Fuel & Advanced Combustion

Lecture
Chemical Reaction

Ideal Gas Model

The ideal gas equation of state is:

$$\boxed{PV = mRT} = m\left(\frac{\overline{R}}{\overline{M}}\right)T = n\overline{R}T$$

where $\overline{R}$ is the Universal Gas Constant (8.314 kJ/kmol K), $\overline{M}$ is the molecular weight and n is the number of moles.

Specific internal energy (units: kJ/kg) $u(T) = \int c_v(T)dT$

Specific enthalpy (units: kJ/kg) $\boxed{h(T) = \int c_p(T)dT}$

Specific entropy (units: kJ/kg K) $s(P,T) = s^o(T) - R\ln(P/P_o)$

(P_o = 1 bar, s^o entropy at P_o)

Ideal Gas Model for Mixtures

The mass m of a mixture is equal to the sum of the mass of n components

$$m = \sum_{i=1}^{n} m_i$$

The mass fraction, x_i, of any given species is defined as:

$$x_i = \frac{m_i}{m} \quad \text{and} \quad \sum_{i=1}^{n} x_i = 1$$

The mixture internal energy U and enthalpy H (units: kJ) is:

$$U = mu = \sum_{i=1}^{n} m_i u_i \qquad H = mh = \sum_{i=1}^{n} m_i h_i$$

where u_i and h_i are mass specific values (units: kJ/kg)

The mixture specific internal energy u and enthalpy h is:

$$u = \frac{U}{m} = \sum_{i=1}^{n} \frac{m_i u_i}{m} = \sum_{i=1}^{n} x_i u_i \qquad h = \frac{H}{m} = \sum_{i=1}^{n} \frac{m_i h_i}{m} = \sum_{i=1}^{n} x_i h_i$$

Ideal Gas Model for Mixtures

The total number of moles in the mixture is:

$$n = \sum_{i=1}^{n} n_i$$

The mole fraction, y_i, of any given species is defined as:

$$y_i = \frac{n_i}{n} \quad \text{and} \quad \sum_{i=1}^{n} y_i = 1$$

The mixture internal energy U and enthalpy H (units: kJ) is:

$$U = \sum_{i=1}^{n} n_i \bar{u}_i \qquad H = \sum_{i=1}^{n} n_i \bar{h}_i$$

where $\bar{u}_i$ and $\bar{h}_i$ are molar specific values (units: kJ/kmol)

The mixture molar specific internal energy and enthalpy (units kJ/ kmol) is:

$$\bar{u} = \sum_{i=1}^{n} y_i \bar{u}_i \qquad \bar{h} = \sum_{i=1}^{n} y_i \bar{h}_i$$

Ideal Gas Model for Mixtures

Mass specific entropy (kJ/kg K) molar specific mixture entropy (kJ/mol K) :

$$s = \sum_{i=1}^{n} x_i \left(s_i^o - R_i \ln(P_i / P) \right) - R \ln\left(P / P_o \right) \qquad \bar{s} = \sum_{i=1}^{n} y_i \left(\bar{s}_i^o - R_i \ln y_i \right) - \bar{R} \ln\left(P / P_o \right)$$

The **mixture molecular weight**, $\overline{M}$, is given by:

$$\boxed{\overline{M} = \frac{m}{n}} = \frac{\sum_{i=1}^{n} m_i}{n} = \sum_{i=1}^{n} \frac{n_i \overline{M}_i}{n} = \sum_{i=1}^{n} y_i \overline{M}_i$$

The **partial pressure** of a component, P_i, in the mixture (units: kPa) is:

$$\boxed{y_i = \frac{n_i}{n}} = \frac{P_i V / RT}{PV / RT} = \frac{P_i}{P} \qquad \text{or} \qquad P_i = y_i P$$

Composition of Standard Dry Air

Air is a mixture of gases including oxygen (O_2), nitrogen(N_2), argon (Ar), carbon dioxide (CO_2), water vapour (H_20)….

For combustion dry air is taken to be composed of 21% O_2 and 79% N_2 by volume (y_{O2}=0.21, y_{N2}=0.79).

$$\frac{n_{N_2}}{n_{O_2}} = \frac{n_{N_2}}{n_{tot}} \cdot \frac{n_{tot}}{n_{O_2}} = \frac{y_{N_2}}{y_{O_2}} = \frac{0.79}{0.21} = 3.76$$

For every mole of O_2 there are 3.76 moles of N_2.

Molecular weight of air is $\overline{M}_{air} = \sum_{i=1}^{n} y_i \overline{M}_i = y_{O_2} \cdot \overline{M}_{O_2} + y_{N_2} \cdot \overline{M}_{N_2}$

$$= 0.21(32) + 0.79(28) = 28.84 \text{ kg/kmol}$$

The amount of water in moist air at temperature T is specified by the **specific humidity** (ω) or the **relative humidity** (Φ) defined as follows:

$$\boxed{\omega = \frac{m_{H_2O}}{m_{air}}} \qquad \Phi = \frac{P_{H_2O}}{P_{sat}(T)} \qquad 0 < \Phi < 1$$

Combustion Stoichiometry

If sufficient oxygen is available, a hydrocarbon fuel can be completely oxidized, the carbon is converted to carbon dioxide (CO_2) and the hydrogen is converted to water (H_2O).

The overall chemical equation for the complete combustion of one mole of propane (C_3H_8) with oxygen is:

$$C_3H_8 + aO_2 \rightarrow bCO_2 + \underset{\text{\# of moles}}{c}\underbrace{H_2O}_{\text{species}}$$

Elements cannot be created or destroyed, so

C balance: $3 = b \quad \rightarrow b = 3$
H balance: $8 = 2c \quad \rightarrow c = 4$
O balance: $2a = 2b + c \quad \rightarrow a = 5$

Thus the stoichiometric reaction is:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

Combustion Stoichiometry

Air contains molecular nitrogen N_2, if products are at a “low” temperature the nitrogen is not significantly affected by the reaction, it is considered inert.

The complete reaction of a general hydrocarbon $C_\alpha H_\beta$ with air is:

$$C_\alpha H_\beta + a(O_2 + 3.76N_2) \rightarrow bCO_2 + cH_2O + dN_2$$

C balance: $\alpha = b \rightarrow b = \alpha$

H balance: $\beta = 2c \rightarrow c = \beta/2$

O balance: $2a = 2b + c \rightarrow a = b + c/2 \rightarrow a = \alpha + \beta/4$

N balance: $2(3.76)a = 2d \rightarrow d = 3.76a/2 \rightarrow d = 3.76(\alpha + \beta/4)$

$$C_\alpha H_\beta + \left(\alpha + \frac{\beta}{4}\right)(O_2 + 3.76N_2) \rightarrow \alpha CO_2 + \frac{\beta}{2}H_2O + 3.76\left(\alpha + \frac{\beta}{4}\right)N_2$$

Example: The stoichiometric reaction of octane (C_8H_{18}) $\alpha = 8$ and $\beta = 18$

$$C_8H_{18} + (12.5)(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O + 47N_2$$

