



South Valley University
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Applied Thermodynamics MPEG223

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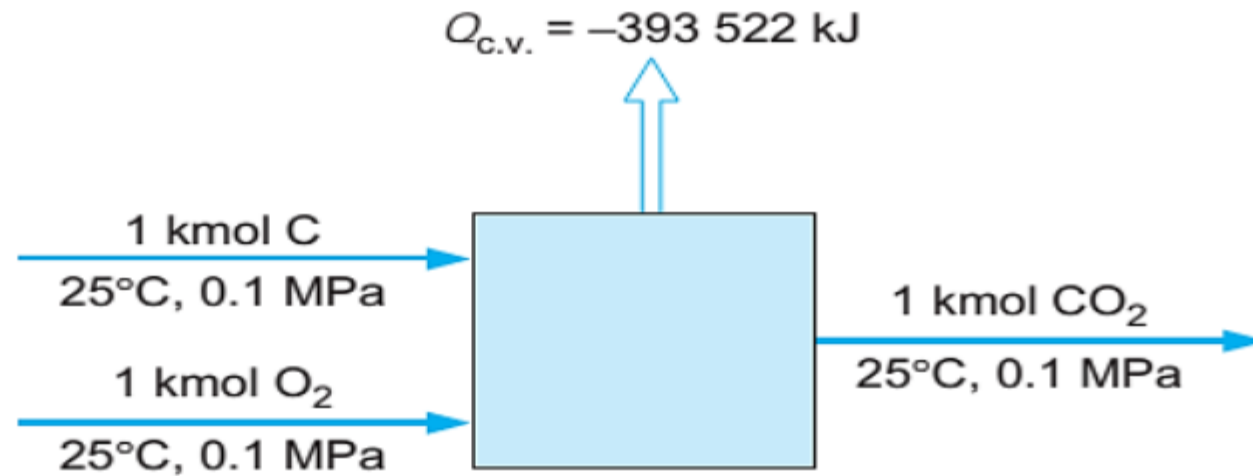
Chemical Reactions

Chapter Contents

The objective of the present chapter is to study chemical reaction, includes;

- ❑ The Combustion Process
 - Theoretical Air
 - Air–Fuel Ratio
 - Excess Air
- ❑ Analysis of the Products of Combustion
- ❑ Enthalpy of Formation
- ❑ First–Law Analysis of Reacting Systems
- ❑ Enthalpy and Internal Energy of Combustion; Heat of Reaction
- ❑ Heating Value
- ❑ Adiabatic Flame Temperature

Enthalpy of Formation



- The chemical reaction can be written;



- Applying the first law to this process, we have;

$$Q_{c.v.} + H_R = H_P$$

$$Q_{c.v} + \sum_R n_i \bar{h}_i = \sum_p n_e \bar{h}_e$$

- ❑ Thus, a measurement of the **heat transfer** would give us the **difference between** the enthalpy of the **products** and the **reactants**,
- ❑ The value of zero to the enthalpy of all the **elements** at the **reference state**.
- ❑ In this case, the enthalpy of the **reactants** is zero, and;

$$Q_{c.v} = H_P = -393\,522 \text{ kJ/kmol}$$

- ❑ The enthalpy of ideal-gas carbon dioxide (CO_2) at 25°C , 0.1 MPa pressure, is called the enthalpy of formation. Thus, for carbon dioxide;

$$\bar{h}_f^0 \text{CO}_2 = -393\,522 \text{ kJ/kmol}$$

Enthalpy of Formation and Absolute Entropy of Various Substances at 25° C, 100 kPa Pressure

