

Thermochemistry

Enthalpy: h Specific enthalpy

$$h = C_p T, \quad C_p - \text{Specific heat Capacity at constant pressure}$$

T - absolute temperature

Standardized enthalpy: h_i

for species

→ is a sum of energy associated with chemical (standard enthalpy of formation, $h_{f,i}^0$) bonds and the sensible enthalpy change associated with the change from standard state to a given state. ($\Delta h_{s,i}$)

$$h_i(T) = h_{fi}^{\circ}(T_{ref}, P_{ref}) + \Delta h_{Si}(T - T_{ref})$$

h_{fi}° → Standard enthalpy of formation of
 ith species is the energy liberated (-ve) or absorbed
 (+ve),
 when the species is formed from the reference
elements/molecules at the Standard/reference
conditions.

1) Standard condition : $T_{ref} = 25^{\circ}\text{C}$,
 $P_{ref} = 1 \text{ atm}$

h_f° of reference elements are set to zero. Reference elements

Example O_2 - Oxygen molecule

at T_{ref} Pref, $h_{fO_2}^\circ = 0$, $h_{fN_2}^\circ = 0$

Atomic $h_{fO}^\circ > 0$ (absorbed)

$h_{fCO_2}^\circ < 0$ (heat is liberated)

Sensible enthalpy change: Δh_{si}

Δh_{si} — heat liberated or absorbed
(-ve) (+ve)

in taking the species from the reference
condition to the given state.

$$\Delta h_{si} = C_{p,i}(T - T_{ref}) \quad \left[C_{p,i} \text{ is assumed to be constant} \right]$$

✓
tables

$$= \int_{T_{ref}} C_{p,i} dT \quad \left[C_{p,i}(T) \text{ function of } T \right]$$



Standardized enthalpy tables

Table A.1 An Introduction to Combustion: Concepts and Applications by Stephen R. Turns, Third Edition, Tata McGraw-Hill, New Delhi, 2012

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Table A.1 Carbon monoxide (CO), MW = 28.010, enthalpy of formation @ 298 K
(kJ/kmol) = -110,541 $\leftarrow \Delta h_f^0$

$T(K)$	\bar{c}_p (kJ/kmol-K)	$(\bar{h}^o(T) - \bar{h}_f^o(298))$ (kJ/kmol)	$\bar{h}_f^o(T)$ (kJ/kmol)	$\bar{s}^o(T)$ (kJ/kmol-K)	$\bar{g}_f^o(T)$ (kJ/kmol)
200	28.687	-2,835	-111,308	186.018	-128,532
298	29.072	0	-110,541	197.548	-137,163
300	29.078	54	-110,530	197.728	-137,328
400	29.433	2,979	-110,121	206.141	-146,332
500	29.857	5,943	-110,017	212.752	-155,403
600	30.407	8,955	-110,156	218.242	-164,470
700	31.089	12,029	-110,477	222.979	-173,499
800	31.860	15,176	-110,924	227.180	-182,473
900	32.629	18,401	-111,450	230.978	-191,386
1,000	33.255	21,697	-112,022	234.450	-200,238
1,100	33.725	25,046	-112,619	237.642	-209,030
1,200	34.148	28,440	-113,240	240.595	-217,768
1,300	34.530	31,874	-113,881	243.344	-226,453
1,400	34.872	35,345	-114,543	245.915	-235,087



Standardized enthalpy tables

An Introduction to Combustion: Concepts and Applications by Stephen R. Turns, Third Edition, Tata McGraw-Hill, New Delhi, 2012

Table A.11 Oxygen (O_2), $MW = 31.999$, enthalpy of formation @ 298 K (kJ/kmol) = 0 Δh_f^0

