

# Thermochemistry

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Dr Guohong Tian  
[g.tian@surrey.ac.uk](mailto:g.tian@surrey.ac.uk)

# The First Law of thermodynamics

For a closed (control mass) system

$${}_1Q_2 - {}_1W_2 = \Delta E_{1-2}$$

**Heat added to  
system in going from  
state 1 to state 2**

**Work done by  
system on  
surroundings in  
going from state 1  
to state 2**

**Change in total  
system energy  
in going from  
state 1 to state 2**

For an open system (control volume)

$$q_{cv} - w_{cv} = (h_0 - h_i) + \frac{1}{2}(v_0^2 - v_i^2) + g(z_0 - z_i)$$

# The First Law of thermodynamics

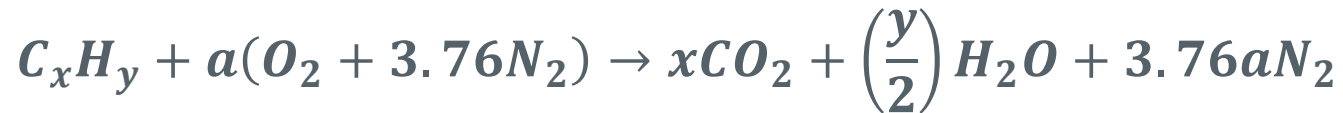
Consider chemical reaction

**Exothermic** reaction: Heat flows out of the system to the surroundings during the reaction

**Endothermic** reaction: Heat flows into the system from the surroundings during the reaction

# Reactant and product mixture

Consider combustion of a hydrocarbon with air



To balance the chemical reaction

$$a = x + y/4$$

We define **stoichiometric air/fuel ratio**

$$\left(\frac{A}{F}\right)_{stoic} = \left(\frac{m_{air}}{m_{fuel}}\right)_{stoic} = \frac{4.76a}{1} \frac{M_{air}}{M_{fuel}}$$

	$\Delta h_R$ (kJ/kg <sub>fuel</sub> )	$\Delta h_R$ (kJ/kg <sub>mix</sub> )	(O/F) <sub>stoic</sub> (kg/kg)	$T_{ad,eq}$ (K)
CH <sub>4</sub> +air	-55,528	-3,066	17.11	2226
H <sub>2</sub> +O <sub>2</sub>	-142,919	-15,880	8.0	3079
C(s)+air	-32,794	-2,645	11.4	2301

### Equivalence ratio

$$\Phi = \frac{(A / F)_{stoic}}{(A / F)} = \frac{(F / A)}{(F / A)_{stoic}}$$

$\Phi > 1$ , fuel rich mixture

$\Phi < 1$ , fuel lean mixture

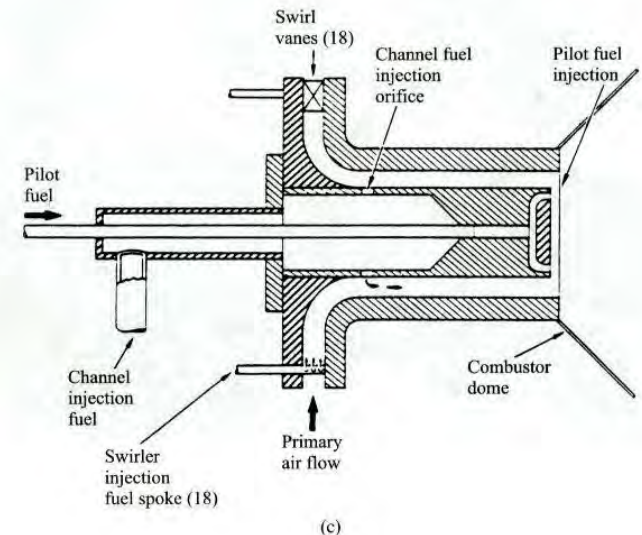
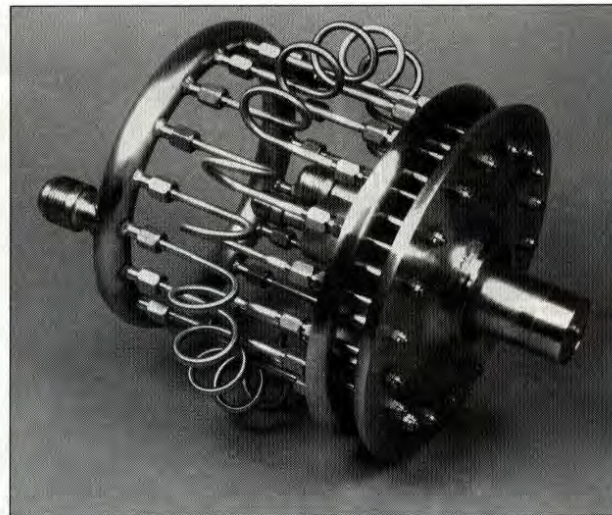
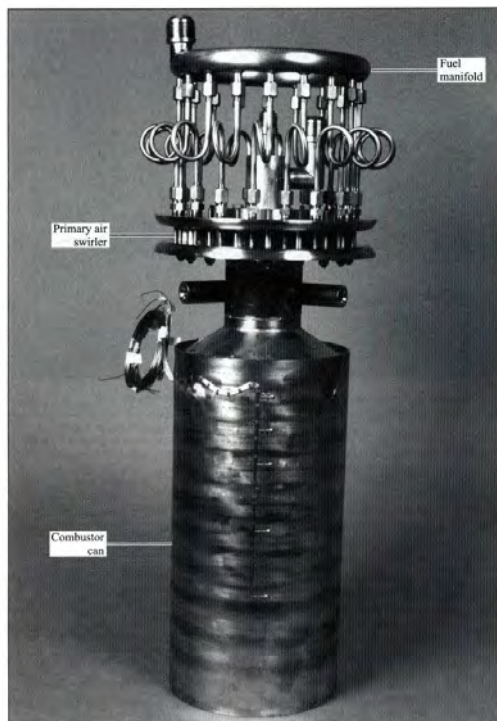
$\Phi = 1$ , stoichiometric mixture