Substance	Formula	<i>M</i> kg/kmol	State	\bar{h}_f^0 kJ/kmol	\bar{s}_f^0 kJ/kmol K
Acetylene	C ₂ H ₂	26.038	gas	+226 731	200.958
Ammonia	NH ₃	17.031	gas	-45 720	192.572
Benzene	C ₆ H ₆	78.114	gas	+82 980	269.562
Carbon dioxide	CO ₂	44.010	gas	-393 522	213.795
Carbon (graphite)	C	12.011	solid	0	5.740
Carbon monoxide	CO	28.011	gas	-110 527	197.653
Ethane	C ₂ H ₆	30.070	gas	-84 740	229.597
Ethene	C ₂ H ₄	28.054	gas	+52 467	219.330
Ethanol	C ₂ H ₅ OH	46.069	gas	-235 000	282.444
Ethanol	C ₂ H ₅ OH	46.069	liq	-277 380	160.554
Heptane	C ₇ H ₁₆	100.205	gas	-187 900	427.805
Hexane	C ₆ H ₁₄	86.178	gas	-167 300	387.979
Hydrogen peroxide	H ₂ O ₂	34.015	gas	-136 106	232.991
Methane	CH ₄	16.043	gas	-74 873	186.251
Methanol	CH ₃ OH	32.042	gas	-201 300	239.709
Methanol	CH ₃ OH	32.042	liq	-239 220	126.809
<i>n</i> -Butane	C ₄ H ₁₀	58.124	gas	-126 200	306.647
Nitrogen oxide	N ₂ O	44.013	gas	+82 050	219.957
Nitromethane	CH ₃ NO ₂	61.04	liq	-113 100	171.80
<i>n</i> -Octane	C ₈ H ₁₈	114.232	gas	-208 600	466.514
<i>n</i> -Octane	C ₈ H ₁₈	114.232	liq	-250 105	360.575
Ozone	O ₃	47.998	gas	+142 674	238.932
Pentane	C ₅ H ₁₂	72.151	gas	-146 500	348.945
Propane	C ₃ H ₈	44.094	gas	-103 900	269.917
Propene	C ₃ H ₆	42.081	gas	+20 430	267.066
Sulfur	S	32.06	solid	0	32.056
Sulfur dioxide	SO ₂	64.059	gas	-296 842	248.212
Sulfur trioxide	SO ₃	80.058	gas	-395 765	256.769
<i>T-T</i> -Diesel	C _{14.4} H _{24.9}	198.06	liq	-174 000	525.90
Water	H ₂ O	18.015	gas	-241 826	188.834
Water	H ₂ O	18.015	liq	-285 830	69.950

- The enthalpy of carbon dioxide (CO_2) in **any other state** would be found by adding the change of enthalpy between ideal gas at 25°C , 0.1 MPa , and the given state to the enthalpy of formation. That is, the enthalpy at any temperature and pressure, $h_{T,P}$, is;

$$\bar{h}_{T,P} = (\bar{h}_f^0)_{298,0.1 \text{ MPa}} + (\Delta\bar{h})_{298,0.1 \text{ MPa} \rightarrow T,P}$$

TABLE A.9

Ideal-Gas Properties of Various Substances (SI Units), Entropies at 0.1-MPa (1-Bar) Pressure, Mole Basis

T K	Nitrogen, Diatomic (N_2) $\bar{h}_{f,298}^0 = 0 \text{ kJ/kmol}$ $M = 28.013 \text{ kg/kmol}$		Nitrogen, Monatomic (N) $\bar{h}_{f,298}^0 = 472\,680 \text{ kJ/kmol}$ $M = 14.007 \text{ kg/kmol}$	
	$(\bar{h} - \bar{h}_{298}^0)$ kJ/kmol	\bar{s}_T^0 kJ/kmol K	$(\bar{h} - \bar{h}_{298}^0)$ kJ/kmol	\bar{s}_T^0 kJ/kmol
0	-8670	0	-6197	0
100	-5768	159.812	-4119	130.593
200	-2857	179.985	-2040	145.001
298	0	191.609	0	153.300
300	54	191.789	38	153.429
400	2971	200.181	2117	159.409
500	5911	206.740	4196	164.047
600	8894	212.177	6274	167.837
700	11937	216.865	8353	171.041
800	15046	221.016	10431	173.816
900	18223	224.757	12510	176.265
1000	21463	228.171	14589	178.455
1100	24760	231.314	16667	180.436
1200	28109	234.227	18746	182.244
1300	31503	236.943	20825	183.908
1400	34936	239.487	22903	185.448
1500	38405	241.881	24982	186.883
1600	41904	244.139	27060	188.224
1700	45430	246.276	29139	189.484
1800	48979	248.304	31218	190.672
1900	52549	250.234	33296	191.796