Combustion Stoichiometry

The stoichiometric mass based air/fuel ratio for $C_\alpha H_\beta$ fuel is:

$$\boxed{(A/F)_s = \frac{m_{air}}{m_{fuel}}} = \frac{\left(\sum n_i \overline{M}_i\right)_{air}}{\left(\sum n_i \overline{M}_i\right)_{fuel}} = \frac{\left(\alpha + \frac{\beta}{4}\right)\overline{M}_{O_2} + 3.76\left(\alpha + \frac{\beta}{4}\right)\overline{M}_{N_2}}{\alpha \overline{M}_C + \beta \overline{M}_H}$$

Substituting the respective molecular weights and dividing top and bottom by α one gets the following expression that only depends on the ratio of the number of hydrogen atoms to hydrogen atoms *(β/α)* in the fuel.

$$\boxed{(A/F)_s = \frac{1}{(F/A)_s}} = \frac{\left(1 + \frac{(\beta/\alpha)}{4}\right)(32 + 3.76 \cdot 28)}{12 + (\beta/\alpha) \cdot 1}$$

Note above equation only applies to stoichiometric mixture

Example: For octane (C_8H_{18}), $\beta/\alpha = 2.25 \rightarrow (A/F)_s = 15.1$

(gasoline $(A/F)_s \approx 14.6$

Fuel Lean Mixture

Fuel-air mixtures with more than stoichiometric air (excess air) can burn

With excess air you have fuel lean combustion

At low combustion temperatures, the extra air appears in the products as O_2 and N_2:

$$C_\alpha H_\beta + \gamma(\alpha + \frac{\beta}{4})(O_2 + 3.76N_2) \rightarrow \alpha CO_2 + \frac{\beta}{2} H_2O + dN_2 + eO_2$$

a fuel lean mixture has excess air, so $\boxed{\gamma > 1}$

Above reaction equation has two unknowns (d, e) and we have two atom balance equations (O, N) so can solve for the unknowns

Fuel Rich Mixture

Fuel-air mixtures with less than stoichiometric air (excess fuel) can burn.

With less than stoichiometric air you have fuel rich combustion, there is insufficient oxygen to oxidize all the C and H in the fuel to CO_2 and H_2O.

Get incomplete combustion where carbon monoxide (CO) and molecular hydrogen (H_2) also appear in the products.

$$C_\alpha H_\beta + \gamma(\alpha + \frac{\beta}{4})(O_2 + 3.76N_2) \rightarrow \alpha CO_2 + \frac{\beta}{2} H_2O + dN_2 + eCO + fH_2$$

a fuel rich mixture has insufficient air → $\boxed{\gamma < 1}$

Above reaction equation has three unknowns (d, e, f) and we only have two atom balance equations (O, N) so cannot solve for the unknowns unless additional information about the products is given.

Off-Stoichiometric Mixtures

The equivalence ratio, ϕ, is commonly used to indicate if a mixture is stoichiometric, fuel lean, or fuel rich.

$$\phi = \frac{(A/F)_s}{(A/F)_{mixture}} = \frac{(F/A)_{mixture}}{(F/A)_s}$$

stoichiometric	$\phi = 1$
fuel lean	$\phi < 1$
fuel rich	$\phi > 1$

Stoichiometric mixture:

$$C_\alpha H_\beta + \left(\alpha + \frac{\beta}{4}\right)(O_2 + 3.76 N_2) \rightarrow \text{Products}$$

Off-stoichiometric mixture:

$$C_\alpha H_\beta + \frac{1}{\phi}\left(\alpha + \frac{\beta}{4}\right)(O_2 + 3.76 N_2) \rightarrow \text{Products}$$

$$\boxed{\gamma = \frac{1}{\phi}}$$

Off-stoichiometric Conditions

Other terminology used to describe how much air is used in combustion:

110% stoichiometric air = 110% theoretical air = 10% excess air

$$C_3H_8 + \gamma(\alpha + \frac{\beta}{4})(O_2 + 3.76N_2) \qquad \boxed{\gamma = 1.1}$$ → mixture is fuel lean

Example: Consider a reaction of octane with 10% excess air, what is ϕ?

Stoichiometric : $C_8H_{18} + 12.5(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O + 47N_2$

10% excess air is: $C_8H_{18} + 1.1(12.5)(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O + aO_2 + bN_2$

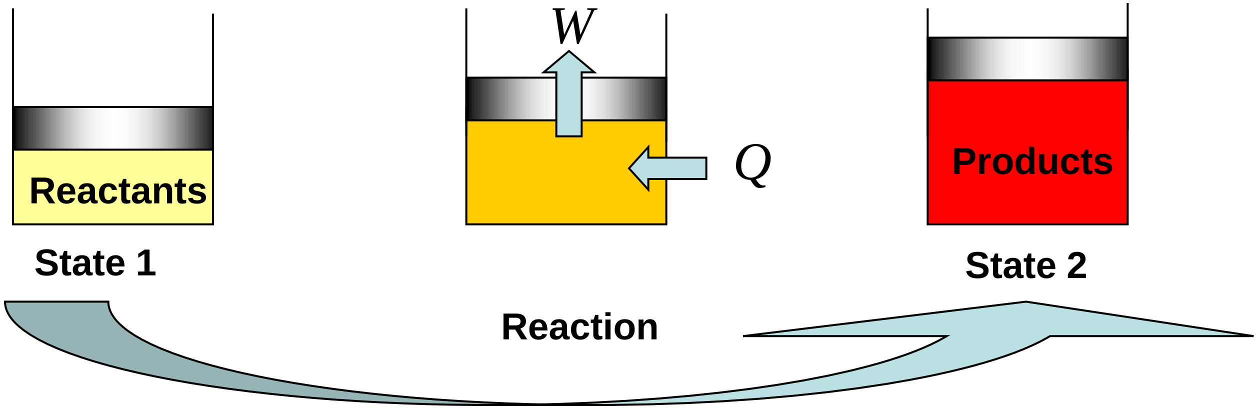
O balance: 1.1(12.5)(2) = 16 + 9 + 2a → a = 1.25,
N balance: 1.1(12.5)(3.76)(2) = 2b → b = 51.7

$$\phi = \frac{(A/F)_s}{(A/F)_{mixture}} = \frac{12.5(4.76)/1}{1.1(12.5)(4.76)/1} = 0.91 \qquad \frac{1}{\phi} = \frac{1}{.91} = 1.1$$

First Law Analysis for Reacting System

Consider a constant pressure process in which n_f moles of fuel react with n_a moles of air to produce n_p moles of product:

$$\underbrace{n_f F + n_a A}_{\text{Reactants}} \rightarrow \underbrace{n_p P}_{\text{Products}}$$



Applying First Law with state 1 being the reactants at P_1, T_1 and state 2 being products at P_2, T_2:

First Law Analysis for Reacting System

$$Q = \Delta U + W$$

$$Q_{1\to 2} = (U_2 - U_1) + P(V_2 - V_1)$$

$$= (U_2 + P_2 V_2) - (U_1 + P_1 V_1)$$

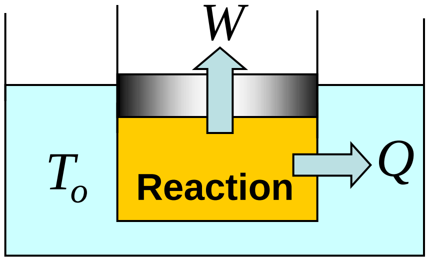
$$= H_2 - H_1$$

$$= H_P - H_R$$

$$\boxed{Q = \sum_P n_i \bar{h}_i (T_p) - \sum_R n_i \bar{h}_i (T_R)}$$

Enthalpy of Reaction

Consider the case where the final temperature of the products is the same as the initial temperature of the reactants (e.g., calorimeter is used to measure Q).



