Thermodynamics of Combustion

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ME 6163: Combustion Engineering
http://zahurul.buet.ac.bd/ME6163/

Overview

1. Properties of Mixtures

2. Combustion Stoichiometry

3. Heat Release Parameters
   Heating Values of Fuels
   Adiabatic Flame Temperature

4. Coal Combustion

5. Chemical Equilibrium
   Equilibrium Composition: HC Fuel Combustion
   Equilibrium Composition: Simple Calculation

Ideal Gas Mixtures[1]

- $m = m_1 + m_2 + m_3 + \cdots + m_k = \sum_{i=1}^{k} m_i$

$$Y_i \equiv \frac{m_i}{m} \quad :\Rightarrow \quad \sum_{i=1}^{k} Y_i = 1$$

- $n = n_1 + n_2 + n_3 + \cdots + n_k = \sum_{i=1}^{k} n_i$

$$X_i \equiv \frac{n_i}{n} \quad :\Rightarrow \quad \sum_{i=1}^{k} X_i = 1$$

m_i = mass of component i
m = total mass of mixture
n_i = number of moles of component i
n = total number of moles in mixture
Y_i = mass fraction of component i
X_i = mole fraction of component i
M_i = molecular mass of component i
M = apparent molecular mass of mixture i

[1] M. Moran et al. (2014). *Fundamentals of Engineering Thermodynamics.* 8th ed. Wiley.

$$m_i = n_i M_i \quad : \quad m = nM$$

- $M = \frac{m}{n} = \frac{m_1 + m_2 + \cdots + m_k}{n} = \frac{n_1 M_1 + n_2 M_2 + \cdots + n_k M_k}{n} = \sum_{i=1}^{k} \left(\frac{n_i}{n}\right) M_i$

$$M = \sum_{i=1}^{k} X_i M_i$$

Dry air: $78.08\% N_2, 20.95\% O_2, 0.93\% Ar, 0.03\% CO_2$

$M = 0.7808 \cdot 28 + 0.2095 \cdot 32 + 0.0093 \cdot 39.94 + 0.0003 \cdot 44 = 28.95$ kg/kmol

- Apparent gas constant, $R = \frac{R_u}{M}$

$R_{air} = \frac{8.314}{28.95} = 0.287$ kJ/kg K

- $M = \frac{m}{n} = \frac{m}{\sum_{i=1}^{k} n_i} = \frac{m}{\sum_{i=1}^{k} \left(\frac{m_i}{M_i}\right)} = \frac{1}{\sum_{i=1}^{k} \left(\frac{m_i/m}{M_i}\right)} = \frac{1}{\sum_{i=1}^{k} \left(\frac{Y_i}{M_i}\right)}$

$$M = \frac{1}{\sum_{i=1}^{k} \left(\frac{Y_i}{M_i}\right)}$$

- $Y_i = \frac{m_i}{m} = \frac{n_i M_i}{\sum n_i M_i} = \frac{n_i M_i/n}{\sum n_i M_i/n} = \frac{X_i M_i}{\sum X_i M_i} \quad :\Rightarrow \quad Y_i = \frac{X_i M_i}{M}$

$$Y_i = \frac{X_i M_i}{M} = \frac{X_i M_i}{\sum X_i M_i} \quad : \quad X_i = \left(\frac{Y_i}{M_i}\right) M = \frac{Y_i/M_i}{\sum Y_i/M_i}$$

Illustrative Example: Mass Fraction to Mole Fraction

$$X_i = \left(\frac{Y_i}{M_i}\right) M = \frac{Y_i/M_i}{\sum Y_i/M_i}$$

i	Y_i	M_i	$\frac{Y_i}{M_i}$	$X_i = \frac{Y_i/M_i}{\sum Y_i/M_i}$
H_2	0.10	2.0	0.050	0.6250
O_2	0.48	32.0	0.015	0.1875
CO	0.42	28.0	0.015	0.1875
	1.00	-	0.080	1.0000

$$M = \frac{1}{\sum Y_i/M_i} = \frac{1}{0.080} = 12.5 \ kg/kmol.$$

- If m_i's are given:
  - $m_i \longrightarrow Y_i = \frac{m_i}{\sum m_i} = \frac{m_i}{m}$
  - $n = \frac{m}{M}$
  - $n_i = X_i n$

Illustrative Example: Mole Fraction to Mass Fraction

$$Y_i = \frac{X_i M_i}{M} = \frac{X_i M_i}{\sum X_i M_i}$$

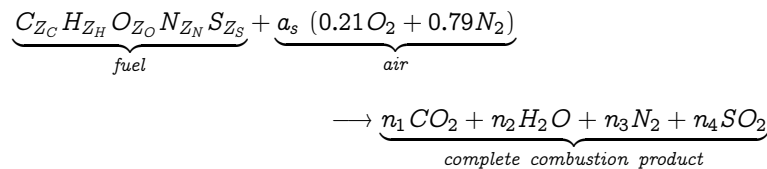| i	X_i	M_i	$X_i M_i$	$Y_i = \frac{X_i M_i}{\sum X_i M_i}$
H_2	0.6250	2.0	1.25	0.10
O_2	0.1875	32.0	6.00	0.48
CO	0.1875	28.0	5.25	0.42
	1.00	-	12.5	1.0000

$$M = \sum X_i M_i = 12.5 \ kg/kmol.$$

- If n_i's are given:
  - $n_i \longrightarrow X_i = \frac{n_i}{\sum n_i} = \frac{n_i}{n}$
  - $m = nM$
  - $m_i = Y_i m$

