Ciências
ULisboa

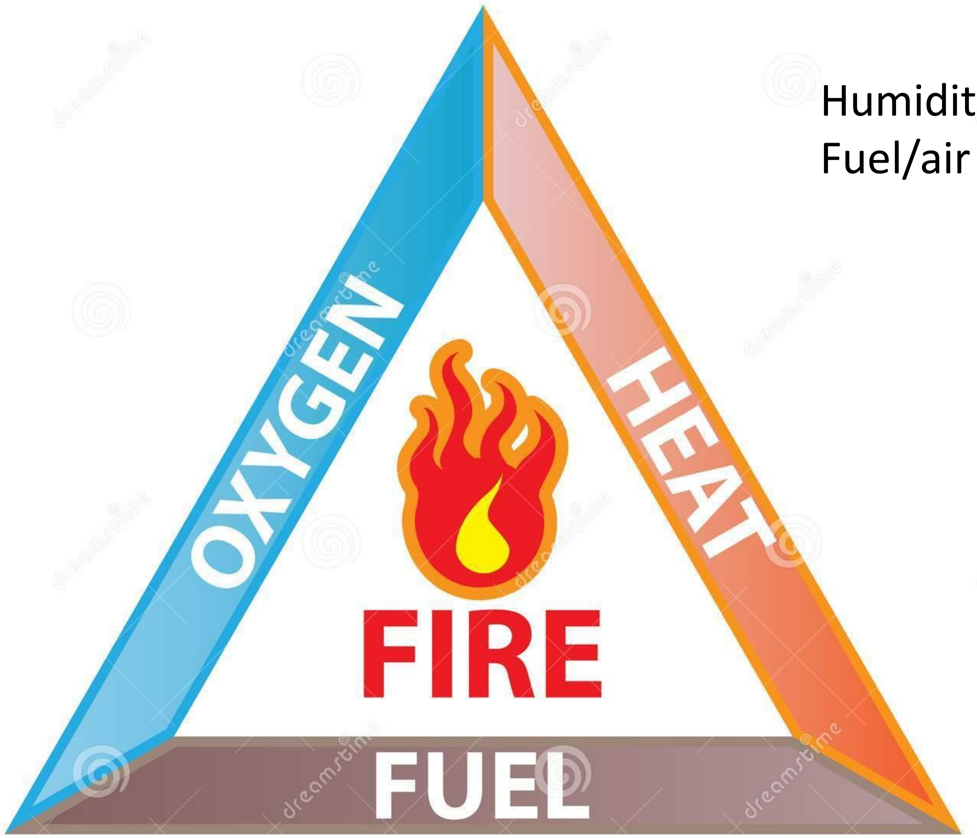
Faculdade
de Ciências
da Universidade
de Lisboa

DISCIPLINA MIEEA 2020

Combustion

Combustion definition

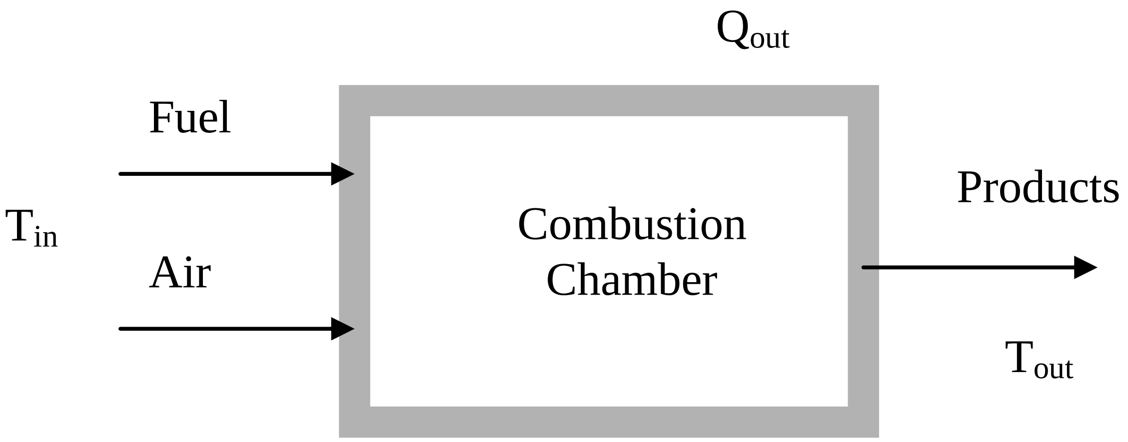
Combustion is essentially burning, fuels react with oxygen to release energy



Humidity
Fuel/air

Thermochemistry

$$fuel + oxidizer \rightarrow products$$



Thermochemistry

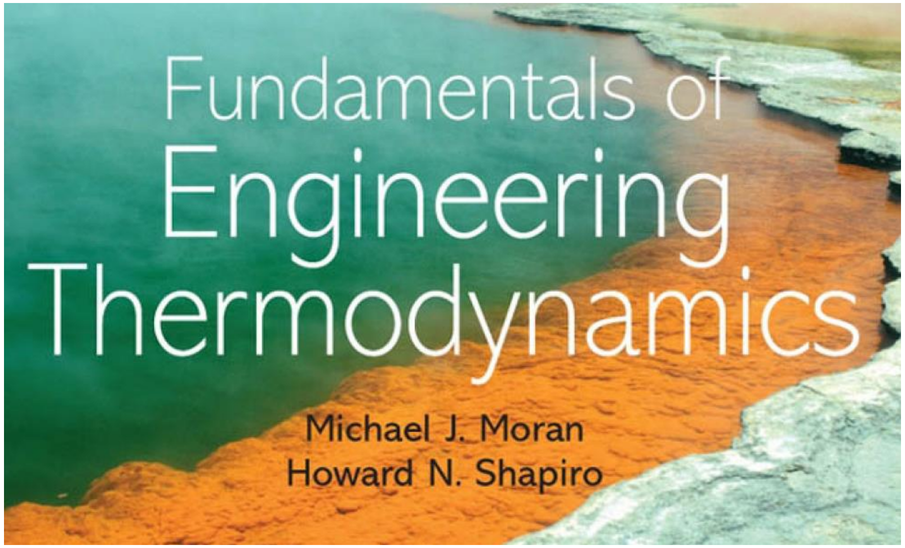
REVIEW

Considering a stoichiometric mixture of isooctane and air, determine:

(a) the mole fraction of fuel
(b) the fuel-air ratio
(c) the mole fraction of H2O in the products
(d) the temperature of products below which H2O starts to condense into liquid at 101.3 kPa

Thermochemistry

Water



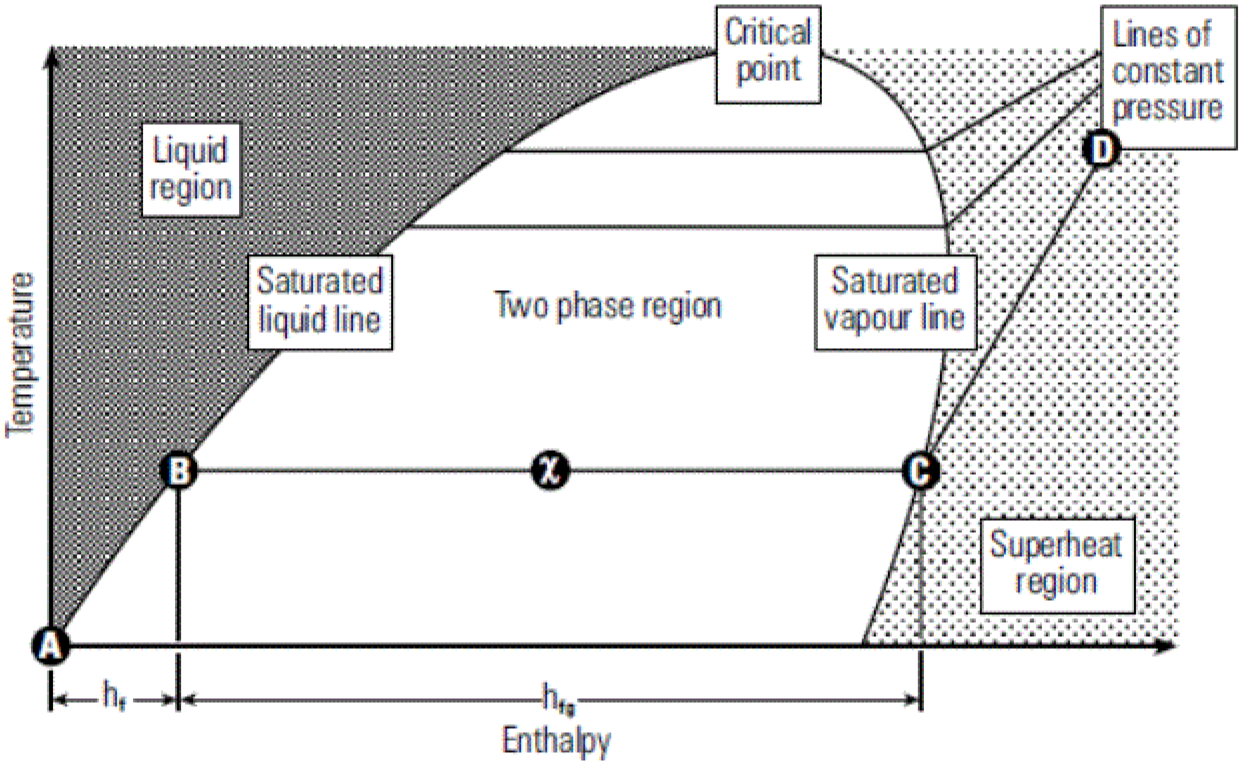
Fundamentals of Engineering Thermodynamics