$T(\text{K})$	\bar{c}_p (kJ/kmol-K)	$(\bar{h}^o(T) - \bar{h}_f^o(298))$ (kJ/kmol)	$\bar{h}_f^o(T)$ (kJ/kmol)	$\bar{s}^o(T)$ (kJ/kmol-K)	$\bar{g}_f^o(T)$ (kJ/kmol)
200	28.473	-2,836	0	193.518	0
298	29.315	0	0	205.043	0
300	29.331	54	0	205.224	0
400	30.210	3,031	0	213.782	0
500	31.114	6,097	0	220.620	0
600	32.030	9,254	0	226.374	0
700	32.927	12,503	0	231.379	0
800	33.757	15,838	0	235.831	0
900	34.454	19,250	0	239.849	0
1,000	34.936	22,721	0	243.507	0
1,100	35.270	26,232	0	246.852	0
1,200	35.593	29,775	0	249.935	0
1,300	35.903	33,350	0	252.796	0
1,400	36.202	36,955	0	255.468	0
1,500	36.490	40,590	0	257.976	0
1,600	36.768	44,253	0	260.339	0
1,700	37.036	47,943	0	262.577	0



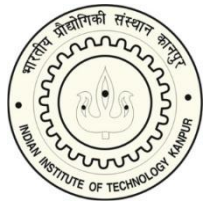
Standardized enthalpy tables

An Introduction to Combustion: Concepts and Applications by Stephen R. Turns, Third Edition, Tata McGraw-Hill, New Delhi, 2012

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Table A.12 Oxygen atom (O), MW = 16.000, enthalpy of formation @ 298 K (kJ/kmol)
 $= 249,197$ Δh_f^0

$T(K)$	\bar{c}_p (kJ/kmol-K)	$(\bar{h}^o(T) - \bar{h}_f^o(298))$ (kJ/kmol)	$\bar{h}_f^o(T)$ (kJ/kmol)	$\bar{s}^o(T)$ (kJ/kmol-K)	$\bar{g}_f^o(T)$ (kJ/kmol)
200	22.477	-2,176	248,439	152.085	237,374
298	21.899	0	249,197	160.945	231,778
300	21.890	41	249,211	161.080	231,670
400	21.500	2,209	249,890	167.320	225,719
500	21.256	4,345	250,494	172.089	219,605
600	21.113	6,463	251,033	175.951	213,375
700	21.033	8,570	251,516	179.199	207,060
800	20.986	10,671	251,949	182.004	200,679
900	20.952	12,768	252,340	184.474	194,246
1,000	20.915	14,861	252,698	186.679	187,772
1,100	20.898	16,952	253,033	188.672	181,263
1,200	20.882	19,041	253,350	190.490	174,724
1,300	20.867	21,128	253,650	192.160	168,159
1,400	20.854	23,214	253,934	193.706	161,572
1,500	20.843	25,299	254,201	195.145	154,966
1 600	20.834	27,383	254,454	196.490	148,342



Enthalpy of formation-fuels

An Introduction to Combustion: Concepts and Applications by Stephen R. Turns, Third Edition, Tata McGraw-Hill, New Delhi, 2012

