

Thermochemistry

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Introduction to Energy changes

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

Definitions

- 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

- 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

- 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

■ 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 ΔE

- 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 ΔE

- $\Delta E = E_{\text{products}} - E_{\text{reactants}}$
- It is heat change measured at constant volume
 ΔE
- 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

- 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

- 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

- 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

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

Enthalpy change ΔH

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

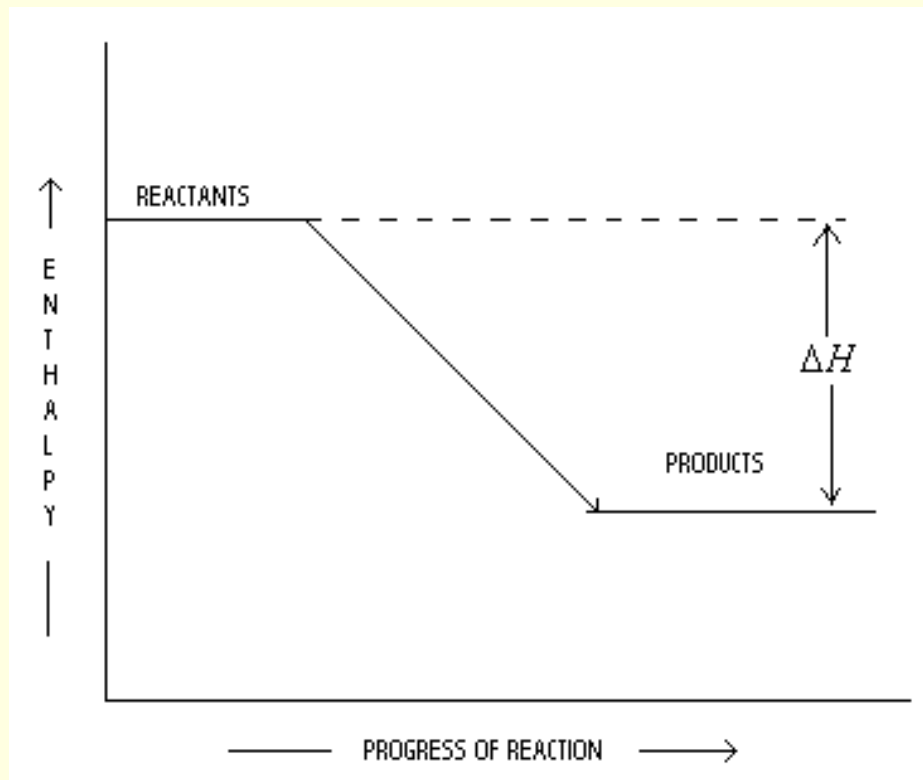
Enthalpy of formation ΔH_f°

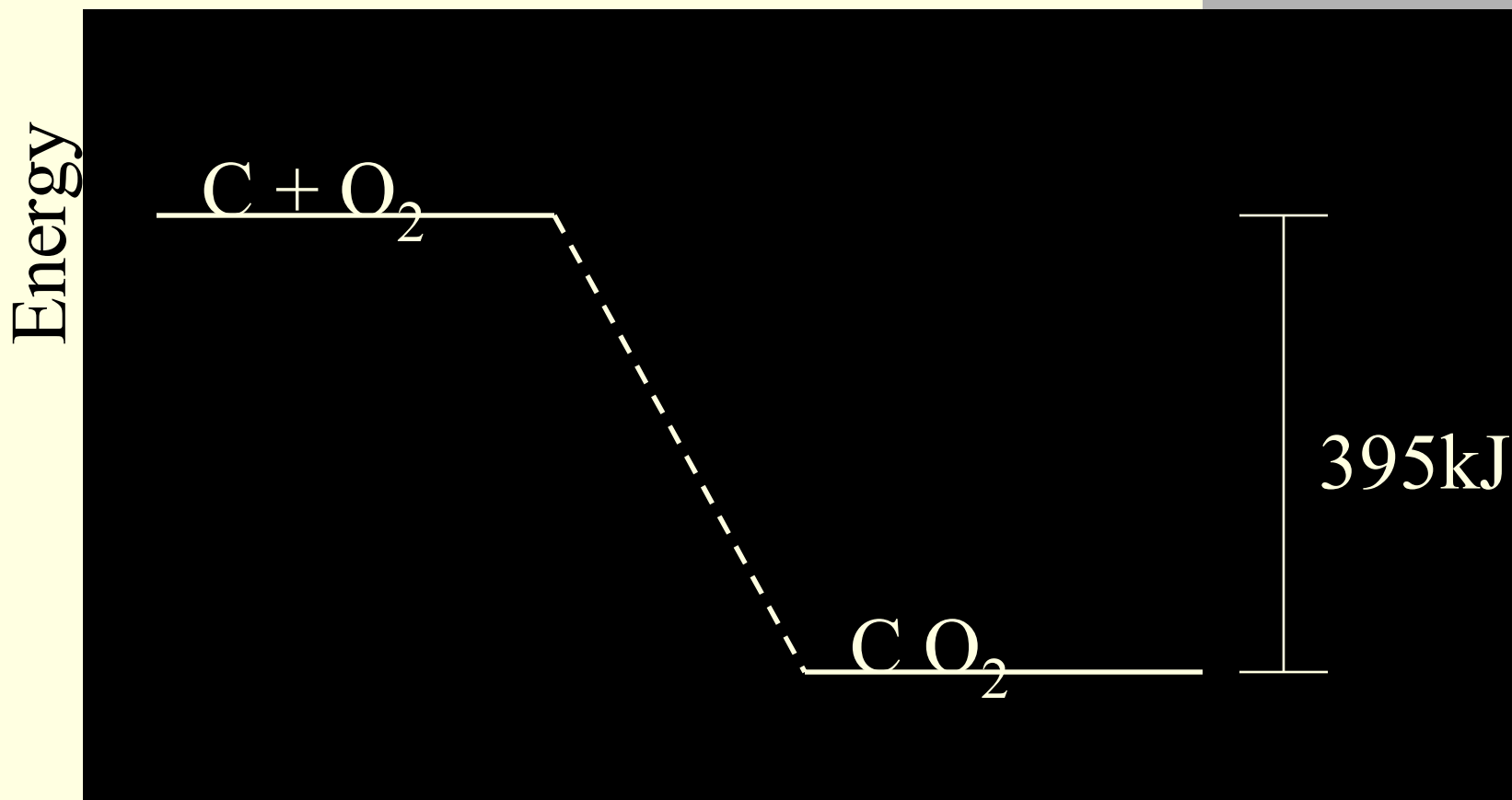
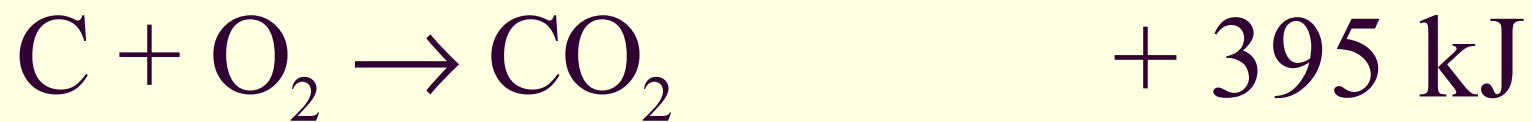
- The heat evolved or absorbed when one mole of substance is formed from its elements in the standard state.
- Standard state 25°C and 1 atmosphere
- Or 298K and 100kPa
- $\text{C}_{(\text{solid})} + \text{O}_{2(\text{gas})} \rightarrow \text{CO}_{2(\text{gas})}$, $\Delta H_f^\circ = -393.5\text{kJ}$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