Combustion Stoichiometry[2]

$$\underbrace{C_{Z_C} H_{Z_H} O_{Z_O} N_{Z_N} S_{Z_S}}_{fuel} + \underbrace{a_s \ (0.21 O_2 + 0.79 N_2)}_{air}$$

$$\longrightarrow \underbrace{n_1 CO_2 + n_2 H_2O + n_3 N_2 + n_4 SO_2}_{complete \ combustion \ product}$$

- Z_i be the number of moles of the ith element per mole of fuel.
- Atom balance:

C : $Z_C = n_1$
H : $Z_H = 2n_2$
O : $Z_O + 2(0.21) a_s = 2n_1 + n_2 + 2n_4 \Rightarrow$
N : $Z_N + 2(0.79) a_s = 2n_3$
S : $Z_S = n_4$

$a_s = \frac{Z_C + \frac{Z_H}{4} + Z_S - \frac{Z_O}{2}}{0.21}$
$n_1 = Z_C$
$n_2 = \frac{Z_H}{2}$
$n_3 = \frac{Z_N}{2} + 0.79 a_s$
$n_4 = Z_S$

[2] A. Culp (1991). *Principles of Energy Conversion*. 2nd ed. McGraw-Hill.

$\left(\frac{A}{F}\right)_{T,M,D} \equiv$ Theoretical (stoichiometric), Molar, Dry air-fuel ratio
$\left(\frac{A}{F}\right)_{T,G,D} \equiv$ Theoretical, Gravimetric, Dry air-fuel ratio
$\left(\frac{A}{F}\right)_s \equiv$ Stoichiometric air-fuel ratio

$$\left[\frac{A}{F}\right]_{T,M,D} = a_s = \frac{Z_C + \frac{Z_H}{4} + Z_S - \frac{Z_O}{2}}{0.21}$$

$$\left[\frac{A}{F}\right]_{T,G,D} = \left[\frac{A}{F}\right]_s = \frac{28.97 \left(\frac{A}{F}\right)_{T,M,D}}{M_{fuel}}$$

$$M_{fuel} = 12 Z_C + Z_H + 16 Z_O + 14 Z_N + 32 Z_S$$

To include the water vapour contained in the atmospheric air:

$$\left[\frac{A}{F}\right]_{T,M,W} = \left[1 + \frac{\omega}{0.622}\right] \left[\frac{A}{F}\right]_{T,M,D}$$

$$\left[\frac{A}{F}\right]_{T,G,W} = (1 + \omega) \left[\frac{A}{F}\right]_{T,G,D}$$

- $X_{s,fuel} = \frac{1}{1+a_s}$, $Y_{s,fuel} = \frac{1}{1+(A/F)_s}$
- $\phi \equiv$ fuel-air equivalence ratio, simply equivalence ratio
- $\lambda \equiv$ relative air-fuel ratio or excess-air factor or dilution coefficient

$$\phi = \lambda^{-1} = \frac{(A/F)_s}{(A/F)_a} = \frac{(F/A)_a}{(F/A)_s}: \quad \phi = \begin{cases} < 1 & : \text{lean mixture} \\ = 1 & : \text{stoichiometric mix.} \\ > 1 & : \text{rich mixture} \end{cases}$$

- Percent excess air $= 100(\lambda - 1]$
- Actual air-fuel ratio,

$$\left[\frac{A}{F}\right]_{A,G,D} = \lambda \left[\frac{A}{F}\right]_{T,G,D}$$

$\left(\frac{A}{F}\right)_{A,M,D} \equiv$ Actual, Molar, Dry air-fuel ratio
$\left(\frac{A}{F}\right)_{T,G,D} \equiv$ Theoretical, Gravimetric, Dry air-fuel ratio

$$\left[\frac{A}{F}\right]_{A,M,D} = \left[\frac{(\%N_2)(Z_c)}{(\%CO + \%CO_2)} - \frac{Z_N}{2}\right]\frac{1}{0.79}$$

Illustrative Example: Dew-point of Combustion Products[3]

Fuel: 92% CH_4, 9% H_2, 14% N_2, 2% O_2, 3% CO_2

Air: 20°C, 1 atm, 80% RH $\rightarrow \omega = 0.01175$

Stoichiometric combustion, $\phi = 1.0$

- $Z_C = 0.75$, $Z_H = 3.06$, $Z_S = 0$, $Z_N = 0.28$, $Z_O = 0.01$
- $\Rightarrow (A/F)_{T,M,D} = 6.975$, $(A/F)_{T,M,W} = 7.108$
- water moles $= 7.108 - 6.975 = 0.132$ (from air moisture)
- Fuel $+ 6.975$ Air $+ 0.132\,H_2O \longrightarrow 0.75\,CO_2 + 1.662\,H_2O + 5.651\,N_2$
- $P_{water} = (1.662/8.063)P_{atm} \rightarrow P_{water} = 20.8$ kPa.
- $T_{dp} = P_{sat}(20.8\ kPa) = 60.9^oC$

[3]Y. Çengel (2014). *Thermodynamics: An Engineering Approach.* 8th ed. McGraw-Hill.
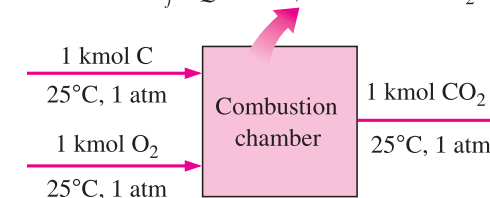

Illustrative Problems[4]:

- Culp Ex. 3.5 ▷ A natural gas with the following molar analysis is burned in a furnace: $CO_2 = 0.5\%$, $CO = 5.0\%$, $CH_4 = 87.0\%$, $C_2H_4 = 3.0\%$ and $N_2 = 4.5\%$. An exhaust analysis gives the following results: 9.39% CO_2, 3.88% O_2 and 0.83% CO. Estimate actual-air fuel ratio and percent excess air.

