

Internal Combustion Engines – MAK 493E

## THERMODYNAMICS of COMBUSTION

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### Thermodynamics of Combustion

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- Properties of mixtures
- Combustion stoichiometry
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- Chemical energy
- Heat of reaction
- Heat of formation
- Chemical equilibrium
- Adiabatic flame temperature
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## Introduction

Thermodynamics deals with equilibrium states and how chemical composition can be calculated for a system of known atomic/molecular composition if two independent thermodynamic properties are known.

Systems undergoing chemical reactions are not in general, in chemical equilibrium - reactions are rate-controlled

Chemical composition at a given instant in time is controlled by the thermodynamic properties, chemical reaction rates and fluid dynamics of the system.

## Introduction

### First Law of Thermodynamics

for a thermodynamic system, the time **rate of change of energy** of the system is equal to the rate at which **work is done** on the system + the rate at which **heat is transferred** to the system.

Neglecting PE and KE within system, energy consists of **internal energy** due to,

- **thermal energy** due to translation, rotation and vibration of molecules - so called **sensible energy**,
- **chemical energy** due to chemical bonds between atoms in the molecules,

For system of mass  $m$ , work done  $W$  and heat transfer rate to the system  $q$ , first law can be written as,

$$\frac{d(mu)}{dt} = \dot{W} + q$$

## Introduction

mechanical work - power is,  $\dot{W} = -pA \frac{dx}{dt} = -p \frac{dV}{dt}$

first law becomes,  $\frac{d(mu)}{dt} = -p \frac{dV}{dt} + q$

thermodynamic properties can be evaluated by assuming that the whole system is uniform or by dividing the system into subsystems that are assumed uniform,

j number of cells with volumes  $V_j$

$$mu = \sum_{j=1}^J \rho_j V_j u_j$$

## Introduction

For a closed system energy balance can be obtained integrating first law equation with-respect-to time,

$$m(u_2 - u_1) = -W_{12} + Q_{12}$$

where

$$W_{12} = \int_{t_1}^{t_2} p \frac{dV}{dt} dt \quad Q_{12} = \int_{t_1}^{t_2} q dt$$

for constant pressure,  $\frac{d(mu + pV)}{dt} = q$

$$\frac{d(mh)}{dt} = q$$

integrating,  $m(h_2 - h_1) = Q_{12}$

## Introduction

If the chemical composition is constant, chemical energy does not change - for ideal gases,

$$u_2 - u_1 = \int_{T_1}^{T_2} c_v dT$$

$$h_2 - h_1 = \int_{T_1}^{T_2} c_p dT$$

$$c_p = c_v + R$$

## Properties of Mixtures

For mixtures of gases, system **mass** is obtained from the sum of masses of separate species,

$$m = \sum_i m_i$$

**density** of system is the sum of species densities,

$$\rho = \sum_i \rho_i$$

**mass fraction** is mass of species  $i$ , divided by total mass,

$$y_i = \frac{m_i}{m} = \frac{\rho_i}{\rho}$$

and by definition

$$\sum_i y_i = 1$$

## Properties of Mixtures

Similarly **mole fraction** is mole of species  $i$ , divided by total number of moles, or ratio of molar concentration of species  $i$  to total molar concentration,

$$x_i = \frac{N_i}{N} = \frac{n_i}{n}$$

and 
$$\sum_i x_i = 1$$

**Molecular weight** is,

$$M = \sum_i \frac{m_i}{N} = \sum_i x_i M_i$$

relation between mole fraction and mass fraction,

$$x_i = \frac{N_i}{N} = \frac{m_i / M_i}{m / M} = \frac{M y_i}{M_i}$$

## Properties of Mixtures

**mixture internal energy and enthalpy per unit mass**,

$$u = \sum_i y_i u_i \quad h = \sum_i y_i h_i$$

**internal energy and enthalpy per mole of mixture**,

$$\hat{u} = \sum_i x_i \hat{u}_i \quad \hat{h} = \sum_i x_i \hat{h}_i$$

**pressure of mixture** – for an ideal gas, is equal to sum of partial  $p$  of component gases if each existed alone in the mixture volume at mixture temperature,

$$\sum_i p_i = \sum_i x_i p = p$$

## Properties of Mixtures

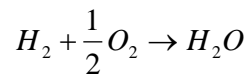
**volume of mixture** – for an ideal gas, is equal to sum of partial volumes which the component gases would occupy if each existed alone at the pressure and temperature of the mixture,

$$\sum_i V_i = \sum_i x_i V = V$$

## Combustion Stoichiometry

When molecules undergo chemical reaction, the reactant atoms are rearranged to form new combinations.

