

## Calculating Heat of Reaction

Names:

### Orientation:

In this activity you will be calculating the heating value for various fuels under several different conditions. Engineers frequently use tabulated data, but it is important to understand assumptions behind those values, and how to calculate correct values if your application does not meet those assumptions. When modeling engines, it is important to understand how the exhaust temperature and equivalence ratio impact the heating value of fuel.

### Learning Objectives:

1. Understand difference in heating values expressed in a: per mole fuel, per kg fuel, and per kg mix basis.
2. Choose the correct property (U or H) for a given combustion type to estimate heat of reaction and adiabatic flame temperatures.

### Targeted Skills:

Identifying assumptions – examining preconceptions/biases

Validating – using alternative methods to test results

Reasoning with theory – explaining data with accepted knowledge

Each team will do the activity for two fuels. Nitromethane ( $\text{CH}_3\text{NO}_2$ ), and one of the following:

- Methane ( $\text{CH}_4$ )
- Propane ( $\text{C}_3\text{H}_8$ )
- Methanol ( $\text{CH}_3\text{OH}$ )
- Iso-octane ( $\text{C}_8\text{H}_{18}$ )

1. Write a balanced reaction for each of your fuels with air under stoichiometric conditions. Verify the mass balance for each atom. See page 69 of the Stone text for more information.
  
2. Sketch and label isothermal and adiabatic reactions on an enthalpy-temperature diagram (no numbers necessary, just trends). Show which line is the reactant-side and which the product-side is.

3. Using the balanced reaction coefficients and separate enthalpies for each species calculate the lower heating value for an isobaric combustion process as:
  - a) per mole of fuel
  - b) per kilogram of fuelAssume standard temperature and pressure conditions for both products and reactants, as well as an equivalence ratio of unity. You can find heats of formation for the fuels  $h_f$  in Table A.3 on page 597 in the text. Compare your results with the calorific values also reported in Table A.3.
  
4. How does the lower heating value change as the mixture is made leaner? How does the heat of reaction change if the water vapor condenses?
  
5. For equivalence ratios of (a) unity, and (b) one-half:  
Calculate the heat of an isobaric, isothermal reaction on a "per kilogram mixture" basis.
  
6. Explain how to estimate the adiabatic isobaric combustion temperature for a stoichiometric mixture. Does this vary with equivalence ratio? Why?

**Table A.3** Boiling points, enthalpy of vaporisation, liquid density and specific heat capacity, molar masses, standard enthalpy of formation, standard state entropy and calorific values for fuels, derived from Daubert and Danner (1989)

Fuel	Formula	Boiling point at 1 atm (°C)	Enthalpy of vaporisation <sup>1</sup> at 298.15 K (MJ/kmol)	Density <sup>1</sup> (kg/m <sup>3</sup> )	C <sub>p,1</sub> <sup>1,2</sup> (kJ/kmol K)
Methane	CH <sub>4</sub>	-161.5	8.171	422.5	57 <sup>a</sup>
Propane	C <sub>3</sub> H <sub>8</sub>	-42.0	18.743	582.5	106.3 <sup>b</sup>
Benzene	C <sub>6</sub> H <sub>6</sub>	80.1	33.790	872.9	135.6
Toluene	C <sub>7</sub> H <sub>8</sub>	110.6	38.341	864.7	156.1
n-Heptane	C <sub>7</sub> H <sub>16</sub>	98.4	36.630	681.5	224.7
Iso-octane	C <sub>8</sub> H <sub>18</sub>	99.2	35.142	690.4	236.4
(2,2,4-Trimethylpentane)					
n-Hexadecane (Cetane)	C <sub>16</sub> H <sub>34</sub>	286.9	79.641	769.7	501.7
α-Methylnaphthalene	C <sub>10</sub> H <sub>7</sub> CH <sub>3</sub>	244.7	59.387	1017.2	224.4 <sup>c</sup>
Methanol	CH <sub>3</sub> OH	64.7	38.012	789.6	81.6
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	78.3	42.512	785.9	113.0
Nitromethane	CH <sub>3</sub> NO <sub>2</sub>	101.2	38.365	1112.7	106.3

  

