

**ESO201A**  
**Lecture#27**  
**(Class Lecture)**

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# Enthalpy of Combustion

## and Enthalpy of Formation

### Introduction

- During a chemical reaction, some chemical bonds that bind the atoms into molecules are broken, and new ones are formed.
- The chemical energy associated with these bonds, in general, is different for the reactants and the products.
- Therefore, a process that involves chemical reactions involves changes in chemical energies, which must be accounted for in an energy balance.
- Assuming the atoms of each reactant remain intact (no nuclear reactions) and  $\Delta KE = 0$ , the energy change of a system during a chemical reaction is due to a change in state and a change in chemical composition. That is,  $\Delta E_{sys} = \Delta E_{state} + \Delta E_{chem}$

## Introduction (contd.)

- $\Delta E_{\text{state}} = 0$  when the state of the products and reactants is the same. Therefore,  $\Delta E_{\text{sys}} = \Delta E_{\text{chem}}$ . By 'state' we mean temperature and pressure, not phase.
- In thermodynamics we are concerned with  $\Delta E$  and not the values of  $E$  at the particular states.
- Therefore, we can choose any state as the reference state and assign a value of zero to the internal energy or enthalpy of a substance at that state.
- When a process involves no changes in chemical composition, the reference state has no effect on the results.
- In the case of chemical reactions there is a change in chemical composition and it becomes necessary to have a common reference state for all substances.

## Introduction (Contd.)

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- The chosen reference state is  $25^\circ\text{C}$  and 1 atm ( $0.1 \text{ MPa}$ ), which is known as the standard reference state.
- Property values at the standard reference state are indicated by a superscript  $(^\circ)$  (such as  $h^\circ$  and  $u^\circ$ ).
- When analyzing reacting systems, we must use property values relative to the standard reference state.
- However, it is not necessary to prepare a new set of property tables for this purpose. We can use the existing tables by subtracting the property values at the standard reference state from the values at the specified state.

## Introduction (contd.)

(4)

- The ideal-gas enthalpy of  $N_2$  at 500 K relative to the standard reference state, for example, is  $\bar{h}_{500\text{ K}} - \bar{h}^\circ = 14581 - 8669$  = 5912 kJ/kmol. See Table A-18 for  $N_2$ . Note that  $\bar{h} = f(T)$  only for ideal gases.

## Enthalpy of Combustion

Consider the formation of  $\text{CO}_2$  from the elements, carbon and oxygen, during a steady-flow combustion process (Fig. 1).

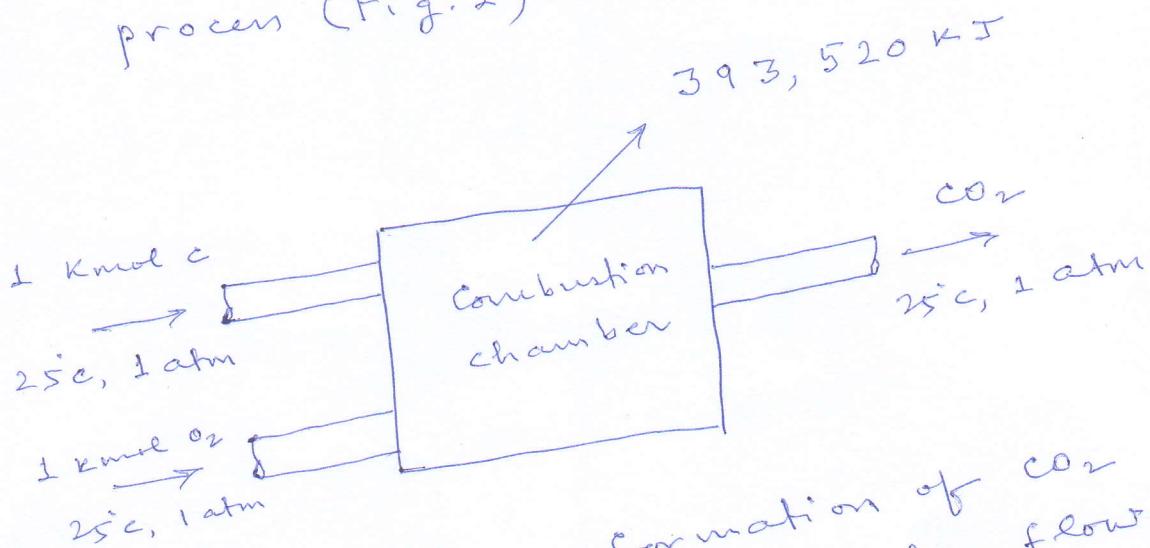


Fig. 1 The formation of  $\text{CO}_2$  during a steady-flow combustion process at 25°C and 1 atm to the surroundings