Michael J. Moran
Howard N. Shapiro

Carla Silva camsilva@fc.ul.pt

Thermochemistry

Water

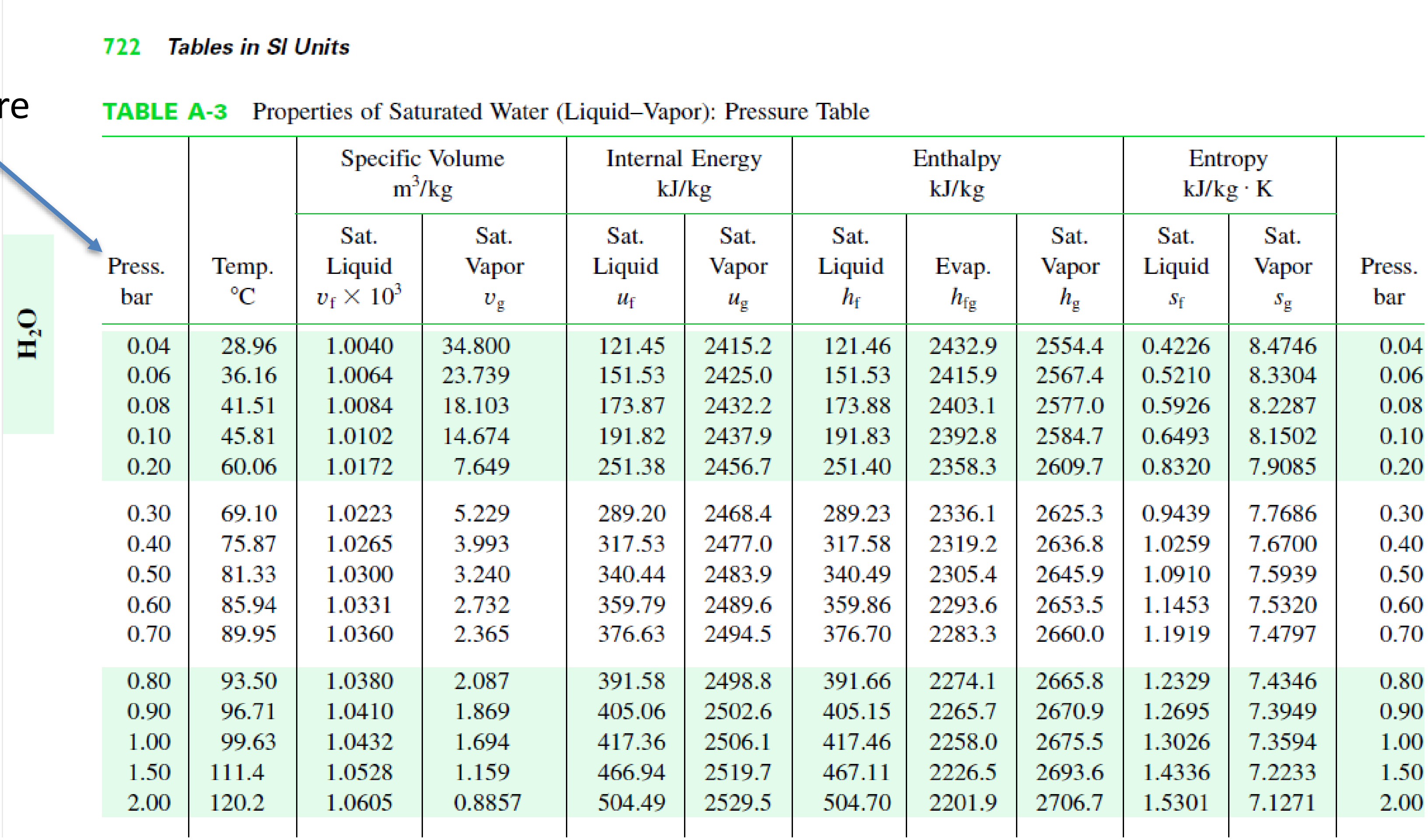


Carla Silva camsilva@fc.ul.pt

Thermochemistry

Water

Partial pressure



722 *Tables in SI Units*

H_2O

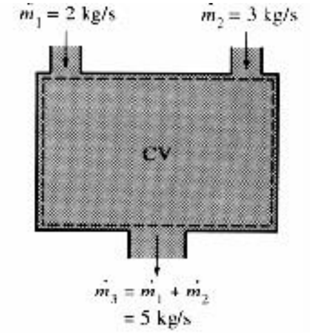
TABLE A-3 Properties of Saturated Water (Liquid–Vapor): Pressure Table

Press. bar	Temp. °C	Specific Volume m^3/kg Sat. Liquid $v_f \times 10^3$	Specific Volume m^3/kg Sat. Vapor v_g	Internal Energy kJ/kg Sat. Liquid u_f	Internal Energy kJ/kg Sat. Vapor u_g	Enthalpy kJ/kg Sat. Liquid h_f	Enthalpy kJ/kg Evap. h_{fg}	Enthalpy kJ/kg Sat. Vapor h_g	Entropy kJ/kg · K Sat. Liquid s_f	Entropy kJ/kg · K Sat. Vapor s_g	Press. bar
0.04	28.96	1.0040	34.800	121.45	2415.2	121.46	2432.9	2554.4	0.4226	8.4746	0.04
0.06	36.16	1.0064	23.739	151.53	2425.0	151.53	2415.9	2567.4	0.5210	8.3304	0.06
0.08	41.51	1.0084	18.103	173.87	2432.2	173.88	2403.1	2577.0	0.5926	8.2287	0.08
0.10	45.81	1.0102	14.674	191.82	2437.9	191.83	2392.8	2584.7	0.6493	8.1502	0.10
0.20	60.06	1.0172	7.649	251.38	2456.7	251.40	2358.3	2609.7	0.8320	7.9085	0.20
0.30	69.10	1.0223	5.229	289.20	2468.4	289.23	2336.1	2625.3	0.9439	7.7686	0.30
0.40	75.87	1.0265	3.993	317.53	2477.0	317.58	2319.2	2636.8	1.0259	7.6700	0.40
0.50	81.33	1.0300	3.240	340.44	2483.9	340.49	2305.4	2645.9	1.0910	7.5939	0.50
0.60	85.94	1.0331	2.732	359.79	2489.6	359.86	2293.6	2653.5	1.1453	7.5320	0.60
0.70	89.95	1.0360	2.365	376.63	2494.5	376.70	2283.3	2660.0	1.1919	7.4797	0.70
0.80	93.50	1.0380	2.087	391.58	2498.8	391.66	2274.1	2665.8	1.2329	7.4346	0.80
0.90	96.71	1.0410	1.869	405.06	2502.6	405.15	2265.7	2670.9	1.2695	7.3949	0.90
1.00	99.63	1.0432	1.694	417.36	2506.1	417.46	2258.0	2675.5	1.3026	7.3594	1.00
1.50	111.4	1.0528	1.159	466.94	2519.7	467.11	2226.5	2693.6	1.4336	7.2233	1.50
2.00	120.2	1.0605	0.8857	504.49	2529.5	504.70	2201.9	2706.7	1.5301	7.1271	2.00

Carla Silva camsilva@fc.ul.pt

Conservation of mass

$$\left(Massa\ que\ entra\right)-\left(Massa\ que\ sai\right)=\left(Variação\ total\ massa\ sistema\right)$$



$$\sum_e \dot{m}_e - \sum_s \dot{m}_s = \frac{dm_{vc}}{dt}$$

Stationary regime

$$\boxed{\sum_e \dot{m}_e = \sum_s \dot{m}_s}\ , \frac{dm_{vc}}{dt} = 0$$

Mass flow (kg/s)

Carla Silva camsilva@fc.ul.pt

Conservation of Energy

1st Law thermodynamics conservation of energy

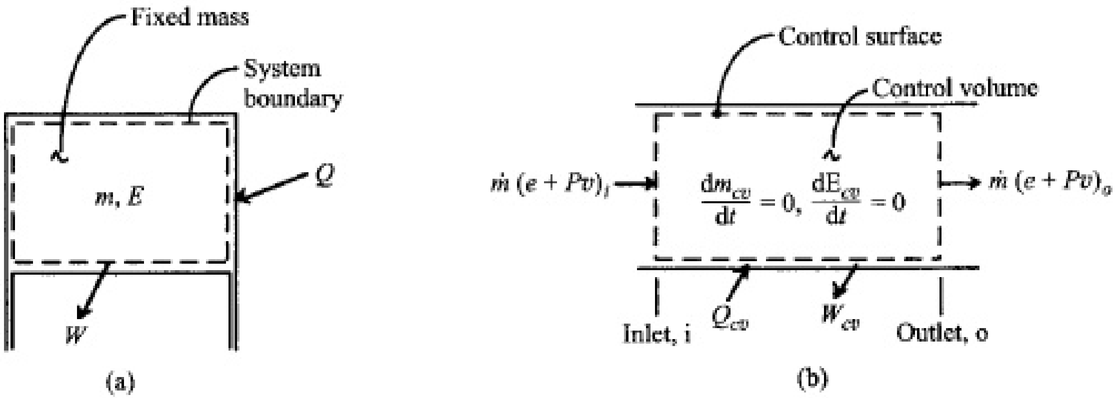
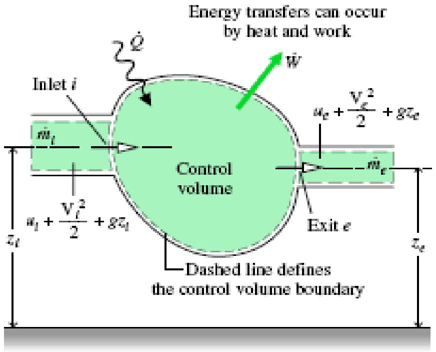


Figure 2.3 (a) Schematic of fixed-mass system with moving boundary above piston. (b) Control volume with fixed boundaries and steady flow.

- Closed system
- Open system

$$\Delta E = \Delta EP + \Delta EC + \Delta U = Q - W$$

Open system



Usando definição de entalpia

$$\frac{dE_{cv}}{dt} = \dot{Q}_{cv} - \dot{W}_{cv} + \dot{m}_i\left(u_i + p_i v_i + \frac{V_i^2}{2} + gz_i\right) - \dot{m}_e\left(u_e + p_e v_e + \frac{V_e^2}{2} + gz_e\right)$$

$$\boxed{\frac{dE_{cv}}{dt} = \dot{Q}_{cv} - \dot{W}_{cv} + \sum_i \dot{m}_i\left(h_i + \frac{V_i^2}{2} + gz_i\right) - \sum_e \dot{m}_e\left(h_e + \frac{V_e^2}{2} + gz_e\right)}$$

Carla Silva camsilva@fc.ul.pt

Thermochemistry

$$reactants(fuel + oxidizer) \rightarrow products$$

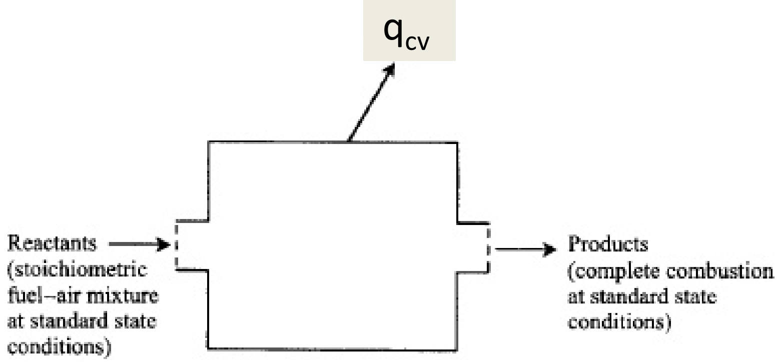


Figure 2.7 Steady-flow reactor used to determine enthalpy of combustion.

$$\dot{m}_i = \dot{m}_e \qquad \text{(kg/s)}$$

$$\dot{E}_{in} - \dot{E}_{out} = \Delta\dot{E}_{CV}$$

$$\dot{Q}_{net} + \underbrace{\sum \dot{m}_i\left(h_i + \cancel{\frac{\vec{V}_i^2}{2}} + \cancel{gz_i}\right)}_{\text{for each inlet}} - \underbrace{\cancel{\dot{W}_{net}}}_{=0} - \underbrace{\sum \dot{m}_e\left(h_e + \cancel{\frac{\vec{V}_e^2}{2}} + \cancel{gz_e}\right)}_{\text{for each exit}} = \underbrace{\cancel{\Delta\dot{E}_{CV}}}_{=0} \qquad \text{(J)}$$