$$P_1=P_2=P_o$$
$$T_1=T_2=T_o$$

The heat released under this situation is referred to as the **enthalpy of reaction,** ΔH_R ,

$$\begin{aligned} Q &= \Delta H_R \\ &= \sum_P n_i \bar{h}_i(T_p) - \sum_R n_i \bar{h}_i(T_R) \\ &= \sum_P n_i \bar{h}_i(T_o) - \sum_R n_i \bar{h}_i(T_o) \quad \text{units : kJ per kg or kmol of fuel} \end{aligned}$$

Heat of Combustion

The maximum amount of energy is released from a fuel when reacted with a stoichiometric amount of air and all the hydrogen and carbon contained in the fuel is converted to CO_2 and H_2O

$$C_\alpha H_\beta + \left(\alpha + \frac{\beta}{4}\right)(O_2 + 3.76N_2) \rightarrow \alpha CO_2 + \frac{\beta}{2} H_2O + 3.76\left(\alpha + \frac{\beta}{4}\right)N_2$$

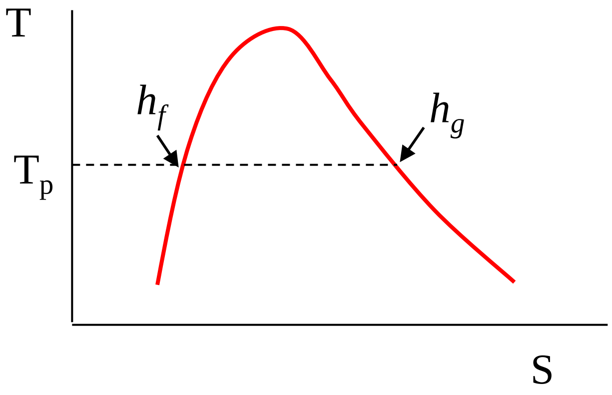
This maximum energy is commonly referred to as the heat of combustion, or the heating value, given per unit mass of fuel or air

$$\Delta H_R = H_P - H_R < 0 \quad \text{(exothermic)}$$

$$\Delta H_R = H_P - H_R > 0 \quad \text{(endothermic)}$$

Heat of Combustion

There are two possible values for the heat of combustion depending on whether the water in the products is taken to be saturated liquid or vapour.



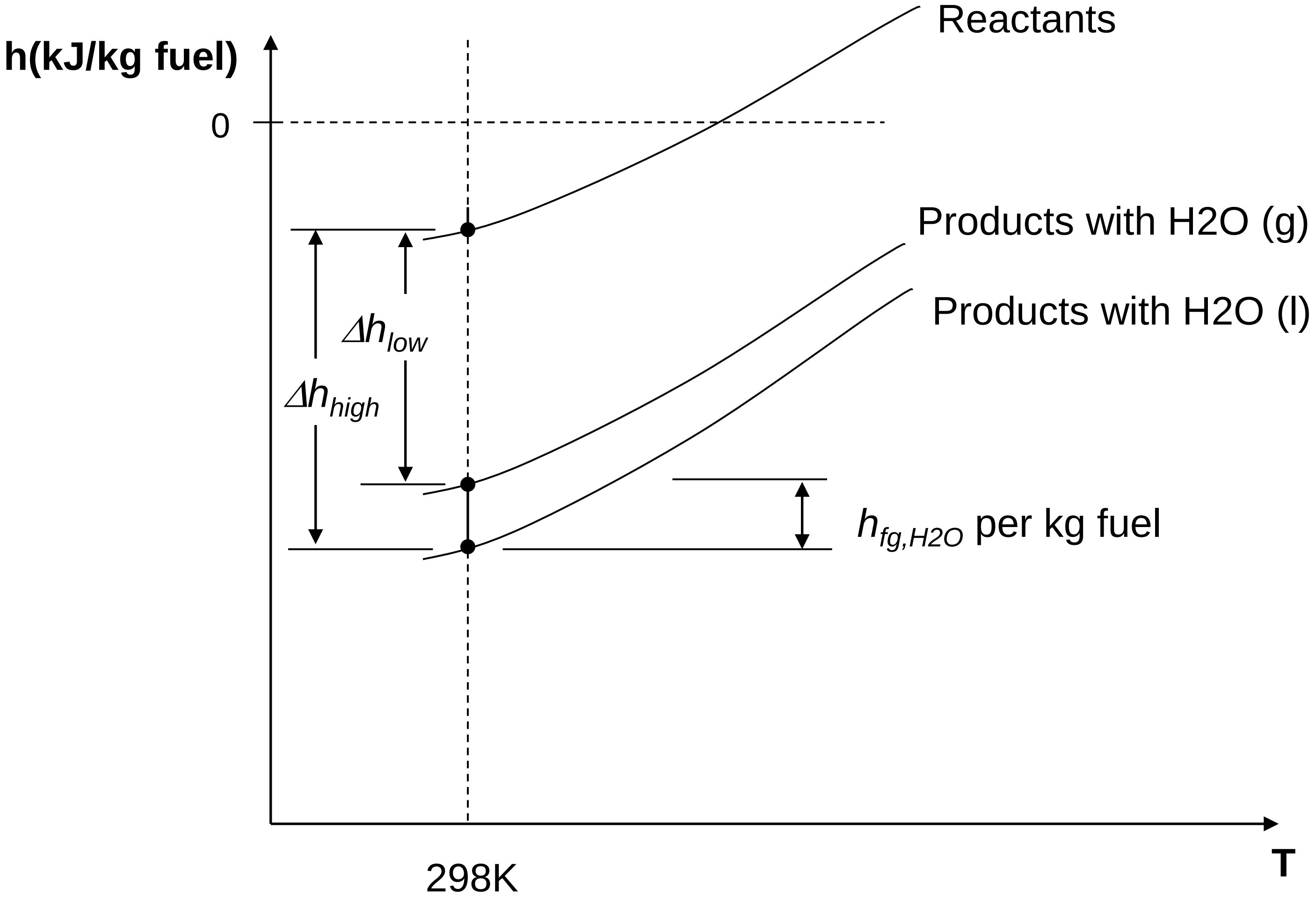
From steam tables:

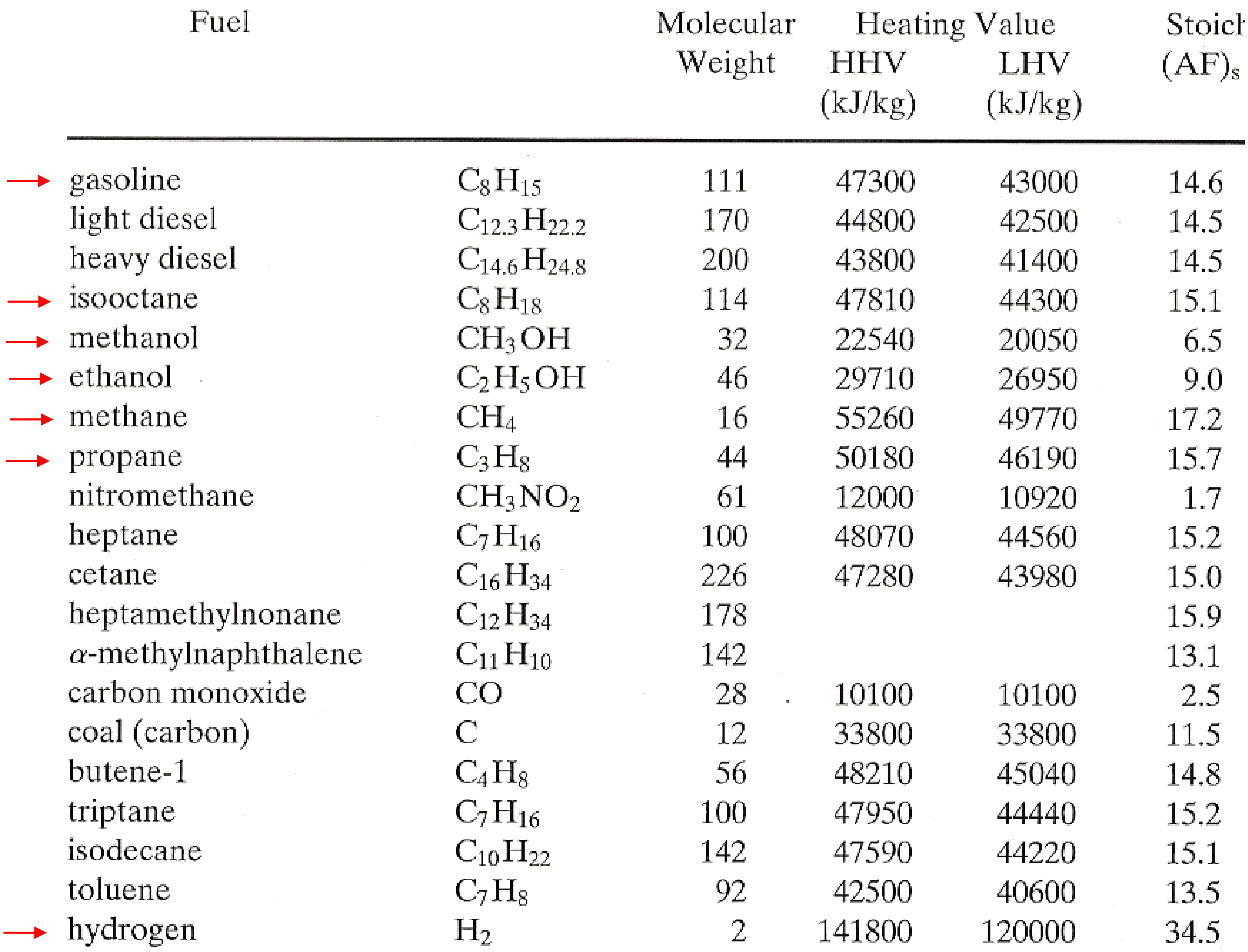
$$h_{fg} = h_g - h_f > 0$$

The term **higher heat of combustion** and **heating value** (HHV) is used when the water in the products is taken to be in the liquid state ($h_{H20} = h_f$)

The term **lower heat of combustion** and **heating value** (LHV) is used when the water in the products is taken to be in the vapour state ($h_{H20} = h_g$)

Heat of Combustion, graphical





	Fuel		Molecular Weight	Heating Value HHV (kJ/kg)	LHV (kJ/kg)	Stoich (AF)$_s$
→	gasoline	C_8H_{15}	111	47300	43000	14.6
	light diesel	$C_{12.3}H_{22.2}$	170	44800	42500	14.5
	heavy diesel	$C_{14.6}H_{24.8}$	200	43800	41400	14.5
→	isooctane	C_8H_{18}	114	47810	44300	15.1
→	methanol	CH_3OH	32	22540	20050	6.5
→	ethanol	C_2H_5OH	46	29710	26950	9.0
→	methane	CH_4	16	55260	49770	17.2
→	propane	C_3H_8	44	50180	46190	15.7
	nitromethane	CH_3NO_2	61	12000	10920	1.7
	heptane	C_7H_{16}	100	48070	44560	15.2
	cetane	$C_{16}H_{34}$	226	47280	43980	15.0
	heptamethylnonane	$C_{12}H_{34}$	178			15.9
	α-methylnaphthalene	$C_{11}H_{10}$	142			13.1
	carbon monoxide	CO	28	10100	10100	2.5
	coal (carbon)	C	12	33800	33800	11.5
	butene-1	C_4H_8	56	48210	45040	14.8
	triptane	C_7H_{16}	100	47950	44440	15.2
	isodecane	$C_{10}H_{22}$	142	47590	44220	15.1
	toluene	C_7H_8	92	42500	40600	13.5
→	hydrogen	H_2	2	141800	120000	34.5

Source: Pulkrabek

Fuel	A/F	Energy density (MJ/L fuel)	Specific energy (MJ/kg air)
Gasoline*	14.6	32	2.9
Butanol	11.2	29.2	3.2
Ethanol	9.0	19.6	3.0
Methanol	6.5	16	3.1
Hydrogen	34.3	**	4.1

* Diesel about 10% more energy per volume than gasoline

** liquefied hydrogen has roughly ¼ the energy density of gasoline

Heat of Formation

Consider the following reactions taking place at atmospheric pressure and with $T_P = T_R = 298$K

$$1/2O_2(g) + H_2(g) \rightarrow H_2O(l) \qquad \overline{Q} = -286{,}000\, kJ/kmol\ H_2O$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \overline{Q} = -394{,}000\, kJ/kmol\ CO_2$$

In these reactions H_2O and CO_2 are formed from their elements in their natural state at standard temperature and pressure (STP) 1 atm and 298K.

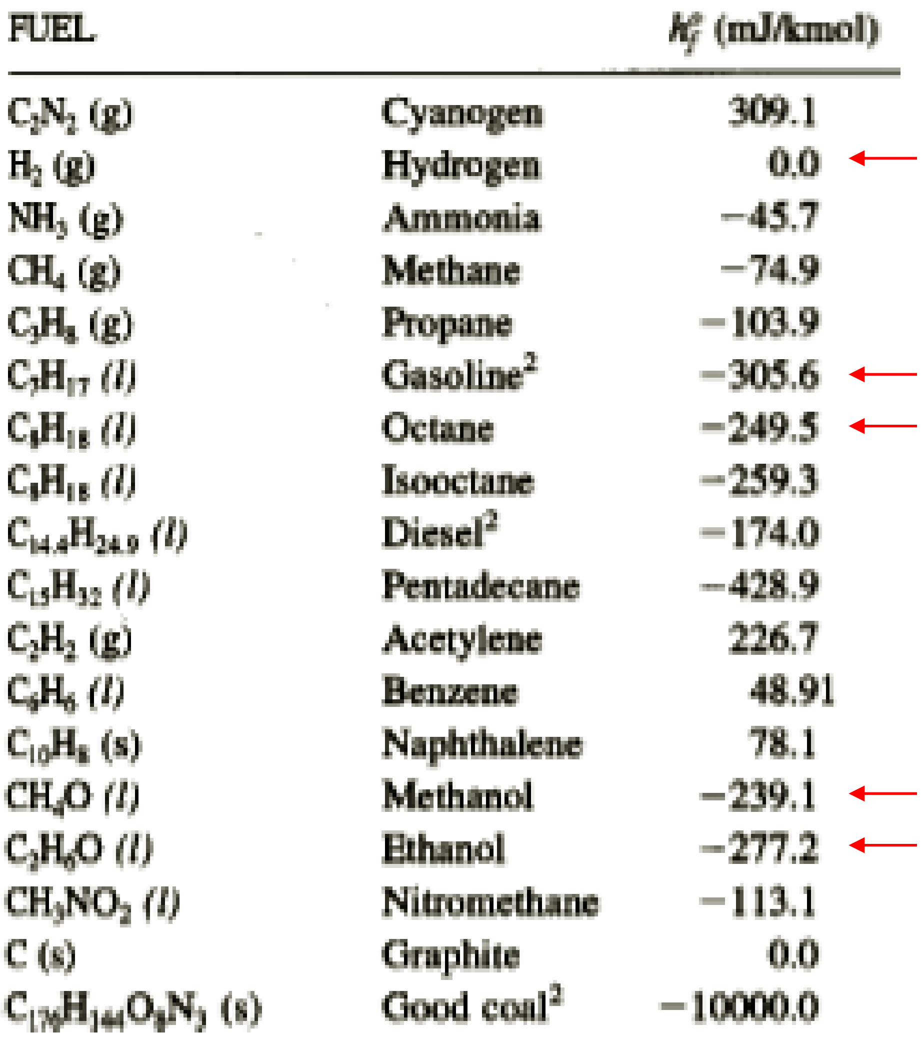
Reactions of this type are called formation reactions and the corresponding measured heat release Q is referred to as the standard heat of formation ($\overline{h}_f^o$) so:

$$\overline{h}^o_{f,\,H_2O} = \overline{Q} = -286{,}000\, kJ/kmol$$

$$\overline{h}^o_{f,\,CO_2} = \overline{Q} = -394{,}000\, kJ/kmol$$

Values for standard heat of formation for different species are tabulated

Heat of Formation for Different Fuels



FUEL		h_f° (mJ/kmol)
C_2N_2 (g)	Cyanogen	309.1
H_2 (g)	Hydrogen	0.0
NH_3 (g)	Ammonia	−45.7
CH_4 (g)	Methane	−74.9
C_3H_8 (g)	Propane	−103.9
C_7H_{17} (*l*)	Gasoline[2]	−305.6
C_8H_{18} (*l*)	Octane	−249.5
C_8H_{18} (*l*)	Isooctane	−259.3
$C_{14.4}H_{24.9}$ (*l*)	Diesel[2]	−174.0
$C_{15}H_{32}$ (*l*)	Pentadecane	−428.9
C_2H_2 (g)	Acetylene	226.7
C_6H_6 (*l*)	Benzene	48.91
$C_{10}H_8$ (s)	Naphthalene	78.1
CH_4O (*l*)	Methanol	−239.1
C_2H_6O (*l*)	Ethanol	−277.2
CH_3NO_2 (*l*)	Nitromethane	−113.1
C (s)	Graphite	0.0
$C_{170}H_{144}O_8N_3$ (s)	Good coal[2]	−10000.0

Enthalpy Scale for a Reacting System

By international convention, the enthalpy of every element in its natural state (e.g., $O_2(g)$, $N_2(g)$, $H_2(g)$, $C(s)$) at STP has been set to zero

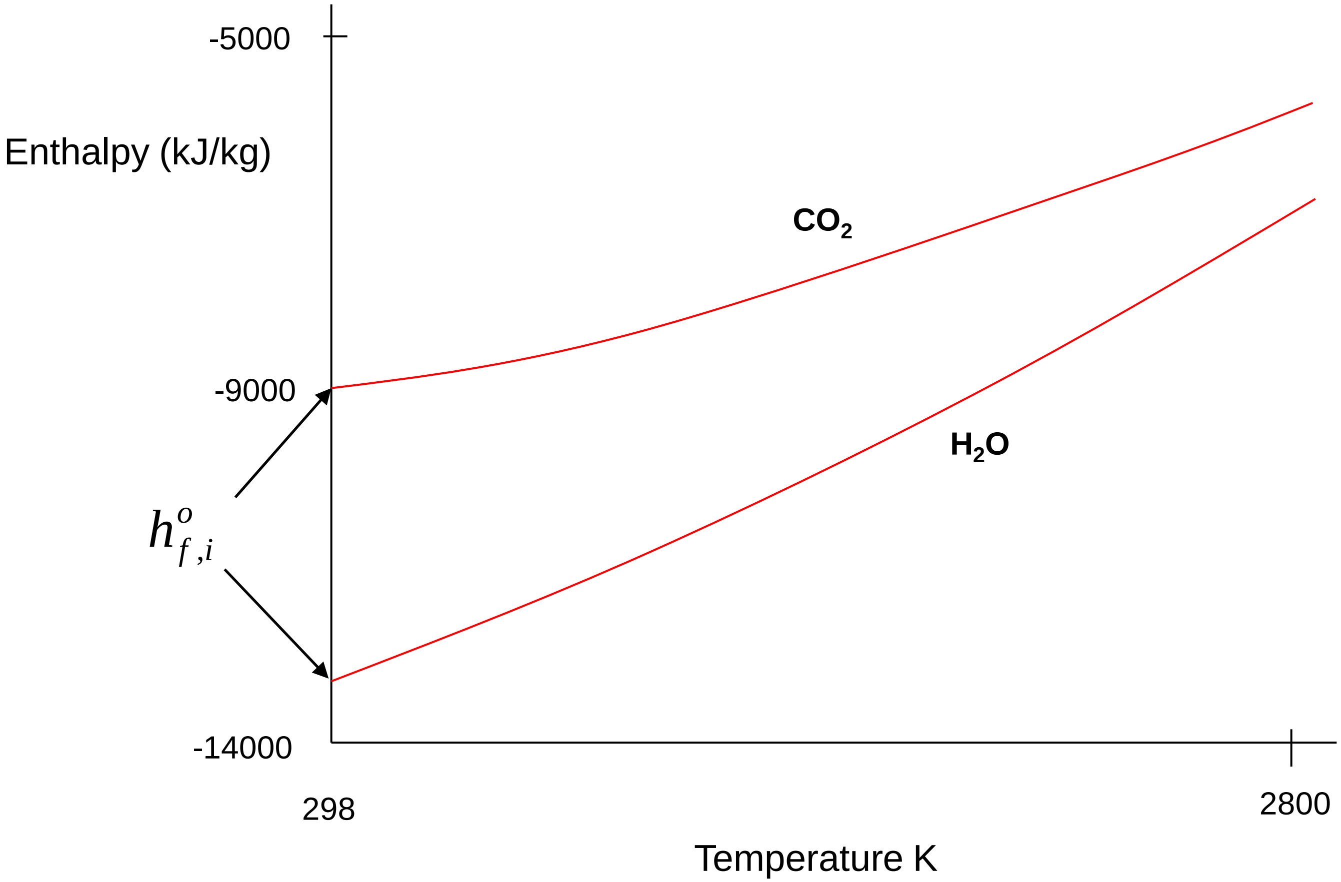
$$\text{i.e,}\quad \bar{h}(1atm,298K) = \bar{h}_f^o = 0$$