First-Law Analysis of Reacting Systems

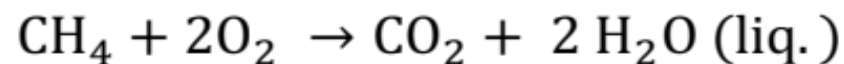
- the first law for a steady-state, steady-flow process in the form;

$$Q_{c.v} + H_R = W_{c.v} + H_P$$

$$Q_{c.v} + \sum_R n_i \bar{h}_i = W_{c.v} + \sum_P n_e \bar{h}_e$$

Tutorial 3: First law of thermodynamics

Consider the following reaction, which occurs in a steady-state, steady-flow process.



The reactants and products are each at a total pressure of 0.1 MPa and 25°C. Determine the heat transfer per kmole of fuel entering the combustion chamber.

Solution.

- Applying the First law of thermodynamics;

$$Q_{c.v} + \sum_R n_i \bar{h}_i = \sum_P n_e \bar{h}_e$$

$$\sum_R n_i \bar{h}_i = (\bar{h}_f^0)_{\text{CH}_4} = -74873 \text{ kJ}$$

$$\sum_P n_e \bar{h}_e = (n \bar{h}_f^0)_{\text{CO}_2} + (n \bar{h}_f^0)_{\text{H}_2\text{O}} = -393522 + 2(-285830) = -965182 \text{ kJ}$$

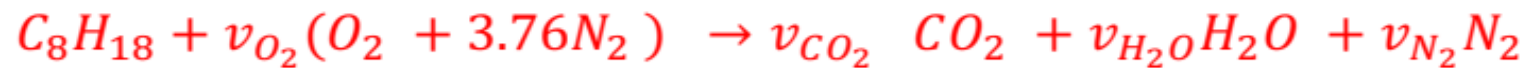
$$Q_{c.v} = -965182 + 74873 = -890309 \text{ kJ}$$

Tutorial 4: First law of thermodynamics

A small gas turbine uses $C_8H_{18}(L)$ for fuel and 400% theoretical air. The air and fuel enter at 25°C , and the products of combustion leave at 900 K. The output of the engine and the fuel consumption are measured, and it is found that the specific fuel consumption is 0.25 kg/s of fuel per megawatt output. Determine the heat transfer from the engine per kmole of fuel.

Solution:

- The theoretical combustion equation is;





- The actual combustion equation is;



- Applying the First law of thermodynamics;

$$Q_{c.v} + \sum_R n_i \bar{h}_i = W_{c.v} + \sum_p n_e \bar{h}_e$$

$$Q_{c.v} + \sum_R n_i (\bar{h}_f^0 + \Delta \bar{h})_i = W_{c.v} + \sum_p n_e (\bar{h}_f^0 + \Delta \bar{h})_e$$

$$\sum_R n_i (\bar{h}_f^0 + \Delta \bar{h})_i = (\bar{h}_f^0)_{C_8H_{18}} = -250\,105 \frac{kJ}{kmol}$$