[4]A. Culp (1991). *Principles of Energy Conversion.* 2nd ed. McGraw-Hill.

Enthalpy of Formation

$\bar{h}_f^\circ = Q = -393{,}520$ kJ/kmol CO_2

1 kmol C, 25°C, 1 atm → Combustion chamber

1 kmol O_2, 25°C, 1 atm → Combustion chamber

→ 1 kmol CO_2, 25°C, 1 atm

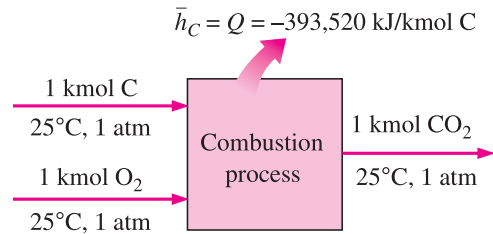T302

- The enthalpy of formation of a compound represents the amount of energy absorbed or released as the component is formed from its stable elements during a steady-flow process at a specified state.
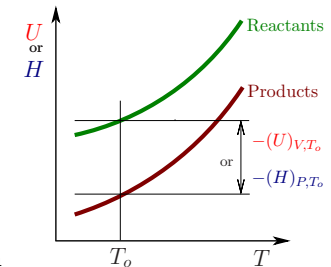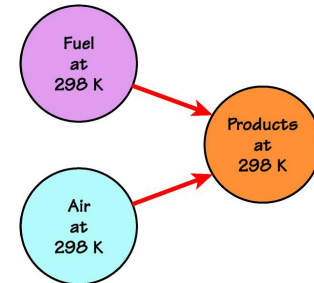
Heat of Combustion

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

1 kmol C
25°C, 1 atm

1 kmol O_2
25°C, 1 atm

Combustion process

1 kmol CO_2
25°C, 1 atm

T303

- The enthalpy of combustion represents the amount of energy released as a fuel is burned during a steady-flow process at a specified state.
- $Heating\ Value = |h_c| = |H_P - H_R| = |\sum_P n_i H_i - \sum_R n_i H_i|$
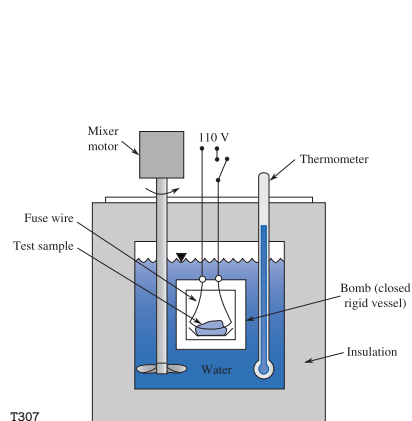

Heating Values of Fuels[5]

Fuel at 298 K

Air at 298 K

Products at 298 K

U or H

Reactants

Products

$-(U)_{V,T_o}$ or $-(H)_{P,T_o}$

T_o T

T296   d001

- The heating value is the heat release per unit mass of the fuel initially at 25°C reacts completely with oxygen (or air) and the products are returned to 25°C.
- Heating value at constant pressure $\equiv Q_{HV,P} = -(\Delta H)_{P,T_o}$
- Heating value at constant volume $\equiv Q_{HV,V} = -(\Delta U)_{V,T_o}$

[5]S. Turns (2012). *An Introduction to Combustion: Concepts and Applications*. 3rd ed. McGraw-Hill.
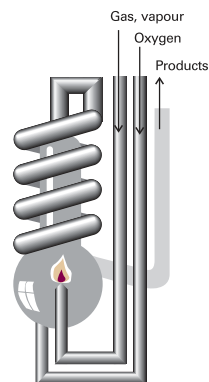

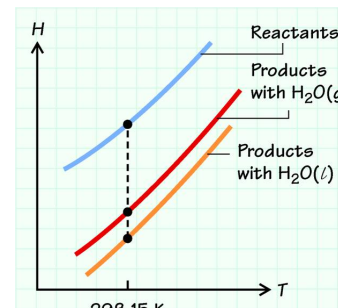$$Q_{HV,P} - Q_{HV,V} = -P(V_{prod} - V_{reac}) = -R_u(n_{prod} - n_{reac})T_o$$

Mixer motor

110 V

Thermometer

Fuse wire

Test sample

Water

Bomb (closed rigid vessel)

Insulation

T307

Gas, vapour
Oxygen
Products

T308

Constant Pressure Flame Calorimeter

Constant Volume Bomb Calorimeter

H

Reactants

Products with $H_2O(g)$

Products with $H_2O(\ell)$

298.15 K

T

LHV = Q_{out}

$(mh_{fg})_{H_2O}$

Fuel 1 kg

Air

Combustion chamber

Products (vapor H_2O)

Products (liquid H_2O)
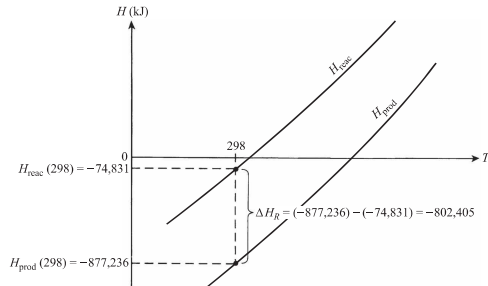
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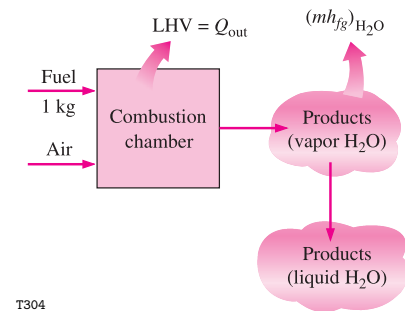
$$Q_{HHV,P} = Q_{LHV,P} + \left[\frac{m_{H_2O}}{m_{fuel}}\right] h_{fg,H_2O}$$

