Reactions for Energy -

Equilibrium Reaction Thermodynamics

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Learning objectives

- Determine how much heat would be liberated during a reaction

Combustion Stoichiometry (1)

Stoichiometric air-fuel mixture:

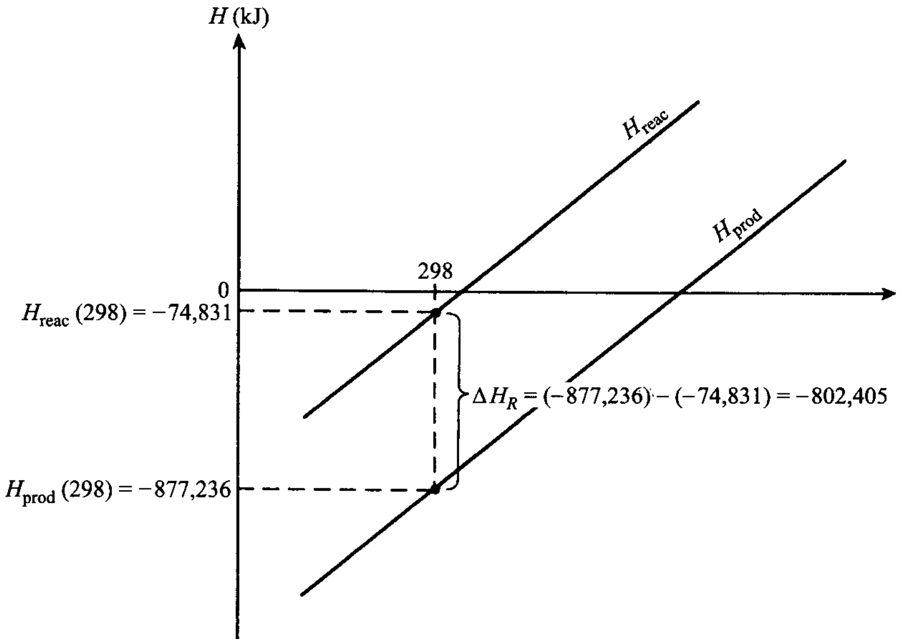
It contains the exact amount of fuel and oxidizer such that after combustion is complete, all the fuel and oxidizer are consumed to form products and the products have the highest negative enthalpies of formation.

Enthalpy of reaction (1)

Heat liberated when a reaction starts at some p and T and ends at the same p and T

Enthalpy of reaction (2)

Example 2: At STP (25^{o}C and 1.013 bar), the reactant enthalpy of a stoichiometric mixture of methane and air, where 1 kmol of fuel reacts, is -74831 kJ. At the same condition (STP), the combustion products have an absolute enthalpy of -877236 kJ. Find out the enthalpy of reaction on a mass basis of the fuel.



Enthalpy of combustion

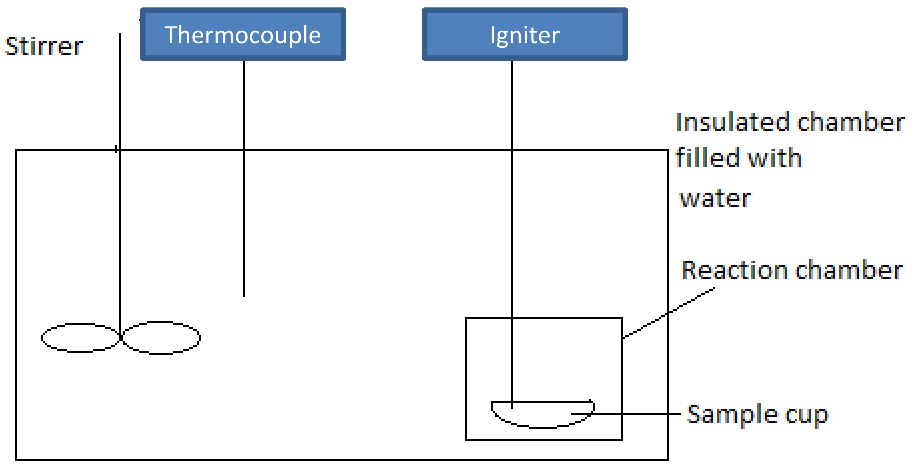
Enthalpy of combustion is numerically equal to the enthalpy of reaction, but with the opposite sign.