Stationary regime

$$q_{cv} = h_{reactants} - h_{products} \qquad \text{(J/kg)}$$

Thermochemistry

$\overline{R} = 8.314\ kJ/kmol.K$ Constante universal dos gases

$Z = \frac{pv}{RT}$ Factor de compressibilidade

$R = \frac{\overline{R}}{M}$ kJ/kg.K

Z=1 é gas perfeito

$$pv = RT$$

$$u = u(T)$$

$$h = h(T) = u(T) + RT$$

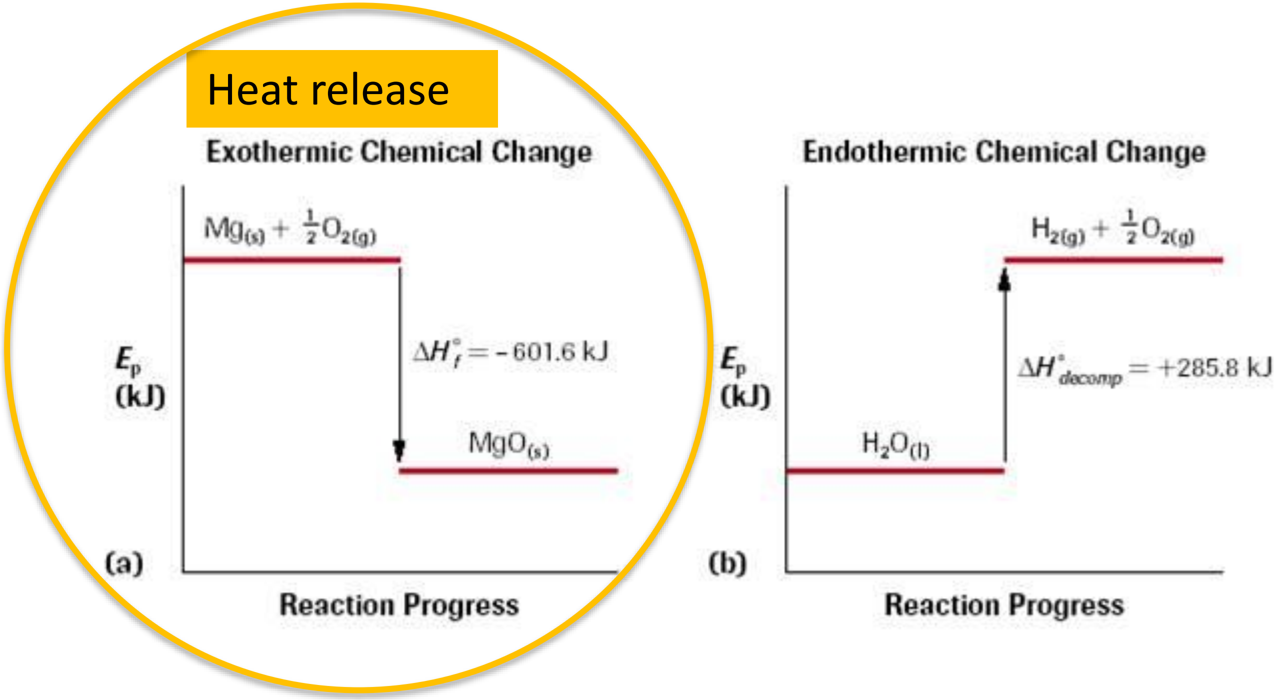
$$c_p(T) = c_v(T) + R$$

$$u(T_2) - u(T_1) = \int_{T_1}^{T_2} c_v(T)dT$$

$$h(T_2) - h(T_1) = \int_{T_1}^{T_2} c_p(T)dT$$

Carla Silva camsilva@fc.ul.pt

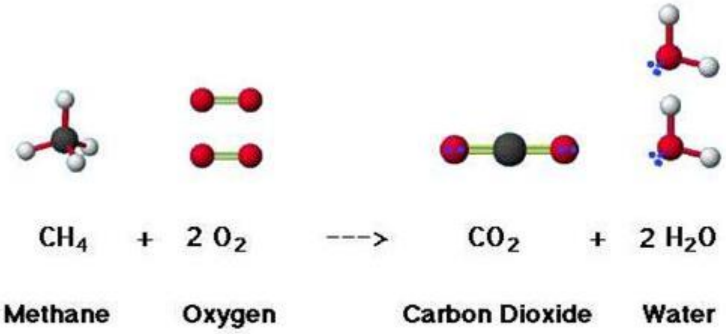
Thermochemistry

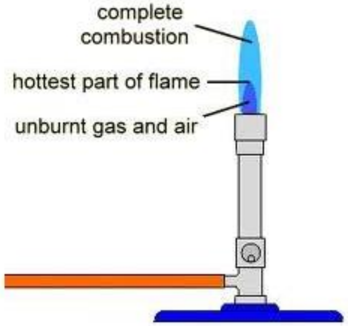


In combustion chemical bonds break, others form, but the energy balance is **exothermic**

Carla Silva camsilva@fc.ul.pt

Thermochemistry





$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O + \text{energy}$$

CONCEPT QUESTIONS

Endothermic or Exothermic?

$+\Delta H$ or $-\Delta H$?

Heat release

Carla Silva camsilva@fc.ul.pt

Thermochemistry

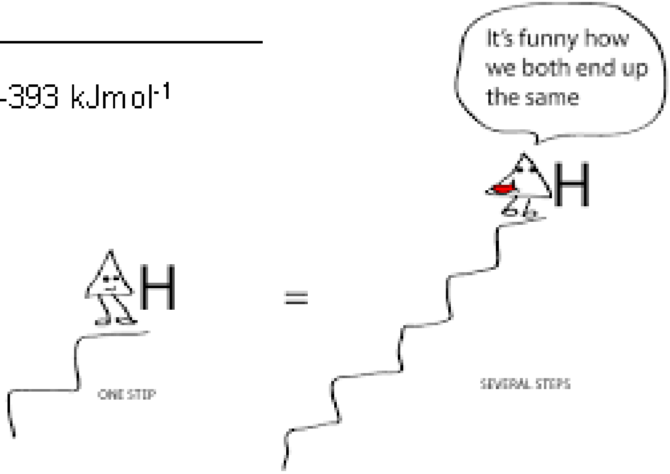
HESS LAW

total enthalpy change during the complete course of a chemical reaction is the same whether the reaction is made in one step or in several steps

$$C + \tfrac{1}{2} O_2 \rightarrow \cancel{CO} \qquad \Delta H = -110\ kJmol^{-1}$$

$$\cancel{CO} + \tfrac{1}{2} O_2 \rightarrow CO_2 \qquad \Delta H = -283\ kJmol^{-1}$$

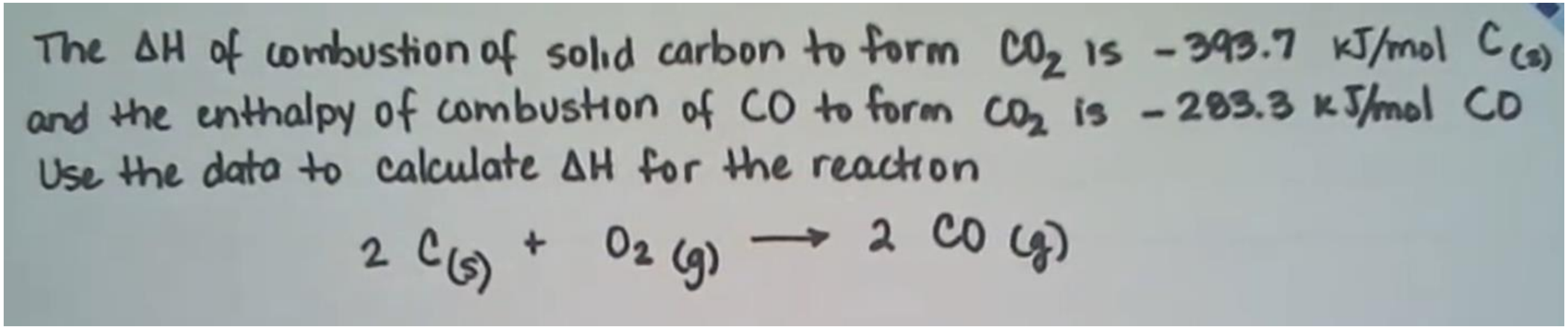
$$C + O_2 \rightarrow CO_2 \qquad \Delta H = -393\ kJmol^{-1}$$



Thermochemistry

HESS LAW

example



The ΔH of combustion of solid carbon to form CO_2 is -393.7 kJ/mol $C_{(s)}$ and the enthalpy of combustion of CO to form CO_2 is -283.3 kJ/mol CO Use the data to calculate ΔH for the reaction

$$2\ C_{(s)} + O_{2}\ (g) \longrightarrow 2\ CO\ (g)$$

Carla Silva camsilva@fc.ul.pt

Thermochemistry

Enthalpy of formation = Energy provided to break bonds- energy released to form bonds

Example:

$$2\,H_{2(g)} + O_{2(g)} \rightarrow 2\,H_2O_{(g)}$$

Bond Energy 298K (kJ/mol)

H-H	436
O=O	499
O-H	463

Carla Silva camsilva@fc.ul.pt

Thermochemistry

$$q_{cv} = \underbrace{h_{reactants} - h_{products}}_{\text{Enthalpy of reaction } = -\Delta h_R} \qquad (J/kg)$$

q_{cv} = Heat of reaction

$$h_i(T) = h^{\circ}_{f,i}(T_{ref}) + \Delta h_{s,i}(T_{ref})$$

- In words first equation says:
  - Absolute enthalpy at T is equal to sum of enthalpy of formation at standard reference state and sensible enthalpy change in going from T_{ref} to T

Products of ideal combustion

$$C_nH_m + S + N_2 + O_2 \rightarrow CO_2 + H_2O + N_2 + O_2$$
$$+ NO_x + CO + SO_x + \text{Soot} + \text{UHC}$$

Fuel

Air

Products of non-ideal combustion

NO_x: Affects ozone (O_3) concentration
CO_2: Absorbs outgoing infrared radiation
CO: Toxic
Soot: Visible

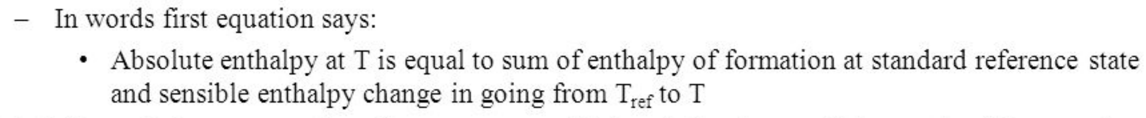
Thermochemistry

$$fuel + oxidizer \rightarrow products$$

Standard reference state

- T_{ref} = 25°C (298.15 K)
- P_{ref} = 1 atm (101.325 kpa = 1 bar)
- $h_{ref} = h^{\circ}_{f,i}(T_{ref})$ =u+pv (J/kg)

$$h_i(T) = h^{\circ}_{f,i}(T_{ref}) + \Delta h_{s,i}(T_{ref}) \qquad \text{(J/kg)}$$



- In words first equation says:
  - Absolute enthalpy at T is equal to sum of enthalpy of formation at standard reference state and sensible enthalpy change in going from T_{ref} to T

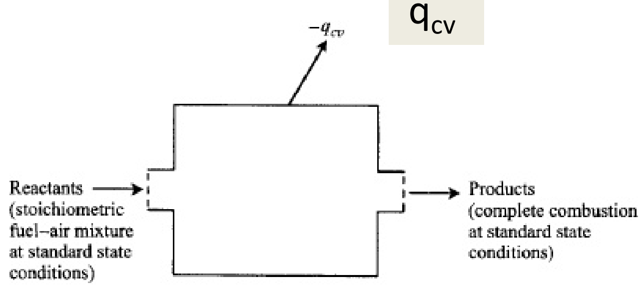
Carla Silva camsilva@fc.ul.pt

Thermochemistry

HEATING VALUE AND ENTHALPY OF REACTION

Constant pressure

q_{cv}



25 °C

Figure 2.7 Steady-flow reactor used to determine enthalpy of combustion.