Table B.1 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

$$\Delta h_f^0$$

Formula	Fuel	MW (kg/kmol)	\bar{h}_f^0 (kJ/kmol)	\bar{g}_f^0 (kJ/kmol)	\bar{s}^0 (kJ/kmol-K)	HHV [†] (kJ/kg)	LHV [†] (kJ/kg)	Boiling pt. (°C)	h_{fg} (kJ/kg)	T_{ad}^{\dagger} (K)	ρ_{liq}^* (kg/m ³)
CH ₄	Methane	16.043	-74,831	-50,794	186.188	55,528	50,016	-164	509	2,226	300
C ₂ H ₂	Acetylene	26.038	226,748	209,200	200.819	49,923	48,225	-84	—	2,539	—
C ₂ H ₄	Ethene	28.054	52,283	68,124	219.827	50,313	47,161	-103.7	—	2,369	—
C ₂ H ₆	Ethane	30.069	-84,667	-32,886	229.492	51,901	47,489	-88.6	488	2,259	370
C ₃ H ₆	Propene	42.080	20,414	62,718	266.939	48,936	45,784	-47.4	437	2,334	514
C ₃ H ₈	Propane	44.096	-103,847	-23,489	269.910	50,368	46,357	-42.1	425	2,267	500
C ₄ H ₈	1-Butene	56.107	1,172	72,036	307.440	48,471	45,319	-63	391	2,322	595
C ₄ H ₁₀	n-Butane	58.123	-124,733	-15,707	310.034	49,546	45,742	-0.5	386	2,270	579
C ₅ H ₁₀	1-Pentene	70.134	-20,920	78,605	347.607	48,152	45,000	30	358	2,314	641
C ₅ H ₁₂	n-Pentane	72.150	-146,440	-8,201	348.402	49,032	45,355	36.1	358	2,272	626
C ₆ H ₆	Benzene	78.113	82,927	129,658	269.199	42,277	40,579	80.1	393	2,342	879
C ₆ H ₁₂	1-Hexene	84.161	-41,673	87,027	385.974	47,955	44,803	63.4	335	2,308	673
C ₆ H ₁₄	n-Hexane	86.177	-167,193	209	386.811	48,696	45,105	69	335	2,273	659
C ₇ H ₁₄	1-Heptene	98.188	-62,132	95,563	424.383	47,817	44,665	93.6	—	2,305	—
C ₇ H ₁₆	n-Heptane	100.203	-187,820	8,745	425.262	48,456	44,926	98.4	316	2,274	684
C ₈ H ₁₆	1-Octene	112.214	-82,927	104,140	462.792	47,712	44,560	121.3	—	2,302	—
C ₈ H ₁₈	n-Octane	114.230	-208,447	17,322	463.671	48,275	44,791	125.7	300	2,275	703
C ₉ H ₁₈	1-Nonene	126.241	-103,512	112,717	501.243	47,631	44,478	—	—	2,300	—
C ₉ H ₂₀	n-Nonane	128.257	-229,032	25,857	502.080	48,134	44,686	150.8	295	2,276	718
C ₁₀ H ₂₀	1-Decene	140.268	-124,139	121,294	539.652	47,565	44,413	170.6	—	2,298	—
C ₁₀ H ₂₂	n-Decane	142.284	-249,659	34,434	540.531	48,020	44,602	174.1	277	2,277	730
C ₁₁ H ₂₂	1-Undecene	154.295	-144,766	129,830	578.061	47,512	44,360	—	—	2,296	—
C ₁₁ H ₂₄	n-Undecane	156.311	-270,286	43,012	578.940	47,926	44,532	195.9	265	2,277	740



Specific Heat Variation with Temperature

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note: specific heats are functions of temperature

constant-pressure specific heat:
(T) (kJ/kmol-K) (molar-specific)
(T) (kJ/kg-K) (mass-specific)