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

- 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
- $\text{CH}_{4(g)} + 2\text{O}_{2(g)} \rightarrow \text{CO}_{2(g)} + 2\text{H}_2\text{O}_{(g)}, \Delta H 890.3 \text{ kJ}$

Exothermic Reaction



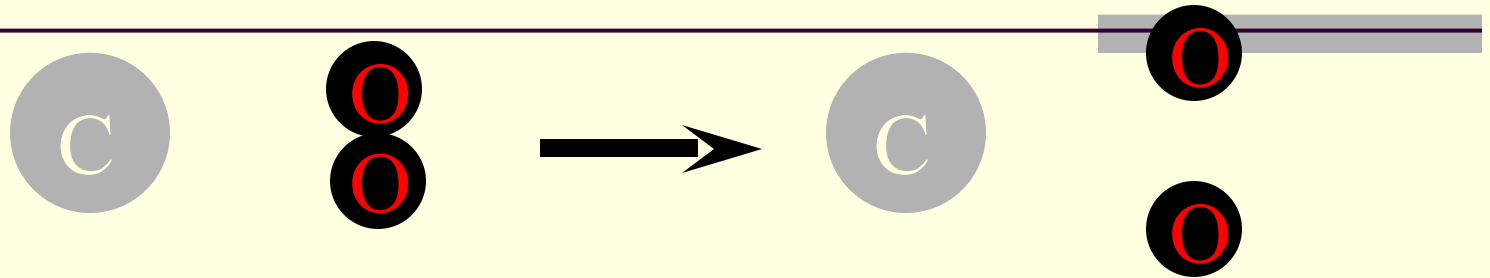


Reactants

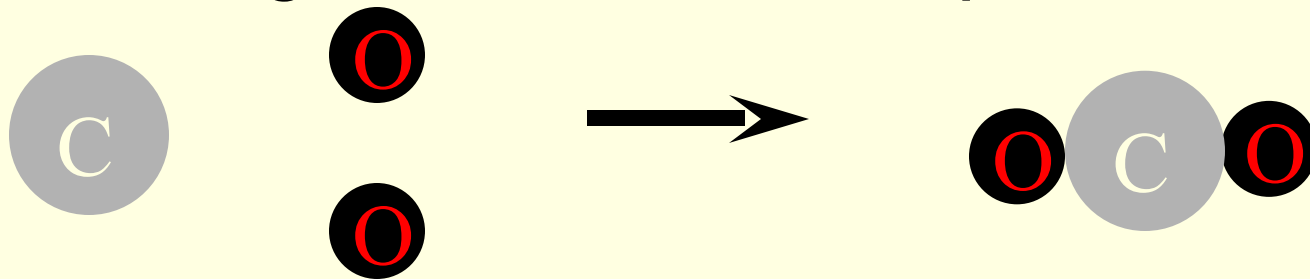


Products

In terms of bonds

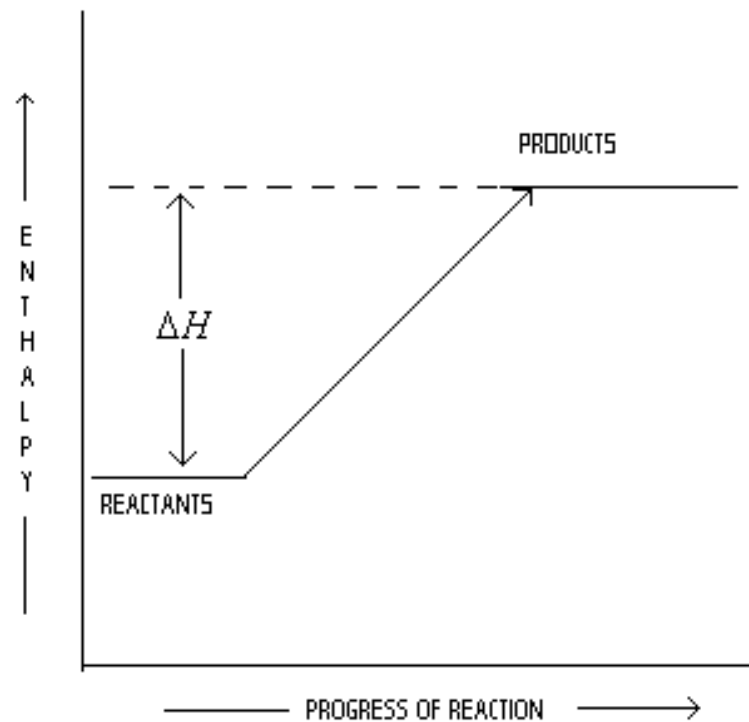


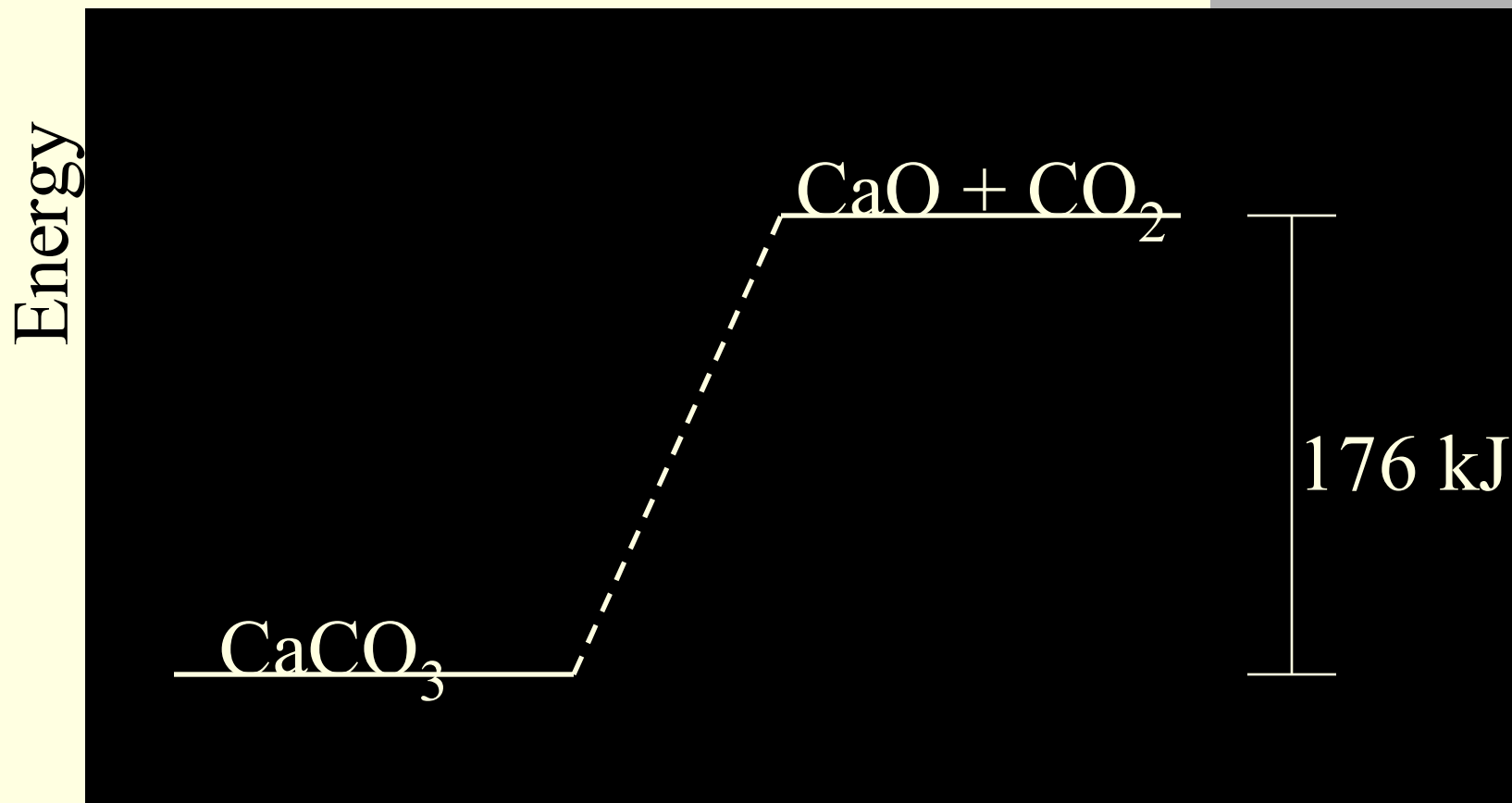
Breaking this bond will require energy.