25 °C

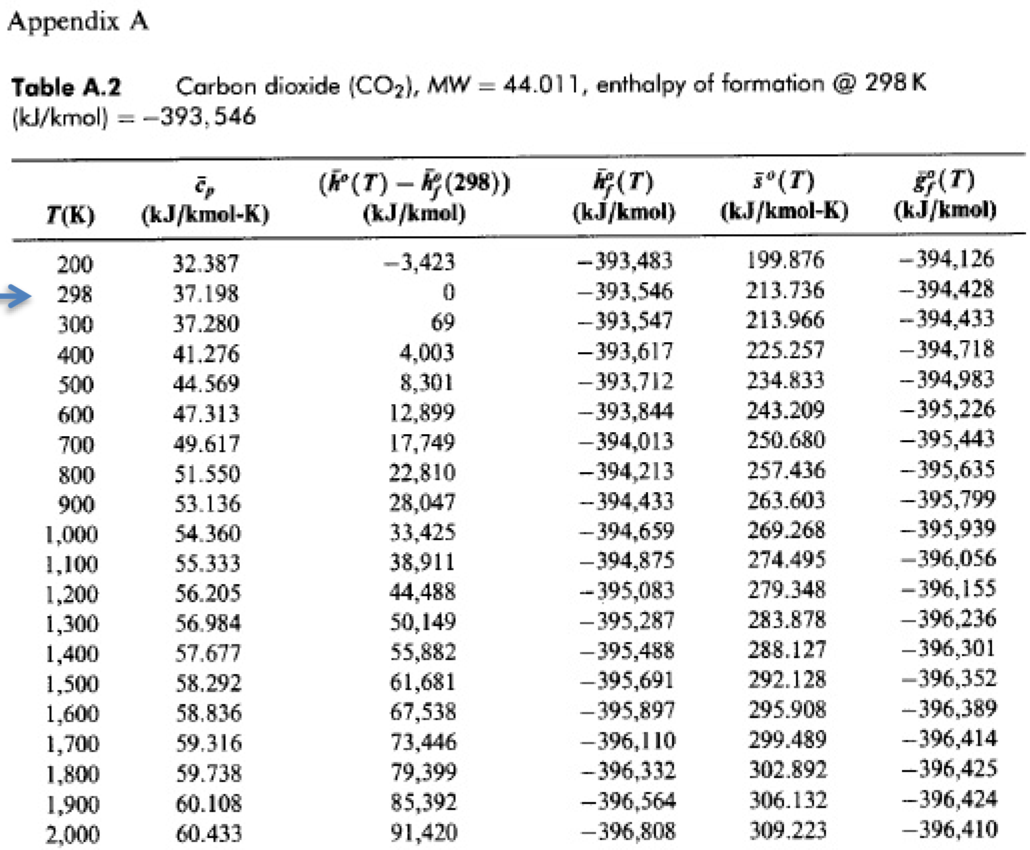
$$C_xH_yO_z + n(0.21O_2 + 0.79N_2) \rightarrow xCO_2 + yH_2O + 0.79 * nN_2$$

HHV = maximum heat release condensing water heat of vaporization **(2443 kJ/kg; 44010 kJ/kmol)**

LHV = q_{cv} in the reaction products is not recovered

Carla Silva camsilva@fc.ul.pt

Thermochemistry



Appendix A

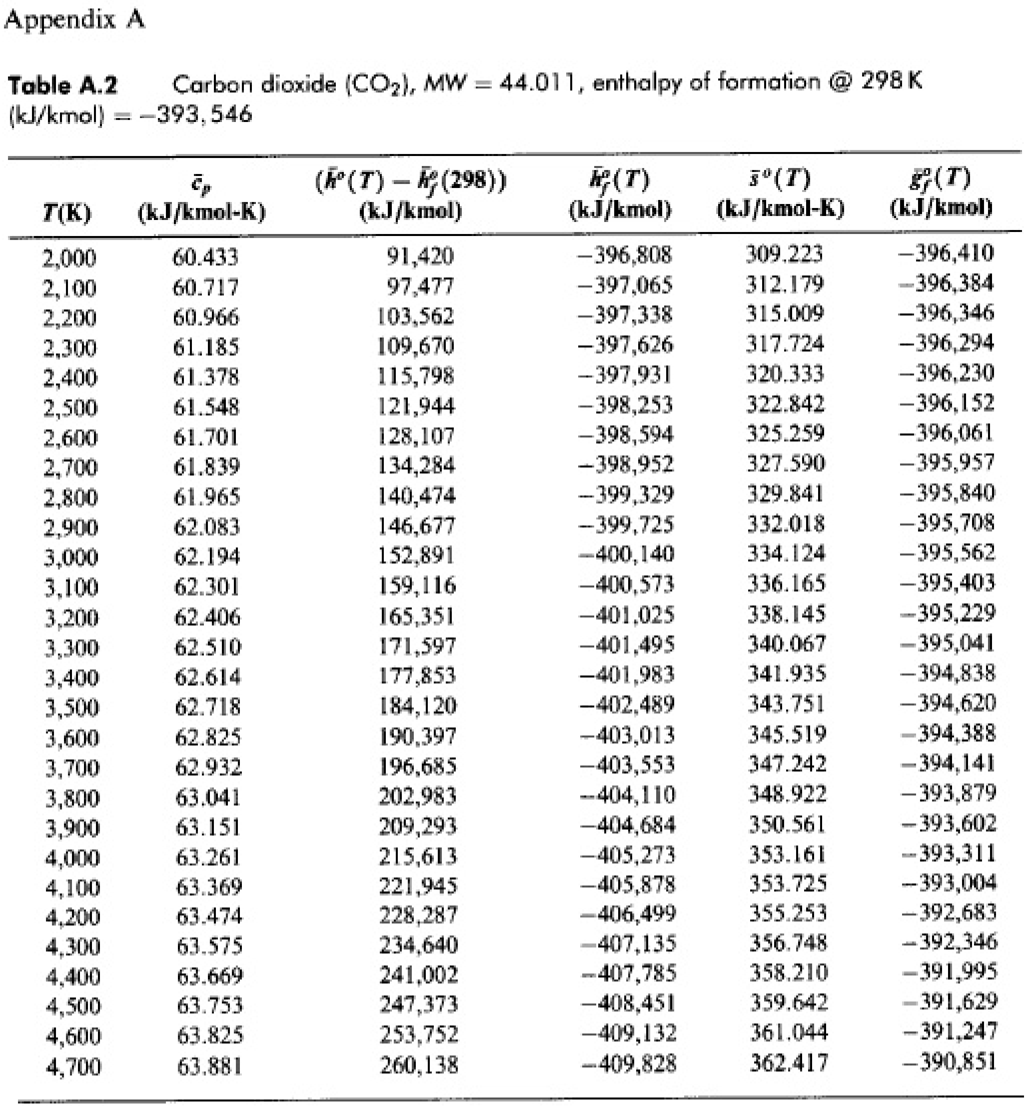
Table A.2 Carbon dioxide (CO_2), $MW = 44.011$, enthalpy of formation @ 298 K (kJ/kmol) = −393, 546

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

CO_2

Carla Silva camsilva@fc.ul.pt

Thermochemistry



Appendix A

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

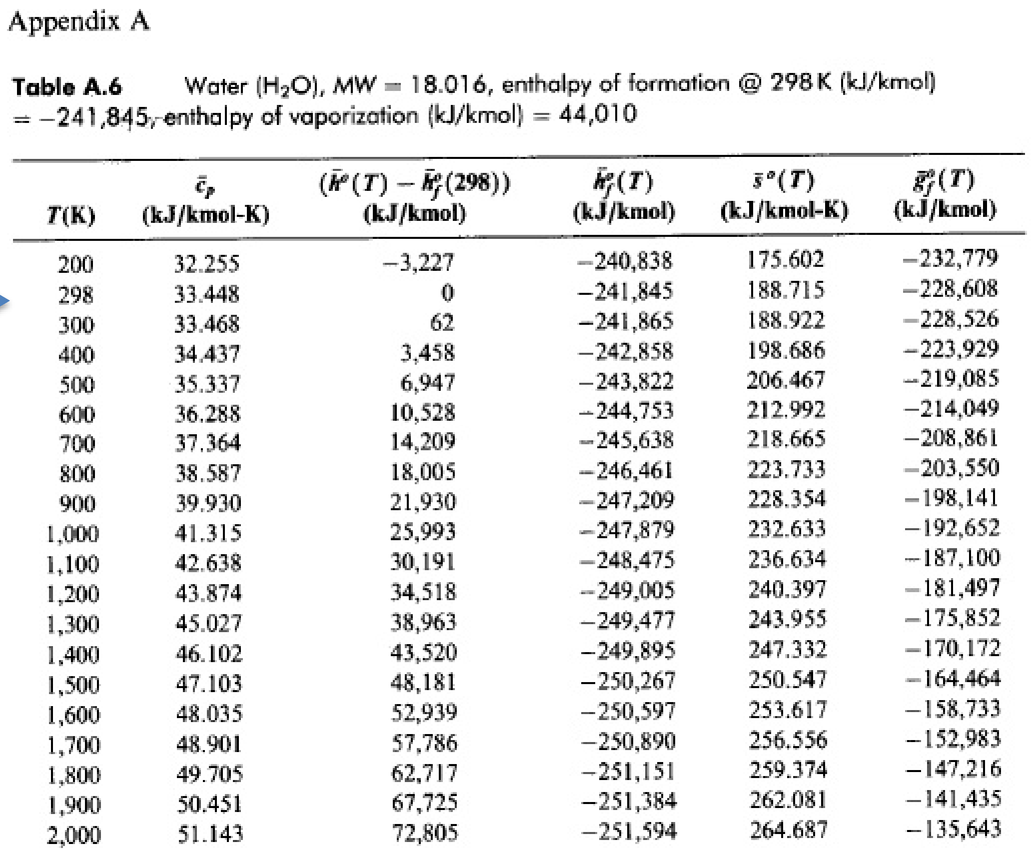
T(K)	$\bar{c}_p$ (kJ/kmol-K)	$(\bar{h}^o(T) - \bar{h}^o_f(298))$ (kJ/kmol)	$\bar{h}^o_f(T)$ (kJ/kmol)	$\bar{s}^o(T)$ (kJ/kmol-K)	$\bar{g}^o_f(T)$ (kJ/kmol)
2,000	60.433	91,420	−396,808	309.223	−396,410
2,100	60.717	97,477	−397,065	312.179	−396,384
2,200	60.966	103,562	−397,338	315.009	−396,346
2,300	61.185	109,670	−397,626	317.724	−396,294
2,400	61.378	115,798	−397,931	320.333	−396,230
2,500	61.548	121,944	−398,253	322.842	−396,152
2,600	61.701	128,107	−398,594	325.259	−396,061
2,700	61.839	134,284	−398,952	327.590	−395,957
2,800	61.965	140,474	−399,329	329.841	−395,840
2,900	62.083	146,677	−399,725	332.018	−395,708
3,000	62.194	152,891	−400,140	334.124	−395,562
3,100	62.301	159,116	−400,573	336.165	−395,403
3,200	62.406	165,351	−401,025	338.145	−395,229
3,300	62.510	171,597	−401,495	340.067	−395,041
3,400	62.614	177,853	−401,983	341.935	−394,838
3,500	62.718	184,120	−402,489	343.751	−394,620
3,600	62.825	190,397	−403,013	345.519	−394,388
3,700	62.932	196,685	−403,553	347.242	−394,141
3,800	63.041	202,983	−404,110	348.922	−393,879
3,900	63.151	209,293	−404,684	350.561	−393,602
4,000	63.261	215,613	−405,273	353.161	−393,311
4,100	63.369	221,945	−405,878	353.725	−393,004
4,200	63.474	228,287	−406,499	355.253	−392,683
4,300	63.575	234,640	−407,135	356.748	−392,346
4,400	63.669	241,002	−407,785	358.210	−391,995
4,500	63.753	247,373	−408,451	359.642	−391,629
4,600	63.825	253,752	−409,132	361.044	−391,247
4,700	63.881	260,138	−409,828	362.417	−390,851