The heat transferred is measured as 393, 520 KJ. Thus, the combustion of carbon is an exothermic reaction (a reaction during which chemical energy is released in the form of heat).

## Enthalpy of Combustion (contd.)

(6)

Since there is no work interactions and  $\Delta KE = 0$ ,  $\Delta PE = 0$ , the energy balance with the combustion chamber as cv gives

$$Q_{in} + H_{react} = Q_{out} + H_{product}$$

$$\Rightarrow (Q_{in} - Q_{out}) = H_{product} - H_{reactant}$$

$$\Rightarrow Q = H_{product} - H_{reactant}$$

$$= -395,520 \text{ kJ/kmol}$$

$$Q = -395,520 \text{ kJ/kmol}$$

$$\Rightarrow \Delta H = \Delta E_{chem}$$

Since  $\Delta E_{state} = 0$ ,  $\Delta E = \Delta E_{chem}$

and since  $\Delta PE = 0$ ,  $\Delta KE = 0$ ,

$$\Delta H = \Delta H_{chem}$$

$\Delta H$  is different for different reactions and this property is the enthalpy of reaction,  $h_R$ .

' $h_R$ ' is defined as the difference between the enthalpy of the products at a specified state and the enthalpy of the reactants at the same state for a complete reaction.

## Enthalpy of Combustion (Contd.)

(7)

For combustion processes, the enthalpy of reaction is usually referred to as the enthalpy of combustion, i.e.

' $\bar{h}_c$ ' represents the amount of heat released during a steady-flow combustion process when 1 kmol (or 1 kg) of fuel is burned completely at a specified temperature and pressure (Fig. 2).

$$\bar{h}_c = Q = -393,520 \text{ kJ/kmol carbon}$$

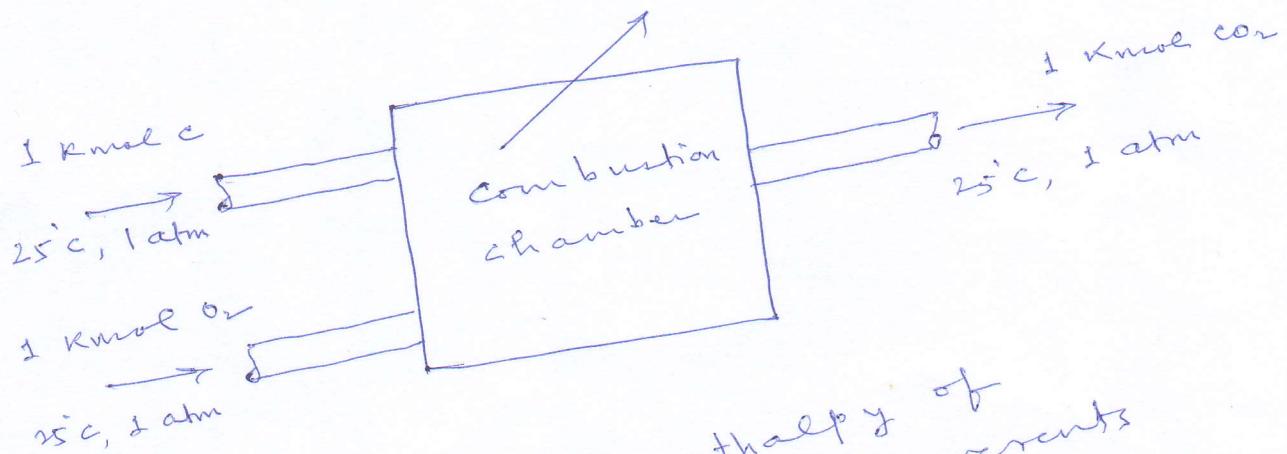


Fig. 2

The enthalpy of combustion represents the amount of energy released as a fuel is burned during a steady-flow process at a specified state.