- $Q_{HHV,P} \equiv$ Higher (Gross) Heating Value
- $Q_{LHV,P} \equiv$ Lower (Net) Heating Value
- $m_{H_2O}/m_{fuel} \equiv$ mass ratio of water produced to fuel burned.
- $h_{fg,H_2O,298K} = 2.445$ MJ/kg for water

Illustrative Example: Methane-Air Combustion[6]

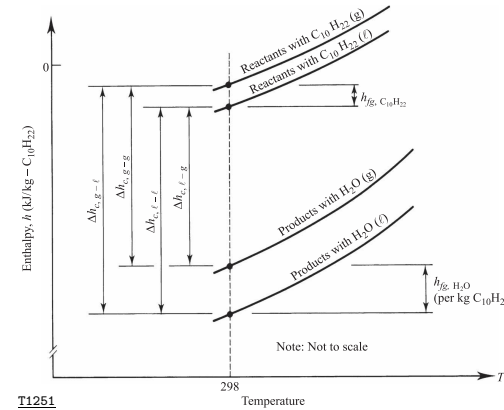
- $CH_4 + a_s\,(0.21\,O_2 + 0.79\,N_2) \longrightarrow n_1\,CO_2 + n_2\,H_2O + n_3\,N_2$

- $a_s = 9.52,\ n_1 = 1.0,\ n_2 = 2.0,\ n_3 = 7.52$

$\Longrightarrow$ LHV = (802.33/16.0) MJ/kg = 50.14 MJ/kg

$\Longrightarrow$ HHV = 50.14 + 2 × 18 /16 ×2.445 = 55.64 MJ/kg

[6]S. Turns (2012). *An Introduction to Combustion: Concepts and Applications.* 3rd ed. McGraw-Hill.

Illustrative Problem: Liquid n-decane ($C_{10}H_{22}$) Combustion[7]

Data for n-decane:

- $\bar{h}_f^o$ = - 249659 kJ/kmol

- h_{fg} = 277 kJ/kmol

- HHV (liq. fuel) = 48.0, LHV (liq. fuel) = 44.6 MJ/kg fuel
- HHV (gaseous fuel) = 48.3, LHV (gaseous fuel) = 44.9 MJ/kg fuel

[7]S. Turns (2012). *An Introduction to Combustion: Concepts and Applications.* 3rd ed. McGraw-Hill.

Higher Heating Values of Some Fuels[8]

Fuel	Heating value		
	MJ/kg	BTU/lb	kJ/mol
Hydrogen	141.8	61,100	286
Methane	55.5	23,900	890
Ethane	51.9	22,400	1,560
Propane	50.35	21,700	2,220
Butane	49.5	20,900	2,877
Gasoline	47.3	20,400	~5,400
Paraffin	46	19,900	16,300
Diesel	44.8	19,300	~4,480
Coal	15–27	8,000–14,000	200–350
Wood	15	6,500	300
Peat	6–15	2,500–6,500	
Methanol	22.7	9,800	726
Ethanol	29.7	12,800	1,368
Propanol	33.6	14,500	2,020
Acetylene	49.9	21,500	1,300
Benzene	41.8	18,000	3,270
Ammonia	22.5	9,690	382
Hydrazine	19.4	8,370	622
Hexamine	30.0	12,900	4,200
Carbon	32.8	14,100	393.5

[8]S. McAllister, J. Chen, and A. Fernandez-Pello (2011). *Fundamentals of Combustion Processes.* Springer.

Adiabatic Flame Temperature
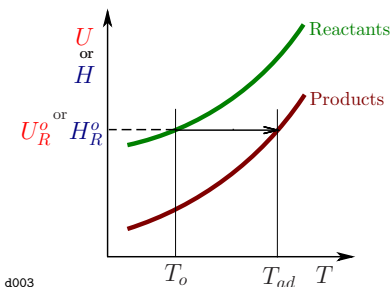
$U_R^o = U_{prod}(T_{ad}, V = \text{constant})$

$H_R^o = H_{prod}(T_{ad}, P = \text{constant})$

Adiabatic Flame Temperature is the product temperature in an ideal adiabatic combustion process. Actual peak temperatures in engines are several hundred degrees less due to:

- heat loss from the flame

- combustion efficiency is less than 100%: a small fraction of fuel does not get burned, and some product components dissociate (endothermic reaction) at high temperatures.

- Adiabatic Constant Pressure Combustion:
- $Q_{out} = 0, \ T = T_{ad,P}$
- $\Rightarrow \displaystyle\sum_{reac} n_i h_i^o = \sum_{prod} n_i(h_i^o + \Delta h_{i,T})$
- $\Rightarrow \displaystyle\sum_{prod} n_i(\Delta h_{i,T}) = \sum_{reac} n_i h_i^o - \sum_{prod} n_i h_i^o$
- Constant Volume Combustion:
- $Q_{out} = 0, \ T = T_{ad,V}$
- $\Rightarrow \displaystyle\sum_{prod} n_i(\Delta h_{i,T}) - n_{prod} R_u T_{ad,V} = \sum_{reac} n_i h_i^o - \sum_{prod} n_i h_i^o - n_{reac} R_u T_0$

Illustrative Problem: Turns Ex. 2.5 & 2.5[9] ▷ Methane-air combustion: adiabatic flame temperature for a) at constant pressure, b) at constant volume.

[9]S. Turns (2012). *An Introduction to Combustion: Concepts and Applications.* 3rd ed. McGraw-Hill.