CO_2

Carla Silva camsilva@fc.ul.pt

Ciências ULisboa

Thermochemistry



Appendix A

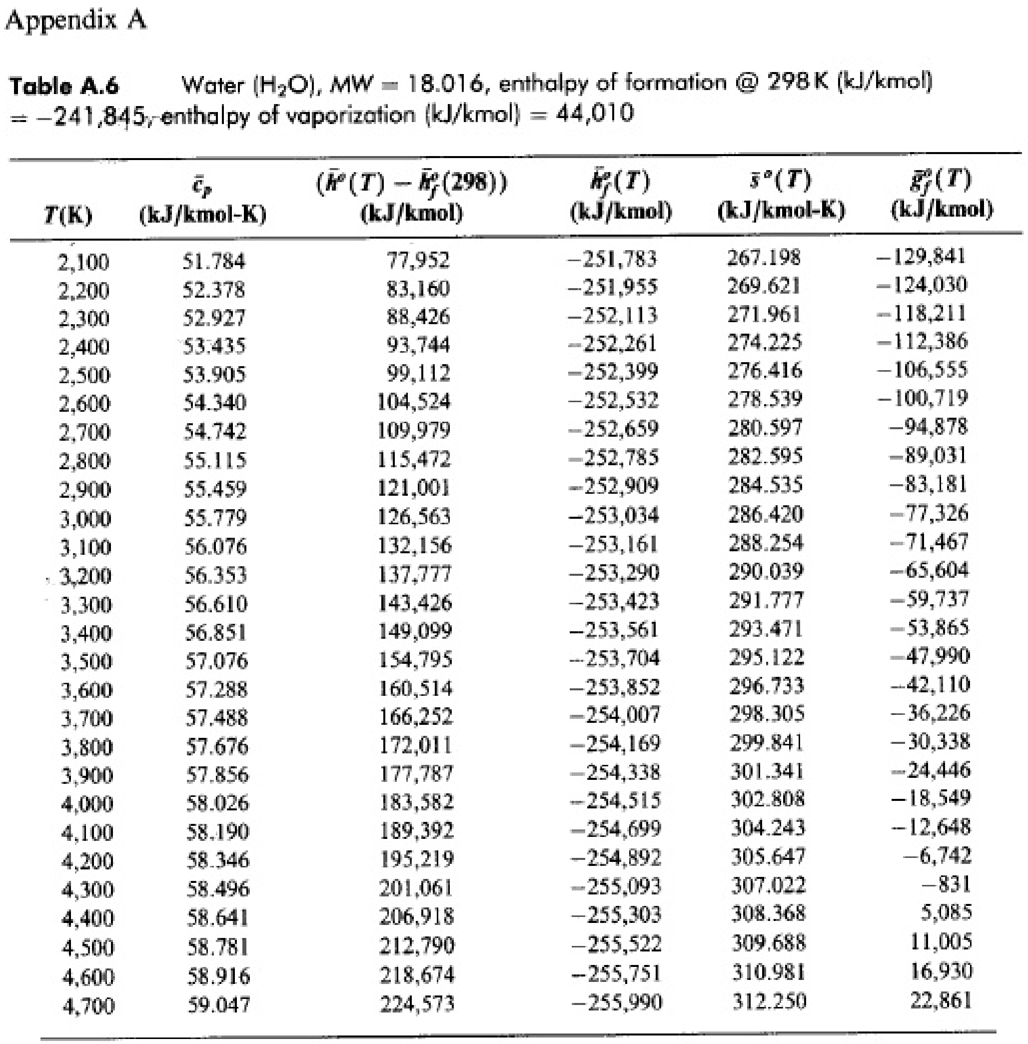
Table A.6 Water (H_2O), MW = 18.016, enthalpy of formation @ 298 K (kJ/kmol) = −241,845, enthalpy of vaporization (kJ/kmol) = 44,010

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	32.255	−3,227	−240,838	175.602	−232,779
298	33.448	0	−241,845	188.715	−228,608
300	33.468	62	−241,865	188.922	−228,526
400	34.437	3,458	−242,858	198.686	−223,929
500	35.337	6,947	−243,822	206.467	−219,085
600	36.288	10,528	−244,753	212.992	−214,049
700	37.364	14,209	−245,638	218.665	−208,861
800	38.587	18,005	−246,461	223.733	−203,550
900	39.930	21,930	−247,209	228.354	−198,141
1,000	41.315	25,993	−247,879	232.633	−192,652
1,100	42.638	30,191	−248,475	236.634	−187,100
1,200	43.874	34,518	−249,005	240.397	−181,497
1,300	45.027	38,963	−249,477	243.955	−175,852
1,400	46.102	43,520	−249,895	247.332	−170,172
1,500	47.103	48,181	−250,267	250.547	−164,464
1,600	48.035	52,939	−250,597	253.617	−158,733
1,700	48.901	57,786	−250,890	256.556	−152,983
1,800	49.705	62,717	−251,151	259.374	−147,216
1,900	50.451	67,725	−251,384	262.081	−141,435
2,000	51.143	72,805	−251,594	264.687	−135,643

H_2O

Carla Silva camsilva@fc.ul.pt

Thermochemistry



Appendix A

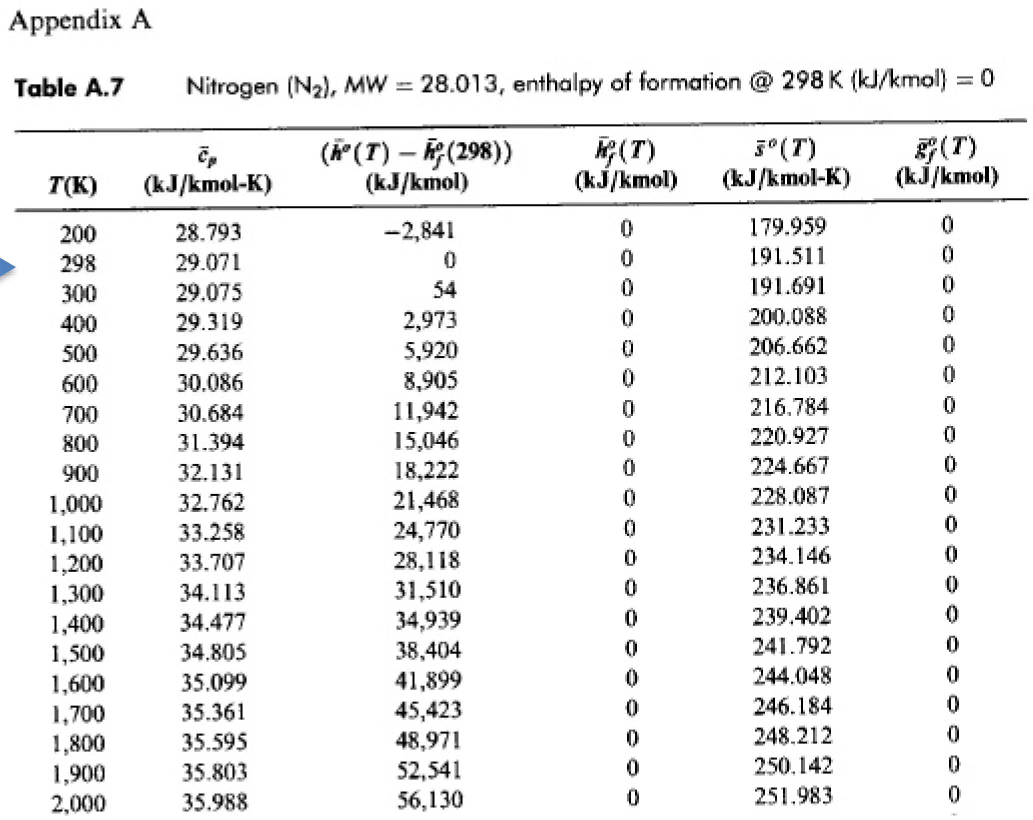
Table A.6 Water (H_2O), $MW = 18.016$, enthalpy of formation @ 298 K (kJ/kmol) $= -241{,}845$, enthalpy of vaporization (kJ/kmol) $= 44{,}010$