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

Endothermic Reaction





Reactants



Products

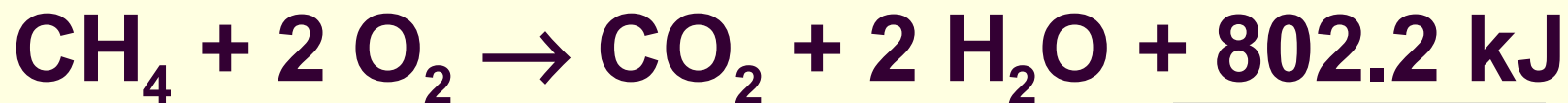
Chemistry Happens in

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 CH_4 releases 802.2 kJ of energy.
- When you make 802.2 kJ you also make 2 moles of water

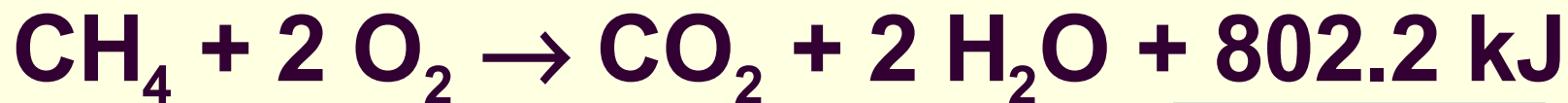
Thermochemical Equations

- 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 CH_4 are burned completely, how much heat will be produced?

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



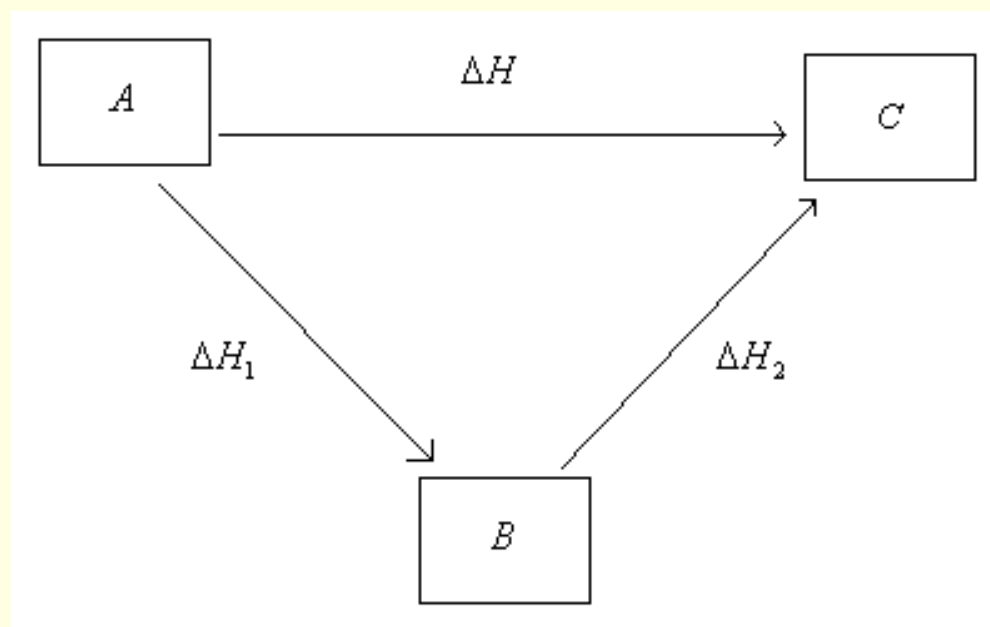
- How many liters of O₂ at STP would be required to produce 23 kJ of heat?
- How many grams of water would be produced with 506 kJ of heat?