For example, hydrogen and oxygen react to form water :



two atoms of hydrogen and one atom of oxygen form one molecule of water - number of atoms of H and O must be the same on both sides

Such reaction equation represents initial and final states and does not indicate actual path of reaction, which may involve many intermediate steps and intermediate species.

## Combustion Stoichiometry

Relative masses of molecules are obtained by multiplying number of moles of each species by the molecular weights (kg/kg-mol)

For hydrogen-oxygen reaction,  $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

$$\begin{aligned} & (1 \text{ mol } H_2) \left( \frac{2 \text{ kg}}{\text{kg - mol } H_2} \right) + \left( \frac{1}{2} \text{ mol } O_2 \right) \left( \frac{32 \text{ kg}}{\text{kg - mol } O_2} \right) \\ & = (1 \text{ mol } H_2O) \left( \frac{18 \text{ kg}}{\text{kg - mol } H_2O} \right) \end{aligned}$$

mass of reactants equals mass of products, although mols of reactants do not equal moles of products - fixed p and T, ideal gas,

$$1 \text{ volume } H_2 + \frac{1}{2} \text{ volume } O_2 = 1 \text{ volume } H_2O$$

## Combustion Stoichiometry

Stoichiometric calculations are done by performing atom balance for each of the elements in mixture.

The theoretical amount of air required to burn a fuel completely to products with no dissociation is defined as **stoichiometric air**.

In most combustion calculations dry air is assumed as a mixture of 79% (vol)  $N_2$  and 21% (vol)  $O_2$  or 3.764 moles of  $N_2$  per mole  $O_2$

Molecular weight of pure air is 28.96, as it also contains small amounts of argon, carbon dioxide, hydrogen etc.

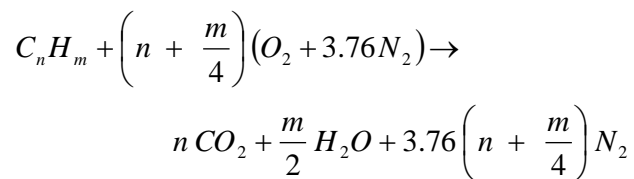
## Dry Air

	% (vol)	% (mass)
N <sub>2</sub>	78.09	75.02
O <sub>2</sub>	20.95	23.15
Ar	0.93	1.28
CO <sub>2</sub>	0.03	0.05

Ne , neon  
He , helium  
Kr , kripton  
Xe , xenon  
H<sub>2</sub> , hydrogen

## IC Engine Combustion

In IC engines, complete combustion of the fuel with air, under ideal conditions - stoichiometric mixture with no dissociation, gives,



Under real engine conditions, CO<sub>2</sub> , CO , H<sub>2</sub> , O<sub>2</sub>, H , O , NO are also produced as a result of the dissociation reactions (parçalanma reaksiyonları).

Sulphur in the fuel produces SO<sub>2</sub> etc.



## Fuel / Air Ratio

Mols of stoichiometric air per mol of fuel,

$$\frac{n_{\text{air-stoich}}}{n_{\text{fuel}}} = 4.76 \left( n + \frac{m}{4} \right)$$

Stoichiometric Fuel / Air ratio by weight,

$$f_{\text{stoich}} = \frac{m_{\text{fuel}}}{m_{\text{air}}} = \frac{M_{\text{fuel}} n_{\text{fuel}}}{M_{\text{air}} n_{\text{air-stoich}}} = \frac{M_{\text{fuel}}}{29.0 \left( n + m/4 \right) 4.76}$$