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)
2,100	51.784	77,952	−251,783	267.198	−129,841
2,200	52.378	83,160	−251,955	269.621	−124,030
2,300	52.927	88,426	−252,113	271.961	−118,211
2,400	53.435	93,744	−252,261	274.225	−112,386
2,500	53.905	99,112	−252,399	276.416	−106,555
2,600	54.340	104,524	−252,532	278.539	−100,719
2,700	54.742	109,979	−252,659	280.597	−94,878
2,800	55.115	115,472	−252,785	282.595	−89,031
2,900	55.459	121,001	−252,909	284.535	−83,181
3,000	55.779	126,563	−253,034	286.420	−77,326
3,100	56.076	132,156	−253,161	288.254	−71,467
3,200	56.353	137,777	−253,290	290.039	−65,604
3,300	56.610	143,426	−253,423	291.777	−59,737
3,400	56.851	149,099	−253,561	293.471	−53,865
3,500	57.076	154,795	−253,704	295.122	−47,990
3,600	57.288	160,514	−253,852	296.733	−42,110
3,700	57.488	166,252	−254,007	298.305	−36,226
3,800	57.676	172,011	−254,169	299.841	−30,338
3,900	57.856	177,787	−254,338	301.341	−24,446
4,000	58.026	183,582	−254,515	302.808	−18,549
4,100	58.190	189,392	−254,699	304.243	−12,648
4,200	58.346	195,219	−254,892	305.647	−6,742
4,300	58.496	201,061	−255,093	307.022	−831
4,400	58.641	206,918	−255,303	308.368	5,085
4,500	58.781	212,790	−255,522	309.688	11,005
4,600	58.916	218,674	−255,751	310.981	16,930
4,700	59.047	224,573	−255,990	312.250	22,861

H_2O

Carla Silva camsilva@fc.ul.pt

Thermochemistry



Appendix A

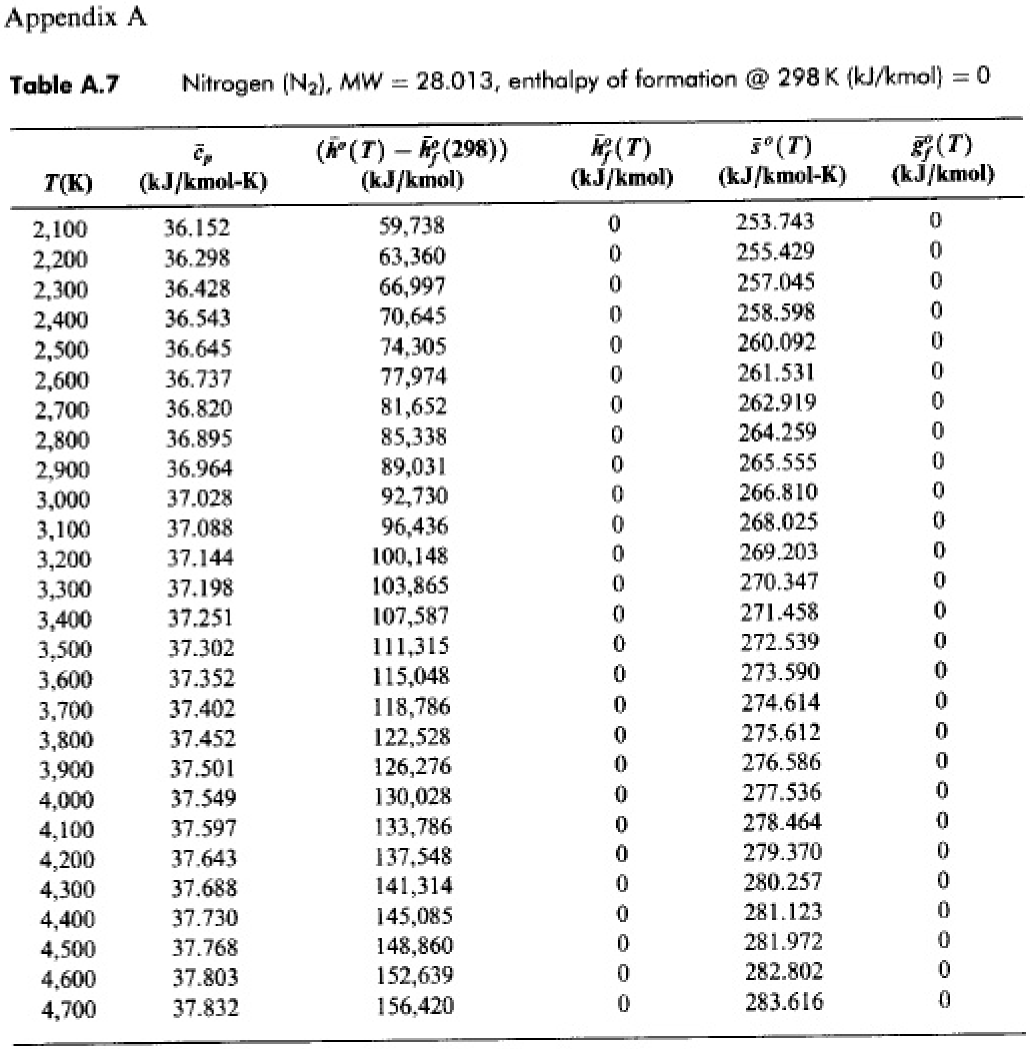
Table A.7 Nitrogen (N_2), MW = 28.013, enthalpy of formation @ 298 K (kJ/kmol) = 0

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	28.793	−2,841	0	179.959	0
298	29.071	0	0	191.511	0
300	29.075	54	0	191.691	0
400	29.319	2,973	0	200.088	0
500	29.636	5,920	0	206.662	0
600	30.086	8,905	0	212.103	0
700	30.684	11,942	0	216.784	0
800	31.394	15,046	0	220.927	0
900	32.131	18,222	0	224.667	0
1,000	32.762	21,468	0	228.087	0
1,100	33.258	24,770	0	231.233	0
1,200	33.707	28,118	0	234.146	0
1,300	34.113	31,510	0	236.861	0
1,400	34.477	34,939	0	239.402	0
1,500	34.805	38,404	0	241.792	0
1,600	35.099	41,899	0	244.048	0
1,700	35.361	45,423	0	246.184	0
1,800	35.595	48,971	0	248.212	0
1,900	35.803	52,541	0	250.142	0
2,000	35.988	56,130	0	251.983	0

N_2

Carla Silva camsilva@fc.ul.pt

Thermochemistry



Appendix A

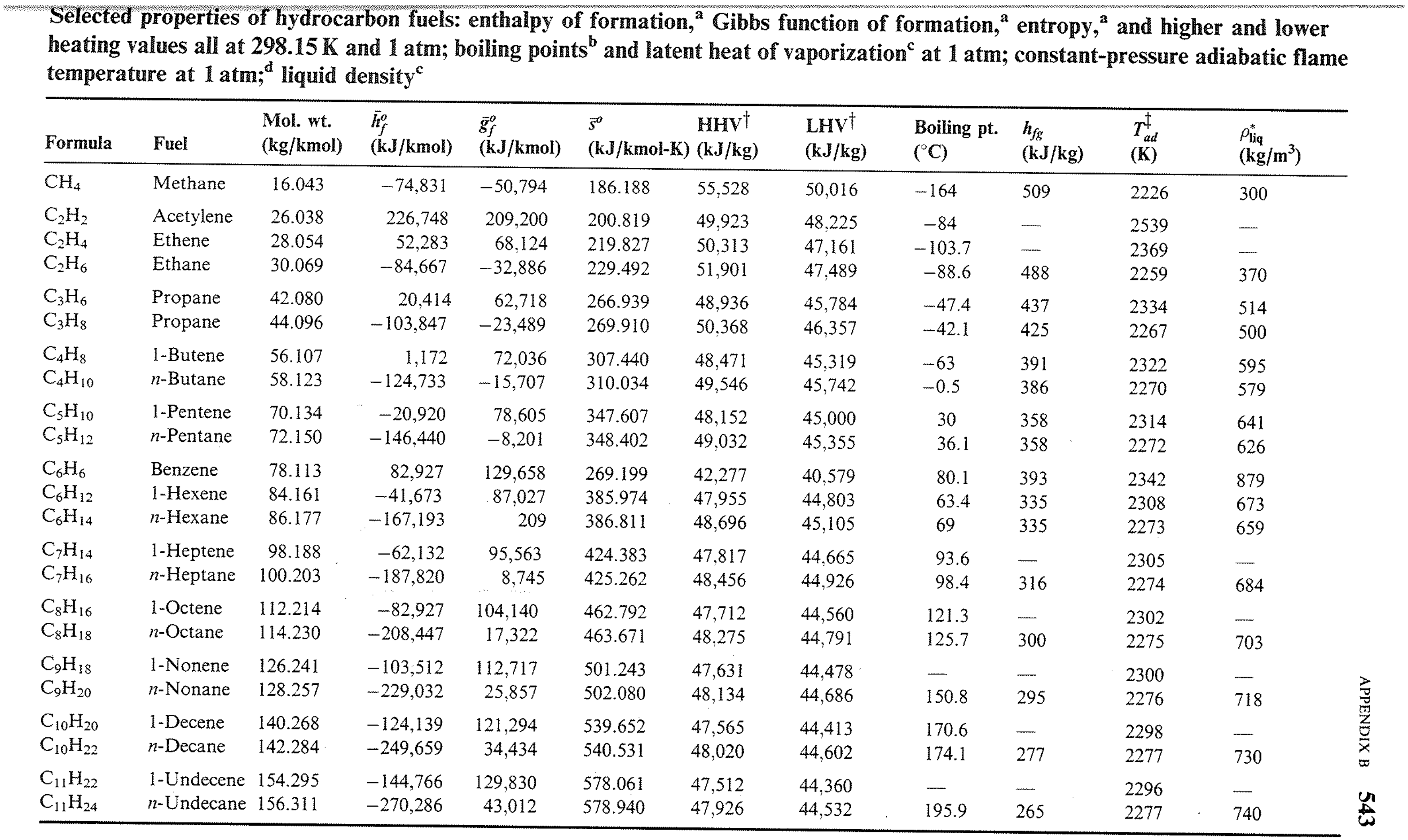
Table A.7 Nitrogen (N_2), MW = 28.013, enthalpy of formation @ 298 K (kJ/kmol) = 0

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)
2,100	36.152	59,738	0	253.743	0
2,200	36.298	63,360	0	255.429	0
2,300	36.428	66,997	0	257.045	0
2,400	36.543	70,645	0	258.598	0
2,500	36.645	74,305	0	260.092	0
2,600	36.737	77,974	0	261.531	0
2,700	36.820	81,652	0	262.919	0
2,800	36.895	85,338	0	264.259	0
2,900	36.964	89,031	0	265.555	0
3,000	37.028	92,730	0	266.810	0
3,100	37.088	96,436	0	268.025	0
3,200	37.144	100,148	0	269.203	0
3,300	37.198	103,865	0	270.347	0
3,400	37.251	107,587	0	271.458	0
3,500	37.302	111,315	0	272.539	0
3,600	37.352	115,048	0	273.590	0
3,700	37.402	118,786	0	274.614	0
3,800	37.452	122,528	0	275.612	0
3,900	37.501	126,276	0	276.586	0
4,000	37.549	130,028	0	277.536	0
4,100	37.597	133,786	0	278.464	0
4,200	37.643	137,548	0	279.370	0
4,300	37.688	141,314	0	280.257	0
4,400	37.730	145,085	0	281.123	0
4,500	37.768	148,860	0	281.972	0
4,600	37.803	152,639	0	282.802	0
4,700	37.832	156,420	0	283.616	0