## Enthalpy of Combustion (Contd.)

(8)

It is expressed as

$$\bar{h}_R = \bar{h}_c = H_{\text{product}} - H_{\text{reactant}}$$

For carbon  $\bar{h}_c = -393,520 \text{ kJ/kmol}$   
at  $25^\circ\text{C}$ , 1 atm (standard reference state).

The enthalpy of combustion of a particular fuel is different at different temperatures and pressures.

(9)

## Enthalpy of Formation

- Although the enthalpy of combustion is a very useful property it is not practical to list the values for so many different fuels and fuel mixtures.
- The enthalpy of combustion is not of much use when the combustion is incomplete.
- A more practical approach would be to have a more fundamental property to represent the chemical energy of an element or a compound at some reference state.
- This property is the enthalpy of formation  $\Delta_f H$ , which can be viewed as the enthalpy of a substance at a specified state due to its chemical composition.

## Enthalpy of Formation (contd.)

- To establish a starting point, we assign the enthalpy of formation of all stable elements (such as O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub> and C) a value of zero at the standard reference state of 25°C and 1 atm. That is,  $\bar{h}_f^{\circ} = 0$  for all stable elements.

Now, reconsider the formation of CO<sub>2</sub> (a compound) from its element C (a compound) from its element C and O<sub>2</sub> at 25°C and 1 atm during a steady-flow process. See Fig. 3.

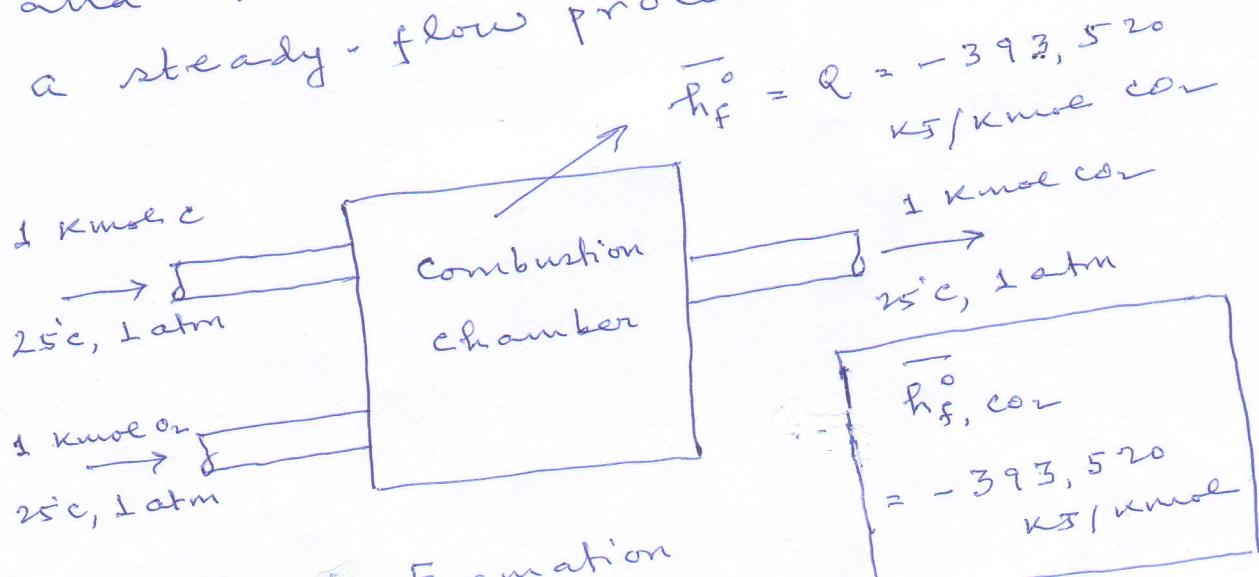


Fig. 3 Formation of CO<sub>2</sub>

## Sign of Enthalpy of Formation

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We have seen that the enthalpy of formation of  $\text{CO}_2$  is negative. This is quite evident because the heat transfer is negative during the steady-flow chemical reaction, and the enthalpy of the carbon dioxide must be less than the sum of enthalpy of the carbon and oxygen, both of which are assigned the zero value.