The percent excess air is, ( $m_{\text{air}}$  actual air used,  $m_{\text{air-stoich}}$  stoichiometric air)

$$\begin{aligned} \% \text{ excess air} &= \frac{100 (m_{\text{air}} - m_{\text{air-stoich}})}{m_{\text{air-stoich}}} \\ &= \frac{100 (n_{\text{air}} - n_{\text{air-stoich}})}{n_{\text{air-stoich}}} = \frac{100 (n_{\text{O}_2} - n_{\text{O}_2\text{-stoich}})}{n_{\text{O}_2\text{-stoich}}} \end{aligned}$$

## Equivalence Ratio

The fuel/air **equivalence ratio** is defined as the actual fuel / air mass ratio, divided by stoichiometric fuel / air mass ratio,

$$\phi = \frac{f}{f_{\text{stoich}}}$$

% excess air is defined as,

$$\% \text{ excess air} = \frac{100 (1 - \phi)}{\phi}$$

**air excess ratio** is defined as,  
(hava fazlalık katsayısı)

$$\lambda = \frac{1}{\phi}$$

## Equivalence Ratio

Stoichiometric mixture,

$$\phi = \lambda = 1.0$$

Lean mixture, (fakir karışım)

$$\phi < 1 \quad \lambda > 1$$

Rich mixture, (zengin karışım)

$$\phi > 1 \quad \lambda < 1$$

## Stoichiometric Combustion

Fuel composition, for 1 kg of fuel,

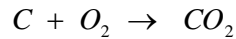
c	kg of carbon
h	kg of hydrogen
o	kg of oxygen
n	kg of nitrogen
s	kg of sulphur
w	kg of water
a	kg of ash, etc

$$c + h + o + n + s + w + a = 1 \text{ kg}$$

## Stoichiometric Combustion

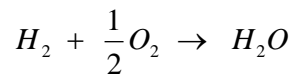
For complete combustion of the fuel the following reactions take place

carbon :



1 mol C + 1 mol O <sub>2</sub>	1 mol CO <sub>2</sub>
12 kg C + 32 kg O <sub>2</sub>	44 kg CO <sub>2</sub>
1 kg C + (32/12) kg O <sub>2</sub>	(44/12) kg CO <sub>2</sub>

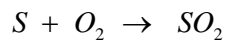
hydrogen :



2 kg H <sub>2</sub> + 16 kg O <sub>2</sub>	18 kg H <sub>2</sub> O
1 kg H <sub>2</sub> + 8 kg O <sub>2</sub>	9 kg H <sub>2</sub> O

## Stoichiometric Combustion

sulphur :



32 kg C + 32 kg O <sub>2</sub>	64 kg CO <sub>2</sub>
1 kg C + 1 kg O <sub>2</sub>	1 kg CO <sub>2</sub>

oxygen required will be,

for c kg carbon	8c/3 kg
for h kg hydrogen	8h kg
for s kg sulphur	s kg

minimum amount of O<sub>2</sub> needed for complete combustion of 1 kg of fuel

$$m_{O-\min} = \frac{8c}{3} + 8h + s - o \quad [\text{kg-O}_2 / \text{kg-fuel}]$$

## Stoichiometric Combustion

$$m_{O-\min} = \frac{8c\sigma}{3} \quad [\text{kg-O}_2 / \text{kg-fuel}]$$

where

$$\sigma = 1 + \frac{3}{8} \left( \frac{8h + s - o}{c} \right)$$

The amount of oxygen in air is 23.3 % by mass,

$$m_{air-\min} = \frac{m_{o-\min}}{0.233} \quad [\text{kg-air} / \text{kg-fuel}]$$

$$m_{air-\min} = 11.44c\sigma \quad [\text{kg-air} / \text{kg-fuel}]$$

## Stoichiometric Combustion

For IC engine fuels  $m_{air-\min} = 14 - 15 \quad [\text{kg-air} / \text{kg-fuel}]$

the ratio of air included in the combustion process, to the theoretically minimum air required gives the air excess ratio,  $\lambda$

$$\lambda = \frac{m_{air}}{m_{air-\min}}$$

equivalence ratio  $\phi = \frac{1}{\lambda}$

## Chemical Energy

To describe the chemical energy released when fuel reacts with air to form products, chemical species in the reactants and products and their states are specified.