MW has units kg/kmol

note: over-bar is used to denote molar specific properties

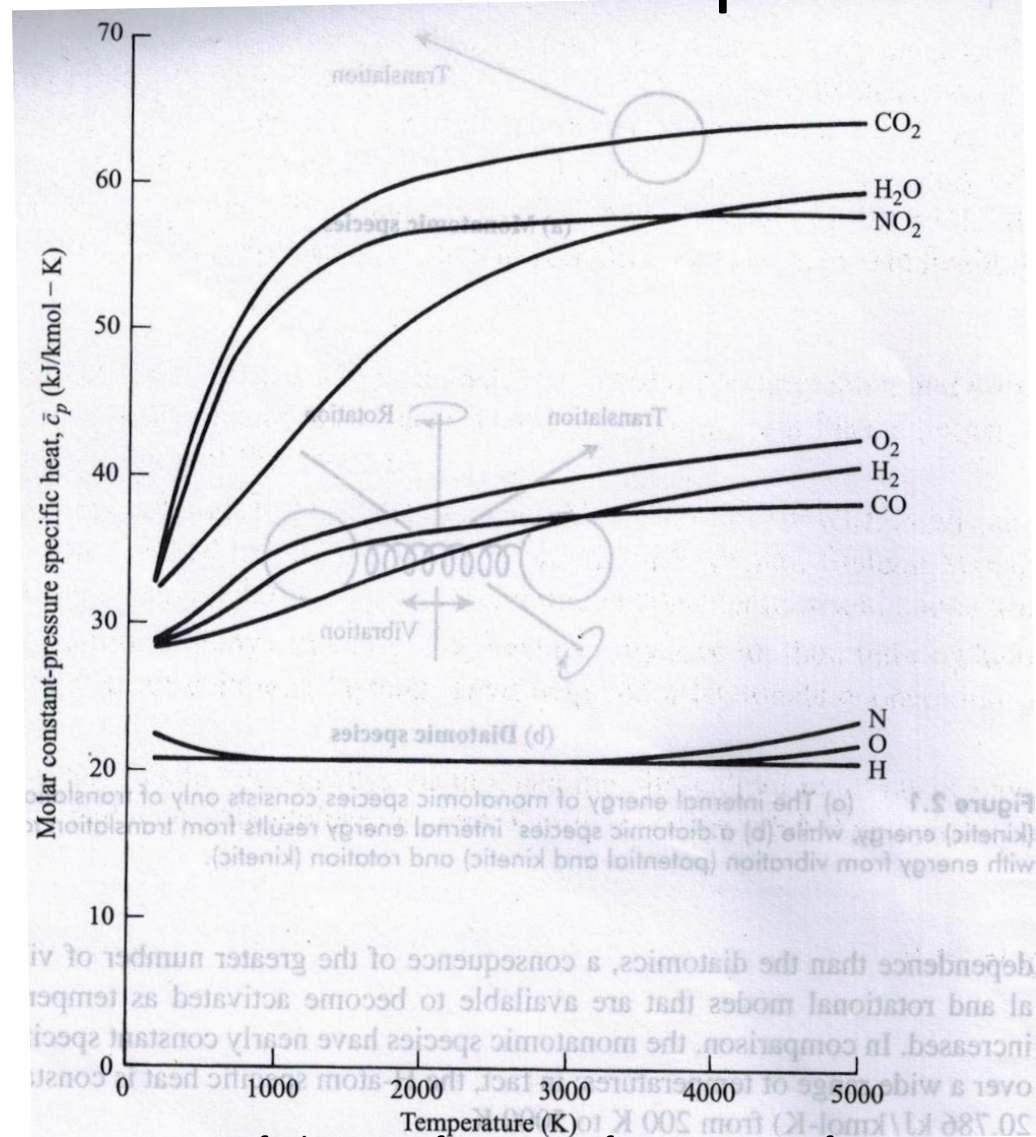


Fig. 2.2 Molar constant-pressure specific heats as functions of temperature for monoatomic (H, N, and O), diatomic (CO , H_2 and O_2), and triatomic (CO_2 , H_2O , and NO_2) species.
(An Introduction to Combustion: Concepts and Applications by Stephen R. Turns, Third Edition, Tata McGraw-Hill, New Delhi, 2012)

Specific Heat as Polynomials

Table A.13 Curvefit coefficients for thermodynamic properties (C-H-N-O system). (An Introduction to Combustion: Concepts and Applications by Stephen R. Turns, Third Edition, Tata McGraw-Hill, New Delhi, 2012)