Heating values (1)

Heating value of a fuel is the maximum amount of heat that can be generated by combustion with air at STP

The amount of heat release from combustion decides the phase of the water in the products

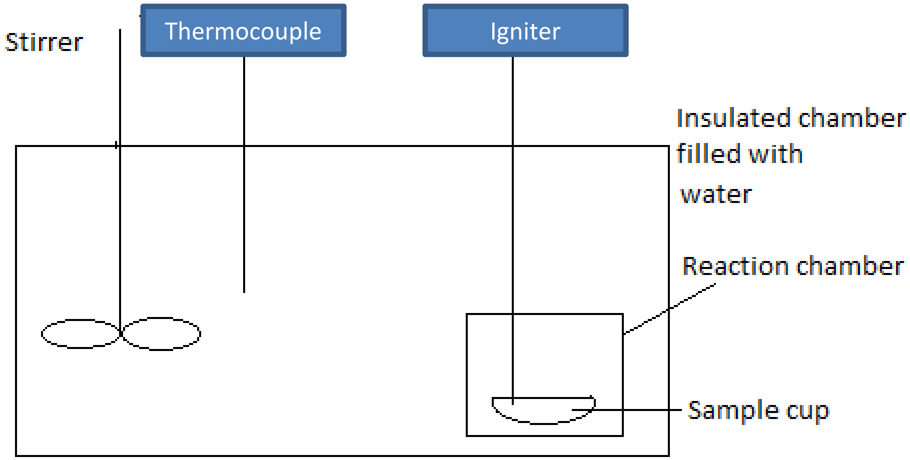
Constant pressure and constant volume reactors are used to determine the heating values



Bomb calorimeter (volume remains constant during reaction)

Heating values (2)

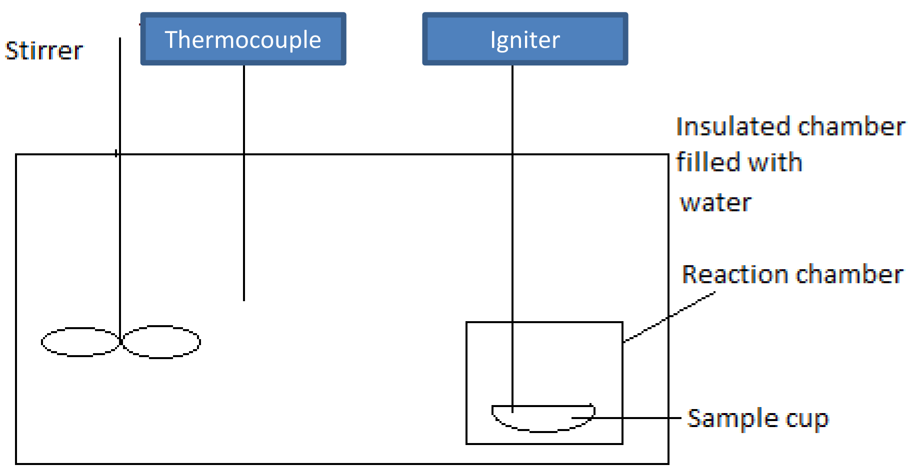
Example 3: A bomb calorimeter burning 1 mol of hydrogen with oxygen molecules measures 282 kJ of heat transfer out of the reacted mixture. Estimate the error in higher heating value measurement compared to heat transfer.



Bomb calorimeter (volume remains constant during reaction)

Heating values (3)

Example 4: The heat released by 1 mol of sugar ($C_{12}H_{22}O_{11}$) in a bomb calorimeter experiment is 5648 kJ/mol. Calculate the enthalpy of combustion per mole of sugar.



Bomb calorimeter (volume remains constant during reaction)

Enthalpy of formation (1)

Enthalpy of formation of a chemical compound is the enthalpy increase associated with the reaction of forming one mole of the given compound from its ‘reference’ elements

Enthalpy of formation at some T & P is the enthalpy of reaction at the same T & P for a compound formed from its reference elements

It is the net change in enthalpy associated with breaking chemical bonds of the standard elements and forming new bonds to create compounds of interest

Table A.3 Hydrogen (H_2), MW = 2.016, 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	28.522	−2,818	0	119.137	0
298	28.871	0	0	130.595	0
300	28.877	53	0	130.773	0
400	29.120	2,954	0	139.116	0
500	29.275	5,874	0	145.632	0
600	29.375	8,807	0	150.979	0
700	29.461	11,749	0	155.514	0
800	29.581	14,701	0	159.455	0
900	29.792	17,668	0	162.950	0
1,000	30.160	20,664	0	166.106	0
1,100	30.625	23,704	0	169.003	0
1,200	31.077	26,789	0	171.687	0
1,300	31.516	29,919	0	174.192	0
1,400	31.943	33,092	0	176.543	0
1,500	32.356	36,307	0	178.761	0
1,600	32.758	39,562	0	180.862	0
1,700	33.146	42,858	0	182.860	0
1,800	33.522	46,191	0	184.765	0
1,900	33.885	49,562	0	186.587	0
2,000	34.236	52,968	0	188.334	0
2,100	34.575	56,408	0	190.013	0
2,200	34.901	59,882	0	191.629	0
2,300	35.216	63,388	0	193.187	0
2,400	35.519	66,925	0	194.692	0
2,500	35.811	70,492	0	196.148	0
2,600	36.091	74,087	0	197.558	0
2,700	36.361	77,710	0	198.926	0
2,800	36.621	81,359	0	200.253	0
2,900	36.871	85,033	0	201.542	0
3,000	37.112	88,733	0	202.796	0
3,100	37.343	92,455	0	204.017	0
3,200	37.566	96,201	0	205.206	0
3,300	37.781	99,968	0	206.365	0
3,400	37.989	103,757	0	207.496	0
3,500	38.190	107,566	0	208.600	0
3,600	38.385	111,395	0	209.679	0
3,700	38.574	115,243	0	210.733	0
3,800	38.759	119,109	0	211.764	0
3,900	38.939	122,994	0	212.774	0
4,000	39.116	126,897	0	213.762	0
4,100	39.291	130,817	0	214.730	0
4,200	39.464	134,755	0	215.679	0
4,300	39.636	138,710	0	216.609	0
4,400	39.808	142,682	0	217.522	0
4,500	39.981	146,672	0	218.419	0
4,600	40.156	150,679	0	219.300	0
4,700	40.334	154,703	0	220.165	0