Adiabatic Flame Temperatures of some Fuels[10]

Fuel	Equivalence ratio, F		
	0.8	1.0	1.2
Gaseous Fuels			
Methane	2020	2250	2175
Ethane	2040	2265	2200
Propane	2045	2270	2210
Octane	2150	2355	2345
Liquid Fuels			
Octane	2050	2275	2215
Cetane	2040	2265	2195
No. 2 fuel oil	2085	2305	2260
Methanol	1755	1975	1810
Ethanol	1935	2155	2045
Solid Fuel (Dry)			
Bituminous coal	1990	2215	2120
Lignite	1960	2185	2075
Wood	1930	2145	2040
RDF[a]	1960	2175	2085
Solid Fuels (25% Moisture)			
Lignite	1760	1990	1800
Wood	1480	1700	1480
RDF[a]	1660	1885	1695

T1254

[10]G. Borman and K. Ragland (1998). *Combustion Engineering.* McGraw-Hill.
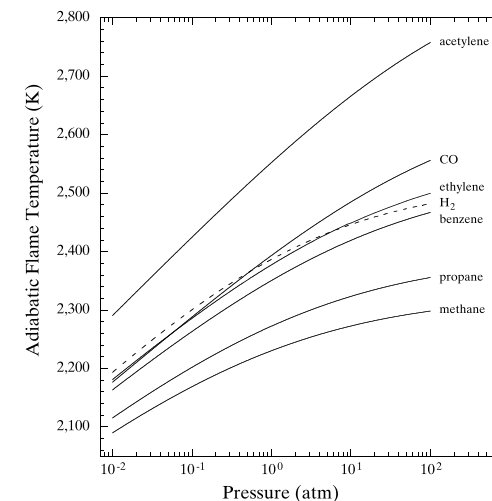
T1265

Increasing pressure suppresses (endothermic) dissociation reactions.

Coal Analysis[11]

1. **Proximate analysis**: gives the mass fraction of fixed carbon (FC), volatile matter (VM), ash (A) and moisture (M) in the coal sample.

2. **Ultimate analysis**: a laboratory analysis that lists the mass fractions of carbon (C), hydrogen (H_2), nitrogen (N_2) and sulphur (S), required for combustion-air calculations.

- Ash is essentially the inorganic matter deposited with the organic materials during the compaction process.

- As moisture and ash fractions can vary widely, a common practice is to report on a moisture-free (dry) and ash-free basis.

- As-burned mass fraction = [dry, ash-free mass fraction][1-M-A]

- As-burned HHV = [dry, ash-free HHV][1-M-A]

[11] A. Culp (1991). *Principles of Energy Conversion*. 2nd ed. McGraw-Hill.

For coal, where the moisture and ash values are as-burned values and all other values are dry, ash-free values:

$$\left[\frac{A}{F}\right]_{T,G,D} = \frac{[2.66\,C + 7.94\,H_2 + 0.998\,S - O_2](1 - M - A)}{0.232}$$

C = mass fraction of coal in dry, ash-free coal
M = as-burned moisture content
A = as-burned ash content

- $HHV = 33950\,C + 144200\left(H_2 - \frac{O_2}{8}\right) + 9400\,S$ (kJ/kg)
- $HHV - LHV = 2400(M + 9H_2)$ (kJ/kg)
- ♣ Mass fractions of C, H_2, O_2, S must be at as-received/as-burned condition.

Illustrative Example: Coal-combustion
Culp Ex.2.1 & 3.1 ▷ Estimate A/F, HHV & LHV

- Proximate analysis of dry, ash-free coal:
  VM = 54.0% & FC = 46.0%

- Ultimate analysis of dry, ash-free coal:
  C = 72.4%, H_2 = 4.7%, O_2 = 18.6%, N_2 = 1.5% & S = 2.8%

- As received condition: M = 39% & A = 8.0%

Criterion for Chemical Equilibrium[12]
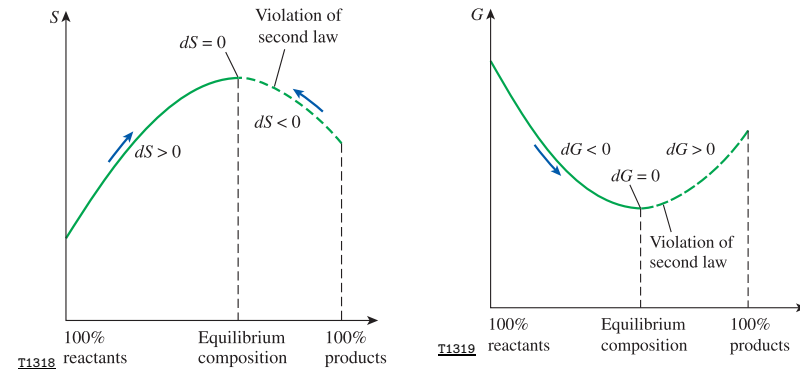
Criteria for adiabatic reactions

Criteria for fixed mass reactions at specified P and T

[12] Y. Çengel (2014). *Thermodynamics: An Engineering Approach*. 8th ed. McGraw-Hill.

Equilibrium Constant, K_p [13]

| Reaction |
| chamber |
| T, P |
| N_A moles of A |
| N_B moles of B |
| N_C moles of C |
| N_D moles of D |

T1320

$$dN_A\, A + dN_B\, B \longrightarrow dN_C\, C + dN_D\, D$$

- $dN_A = -\epsilon\nu_A, \ dN_B = -\epsilon\nu_B$
- $dN_C = +\epsilon\nu_C, \ dN_D = +\epsilon\nu_D$
- ϵ is a proportionality constant.

$$\Rightarrow \nu_A\, A + \nu_B\, B \rightleftharpoons \nu_C\, C + \nu_D\, D$$

- $G_{mix} = \sum_{R\to P} N_i g_{i,T} = \sum_{R\to P} N_i(g_{i,T}^o + R_u T \ln(\frac{P_i}{P_0}))$

- For fixed T & P, equilibrium condition:

$$\Rightarrow dG_{mix} = 0 = \sum_{R\to P} dN_i(g_{i,T}^o + R_u T \ln(\frac{P_i}{P_0}))$$

[13]S. Turns (2012). *An Introduction to Combustion: Concepts and Applications.* 3rd ed. McGraw-Hill.