Fuel	Formula	M (kg/kmol)	H <sub>f</sub> (MJ/kmol)	S <sup>0,3</sup> (kJ/kmol K)	Calorific values <sup>4</sup> at 298.15 K	
					(MJ/kmol)	(MJ/kg)
Methane	CH <sub>4</sub>	16.043	-74.52	186.27	802.64	50.031
Propane	C <sub>3</sub> H <sub>8</sub>	44.096	-104.68	270.2	2043.15	46.334
Benzene	C <sub>6</sub> H <sub>6</sub>	78.114	82.93	269.20	3169.47	40.575
Toluene	C <sub>7</sub> H <sub>8</sub>	92.141	50.00	319.74	3771.88	40.936
n-Heptane	C <sub>7</sub> H <sub>16</sub>	100.204	-187.65	427.98	4501.53	44.924
Iso-octane	C <sub>8</sub> H <sub>18</sub>	114.231	-224.01	422.96	5100.50	44.651
(2,2,4-Trimethylpentane)						
n-Hexadecane (Cetane)	C <sub>16</sub> H <sub>34</sub>	226.446	-374.17	781.02	10033.03	44.307
α-Methylnaphthalene	C <sub>10</sub> H <sub>7</sub> CH <sub>3</sub>	142.2	116.86	377.44	5654.61	39.765
Methanol	CH <sub>3</sub> OH	32.042	-200.94	239.88	676.22	21.104
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	46.069	-234.95	280.64	1277.55	27.731
Nitromethane	CH <sub>3</sub> NO <sub>2</sub>	61.040	-74.73	275.01	681.52	11.165

Note 1: Properties have been evaluated at 25°C, except when a substance is a gas at this temperature, in which case the evaluation refers to the normal boiling point.

Note 2: These data were obtained from the *Handbook of Chemistry and Physics* (70th edn, CRC Press, 1990), with the exception of the following data:

a Y. S. Touloukian and T. Makita, *Specific Heat, nonmetallic liquids and gases* (Plenum, 1970);

b *International Critical Tables, Vol V* (McGraw-Hill, 1929);

c Daubert and Danner (1989).

Note 3:

The entropy values tabulated here for the standard state (S<sup>0</sup>) refer to a pressure of 1 atm (1.01325 bar), while the entropy values evaluated in tables A.4 and A.5 use a pressure of 1 bar as the datum; this accounts for the slight differences in the numerical values for entropy at 298.15 K. The standard state values can refer to a hypothetical state, and this is indeed the case for many of these fuels, which cannot exist as a vapour at a pressure of 1 atm and a temperature of 298.15 K.

Note 4:

The calorific values have been determined from the difference in the enthalpies of formation of the fuel and products, with all reactants and products in the vapour phase; this is known as the Net or Lower Calorific Value (LCV). When the water vapour in the products of combustion has been condensed to its liquid state, the calorific value of the fuel is known as the Gross or Higher Calorific Value (HCV). Thus

$$\text{HCV} = \text{LCV} + (n \times H_{fg})_{\text{H}_2\text{O}}$$

where the enthalpy of condensation of the water vapour,  $H_{fg} = 43.99$  MJ/kmol H<sub>2</sub>O.

