.5 \text{ kJ}$
- For 0.5 moles =  $0.5 \times -393.5 \text{ kJ}$
- For 10 moles =  $10 \times -393.5 \text{ kJ}$

# Calculation of Enthalpy of reaction

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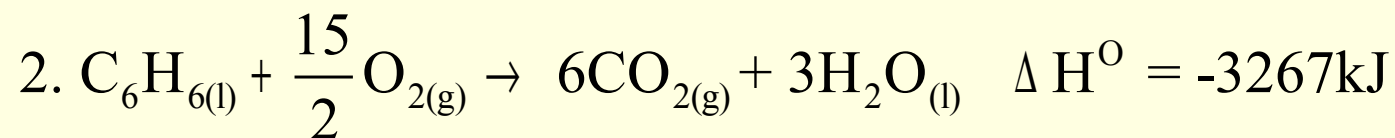
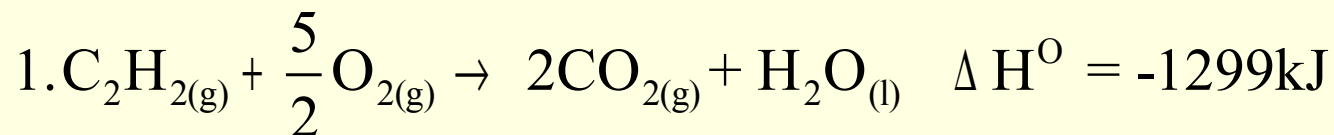


$$\Delta H^{\circ}_{\text{reaction}} = \sum \Delta H^{\circ}_{f \text{ products}} - \sum \Delta H^{\circ}_{f \text{ reactants}}$$

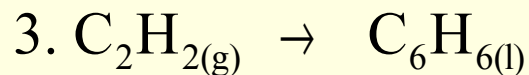
# Problem

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The enthalpy changes for the reactions are



Using only the above data, find  $\Delta H_f^\circ$  for the following reaction:

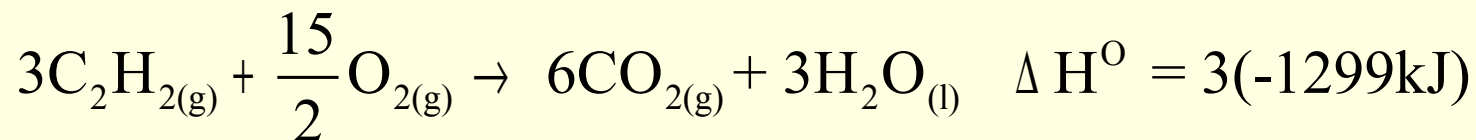


Is the reaction endothermic or exothermic?

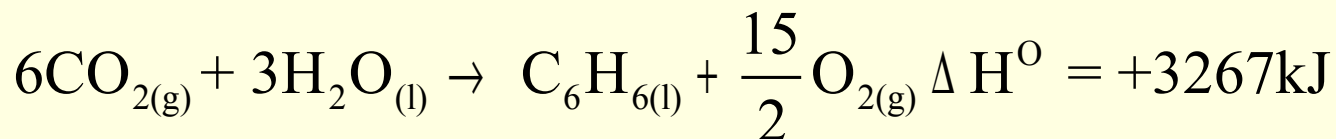
# Solution

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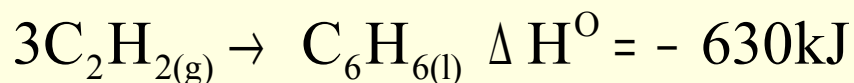
Multiply equation 1 by 3



Reverse equation 2



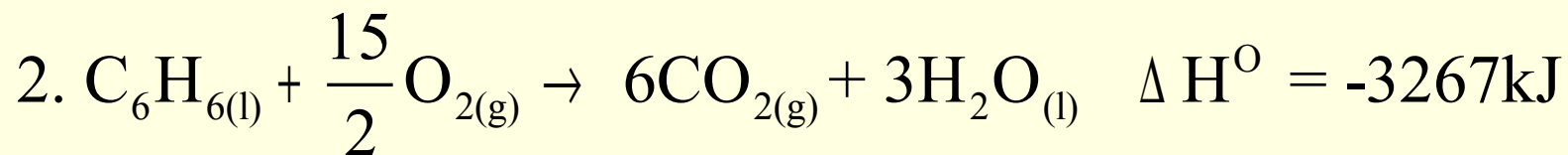
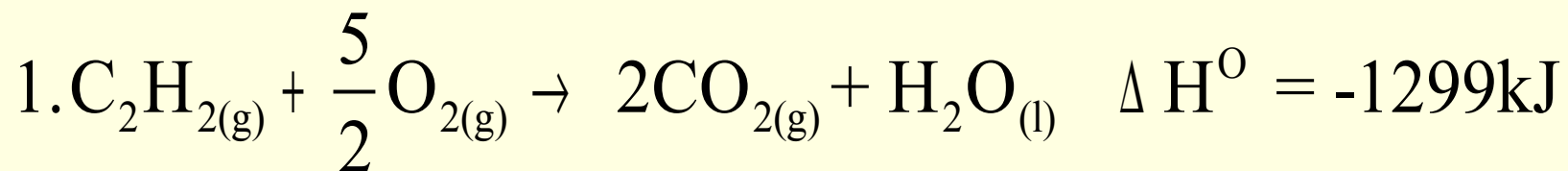
Cancel out common terms on either side of the reaction.



Since  $\Delta H$  is negative or less than zero the reaction is exothermic

Calculate enthalpy of formation for the following reactants given the eqns.

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# Bond Energy and Enthalpy

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- Bond dissociation energy is the energy required to break one mole of bonds of a particular type between the atoms in the gaseous state
- Bond energy: Average bond dissociation energy required to break bonds in a substance is called bond energy (O-H in water or C-H in methane)

# Enthalpy from bond energies

- One way of determining the enthalpy values is by using the equation below. In this method use only positive values for bond energies.
- Alternatively consider bond dissociation energy for bonds broken to be positive (+q) and bonds energies for bonds formed as negative (-q) and take the algebraic sum as the resultant value for enthalpy of the reaction

$$\Delta H_{\text{reaction}}^{\circ} = \sum \text{Bond energies of bonds broken} - \sum \text{Bond energies of bonds formed}$$

# Different methods used to determine Enthalpy

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- Calorimetry:  $q = mc\Delta T$
- Hess's Law of summation
  - Equations addition method
- Heats of formation method
  - $\Delta H^{\circ}_{\text{rxn}} = \sum H^{\circ}_{\text{products}} - \sum H^{\circ}_{\text{reactants}}$
- Bond dissociation energy method

# Enthalpy Calculation

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- Relation between  $C_v$  and  $C_p$
- $\Delta H = \Delta E + P \Delta V$
- Enthalpy of reactions can also be calculated using the above equation