- $[\nu_C g_{C,T}^o + \nu_D g_{D,T}^o - \nu_A g_{A,T}^o - \nu_B g_{B,T}^o] = -R_u T \sum_{R\to P} \nu_i \ln\left(\frac{P_i}{P_0}\right)$

$$\implies \Delta G_T^o = -R_u T \ln\left[\frac{(P_C/P_0)^{\nu_C}(P_D/P_0)^{\nu_D}}{(P_A/P_0)^{\nu_A}(P_B/P_0)^{\nu_B}}\right] = -R_u T \ln(K_P)$$

- $K_P = \exp\left[-\frac{\Delta G_T^o}{R_u T}\right]$

- Equilibrium constant, $K_P \equiv \frac{(P_C/P_0)^{\nu_C}(P_D/P_0)^{\nu_D}}{(P_A/P_0)^{\nu_A}(P_B/P_0)^{\nu_B}}$

- $K_P = e^{(-\Delta G_T^o/R_u T)} = e^{-\Delta H^o/R_u T}\, \dot{e}^{\Delta S^o/R_u}$

- For $K_P > 0$, which favours products, ΔH^o should be negative, exothermic reaction.

- For gaseous mixture, $P_i = X_i P$, and if $\Delta\nu = \nu_C + \nu_D - \nu_A - \nu_B$,

$$\Rightarrow K_P = \frac{X_C^{\nu_C} X_D^{\nu_D}}{X_A^{\nu_A} X_B^{\nu_B}}\left[\frac{P}{P_0}\right]^{\Delta\nu} = \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}}\left[\frac{P/P_0}{N_T}\right]^{\Delta\nu}$$

- N_T is the total number of moles present in the reaction vessel.

Illustrative Example[14]: Dissociation of CO_2 at 2500 K, 10 atm

	CO_2	$\rightleftharpoons$	CO	$+$	$\frac{1}{2} O_2$
$T = 298$ K	1		0		0
$T = 2500$ K	1 - α		α		$\alpha/2$
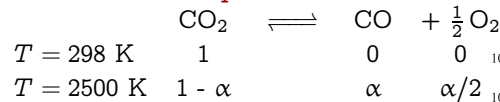
- $\Delta G_{2500}^o = [g_{CO} + 0.5 g_{O2} - g_{CO2}]_{2500}$

- $\Rightarrow K_P = \exp(-\Delta G_T^o/R_u T) = 0.0363$

- $K_P = \frac{X_{CO} X_{O2}^{0.5}}{X_{CO2}}\left(\frac{P}{P_0}\right)^{1+0.5-1}$

- $\Rightarrow 0.036 = \frac{\left(\frac{\alpha}{1+\alpha/2}\right)\left(\frac{\alpha/2}{1+\alpha/2}\right)^{1/2}}{\left(\frac{1-\alpha}{1+\alpha/2}\right)} 10^{0.5}$

- $\implies \alpha = 0.06205 \ \to X_{CO} = 0.0602$

T1213
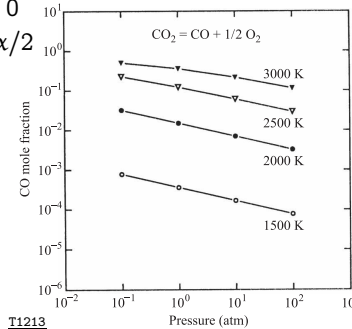
[14]S. Turns (2012). *An Introduction to Combustion: Concepts and Applications.* 3rd ed. McGraw-Hill.

Illustrative Example[15]: Effects of pressure and inert-addition on equilibrium composition

1 atm   *5 atm*   *N_2 addition*

- $x = 0.34$
- $y = 0.67$
- $z = 0.66$

- $x = 0.193$
- $y = 0.5965$
- $z = 0.807$

- $x = 0.47$
- $y = 0.736$
- $z = 0.53$

[15]K. Wark and D. Richards (1999). *Thermodynamics.* 6th ed. McGraw-Hill.

Observations: K_p of Ideal Gas Mixture[16]

- The K_p of a reaction depends solely on temperature only.
- The K_p of the reverse reaction is $1/K_p$.
  - $K_p = 0.1147 \times 10^{11}$ for $H_2 + \frac{1}{2} O_2 \rightleftharpoons H_2O$ at 1000 K
  - $K_p = 8.718 \times 10^{-11}$ for $H_2O \rightleftharpoons H_2 + \frac{1}{2} O_2$ at 1000 K
- The larger the K_p, the more complete the reaction.
  - $K_p > 1000 \rightarrow$ reaction proceeds to completion,
  - $K_p < 0.001 \rightarrow$ reaction assumed not occurring.
- The mixture pressure affects the equilibrium composition.
- The presence of inert gases affects the equilibrium composition.
- Equilibrium calculations provide information on the equilibrium composition of a reaction, not on the reaction rate.

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[16]Y. Çengel (2014). *Thermodynamics: An Engineering Approach.* 8th ed. McGraw-Hill.