Table A.4 Thermodynamic data for gaseous species

'ABSOLUTE' MOLAR ENTHALPY (MJ/kmol)													
T (K)	Air	N <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub>	CO	CO <sub>2</sub>	H <sub>2</sub> O	NO	Ar	OH	O	H	T (K)
0	-8.774	-8.823	-8.709	-8.222	-119.363	-402.239	-251.763	81.717	-6.201	32.721	243.041	211.787	0
100	-5.784	-5.812	-5.755	-5.584	-116.336	-399.897	-248.414	84.423	-4.121	33.180	245.154	213.866	100
200	-2.855	-2.864	-2.858	-2.804	-113.387	-396.934	-245.097	87.231	-2.041	37.716	247.264	215.944	200
<b>298.15</b>	<b>0.0</b>	<b>0.0</b>	<b>0.0</b>	<b>0.0</b>	<b>-110.525</b>	<b>-393.512</b>	<b>-241.824</b>	<b>90.080</b>	<b>0.000</b>	<b>40.277</b>	<b>249.333</b>	<b>217.984</b>	<b>298.15</b>
300	0.053	0.053	0.054	0.056	-110.471	-393.443	-241.761	90.135	0.038	40.326	249.372	218.023	300
400	2.973	2.969	3.028	2.959	-107.550	-389.509	-238.371	93.125	2.118	43.005	251.477	220.101	400
T (K)	Air	N <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub>	CO	CO <sub>2</sub>	H <sub>2</sub> O	NO	Ar	OH	O	H	T (K)
500	5.930	5.909	6.089	5.880	-104.594	-385.208	-234.899	96.195	4.198	45.752	253.580	222.180	500
600	8.942	8.893	9.247	8.811	-101.584	-380.605	-231.326	99.337	6.278	48.564	255.681	224.259	600
700	12.018	11.934	12.500	11.750	-98.505	-375.753	-227.639	102.547	8.358	51.437	257.780	226.337	700
800	15.164	15.042	15.837	14.704	-95.353	-370.699	-223.831	105.817	10.438	54.369	259.876	228.416	800
900	18.379	18.219	19.244	17.681	-92.128	-365.477	-219.899	109.143	12.518	57.358	261.971	230.495	900
T (K)	Air	N <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub>	CO	CO <sub>2</sub>	H <sub>2</sub> O	NO	Ar	OH	O	H	T (K)
1000	21.655	21.459	22.708	20.686	-88.838	-360.112	-215.841	112.518	14.598	60.399	264.063	232.573	1000
1100	24.984	24.756	26.213	23.729	-85.496	-354.624	-211.652	115.939	16.678	63.492	266.154	234.652	1100
1200	28.357	28.100	29.754	26.814	-82.107	-349.051	-207.337	119.400	18.758	66.633	268.243	236.730	1200
1300	31.772	31.489	33.328	29.942	-78.676	-343.395	-202.904	122.897	20.838	69.820	270.330	238.809	1300
1400	35.224	34.917	36.934	33.112	-75.208	-337.664	-198.359	126.427	22.918	73.050	272.416	240.888	1400
T (K)	Air	N <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub>	CO	CO <sub>2</sub>	H <sub>2</sub> O	NO	Ar	OH	O	H	T (K)
1500	38.711	38.380	40.571	36.323	-71.707	-331.867	-193.711	129.986	24.998	76.322	274.501	242.966	1500
1600	42.228	41.876	44.237	39.574	-68.176	-326.012	-188.966	133.572	27.078	79.634	276.585	245.045	1600
1700	45.774	45.400	47.931	42.865	-64.618	-320.105	-184.131	137.180	29.158	82.982	278.668	247.124	1700
1800	49.345	48.949	51.652	46.194	-61.037	-314.151	-179.212	140.808	31.238	86.365	280.751	249.202	1800
1900	52.940	52.522	55.399	49.560	-57.435	-308.158	-174.215	144.454	33.318	89.781	282.833	251.281	1900
T (K)	Air	N <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub>	CO	CO <sub>2</sub>	H <sub>2</sub> O	NO	Ar	OH	O	H	T (K)
2000	56.556	56.114	59.171	52.962	-53.815	-302.128	-169.146	148.116	35.398	93.228	284.915	253.359	2000
2100	60.190	59.725	62.967	56.399	-50.178	-296.068	-164.009	151.792	37.478	96.705	286.997	255.438	2100
2200	63.842	63.351	66.787	59.870	-46.527	-289.981	-158.810	155.480	39.558	100.208	289.079	257.517	2200
2300	67.510	66.991	70.630	63.373	-42.863	-283.870	-153.553	159.179	41.638	103.738	291.162	259.595	2300
2400	71.192	70.644	74.495	66.908	-39.189	-277.737	-148.243	162.886	43.718	107.292	293.246	261.674	2400
T (K)	Air	N <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub>	CO	CO <sub>2</sub>	H <sub>2</sub> O	NO	Ar	OH	O	H	T (K)
2500	74.887	74.308	78.381	70.474	-35.504	-271.587	-142.883	166.602	45.797	110.868	295.330	263.753	2500
2600	78.595	77.981	82.288	74.068	-31.811	-265.420	-137.478	170.326	47.877	114.465	297.416	265.831	2600
2700	82.313	81.664	86.216	77.691	-28.111	-259.239	-132.031	174.055	49.957	118.083	299.503	267.910	2700
2800	86.041	85.354	90.163	81.341	-24.403	-253.045	-126.545	177.790	52.037	121.718	301.592	269.988	2800
2900	89.779	89.051	94.130	85.016	-20.689	-246.838	-121.022	181.531	54.117	125.371	303.684	272.067	2900

(continued)

Table A.4 Thermodynamic data for gaseous species (continued)