Consider the following identity:

$$\bar{h}(P,T) = \bar{h}(1atm,298K) + [\bar{h}(P,T) - \bar{h}(1atm,298K)]$$

Therefore, the enthalpy of the i'th component in a mixture is:

$$\boxed{\bar{h}_i(P,T) = \underbrace{\bar{h}_{f,i}^o}_{\text{chemical enthalpy 298K}} + \underbrace{[\bar{h}_i(P,T) - \bar{h}_i(1atm,298K)]}_{\text{sensible enthalpy} = \int_{298K}^{T} c_{p,i}\,dT}}$$



The data is also found in the JANNAF tables provided at course web site

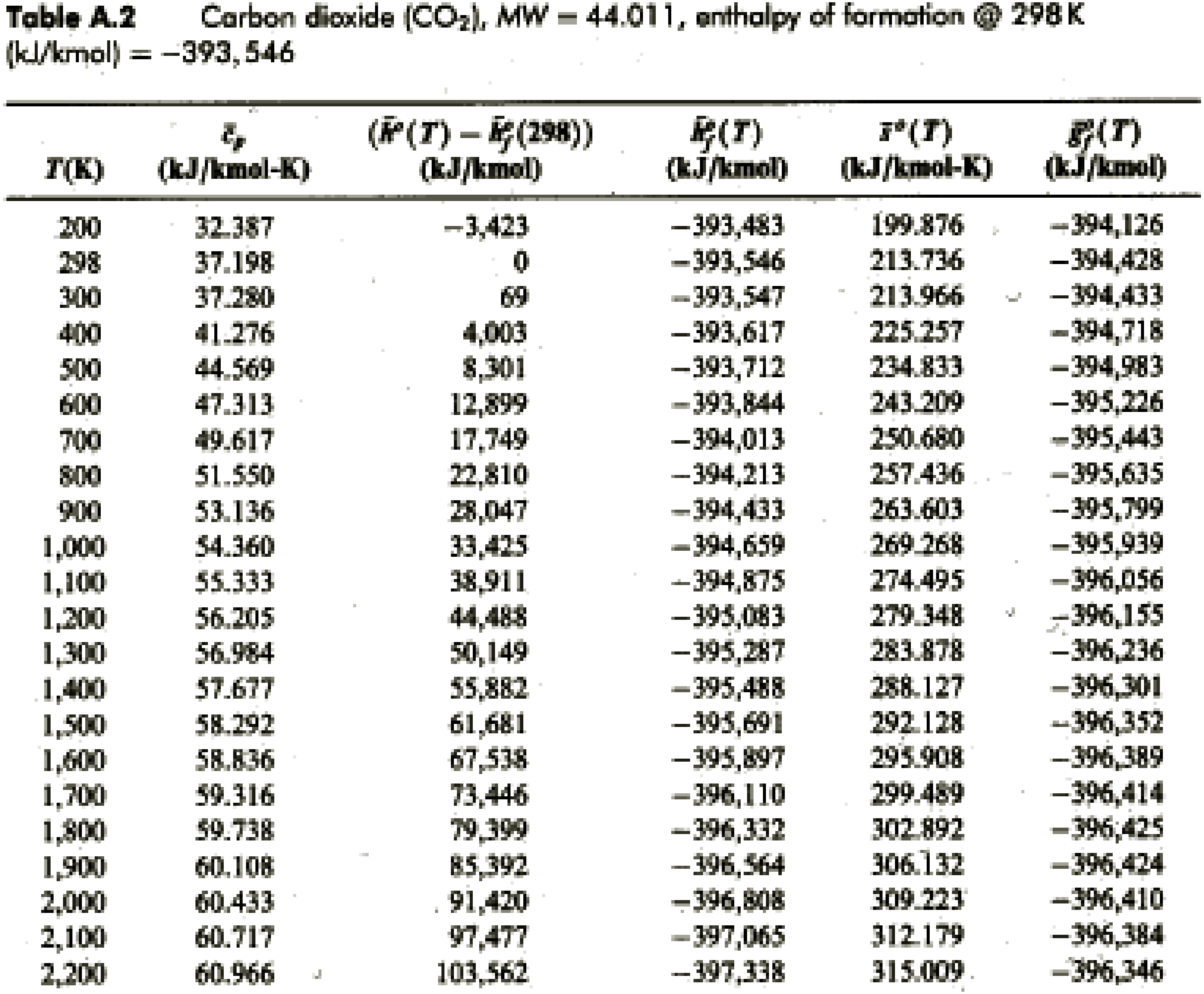
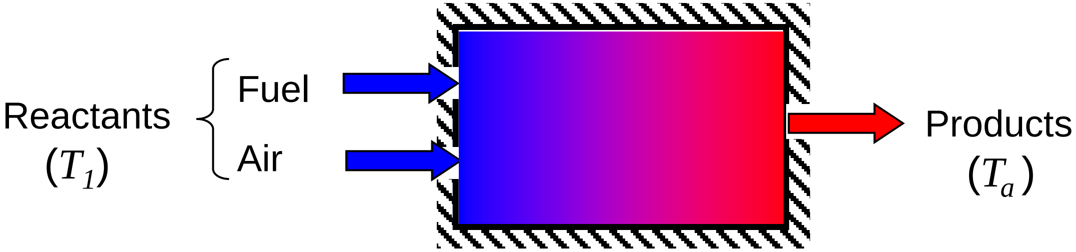


Table A.2 Carbon dioxide (CO_2), MW = 44.011, enthalpy of formation @ 298 K (kJ/kmol) = −393,546

T(K)	$\bar{c}_p$ (kJ/kmol-K)	$(\bar{h}^o(T) - \bar{h}^o_f(298))$ (kJ/kmol)	$\bar{h}^o_f(T)$ (kJ/kmol)	$\bar{s}^o(T)$ (kJ/kmol-K)	$\bar{g}^o_f(T)$ (kJ/kmol)
200	32.387	−3,423	−393,483	199.876	−394,126
298	37.198	0	−393,546	213.736	−394,428
300	37.280	69	−393,547	213.966	−394,433
400	41.276	4,003	−393,617	225.257	−394,718
500	44.569	8,301	−393,712	234.833	−394,983
600	47.313	12,899	−393,844	243.209	−395,226
700	49.617	17,749	−394,013	250.680	−395,443
800	51.550	22,810	−394,213	257.436	−395,635
900	53.136	28,047	−394,433	263.603	−395,799
1,000	54.360	33,425	−394,659	269.268	−395,939
1,100	55.333	38,911	−394,875	274.495	−396,056
1,200	56.205	44,488	−395,083	279.348	−396,155
1,300	56.984	50,149	−395,287	283.878	−396,236
1,400	57.677	55,882	−395,488	288.127	−396,301
1,500	58.292	61,681	−395,691	292.128	−396,352
1,600	58.836	67,538	−395,897	295.908	−396,389
1,700	59.316	73,446	−396,110	299.489	−396,414
1,800	59.738	79,399	−396,332	302.892	−396,425
1,900	60.108	85,392	−396,564	306.132	−396,424
2,000	60.433	91,420	−396,808	309.223	−396,410
2,100	60.717	97,477	−397,065	312.179	−396,384
2,200	60.966	103,562	−397,338	315.009	−396,346

Adiabatic Flame Temperature

Consider the following adiabatic constant pressure process:



For a constant pressure process, the final products temperature, T_a, is known as the adiabatic flame temperature (AFT).

$$Q = \sum_P n_i \bar{h}_i(T_p) - \sum_R n_i \bar{h}_i(T_R) = 0$$

$$\sum_P n_i \bar{h}_i(T_a) = \sum_R n_i \bar{h}_i(T_1)$$

For a given reaction where the n_i's are known for both the reactants and the products, T_a can be calculated explicitly.