Equilibrium with Simultaneous Reactions[17]

Illustrative Example:
Moran Ex.14.9 ▷ A system consisting initially of 1 kmol of CO_2, 12 kmol of O_2, and 12 kmol of N_2 forms an equilibrium mixture of CO_2, CO, O_2, N_2, and NO at 3000 K, 1 atm. Determine the composition of the equilibrium mixture.
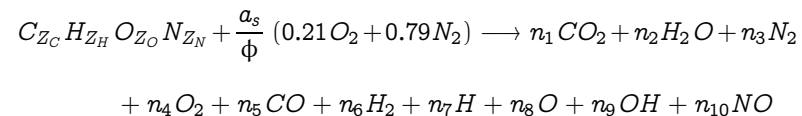$CO_2 + \frac{1}{2} N_2 + \frac{1}{2} O_2 \longrightarrow a\, CO + b\, NO + c\, CO_2 + d\, O_2 + e\, N_2$

- $c = 1 - a$, $d = 0.5(1 + a - b)$, $e = 0.5(1 - b)$

- Two independent reactions:
  1. $CO_2 \rightleftharpoons CO + \frac{1}{2} O_2 \Rightarrow K_1 = \frac{a}{1-a} \frac{\sqrt{1+a-b}}{\sqrt{a+4}}$
  2. $\frac{1}{2} N_2 + \frac{1}{2} O_2 \rightleftharpoons NO \Rightarrow K_2 = \frac{2b}{\sqrt{(1-b)(1+a-b)}}$
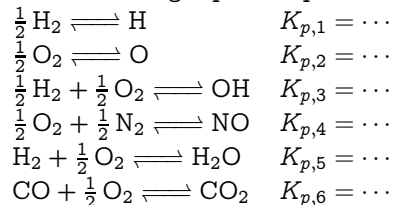
- At 3000 K & 1 atm, $K_1 = 0.327$, $K_2 = 0.1222$

$\Rightarrow$ $a = 0.374$, $b = 0.0674$, $c = 0.626$, $d = 0.653$, $e = 0.466$

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[17]M. Moran et al. (2014). *Fundamentals of Engineering Thermodynamics.* 8th ed. Wiley.


Chemical Equilibrium using Equilibrium Constants[18]

$$C_{Z_C} H_{Z_H} O_{Z_O} N_{Z_N} + \frac{a_s}{\phi} \left(0.21 O_2 + 0.79 N_2\right) \longrightarrow n_1 CO_2 + n_2 H_2O + n_3 N_2$$

$$+ n_4 O_2 + n_5 CO + n_6 H_2 + n_7 H + n_8 O + n_9 OH + n_{10} NO$$

Additional six gas-phase equilibrium reactions are required.

$\frac{1}{2} H_2 \rightleftharpoons H$ $K_{p,1} = \cdots$

$\frac{1}{2} O_2 \rightleftharpoons O$ $K_{p,2} = \cdots$

$\frac{1}{2} H_2 + \frac{1}{2} O_2 \rightleftharpoons OH$ $K_{p,3} = \cdots$

$\frac{1}{2} O_2 + \frac{1}{2} N_2 \rightleftharpoons NO$ $K_{p,4} = \cdots$

$H_2 + \frac{1}{2} O_2 \rightleftharpoons H_2O$ $K_{p,5} = \cdots$

$CO + \frac{1}{2} O_2 \rightleftharpoons CO_2$ $K_{p,6} = \cdots$
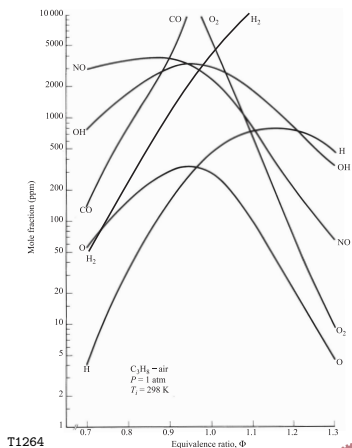
- 10 unknowns: $n_1, n_2, \cdots, n_{10}$
- 4 atom balance equations + 6 K_p equations.

[18]C. Ferguson and A. Kirkpatrick (2015). *Internal Combustion Engines: Applied Thermosciences.* Wiley.


Equilibrium Composition: Detailed Chemistry[19]
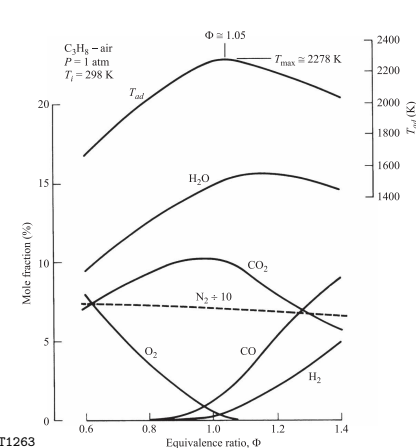
[19]S. Turns (2012). *An Introduction to Combustion: Concepts and Applications.* 3rd ed. McGraw-Hill.

- Major products of lean combustion are H_2O, CO_2, O_2 and N_2; while, for rich combustion they are H_2O, CO_2, CO, H_2 and N_2.
- Maximum flame temperature is at slightly rich condition ($\phi \simeq 1.05$) as a result of both the heat of combustion & heat capacity of products decaying beyond $\phi = 1.0$.
- Between $1.0 \leqq \phi \leqq \phi(T_{max})$ heat capacities decays more rapidly with ϕ than ΔH_c and beyond $\phi(T_{max})$, ΔH_c falls more rapidly than does the heat capacity.
- Increase in temperature promotes dissociation (endothermic) reactions and increase in pressure decreases dissociation in case of HC combustion.
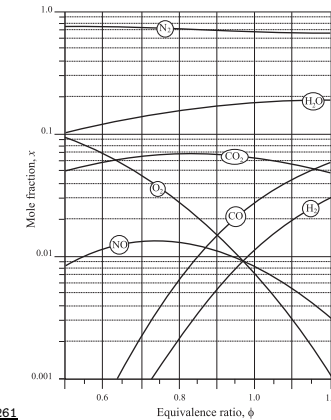