Therefore, a negative enthalpy of formation for a compound indicates that heat is released during the formation of that compound from its stable elements. A positive value indicates heat is absorbed.

## Enthalpy of Formation

(contd.)

$$\bar{h}_{f, \text{CO}_2}^\circ = Q = H_{\text{prod}} - H_{\text{react}}^\circ$$

$$= -393,520 \text{ kJ/kmol}$$

Note  $H_{\text{react}}^\circ = 0$  since both reactants are elements at the standard reference state. The enthalpy of (hypothetical) ideal-gas  $\text{CO}_2$  at  $25^\circ\text{C}$ ,  $0.1 \text{ MPa}$  is called the enthalpy of formation of  $\text{CO}_2$ . Therefore,  $\bar{h}_{f, \text{CO}_2}^\circ = -393,520 \text{ kJ/kmol}$  at the standard reference state.

The enthalpy of  $\text{CO}_2$  in any other state, relative to this base in which the enthalpy of the elements is zero, would be found by adding the change of enthalpy between ideal gas at  $25^\circ\text{C}$ ,  $0.1 \text{ MPa}$ , and the given state to the enthalpy of formation. That is, the enthalpy at any temperature and pressure,  $\bar{h}_{T, P}$ , is

$$\bar{h}_{T, P} = (\bar{h}_f)_{298 \text{ K}, 0.1 \text{ MPa}}$$

$$+ (\Delta \bar{h})_{298 \text{ K}, 0.1 \text{ MPa} \rightarrow T, P}$$

where  $(\Delta \bar{h})_{298 \text{ K}, 0.1 \text{ MPa} \rightarrow T, P}$  represents the difference in enthalpy between any given state and the enthalpy of ideal gas at  $298 \text{ K}$ ,  $0.1 \text{ MPa}$ .

For gases, the change of enthalpy can be found by one of the following procedures.

1. Assume ideal-gas behaviour between  $25^\circ\text{C}$ ,  $0.1 \text{ MPa}$ , and the given state. In this case, the enthalpy is a function of temperature only and can be found from the ideal-gas property table or by an equation for  $\bar{f}_0$  (if the table is not available).
2. If a real-substance behaviour reference state is used (as for solid or liquid) then  $\bar{\Delta h}$  can be usually found from a table of thermodynamic properties or from specific heat data.
3. If the deviation from ideal-gas behaviour is significant but no tables of thermodynamic properties are available, the value of  $\bar{\Delta h}$  can be found from the generalized tables or charts and the values for  $\bar{f}_0$  or  $\bar{\Delta h}$  at  $0.1 \text{ MPa}$  pressure. The generalized chart for obtaining  $\bar{\Delta h}$  corresponding to  $P_R$  (reduced pressure) is not available in our textbook.

## Enthalpy of Formation

(contd.)

Table A-26 gives the values of the enthalpy of formation (in  $\text{kJ}/\text{kmol}$ ) at the standard reference state.

It may be noted that two  $\bar{h}_f^\circ$  values are given for  $\text{H}_2\text{O}$  in Table A-26, one for liquid water and the other for water vapour.

$$\bar{h}_f^\circ, \text{H}_2\text{O}(\text{g}) = -241,820 \text{ kJ/kmol}$$

$$\bar{h}_f^\circ, \text{H}_2\text{O}(\text{l}) = -285,830 \text{ kJ/kmol}$$

$$\begin{aligned} \bar{h}_f^\circ, \text{H}_2\text{O}(\text{g}) - \bar{h}_f^\circ, \text{H}_2\text{O}(\text{l}) \\ = -241,820 - (-285,830) \\ = 44010 \text{ kJ/kmol} = \bar{h}_{fg, \text{H}_2\text{O}} \end{aligned}$$

## Heating Value of Fuel

Heating value of a fuel is defined as the amount of heat released when a fuel is burned completely in a steady-flow process and the products are returned to the state of the reactants. In other words, the heating value of a fuel is equal to the absolute value of the enthalpy of combustion of the fuel.