Adiabatic Flame Temperature

$$\sum_P n_i \bar{h}_i(T_a) = \sum_R n_i \bar{h}_i(T_1)$$

$$\sum_P n_i \left[\bar{h}^o_{f,i} + \left(\bar{h}_i(T_a) - \bar{h}_i(298K)\right)\right] = \sum_R n_i \left[\bar{h}^o_{f,i} + \left(\bar{h}_i(T_1) - \bar{h}_i(298K)\right)\right]$$

$$\underbrace{\sum_P n_i \left(\bar{h}_i(T_a) - \bar{h}_i(298K)\right)}_{\boxed{\text{Sensible heat of products}}} = \underbrace{\sum_R n_i \left(\bar{h}_i(T_1) - \bar{h}_i(298K)\right)}_{\substack{\text{Sensible heat of reactants} \\ \text{(equal to 0 if } T_1 = 298\text{K)}}} - \underbrace{\left[\sum_P n_i \bar{h}^o_{f,i} - \sum_R n_i \bar{h}^o_{f,i}\right]}_{\boxed{\Delta H^o_R}}$$

$$OR \qquad \sum_P n_i \int_{298}^{T_a} c_{p,i}\, dT = \sum_R n_i \int_{298}^{T_i} c_{p,i}\, dT - \left[\sum_P n_i \bar{h}^o_{f,i} - \sum_R n_i \bar{h}^o_{f,i}\right]$$

Adiabatic Flame Temperature, example

$$C_8H_{18}(l) + 12.5(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O + 47N_2$$

Consider constant pressure complete combustion of stoichiometric liquid butane-air initially at 298K and 1 atm

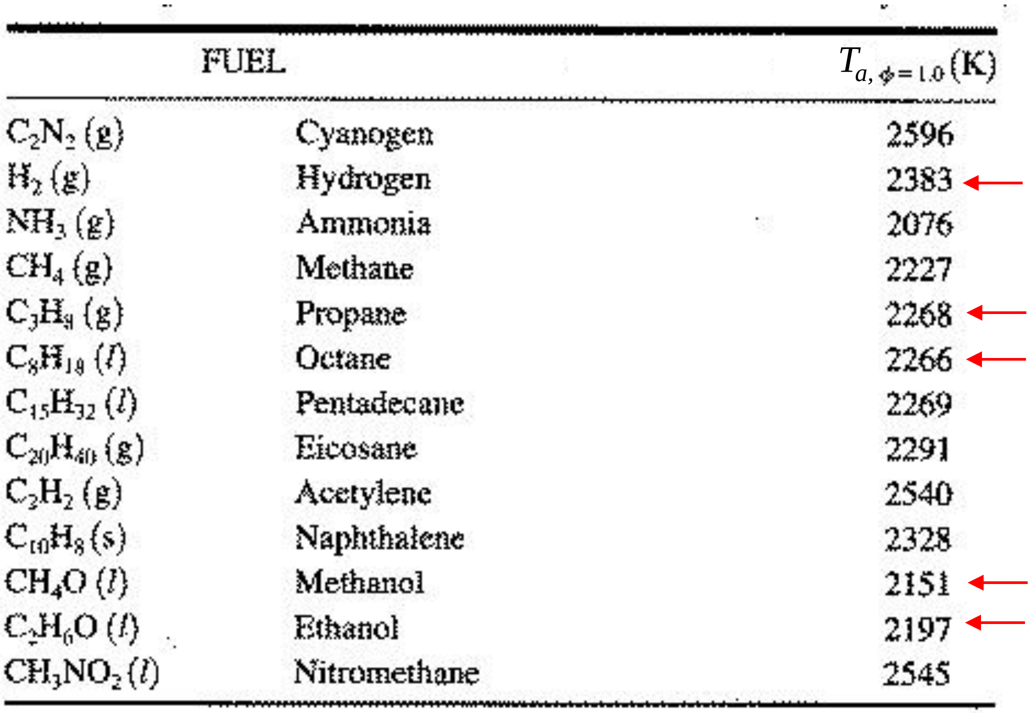
$$\sum_P n_i\{\bar{h}_i(T_a) - \bar{h}_i(298K)\} = \left[\sum_R n_i\left(\cancel{\bar{h}_i(T_1) - \bar{h}_i(298K)}\right)\right] - \left[\sum_P n_i\bar{h}^o_{f,i} - \sum_R n_i\bar{h}^o_{f,i}\right]$$

Note: $\bar{h}^o_{f,O_2} = \bar{h}^o_{f,N_2} = 0$

$$8\left\{\bar{h}_{CO_2}(T_a) - \bar{h}_{CO_2}(298K)\right\} + 9\left\{\bar{h}_{H_2O}(T_a) - \bar{h}_{H_2O}(298K)\right\} + 47\left\{\bar{h}_{N_2}(T_a) - \bar{h}_{N_2}(298K)\right\}$$
$$= -\left[8\bar{h}^o_{f,CO_2} + 9\bar{h}^o_{f,H_2O} - \bar{h}^o_{f,C_8H_{18}}\right]$$

Look up enthalpy of formation values and iterate $T_a \rightarrow$ 2410K

Adiabatic Flame Temperature with products at equilibrium



FUEL		$T_{a,\phi=1.0}$ (K)
C_2N_2 (g)	Cyanogen	2596
H_2 (g)	Hydrogen	2383 ←
NH_3 (g)	Ammonia	2076
CH_4 (g)	Methane	2227
C_3H_8 (g)	Propane	2268 ←
C_8H_{18} (*l*)	Octane	2266 ←
$C_{15}H_{32}$ (*l*)	Pentadecane	2269
$C_{20}H_{40}$ (g)	Eicosane	2291
C_2H_2 (g)	Acetylene	2540
$C_{10}H_8$ (s)	Naphthalene	2328
CH_4O (*l*)	Methanol	2151 ←
C_2H_6O (*l*)	Ethanol	2197 ←
CH_3NO_2 (*l*)	Nitromethane	2545