### Percent excess air

$$\% \text{ excess} = \frac{(1 - \Phi)}{\Phi} \cdot 100\%$$

## Example 1

A small, low-emission, stationary gas turbine engine operates at full load (3950 kW) at an equivalence ratio of 0.286 (lean) 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.



Known:  $\Phi = 0.286$ ,  $M_{air} = 28.85 \text{ kg/kmol}$ ,  $\dot{m}_{air} = 15.9 \text{ kg/s}$

Calculate:  $\dot{m}_{fuel}$ ,  $A/F$

$$M_{fuel} = 1.16(12.01) + 4.32(1.008) = 18.286 \text{ kg/kmol}$$

$$(A/F)_{stoic} = 4.76a \frac{M_{air}}{M_{fuel}}$$

$$a = x + \frac{y}{4} = 1.16 + \frac{4.32}{4} = 2.24$$

$$(A/F)_{stoic} = \frac{4.76(2.24)28.85}{18.286} = 16.82$$

$$(A/F) = \frac{(A/F)_{stoic}}{\Phi} = \frac{16.82}{0.286} = 58.8$$

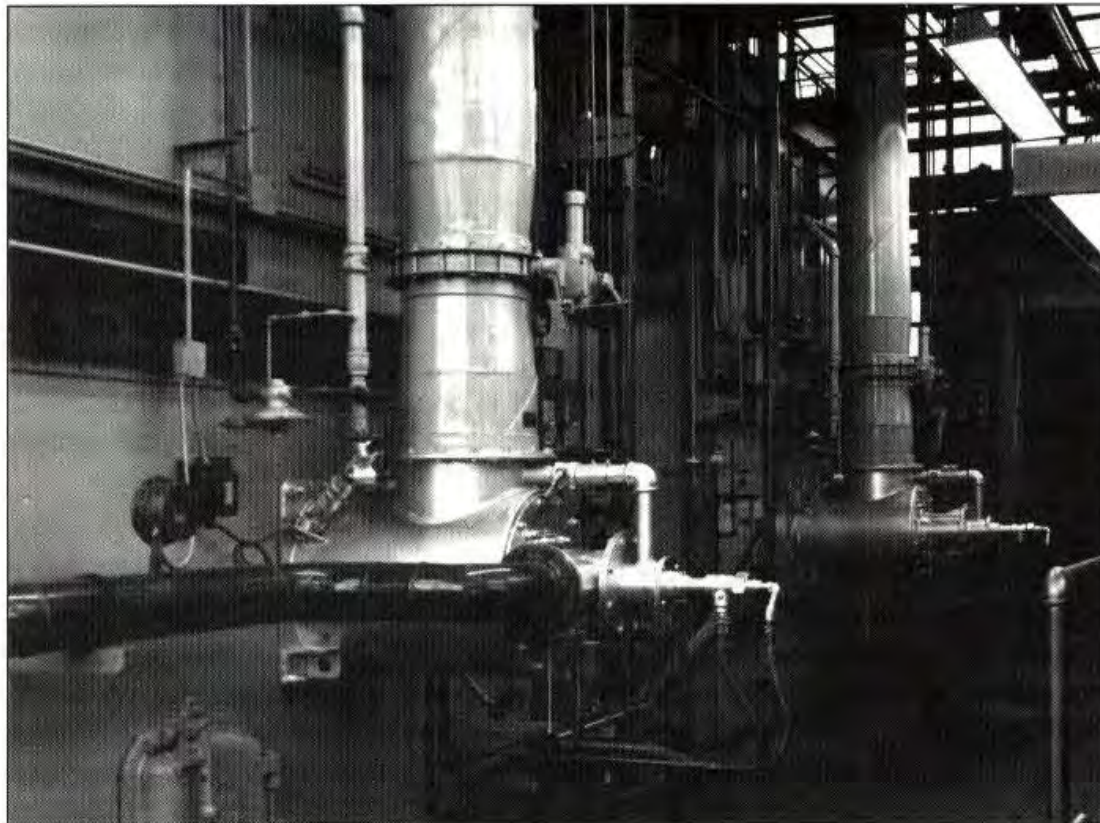
$$\dot{m}_{fuel} = \frac{\dot{m}_{air}}{A/F} = \frac{15.9}{58.8} = 0.270 \text{ kg/s}$$

Comments: at full load, there is excessive air in a gas turbine engine.