N_2

Carla Silva camsilva@fc.ul.pt

Thermochemistry



Selected properties of hydrocarbon fuels: enthalpy of formation,[a] Gibbs function of formation,[a] entropy,[a] and higher and lower heating values all at 298.15 K and 1 atm; boiling points[b] and latent heat of vaporization[c] at 1 atm; constant-pressure adiabatic flame temperature at 1 atm;[d] liquid density[c]

Formula	Fuel	Mol. wt. (kg/kmol)	$\bar{h}_f^o$ (kJ/kmol)	$\bar{g}_f^o$ (kJ/kmol)	$\bar{s}^o$ (kJ/kmol-K)	HHV† (kJ/kg)	LHV† (kJ/kg)	Boiling pt. (°C)	h_{fg} (kJ/kg)	$T_{ad}^{\ddagger}$ (K)	ρ_{liq}^{*} (kg/m^3)
CH_4	Methane	16.043	−74,831	−50,794	186.188	55,528	50,016	−164	509	2226	300
C_2H_2	Acetylene	26.038	226,748	209,200	200.819	49,923	48,225	−84	—	2539	—
C_2H_4	Ethene	28.054	52,283	68,124	219.827	50,313	47,161	−103.7	—	2369	—
C_2H_6	Ethane	30.069	−84,667	−32,886	229.492	51,901	47,489	−88.6	488	2259	370
C_3H_6	Propene	42.080	20,414	62,718	266.939	48,936	45,784	−47.4	437	2334	514
C_3H_8	Propane	44.096	−103,847	−23,489	269.910	50,368	46,357	−42.1	425	2267	500
C_4H_8	1-Butene	56.107	1,172	72,036	307.440	48,471	45,319	−63	391	2322	595
C_4H_{10}	*n*-Butane	58.123	−124,733	−15,707	310.034	49,546	45,742	−0.5	386	2270	579
C_5H_{10}	1-Pentene	70.134	−20,920	78,605	347.607	48,152	45,000	30	358	2314	641
C_5H_{12}	*n*-Pentane	72.150	−146,440	−8,201	348.402	49,032	45,355	36.1	358	2272	626
C_6H_6	Benzene	78.113	82,927	129,658	269.199	42,277	40,579	80.1	393	2342	879
C_6H_{12}	1-Hexene	84.161	−41,673	87,027	385.974	47,955	44,803	63.4	335	2308	673
C_6H_{14}	*n*-Hexane	86.177	−167,193	209	386.811	48,696	45,105	69	335	2273	659
C_7H_{14}	1-Heptene	98.188	−62,132	95,563	424.383	47,817	44,665	93.6	—	2305	—
C_7H_{16}	*n*-Heptane	100.203	−187,820	8,745	425.262	48,456	44,926	98.4	316	2274	684
C_8H_{16}	1-Octene	112.214	−82,927	104,140	462.792	47,712	44,560	121.3	—	2302	—
C_8H_{18}	*n*-Octane	114.230	−208,447	17,322	463.671	48,275	44,791	125.7	300	2275	703
C_9H_{18}	1-Nonene	126.241	−103,512	112,717	501.243	47,631	44,478	—	—	2300	—
C_9H_{20}	*n*-Nonane	128.257	−229,032	25,857	502.080	48,134	44,686	150.8	295	2276	718
$C_{10}H_{20}$	1-Decene	140.268	−124,139	121,294	539.652	47,565	44,413	170.6	—	2298	—
$C_{10}H_{22}$	*n*-Decane	142.284	−249,659	34,434	540.531	48,020	44,602	174.1	277	2277	730
$C_{11}H_{22}$	1-Undecene	154.295	−144,766	129,830	578.061	47,512	44,360	—	—	2296	—
$C_{11}H_{24}$	*n*-Undecane	156.311	−270,286	43,012	578.940	47,926	44,532	195.9	265	2277	740

Carla Silva camsilva@fc.ul.pt

Thermochemistry

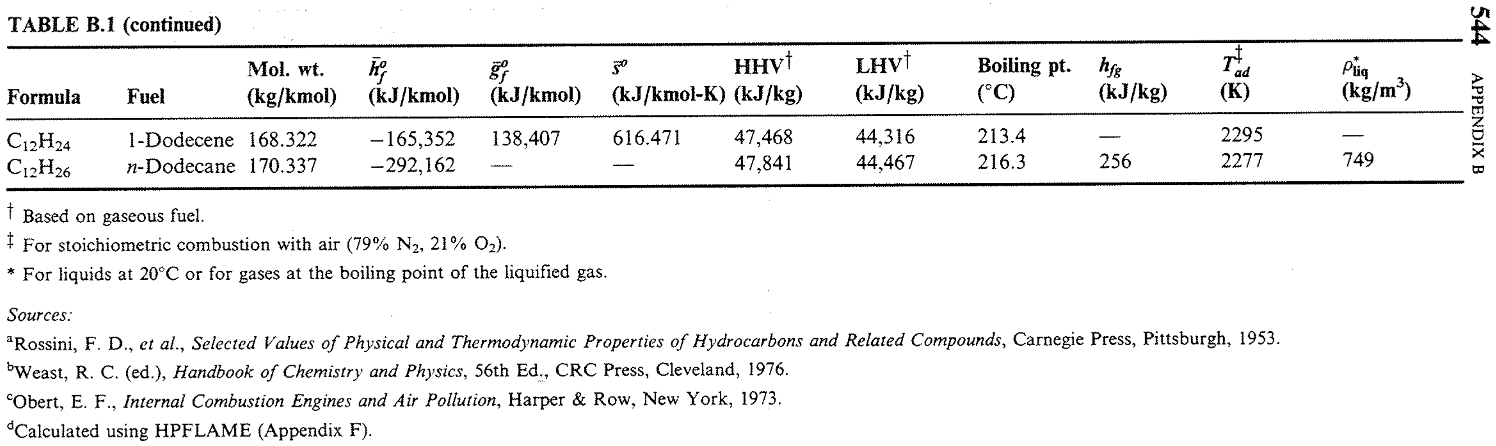


TABLE B.1 (continued)

Formula	Fuel	Mol. wt. (kg/kmol)	$\bar{h}_f^o$ (kJ/kmol)	$\bar{g}_f^o$ (kJ/kmol)	$\bar{s}^o$ (kJ/kmol-K)	HHV† (kJ/kg)	LHV† (kJ/kg)	Boiling pt. (°C)	h_{fg} (kJ/kg)	$T_{ad}^{\ddagger}$ (K)	ρ_{liq}^{*} (kg/m^3)
$C_{12}H_{24}$	1-Dodecene	168.322	−165,352	138,407	616.471	47,468	44,316	213.4	—	2295	—
$C_{12}H_{26}$	*n*-Dodecane	170.337	−292,162	—	—	47,841	44,467	216.3	256	2277	749

† Based on gaseous fuel.

‡ For stoichiometric combustion with air (79% N_2, 21% O_2).

* For liquids at 20°C or for gases at the boiling point of the liquified gas.

Sources:

[a] Rossini, F. D., *et al.*, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Carnegie Press, Pittsburgh, 1953.

[b] Weast, R. C. (ed.), *Handbook of Chemistry and Physics*, 56th Ed., CRC Press, Cleveland, 1976.

[c] Obert, E. F., *Internal Combustion Engines and Air Pollution*, Harper & Row, New York, 1973.

[d] Calculated using HPFLAME (Appendix F).

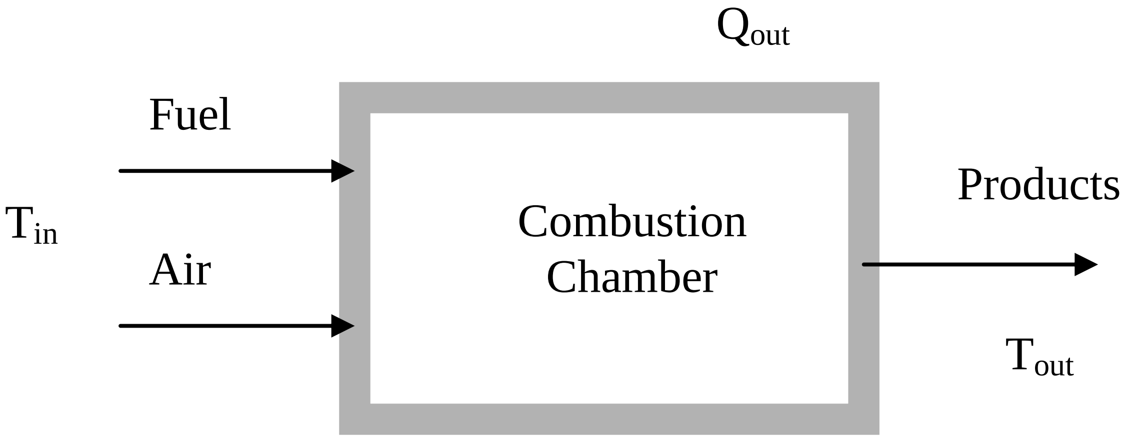
Carla Silva camsilva@fc.ul.pt

Thermochemistry

Fuel	Chemical formula	LHV (MJ/kg)	Density (kg/L)	LHV (MJ/L)	CO_2 (kg/L)	CO_2 (g/MJ)
Gasolina	$C_nH_{1.87n}$	44	0.72-0.78	31.7	2.28	66.6-72.1
Gasóleo	$C_nH_{1.8n}$	42.5	0.84-0.88	35.7	2.68	75.0
Etanol	C_2H_6O	26.9	0.785	21.1	1.50	71.1
Biodiesel	$C_nH_{2n}O_2$	37.1	0.88	32.6	2.47-2.80	75.8-85.8
Gás natural	$\sim CH_4$	50	0.72 (kg/m³)*	36.0 (MJ/m³)	1.98 (kg/m³)	55.0
GPL	$\sim C_3H_8$	46.4	0.51 (2 kg/m³)*	23.7	1.53	64.7

Carla Silva camsilva@fc.ul.pt

Thermochemistry



- Maximum heat release, max Q_{out}: $T_{out}=T_{in}$
- Maximum flame temperature, adiabatic combustion chamber, T_{ad}:

Hreag(T_{in})=Hprod (T_{ad})(constant pressure, e.g. Diesel engine, gas turbine, furnace)

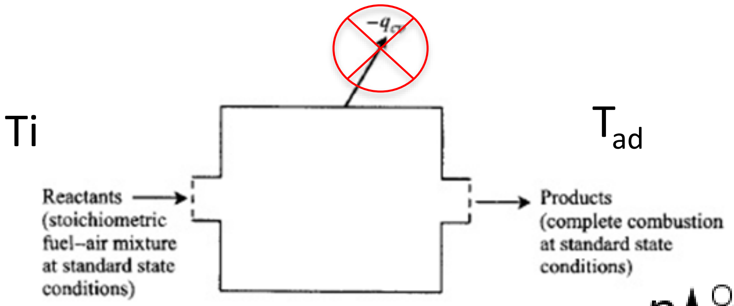
Hreag(T_{in})=Hprod (T_{ad})-R($n_{prod}T_{ad}$-$n_{reag}T_{in}$) (constant volume, e.g. gasoline engine)