universal gas

$R_{\text{gas}} = 8.314 \text{ kJ/kmol} \cdot \text{K}$

Species	T (K)	a_1	a_2	a_3	a_4	a_5	a_6	a_7
CO	1000–5000	0.03025078E+02	0.14426885E-02	-0.05630827E-05	0.10185813E-09	-0.06910951E-13	-0.14268350E+05	0.06108217E+02
	300–1000	0.03262451E+02	0.15119409E-02	-0.03881755E-04	0.05581944E-07	-0.02474951E-10	-0.14310539E+05	0.04848897E+02
CO ₂	1000–5000	0.04453623E+02	0.03140168E-01	-0.12784105E-05	0.02393996E-08	-0.16690333E-13	-0.04896696E+06	-0.09553959E+01
	300–1000	0.02275724E+02	0.09922072E-01	-0.10409113E-04	0.06866686E-07	-0.02117280E-10	-0.04837314E+06	0.10188488E+02
H ₂	1000–5000	0.02991423E+02	0.07000644E-02	-0.05633828E-06	-0.09231578E-10	0.15827519E-14	-0.08350340E+04	-0.13551101E+01
	300–1000	0.03298124E+02	0.08249441E-02	-0.08143015E-05	-0.09475434E-09	0.04134872E-11	-0.10125209E+04	-0.03294094E+02
H	1000–5000	0.02500000E+02	0.00000000E+00	0.00000000E+00	0.00000000E+00	0.00000000E+00	0.02547162E+06	-0.04601176E+01
	300–1000	0.02500000E+02	0.00000000E+00	0.00000000E+00	0.00000000E+00	0.00000000E+00	0.02547162E+06	-0.04601176E+01
OH	1000–5000	0.02882730E+02	0.10139743E-02	-0.02276877E-05	0.02174683E-09	-0.05126305E-14	0.03886888E+05	0.05595712E+02
	300–1000	0.03637266E+02	0.01850910E-02	-0.16761646E-05	0.02387202E-07	-0.08431442E-11	0.03606781E+05	0.13588605E+01
H ₂ O	1000–5000	0.02672145E+02	0.03056293E-01	-0.08730260E-05	0.12009964E-09	-0.06391618E-13	-0.02989921E+06	0.06862817E+02
	300–1000	0.03386842E+02	0.03474982E-01	-0.06354696E-04	0.06968581E-07	-0.02506588E-10	-0.03020811E+06	0.02590232E+02
N ₂	1000–5000	0.02926640E+02	0.14879768E-02	-0.05684760E-05	0.10097038E-09	-0.06753351E-13	-0.09227977E+04	0.05980528E+02
	300–1000	0.03298677E+02	0.14082404E-02	-0.03963222E-04	0.05641515E-07	-0.02444854E-10	-0.10208999E+04	0.03950372E+02
N	1000–5000	0.02450268E+02	0.10661458E-03	-0.07465337E-06	0.01879652E-09	-0.10259839E-14	0.05611604E+06	0.04448758E+02
	300–1000	0.02503071E+02	-0.02180018E-03	0.05420529E-06	-0.05647560E-09	0.02099904E-12	0.05609890E+06	0.04167566E+02
NO	1000–5000	0.03245435E+02	0.12691383E-02	-0.05015890E-05	0.09169283E-09	-0.06275419E-13	0.09800840E+05	0.06417293E+02
	300–1000	0.03376541E+02	0.12530634E-02	-0.03302750E-04	0.05217810E-07	-0.02446262E-10	0.09817961E+05	0.05829590E+02
NO ₂	1000–5000	0.04682859E+02	0.02462429E-01	-0.10422585E-05	0.01976902E-08	-0.13917168E-13	0.02261292E+05	0.09885985E+01
	300–1000	0.02670600E+02	0.07838500E-01	-0.08063864E-04	0.06161714E-07	-0.02320150E-10	0.02896290E+05	0.11612071E+02
O ₂	1000–5000	0.03697578E+02	0.06135197E-02	-0.12588420E-06	0.01775281E-09	-0.11364354E-14	-0.12339301E+04	0.03189165E+02
	300–1000	0.03212936E+02	0.11274864E-02	-0.05756150E-05	0.13138773E-08	-0.08768554E-11	-0.10052490E+04	0.06034737E+02
O	1000–5000	0.02542059E+02	-0.02755061E-03	-0.03102803E-07	0.04551067E-10	-0.04368051E-14	0.02923080E+06	0.04920308E+02
	300–1000	0.02946428E+02	-0.16381665E-02	0.02421031E-04	-0.16028431E-08	0.03890696E-11	0.02914764E+06	0.02963995E+02

- For computation: polynomial fits are used for \bar{c}_p :

$$\frac{\bar{c}_p}{R_u} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

$$\int_{T_{\text{ref}}}^T \bar{c}_p dT \left\} \begin{array}{l} \text{sensible enthalpy} \\ \text{(going from } T_{\text{ref}} \rightarrow T) \end{array} \right.$$



Example problem

An Introduction to Combustion: Concepts and Applications by Stephen R. Turns, Third Edition, Tata McGraw-Hill, New Delhi, 2012

A gas stream of 1 atm contains a mixture of CO , CO_2 , N_2 , in which mole fractions of CO and CO_2 are 0.1 and 0.2 respectively. The gas stream temperature is 1200 K. Determine the standardized enthalpy of the mixture on both a mole basis (kJ/kmol) and a mass basis (kJ/kg). Also determine the mass fractions of the three component gases.