Heat of vaporization of liquid fuels and heat of pyrolysis of solid fuels is small compared with the chemical energy released by combustion. But effect of water condensation can be important.

For lean HC-air mixtures with low  $T$ , products may be assumed to be complete (usually  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{O}_2$  and  $\text{N}_2$ ). But with high product  $T$  and rich mixtures it is generally necessary to include other species and assume chemical equilibrium to determine species mole fractions. If products are not in chemical equilibrium, then chemical kinetic analysis (or measurements) is required to determine end state.

## Heat of Reaction

Consider F and A mixture of mass  $m$ , constant-volume combustion with heat transfer,  $Q_v$ , from state 1 to state 2

$$m[(u_2 - u_1)_{sensible} + (u_2 - u_1)_{chemical}] = Q_v$$

for  $n$  species,  $u$  at state 1 can be obtained by,

$$\begin{aligned}(u_1)_{sensible} &= (u(T_1))_{sensible} = \sum_{i=1}^n y_i (u_i(T_1))_{sensible} \\ &= \sum_{i=1}^n y_i \int_{T_o}^{T_1} (c_{v,i})_r dT = \int_{T_o}^{T_1} (c_v)_r dT\end{aligned}$$

$T_o$  is ref temperature,  $(c_v)_r$  is specific heat of reactant mixture

## Heat of Reaction

Similarly, 
$$(u_2)_{sensible} = \int_{T_o}^{T_2} (c_v)_p dT$$

If heat transfer is just large enough to bring products' temperature back to the reactants temperature, and if this T is taken as the ref T, T<sub>o</sub> for sensible energy, then

$$(u_2 - u_1)_{sensible} = 0$$

and Q<sub>v</sub> is the chemical energy released by the reaction  
(sabit hacimdeki reaksiyon ısısı)

The quantity [(1+f)/f](-Q<sub>v</sub>/m) is the **lower heating value** (LHV) of the fuel for constant-volume combustion.

If the water in the products is condensed, that quantity becomes the **higher heating value** (HHV) of the fuel for constant-V combustion

## Heat of Reaction

If reaction takes place at constant pressure,

$$m[(h_2 - h_1)_{sensible} + (h_2 - h_1)_{chemical}] = Q_p$$

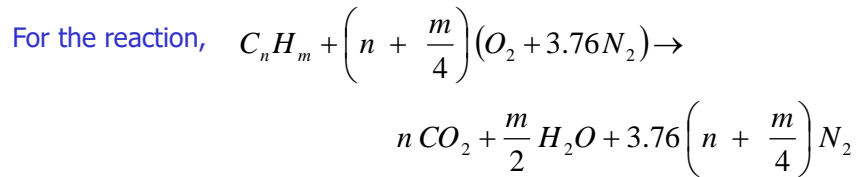
again if T<sub>1</sub> = T<sub>2</sub> = T<sub>o</sub>, then Q<sub>p</sub> is the chemical energy released.

For constant-pressure case, if moles of gaseous products N<sub>p</sub> are larger than moles of gaseous reactants N<sub>r</sub>, then some of the chemical is expended to push aside the ambient pressure. Thus,

$$Q_p - Q_v = \Delta(pV) = (N_p - N_r)\hat{R}T_o = \Delta N\hat{R}T_o$$

Here "overbar" shows quantity per mole

## Heat of Reaction



assume fuel is in gas phase and gaseous water,

$$\Delta N = \frac{m}{4} - 1$$

if  $m > 4$ ,  $\Delta N > 0$ , since both  $Q_v$  and  $Q_p$  are negative,  $|Q_v| > |Q_p|$   
for most cases of interest, the difference is negligible.