Carla Silva camsilva@fc.ul.pt

Thermochemistry

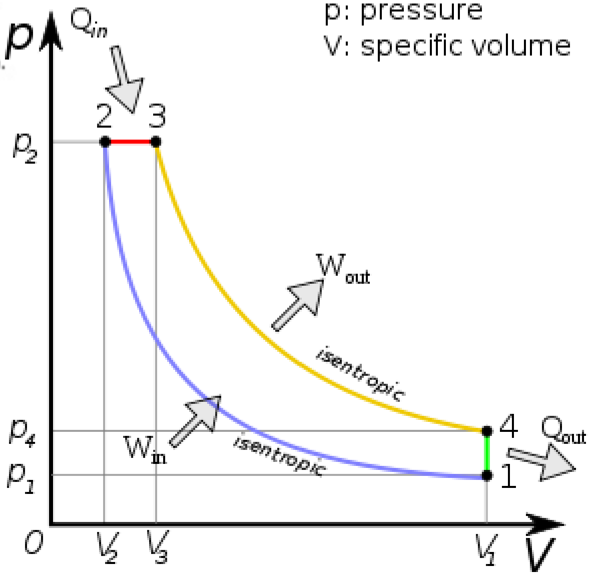
Adiabatic flame temperature = T_{ad}

Constant pressure

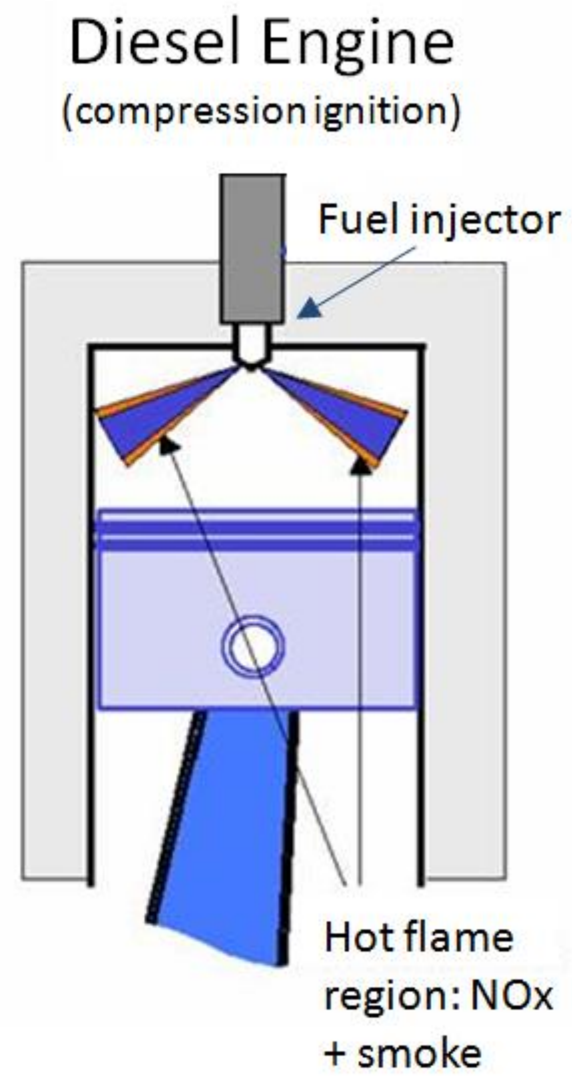


Steady-flow reactor used to determine enthalpy of combustion.

ΔH=0 for constant pressure

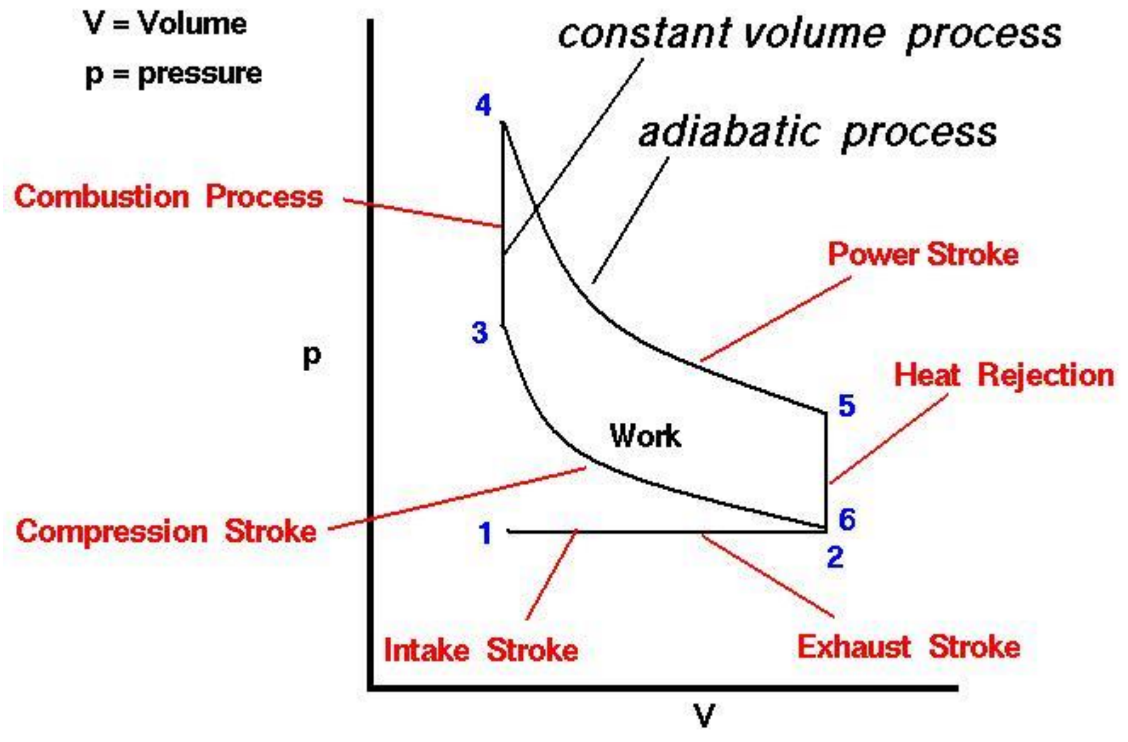


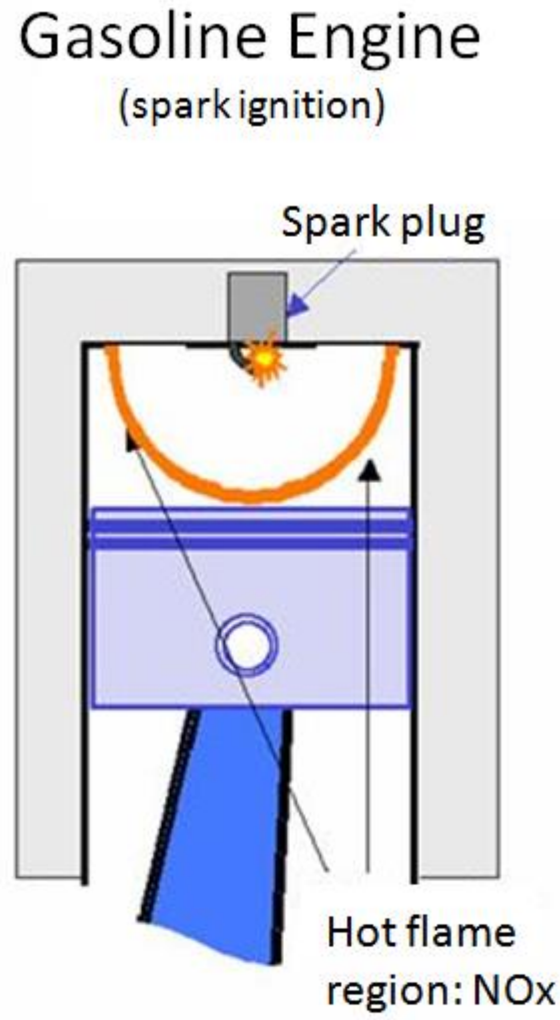
p: pressure
V: specific volume



Thermochemistry

Adiabatic flame temperature = T_{ad} { Constant volume





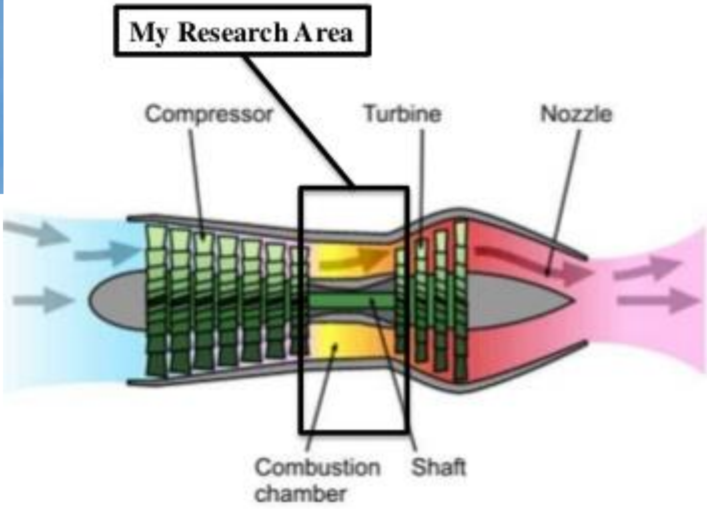
Carla Silva camsilva@fc.ul.pt

Thermochemistry

P#3 Determine the reference enthalpy of combustion of methane, CH_4, with air with λ=1. what is the lower and higher heating value for methane combustion?

Thermochemistry

P#4 A small, low-emission, stationary gas-turbine engine (see Fig. 2.4) operates at full load (3950 kW) at an equivalence ratio of 0.286 with an air flowrate of 15.9 kg/s. The equivalent composition of the fuel (natural gas) is $C_{1.16}H_{4.32}$. Determine the fuel mass flowrate and the operating air–fuel ratio for the engine.



Carla Silva camsilva@fc.ul.pt

Thermochemistry

P#5 Determine the upper and lower heating values at 298 K of gaseous n-decane, $C_{10}H_{22}$, per mol of fuel and per kg of fuel, and (A/F)st (molar and mass basis). If the enthalpy of vaporization of n-decade is 359 kJ/kgfuel at 298 K, what are the upper and lower heating values of liquid n-decane?

Thermochemistry

P#6 Estimate the constant-pressure adiabatic flame temperature for the combustion of a stoichiometric CH_4-air mixture. The pressure is 1 atm and the initial reactant temperature is 298 K. Make the necessary assumptions.

Carla Silva camsilva@fc.ul.pt

Thermochemistry

P#7 Estimate the constant-volume adiabatic flame temperature for the combustion of a stoichiometric CH4-air mixture. The initial pressure is 1 atm and the initial reactant temperature is 298 K. Make the necessary assumptions.

Thanks

Ciências
ULisboa

Faculdade
de Ciências
da Universidade
de Lisboa