Adiabatic Flame Temperature, example

Now consider octane air with 10% excess air

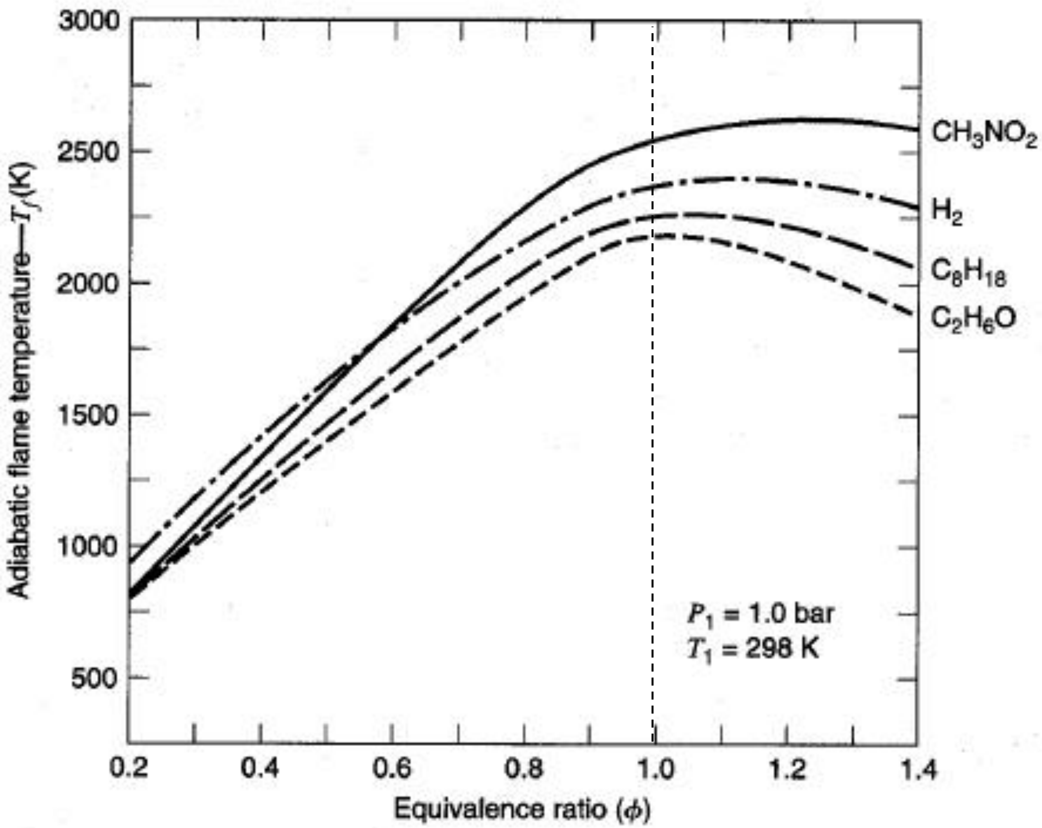
$$C_8H_{18} + 1.1(12.5)(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O + 1.25O_2 + 51.7N_2$$

$$\begin{aligned} 8\left\{\bar{h}_{CO_2}(T_a) - \bar{h}_{CO_2}(298K)\right\} + 9\left\{\bar{h}_{H_2O}(T_a) - \bar{h}_{H_2O}(298K)\right\} + 1.25\left\{\bar{h}_{O_2}(T_a) - \bar{h}_{O_2}(298K)\right\} \\ + 51.7\left\{\bar{h}_{N_2}(T_a) - \bar{h}_{N_2}(298K)\right\} = -\underbrace{\left[8\bar{h}^o_{f,CO_2} + 9\bar{h}^o_{f,H_2O} - \bar{h}^o_{f,C_8H_{18}}\right]}_{\Delta H_R \text{ same as for } \phi = 1} \end{aligned}$$

Look up values and iteration gives T_a = 2262K

Excess air adds 6 moles of diatomic molecules (O_2 and N_2) into the products that does not contribute to heat release just soaks it up.

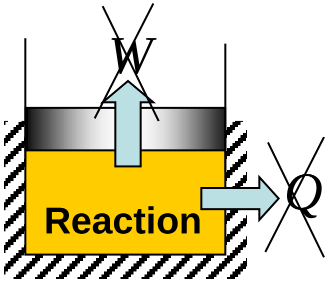
Adiabatic Flame Temperature with products at equilibrium



nitromethane
hydrogen
octane
ethanol

Constant Volume AFT

Consider the case where the piston is fixed and the cylinder is perfectly insulated so the process is adiabatic (Q = 0)



$$Q = \sum_P n_i \bar{u}_i (T_p) - \sum_R n_i \bar{u}_i (T_R) = 0$$

$$\sum_P n_i \bar{u}_i (T_a) = \sum_R n_i \bar{u}_i (T_1)$$

Note $\boxed{h = u + pv = u + RT,}$ so

$$\sum_P n_i (\bar{h}_i (T_a) - \bar{R} T) = \sum_R n_i (\bar{h}_i (T_1) - \bar{R} T)$$

Constant Volume AFT

$$\sum_P n_i\left[\bar{h}^o_{f,i} + \left(\bar{h}_i(T_a) - \bar{h}_i(298K)\right) - \bar{R}T_i\right] = \sum_R n_i\left[\bar{h}^o_{f,i} + \left(\bar{h}_i(T_1) - \bar{h}_i(298K)\right) - \bar{R}T_i\right]$$

$$\sum_P n_i\left(\bar{h}_i(T_a) - \bar{h}_i(298K)\right) = \left[\sum_R n_i\left(\bar{h}_i(T_1) - \bar{h}_i(298K)\right)\right] - \left[\sum_P n_i\bar{h}^o_{f,i} - \sum_R n_i\bar{h}^o_{f,i}\right]$$
$$\underbrace{+\sum_p n_i\bar{R}T_a - \sum_R n_i\bar{R}T_1}$$

Extra term compared to constant pressure AFT (term > 0)

The AFT for a constant volume process is larger than for a constant pressure process.

The AFT is lower for constant pressure process since there is Pdv work done

Constant Volume Combustion Pressure

Assuming ideal gas behaviour:

$$V_R = V_P$$

$$\frac{n_R \bar{R} T_R}{P_R} = \frac{n_p \bar{R} T_p}{P_p}$$

$$\frac{P_p}{P_R} = \left(\frac{n_p}{n_R}\right)\left(\frac{T_p}{T_R}\right) \quad \rightarrow \quad \boxed{\frac{P_{CV}}{P_i} = \left(\frac{n_p}{n_R}\right)\left(\frac{T_a}{T_i}\right)}$$

For large hydrocarbons like octane the mole ratio term is close to one

$$C_8H_{18}(l) + 12.5(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O + 47N_2$$

$$\frac{n_p}{n_R} = \frac{8+9+47}{1+12.5(4.76)} = \frac{64}{60.5} = 1.06$$

Engine Fuel Comparison

Stoichiometric octane-air (ΔH_R= 47.9 MJ/kg-fuel):

$$C_8H_{18} + 12.5(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O + 47N_2$$

$$\frac{P_{CV}}{P_i} = \left(\frac{n_p}{n_R}\right)\left(\frac{T_a}{T_i}\right) = \left(\frac{64}{60.5}\right)\left(\frac{2266}{298}\right) = 1.06 \cdot 7.604 = 8.1$$

Stoichiometric hydrogen-air (ΔH_R= 141.6 MJ/kg-fuel):

$$H_2 + 0.5(O_2 + 3.76N_2) \rightarrow 1H_2O + 1.88N_2$$

$$\frac{P_{CV}}{P_i} = \left(\frac{n_p}{n_R}\right)\left(\frac{T_a}{T_i}\right) = \left(\frac{2.88}{3.38}\right)\left(\frac{2383}{298}\right) = 0.85 \cdot 8.0 = 6.8$$

Stoichiometric ethanol-air (ΔH_R= 29.7 MJ/kg-fuel):

$$C_2H_6O + 3.5(O_2 + 3.76N_2) \rightarrow 2CO_2 + 3H_2O + 13.2N_2$$

$$\frac{P_{CV}}{P_i} = \left(\frac{n_p}{n_R}\right)\left(\frac{T_a}{T_i}\right) = \left(\frac{18.2}{17.7}\right)\left(\frac{2197}{298}\right) = 1.02 \cdot 7.37 = 7.5$$