Example 2.3. S. Turns. Combustion book (12)

$$X_{CO} = 0.1, X_{CO_2} = 0.2, X_{N_2} = 1 - (X_{CO} + X_{CO_2}) = 1 - (0.1 + 0.2)$$

$$X_{N_2} = 0.7$$

Standardized enthalpy, $h_{mix} = \sum X_i h_i$

$$h_{CO} = h_{f,CO}^{\circ} + \Delta h_{s,CO}(T=1200) = h_{f,CO}^{\circ} + (h(1200) - h_f^{\circ}(298))_{CO}$$

[From table]

$$= -110541 + 28440 = -82101 \text{ kJ/kmol.}$$

... 1°(298)



Example problem

An Introduction to Combustion: Concepts and Applications by Stephen R. Turns, Third Edition, Tata McGraw-Hill, New Delhi, 2012

$$= -110541 + 44488 = -$$

$$h_{CO_2} = h_{fCO_2}^{\circ} + \Delta h_{sCO_2}(1200) = h_{fCO_2}^{\circ} + (h(1200) - h_f^{\circ}(298))_{CO_2}$$

$$= -393546 + 44488 = -349058 \text{ kJ/kmol.}$$

$$h_{N_2} = h_{fN_2}^{\circ} + \Delta h_{sN_2}(1200) = h_{fN_2}^{\circ} + (h(1200) - h_f^{\circ}(298))_{N_2}$$

$$= 0 + 28118 = 28118 \text{ kJ/kmol}$$

$$h_{mix} = 0.1 \times (-82101) + 0.2 \times (-349058) + 0.7 \times 28118$$

$$h_{mix} = -58339.1 \text{ kJ/kmol.} \quad \text{Std. Enthalpy of mixture / kmol}$$

$$M_{W_{CO}} = 12 + 16 = 28, \quad M_{W_{CO_2}} = 12 + 32 = 44, \quad M_{W_{N_2}} = 28 \text{ kg/kmol}$$



Example problem

An Introduction to Combustion: Concepts and Applications by Stephen R. Turns, Third Edition, Tata McGraw-Hill, New Delhi, 2012

$$M_{w_{CO}} = 12 + 16 = 28 \quad w_{CO_2}$$

$$M_{w_{mix}} = \sum X_i M_{w_i} = 0.1 \times 28 + 0.2 \times 44 + 0.7 \times 28 = 31.2 \text{ kg/kmol.}$$

$$h_{mix} = \frac{-58339.1}{31.2} \text{ kJ/kg} = -1869.84 \text{ kJ/kg} = h_{mix}$$

Mass fraction: $Y_i = X_i \frac{M_{w_i}}{M_{w_{mix}}}$

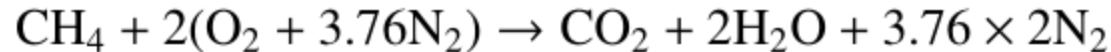
$$Y_{CO} = 0.1 \times \frac{28}{31.2} = 0.0897, \quad Y_{CO_2} = 0.2 \times \frac{44}{31.2} = 0.282$$

$$Y_{N_2} = 0.7 \times \frac{28}{31.2} = 0.628$$



Example problem: heat of reaction

An Introduction to Combustion: Concepts and Applications by Stephen R. Turns, Third Edition, Tata McGraw-Hill, New Delhi, 2012



$$h_{f,\text{CH}_4}^0 = -74831, \quad h_{f,\text{O}_2}^0 = h_{f,\text{N}_2}^0 = 0 \text{ KJ/Kmol}$$

$$h_{f,\text{CO}_2}^0 = -393546, \quad h_{f,\text{H}_2\text{O}}^0 = -241845 \text{ KJ/Kmol}$$

$$\begin{aligned} H_{\text{prod}} &= 1 \times h_{f,\text{CO}_2}^0 + 2 \times h_{f,\text{H}_2\text{O}}^0 + 3.76 \times h_{f,\text{N}_2}^0 \\ &= 1 \times -393546 + 2 \times -241845 + 3.76 \times 0 = -877236 \text{ KJ} \end{aligned}$$