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
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

Enthalpy of formation (2)

Standard enthalpy of formation of common combustion species

	Δh_0 (MJ/kmol)	Species	Δh_0 (MJ/kmol)
H_2O (g)	-241.83	H	217.99
H_2O (l)	-285.83	N	472.79
CO_2	-393.52	NO	90.29
CO	-110.53	NO2	33.10
CH4	-74.87	O	249.19
Iso-octane	-259.23	OH	39.46
Methanol	-201.54	C (g)	715
Acetylene	226.73		

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]

Formula	Fuel	MW (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)	$T_{ad}^{‡}$ (K)	ρ_{liq}^{*} (kg/m³)
CH_4	Methane	16.043	−74,831	−50,794	186.188	55,528	50,016	−164	509	2,226	300
C_2H_2	Acetylene	26.038	226,748	209,200	200.819	49,923	48,225	−84	—	2,539	—
C_2H_4	Ethene	28.054	52,283	68,124	219.827	50,313	47,161	−103.7	—	2,369	—
C_2H_6	Ethane	30.069	−84,667	−32,886	229.492	51,901	47,489	−88.6	488	2,259	370
C_3H_6	Propene	42.080	20,414	62,718	266.939	48,936	45,784	−47.4	437	2,334	514
C_3H_8	Propane	44.096	−103,847	−23,489	269.910	50,368	46,357	−42.1	425	2,267	500
C_4H_8	1-Butene	56.107	1,172	72,036	307.440	48,471	45,319	−63	391	2,322	595
C_4H_{10}	*n*-Butane	58.123	−124,733	−15,707	310.034	49,546	45,742	−0.5	386	2,270	579
C_5H_{10}	1-Pentene	70.134	−20,920	78,605	347.607	48,152	45,000	30	358	2,314	641
C_5H_{12}	*n*-Pentane	72.150	−146,440	−8,201	348.402	49,032	45,355	36.1	358	2,272	626
C_6H_6	Benzene	78.113	82,927	129,658	269.199	42,277	40,579	80.1	393	2,342	879
C_6H_{12}	1-Hexene	84.161	−41,673	87,027	385.974	47,955	44,803	63.4	335	2,308	673
C_6H_{14}	*n*-Hexane	86.177	−167,193	209	386.811	48,696	45,105	69	335	2,273	659
C_7H_{14}	1-Heptene	98.188	−62,132	95,563	424.383	47,817	44,665	93.6	—	2,305	—
C_7H_{16}	*n*-Heptane	100.203	−187,820	8,745	425.262	48,456	44,926	98.4	316	2,274	684
C_8H_{16}	1-Octene	112.214	−82,927	104,140	462.792	47,712	44,560	121.3	—	2,302	—
C_8H_{18}	*n*-Octane	114.230	−208,447	17,322	463.671	48,275	44,791	125.7	300	2,275	703
C_9H_{18}	1-Nonene	126.241	−103,512	112,717	501.243	47,631	44,478	—	—	2,300	—
C_9H_{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

Absolute enthalpy (1)

Sum of energy associated with chemical bonds and energy associated with temperature

When phase change is encountered, absolute enthalpy would include latent heat

Absolute enthalpy (2)

Example 5: A gas stream at 1 atm contains a mixture of CO, CO_2 and N_2 in which the CO mole fraction is 0.1 and CO_2 mole fraction is 0.2. The gas stream temperature is 1200 K. Determine the absolute enthalpy of the mixture.

Heating values (2)

Example 6: Determine the higher and lower heating values of gaseous n-decane, $C_{10}H_{22}$ per kmol and per kg of fuel. The latent heat of vaporization of water is 44010 kJ/kmol. If the enthalpy of vaporization of n-decane is 359 kJ/kg fuel at STP, what are the LHV and HHV of liquid n-decane?

Hess law

In a chemical reaction, the resultant enthalpy is the same, irrespective of the number of steps.

Next Lecture

- **Adiabatic flame temperature**