Hess's Law

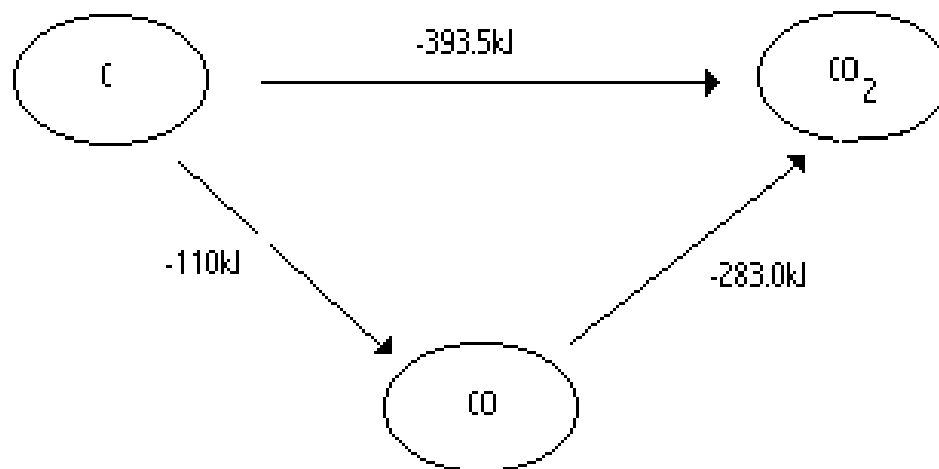
- The heat change (evolved or absorbed) in a particular reaction is the same whether the reaction takes place in one step or in a number of steps

Hess's Law

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



Hess's Law



Problem

- If the standard enthalpy of formation of CO_2 from its elements is -393.5kJ what will be the standard enthalpy of formation for
 - 2 moles of CO_2
 - 0.5 moles of CO_2
 - 10 moles of CO_2

Solution

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

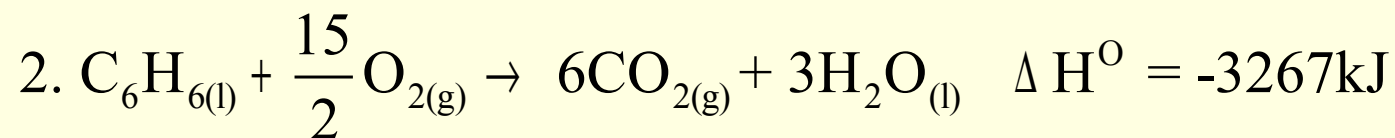
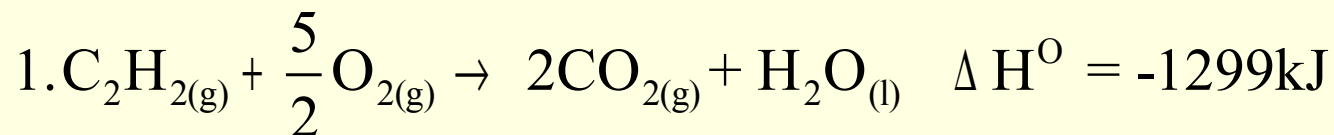
Calculation of Enthalpy of reaction



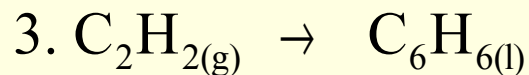
$$\Delta H^{\circ}_{\text{reaction}} = \sum \Delta H^{\circ}_{f \text{ products}} - \sum \Delta H^{\circ}_{f \text{ reactants}}$$