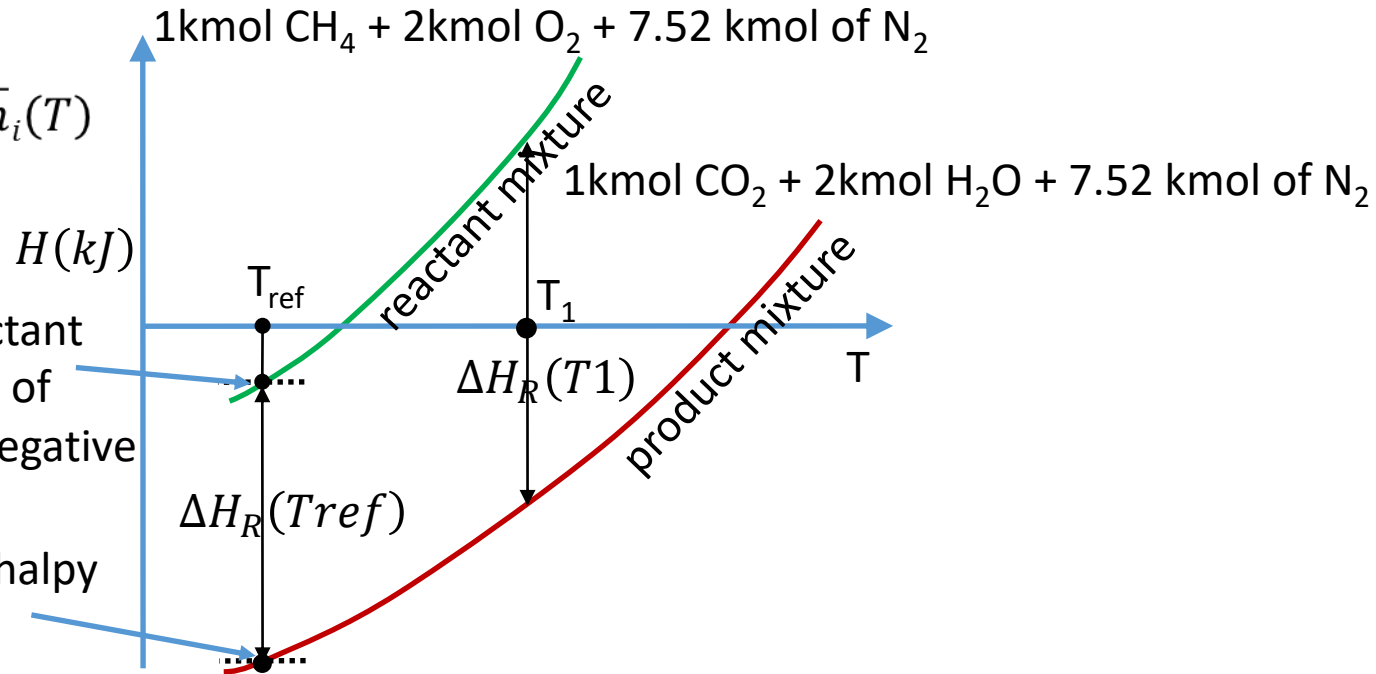
$$\begin{aligned} H_{\text{reac}} &= 1 \times h_{f,\text{CH}_4}^0 + 2 \times h_{f,\text{O}_2}^0 + 3.76 \times h_{f,\text{N}_2}^0 \\ &= 1 \times -74831 + 2 \times 0 + 3.76 \times 0 = -74831 \text{ KJ} \end{aligned}$$

$$\Delta H_R = h_{\text{prod}} - h_{\text{reac}} = -877236 - (-74831) = -802405 \text{ KJ}$$

- The above change in Enthalpy is obtained by burning one mole of Methane, which is the fuel.
- Hence, $\Delta H_R = \Delta h_R = -802405 \text{ KJ/Kmol}_{\text{fuel}} = -802405/M_{\text{w}_{\text{fuel}}} \text{ KJ/Kg}_{\text{fuel}} = -802405/16 = -50150 \text{ KJ/Kg}_{\text{fuel}}$.