Product of Combustion at TDC in Otto Cycle[20]
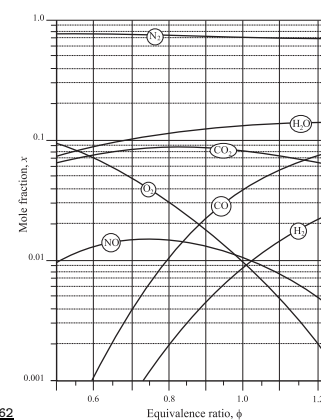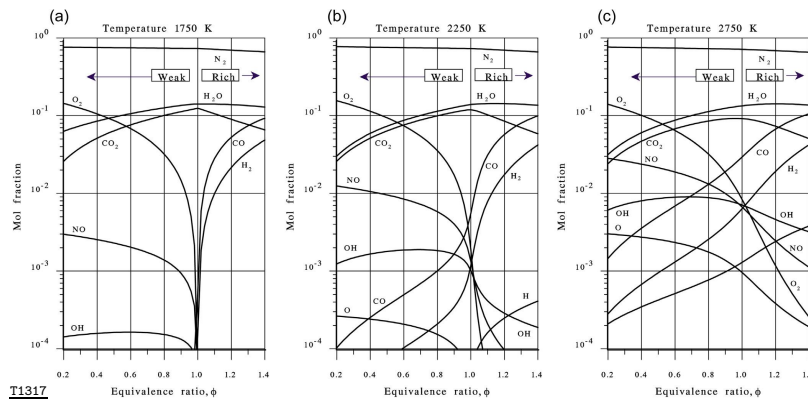

Octane combustion   *Methane combustion*

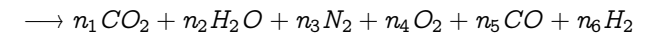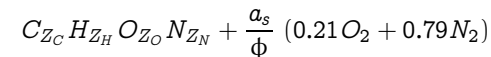[20] D. Winterbone (1997). *Advanced Thermodynamics for Engineers.* Arnold.

Equilibrium Composition: iso-octane at 30 bar[21]

[21] J. Heywood (2018). *Internal Combustion Engine Fundamentals.* 2nd ed. McGraw-Hill.

Low Temperature Combustion (T < 1000 K)[22]

$$C_{Z_C} H_{Z_H} O_{Z_O} N_{Z_N} + \frac{a_s}{\phi} \left(0.21 O_2 + 0.79 N_2\right)$$

$$\longrightarrow n_1 CO_2 + n_2 H_2O + n_3 N_2 + n_4 O_2 + n_5 CO + n_6 H_2$$

- if $\phi = 1$: $n_4 = n_5 = n_6 = 0$
- if $\phi < 1$: $n_5 = n_6 = 0$
- if $\phi > 1$: additional equation is required.
  Water-gas shift equation: $CO_2 + H_2 \leftrightarrows CO + H_2O$

$$K(T) = \frac{n_2 n_5}{n_1 n_6}$$

$$\ln K(T) = 2.743 - \frac{1.761}{t} - \frac{1.611}{t^2} + \frac{0.2803}{t^3} \qquad \left(t = \frac{T}{1000}\right)$$

[22] C. Ferguson and A. Kirkpatrick (2015). *Internal Combustion Engines: Applied*
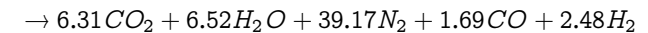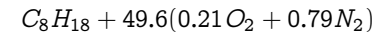
Species	n_i	$\phi \leq 1$	$\phi > 1$
CO_2	n_1	Z_C	$Z_C - n_5$
H_2O	n_2	$Z_H/2$	$Z_H/2 - d_1 + n_5$
N_2	n_3	$Z_N/2 + 0.79a_s/\phi$	$Z_N/2 + 0.79a_s/\phi$
O_2	n_4	$0.42a_s$	0
CO	n_5	0	n_5
H_2	n_6	0	$d_1 - n_5$

- $d_1 = 0.42a_s(1 - 1/\phi)$
- $c_1 = -Z_C d_1 K$
- $b_1 = Z_H/2 + KZ_C - d_1(1 - K)$
- $a_1 = 1 - K$
- $n_5 = \frac{-b_1 + \sqrt{b_1^2 - 4a_1 c_1}}{2a_1}$

Illustrative Example: Octane ($\phi = 1.2$) combustion at 1000 K[23]

- $Z_C = 8$, $Z_H = 18$ $\rightarrow a_s = 59.52$
- $d_1 = 4.167$
- $\ln K = -0.34 \rightarrow K = 0.705$
  [$\ln K_P = -\Delta G_T^o / R_u T$, $K_P = 0.693$]
- $a_1 = 0.295$, $b_1 = 13.41$, $c_1 = -23.50$
- $n_5 = 1.690$ $\rightarrow n_1 = 6.31$, $n_2 = 6.52$, $n_3 = 39.17$, $n_6 = 2.48$
- $N = \sum n_i = 56.17$

$$C_8H_{18} + 49.6(0.21O_2 + 0.79N_2)$$

$$\rightarrow 6.31CO_2 + 6.52H_2O + 39.17N_2 + 1.69CO + 2.48H_2$$

- $Y_5 = Y_{CO} = n_5/N = 0.03 = 30000$ ppm

[23]C. Ferguson and A. Kirkpatrick (2015). *Internal Combustion Engines: Applied Thermosciences*. Wiley.

Heat Release: Product Leaving at High Temperature[24]

Illustrative Problem:

Wark Ex. 13.7 ▷ Methane gas initially at 400 K is burned with 50% excess air which enters the combustion chamber at 500 K. Product leaves the chamber at 1800 K and 1 atm. Estimate heat release per kmol of methane.

[24]K. Wark and D. Richards (1999). *Thermodynamics*. 6th ed. McGraw-Hill.

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