Problem

The enthalpy changes for the reactions are



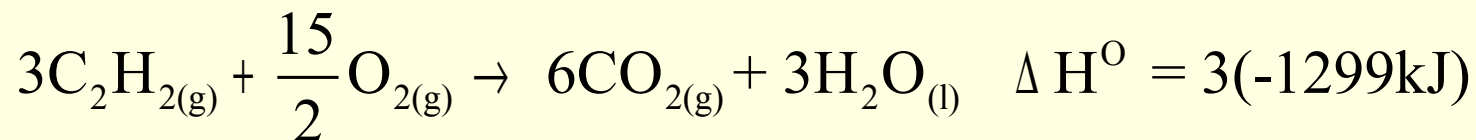
Using only the above data, find ΔH_f° for the following reaction:



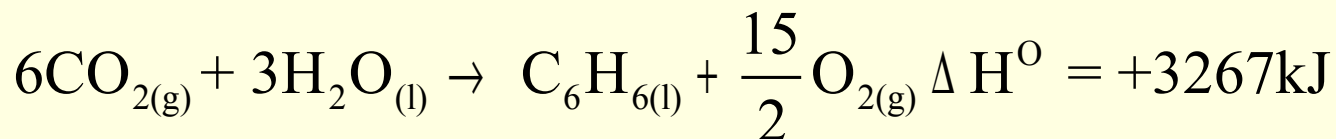
Is the reaction endothermic or exothermic?

Solution

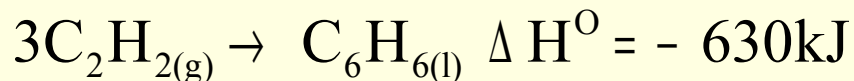
Multiply equation 1 by 3



Reverse equation 2

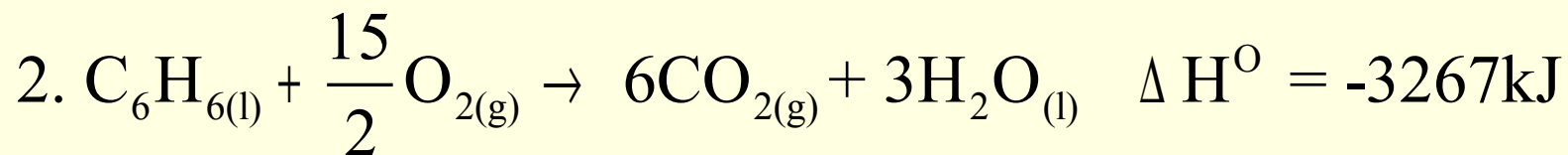
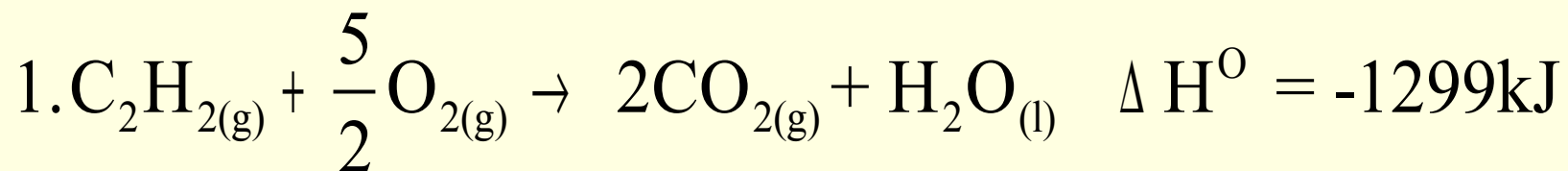


Cancel out common terms on either side of the reaction.



Since ΔH is negative or less than zero the reaction is exothermic

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



Bond Energy and Enthalpy

- 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

- 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

- 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