## Heat of Reaction

Heat of reaction can be obtained for reactions at T other than  $T_o$

$$Q_p = m \int_{T_1}^{T_o} (c_p)_r dT + Q_p(T_o) + m \int_{T_o}^{T_2} (c_p)_p dT$$

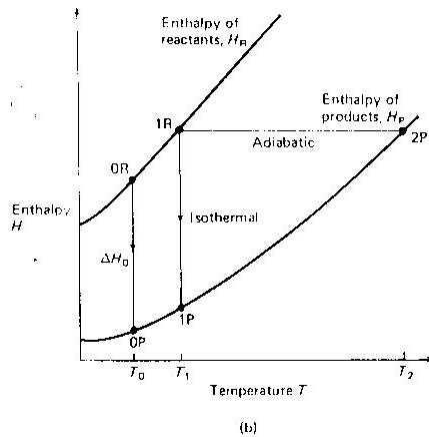
$$Q_p - Q_p(T_o) = m(h_{s2} - h_{s1})$$

$h_s$  is the sensible enthalpy

$Q_p(T_o)$  is negative for an exothermic reaction

## Heat of Reaction

### Enthalpy of reactants and products



## Heat of Formation

Heat of reaction of fuels combusting in air or oxygen with starting and ending points at 25 °C and 1 atm gives fuel heating value. These values are tabulated for common fuels.

This cannot be applied to all reactions - needs enormous amounts of tabulated data. Instead selected reactions and their heat of reactions can be added to obtain any given reaction and its heat of reaction.

**Heat of formation** of a particular species is defined as the heat of reaction per mole of product formed isothermally from elements in their standard states. **Standard state** is chosen as the most stable form of the element at 1 atm and 25 °C

Heat of Formation of elements,  $\Delta h^\circ$  in their standard state is assigned a value of zero. These are given in **JANAF tables**.



## Heat of Formation

Absolute enthalpy of a substance can be calculated from, sensible enthalpy relative to reference T plus the heat of formation at ref T,

$$\hat{h} = \int_{T_o}^T \hat{c}_p dT + \Delta\hat{h}^o$$

where  $\Delta\hat{h}^o$  is the heat of formation

Here overbar, " ^ " shows quantity per mole

## Adiabatic Flame Temperature

at constant-pressure combustion

$$(H_R)_{T_R} = (H_P)_{T_P}$$
$$H_R(T_R) - H_P(T_P) + \Delta H_o = 0$$

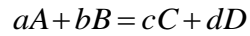
at constant-volume combustion

$$U_R(T_R) - U_P(T_P) + \Delta U_o = 0$$



## Chemical Equilibrium

Considering the following reaction,

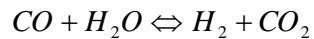


for chemical equilibrium, the equilibrium constants,

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b} = \frac{x_C^c x_D^d}{x_A^a x_B^b} p^{c+d-a-b}$$

## Dissociation Reactions

For example,



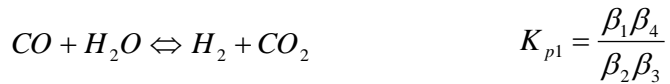
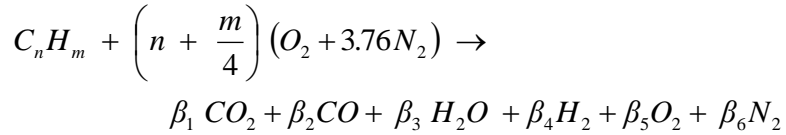
$$k_f = A_f \exp(-E_f / RT)$$

$$k_b = A_b \exp(-E_b / RT)$$

here  $k_f$  and  $k_b$  are the forward and backward reaction rate constants,  
A is the pre-exponential factor, E is the activation energy.

## Dissociation Reactions

Combustion with dissociation,  $\lambda = 1$



## Dissociation Reactions

Carbon balance,  $n = \beta_1 + \beta_2$

Hydrogen balance,  $m/2 = \beta_3 + \beta_4$

Oxygen balance,  $2(n + m/4) = 2\beta_1 + 2\beta_2 + \beta_3 + 2\beta_5$

Equation of state,  $pV = NRT$

main reaction equation + 6 equations to find the values of 6 unknowns

$$\beta_i \quad i=1,2, \dots 6$$

## Dissociation Effects on Flame Temperature

Flame temperature reduces as a result of dissociation reactions.