'ABSOLUTE' MOLAR ENTHALPY (MJ/kmol)													
T (K)	Air	N <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub>	CO	CO <sub>2</sub>	H <sub>2</sub> O	NO	Ar	OH	O	H	T (K)
3000	93.527	92.754	98.116	88.716	-16.969	-240.621	-115.467	185.276	56.197	129.040	305.777	274.146	3000
3100	97.282	96.464	102.120	92.439	-13.244	-234.393	-109.881	189.026	58.277	132.724	307.872	276.224	3100
3200	101.046	100.179	106.142	96.185	-9.514	-228.155	-104.266	192.780	60.357	136.421	309.971	278.303	3200
3300	104.818	103.900	110.182	99.953	-5.778	-221.907	-98.625	196.538	62.437	140.132	312.072	280.382	3300
3400	108.597	107.625	114.238	103.741	-2.039	-215.650	-92.959	200.300	64.517	143.855	314.177	282.460	3400
T (K)	Air	N <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub>	CO	CO <sub>2</sub>	H <sub>2</sub> O	NO	Ar	OH	O	H	T (K)
3500	112.383	111.356	118.312	107.549	1.706	-209.383	-87.271	204.066	66.597	147.589	316.284	284.539	3500
3600	116.177	115.091	122.402	111.377	5.455	-203.106	-81.561	207.836	68.677	151.334	318.396	286.617	3600
3700	119.978	118.832	126.507	115.223	9.209	-196.819	-75.832	211.610	70.757	155.089	320.511	288.696	3700
3800	123.786	122.577	130.627	119.086	12.968	-190.522	-70.083	215.389	72.837	158.853	322.630	290.775	3800
3900	127.600	126.326	134.762	122.968	16.731	-184.215	-64.317	219.171	74.917	162.627	324.754	292.853	3900
T (K)	Air	N <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub>	CO	CO <sub>2</sub>	H <sub>2</sub> O	NO	Ar	OH	O	H	T (K)
4000	131.421	130.081	138.911	126.866	20.499	-177.898	-58.533	222.958	76.997	166.409	326.881	294.932	4000
4100	135.249	133.840	143.074	130.781	24.272	-171.570	-52.733	226.748	79.077	170.200	329.014	297.011	4100
4200	139.083	137.604	147.249	134.713	28.049	-165.232	-46.918	230.543	81.157	173.998	331.150	299.089	4200
4300	142.923	141.373	151.436	138.662	31.831	-158.884	-41.088	234.342	83.237	177.805	333.292	301.168	4300
4400	146.769	145.147	155.634	142.627	35.617	-152.526	-35.242	238.145	85.317	181.620	335.439	303.246	4400
T (K)	Air	N <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub>	CO	CO <sub>2</sub>	H <sub>2</sub> O	NO	Ar	OH	O	H	T (K)
4500	150.621	148.925	159.842	146.610	39.408	-146.159	-29.383	241.951	87.397	185.443	337.590	305.325	4500
4600	154.478	152.707	164.060	150.610	43.202	-139.783	-23.509	245.761	89.477	189.273	339.747	307.404	4600
4700	158.340	156.493	168.286	154.628	47.000	-133.400	-17.621	249.574	91.557	193.112	341.909	309.482	4700
4800	162.206	160.282	172.519	158.665	50.801	-127.012	-11.719	253.390	93.636	196.960	344.076	311.561	4800
4900	166.075	164.074	176.758	162.722	54.604	-120.619	-5.803	257.207	95.716	200.816	346.249	313.640	4900
5000	169.947	167.868	181.001	166.800	58.409	-114.224	0.127	261.025	97.796	204.682	348.427	315.718	5000
T (K)	Air	N <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub>	CO	CO <sub>2</sub>	H <sub>2</sub> O	NO	Ar	OH	O	H	T (K)

Note: The term 'ABSOLUTE' Molar Enthalpy adopted in this table, uses a datum of zero enthalpy for elements when they are in their standard state at a temperature of 25°C. The enthalpy of any molecule at 25°C will thus correspond to its enthalpy of formation,  $\Delta H_f^\circ$ . The tables have been extrapolated below 300 K, and these data should be used with caution. The enthalpies have been evaluated by the integration of a polynomial function that describes the molar specific heat capacity ( $C_p$ ) variation with temperature. The difference in Enthalpy of Reactants and Products at 25°C will thus correspond to the Constant Pressure Calorific Value of the reaction.

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