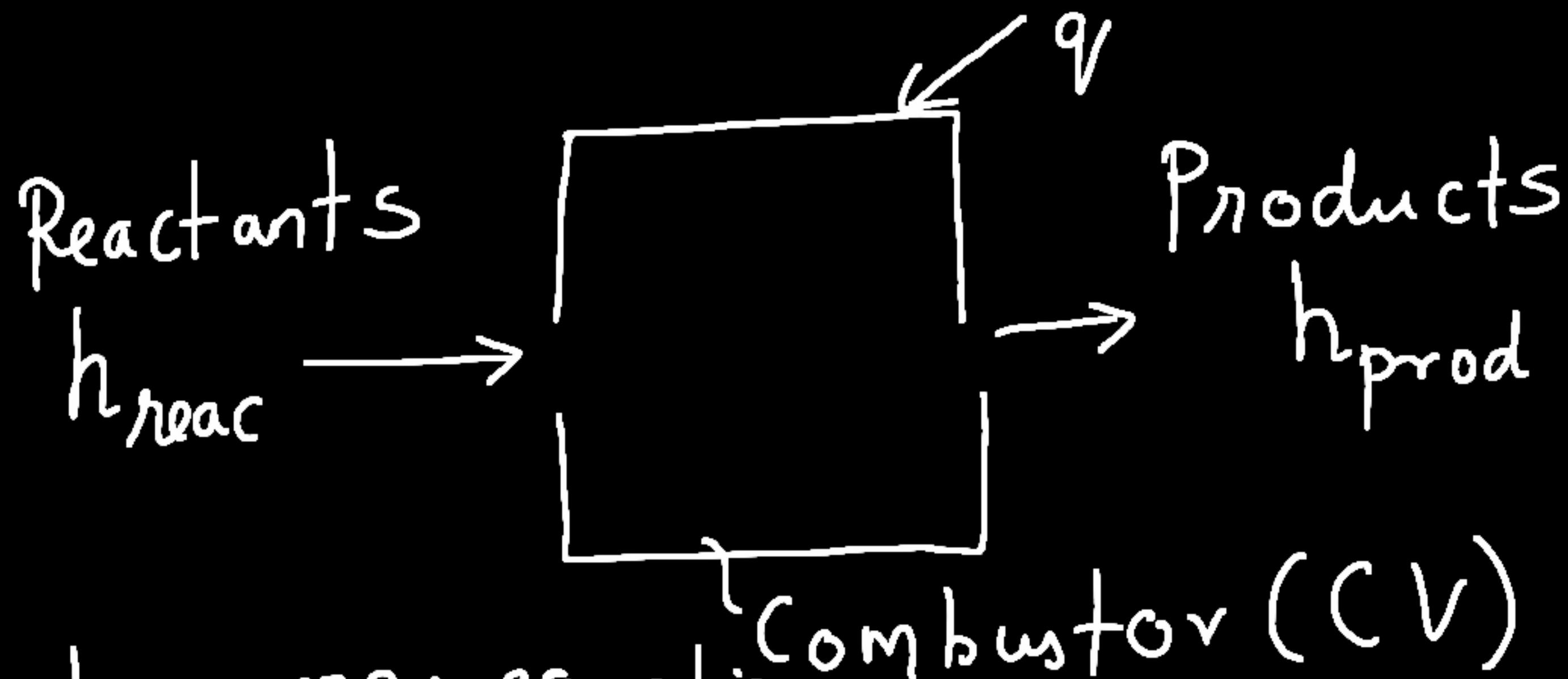
Enthalpy of Reaction

- $H_{mixture}(T) = \sum_i N_i \bar{h}_i(T)$



- note:** enthalpy of reaction (ΔH_R) is at a particular temperature (in this case it is calculated at T_{ref}), at a different temperature (say T_1) ΔH_R may be different

Enthalpy of combustion/reaction (Δh_R)



Apply energy equation

to CV $h_{\text{reac}} + q = h_{\text{prod}}$

$\Delta h_R \leftarrow q = h_{\text{prod}} - h_{\text{reac}}$
(Same T & P)

-ve Exothermic
+ve Endothermic