Substance	Formula	M kg/kmol	State	\bar{h}_f^0 kJ/kmol	\bar{s}_f^0 kJ/kmol K
<i>n</i> -Octane	C_8H_{18}	114.232	liq	-250 105	360.575



$$\sum_p n_e (\bar{h}_f^0 + \Delta \bar{h})_e = n_{CO_2} (\bar{h}_f^0 + \Delta \bar{h})_{CO_2} + n_{H_2O} (\bar{h}_f^0 + \Delta \bar{h})_{H_2O} + n_{O_2} (\bar{h}_f^0 + \Delta \bar{h})_{O_2} + n_{N_2} (\bar{h}_f^0 + \Delta \bar{h})_{N_2}$$

$$= 8(-393\,522 + 28\,030) + 9(-241\,826 + 21\,937) + 37.5(19\,241) + 188(18\,223) = -755\,476 \frac{kJ}{kmol}$$

$$W_{c.v} = \frac{1000}{0.25} * 114.23 = 456\,920 \text{ kJ/kmol}$$

$$Q_{c.v} - 250\,105 = 456\,920 - 755\,476$$

$$Q_{c.v} = -48\,451 \text{ kJ/kmol}$$

<i>T</i> K	Nitrogen, Diatomic (N₂) $\bar{h}_{f,298}^0 = 0 \text{ kJ/kmol}$ $M = 28.013 \text{ kg/kmol}$		Nitrogen, Monatomic (N) $\bar{h}_{f,298}^0 = 472\,680 \text{ kJ/kmol}$ $M = 14.007 \text{ kg/kmol}$	
	$(\bar{h} - \bar{h}_{298}^0)$ kJ/kmol	\bar{s}_T^0 kJ/kmol K	$(\bar{h} - \bar{h}_{298}^0)$ kJ/kmol	\bar{s}_T^0 kJ/kmol
900	18223	224.757	12510	176.265

Enthalpy and Internal Energy of Combustion; Heat of Reaction

- The enthalpy of combustion, h_{RP} , is defined as the difference between the enthalpy of the products and the enthalpy of the reactants when complete combustion occurs at a given temperature and pressure.

$$Q_{c.v} + \sum_R n_i \bar{h}_i = \sum_p n_e \bar{h}_e \rightarrow Q_{c.v} = \bar{h}_{PR} = H_p - H_R$$

$$\bar{h}_{PR} = \sum_p n_e (\bar{h}_f^0 + \Delta \bar{h})_e - \sum_R n_i (\bar{h}_f^0 + \Delta \bar{h})_i$$

- The internal energy of combustion is defined in a **similar manner**.

$$Q_{c.v} + \sum_R n_i \bar{U}_i = \sum_p n_e \bar{U}_e$$

$$\bar{u}_{PR} = \sum_p n_e (\bar{h}_f^0 + \Delta \bar{h} - \bar{R}T) - \sum_R n_i (\bar{h}_f^0 + \Delta \bar{h} - \bar{R}T)$$

Heating Value

- ❑ This represents the heat transferred from the chamber during combustion/reaction at constant temperature.
- ❑ In the case of a **constant pressure** or steady-flow process, it is equal to the **negative of the enthalpy of combustion**.
- ❑ In the case of a **constant-volume** process, the heat transfer is equal to the **negative of the internal energy of combustion**.
- ❑ When the term heating value is used, the terms **higher** and **lower** heating value are used.
- ❑ The **higher** heating value is the heat transfer with **liquid water** in the products,
- ❑ The **lower** heating value is the heat transfer **with vapor water** in the products.

Adiabatic Flame Temperature

- ❑ Consider a given **combustion process** that takes place **adiabatically** and with no work or changes in kinetic or potential energy involved.
- ❑ For such a process the temperature of the products is referred to as the adiabatic flame temperature.
- ❑ For a given fuel and given pressure and temperature of the reactants, the **maximum** adiabatic flame temperature that can be achieved is with a **stoichiometric mixture**.
- ❑ The adiabatic flame temperature can be controlled by the amount of **excess air** that is used.
- ❑ This is important, for example, in gas turbines, where the maximum permissible temperature is determined by **metallurgical considerations**.

The End of Lecture