That is,

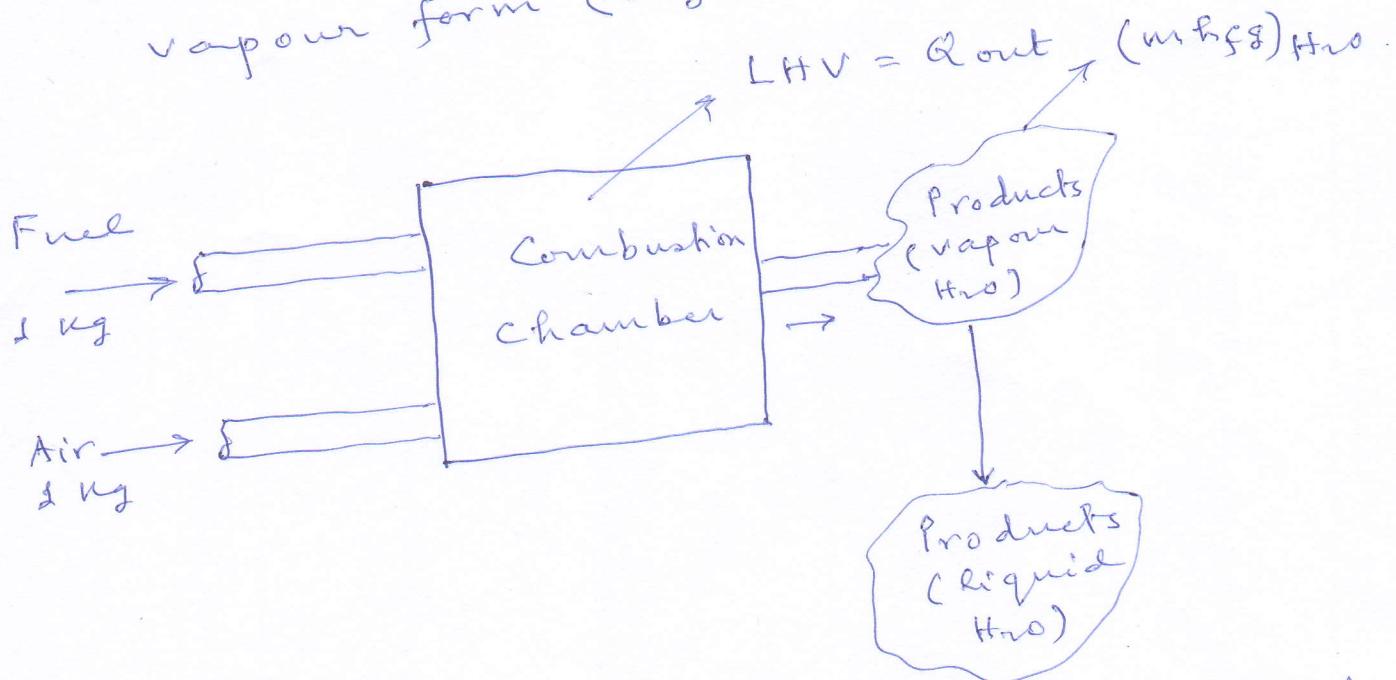
$$\text{Heating value} = |\dot{h}_c| \quad (\text{kJ/kg fuel})$$

Higher Heating Value (HHV)

and Lower Heating Value (LLV)

The heating value depends on the phase of the H<sub>2</sub>O in the products.

The heating value is called the higher heating value (HHV) when the H<sub>2</sub>O in the products is in the liquid form, and it is called the lower heating value (LLV) when the H<sub>2</sub>O in the products is in the vapour form (Fig. 4).



$$HHV = LHV + (m_{H_2O})_{H_2O} \text{ (kg/kg of fuel)}$$

Fig. 4 The relationship between HHV and LHV

The two heating values are related by

$$\boxed{HHV = LHV + (m h_{fg})_{H2O} \text{ (kJ/kg fuel)}}$$

where  $m$  is the mass of  $H_2O$  in the products per unit mass of fuel and  $h_{fg}$  is the enthalpy of vaporization of water at the specified temperature.  $HHV$  and  $LHV$  of common fuels are listed in Table A-2 at the state of 1 atm, 25°C.