## Example 2

A natural gas-fired industrial boiler operates with an oxygen concentration of 3 mole percent in the flue gases. Determine the operating air/fuel ratio and the equivalence ratio. Treat the nature gas as methane.





Known  $x_{O_2} = 0.03$ ,  $M_{fuel} = 16.04 \text{ kg/kmol}$ ,  $M_{air} = 28.85 \text{ kg/kmol}$

Calculate: (A/F) and  $\Phi$

First assume complete combustion and obtain A/F. complete combustion means all carbon atoms form carbon dioxide and hydrogen atoms form water.



From mass conservation,

$$2a = 2 + 2 + 2b$$

*why gas phase*

The definition of mole fraction

$$x_{O_2} = \frac{N_{O_2}}{N_{mix}} = \frac{b}{1 + 2 + b + 3.76a} = \frac{a - 2}{1 + 4.76a}.$$

As  $x_{O_2} = 0.03$

$$0.03 = \frac{a - 2}{1 + 4.76a}$$

Therefore  $a = 2.368$

$$(A/F) = 4.76a \frac{M_{air}}{M_{fuel}} = 4.76 \frac{(2.368)28.85}{16.04} = 20.3$$

We also need to calculate  $(A/F)_{stoic}$  to calculate equivalence ratio.

At stoichiometric condition,  $a=2$

$$(A/F)_{stoic} = 4.76 \frac{(2)28.85}{16.04} = 17.1$$

Therefore

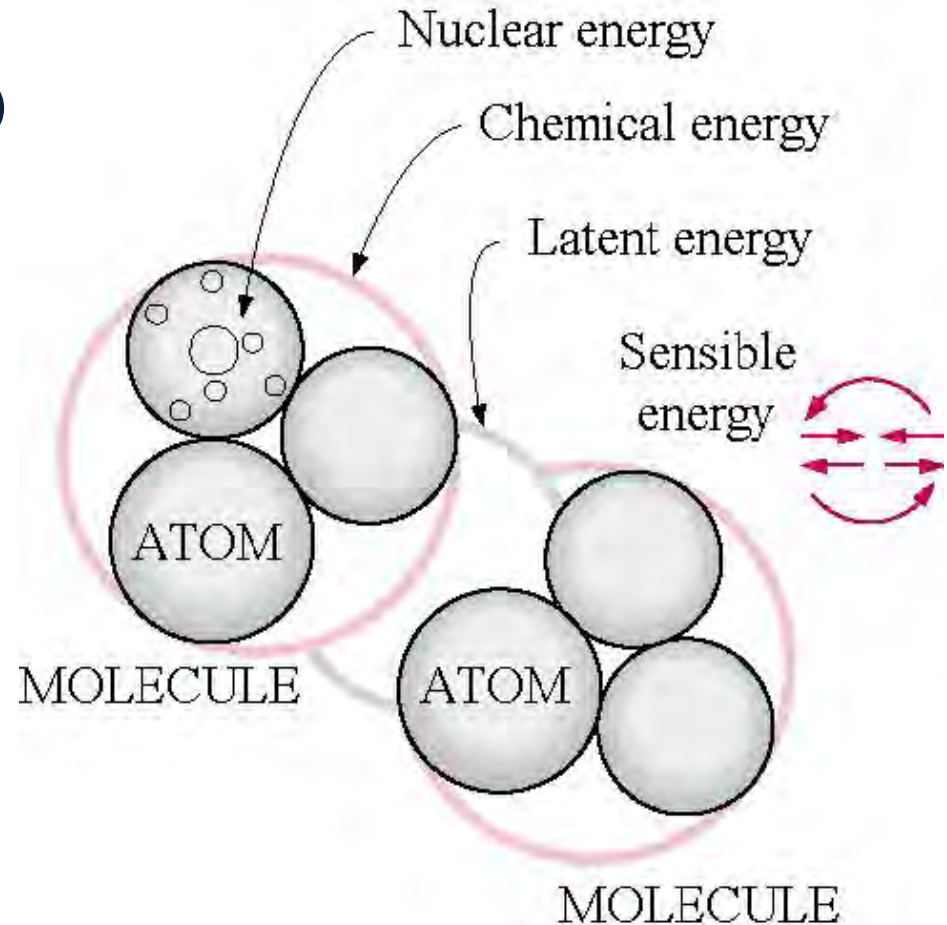
$$\Phi = \frac{(A/F)_{stoic}}{(A/F)} = \frac{17.1}{20.3} = 0.84$$

# Energy from combustion

## Microscopic view of energy

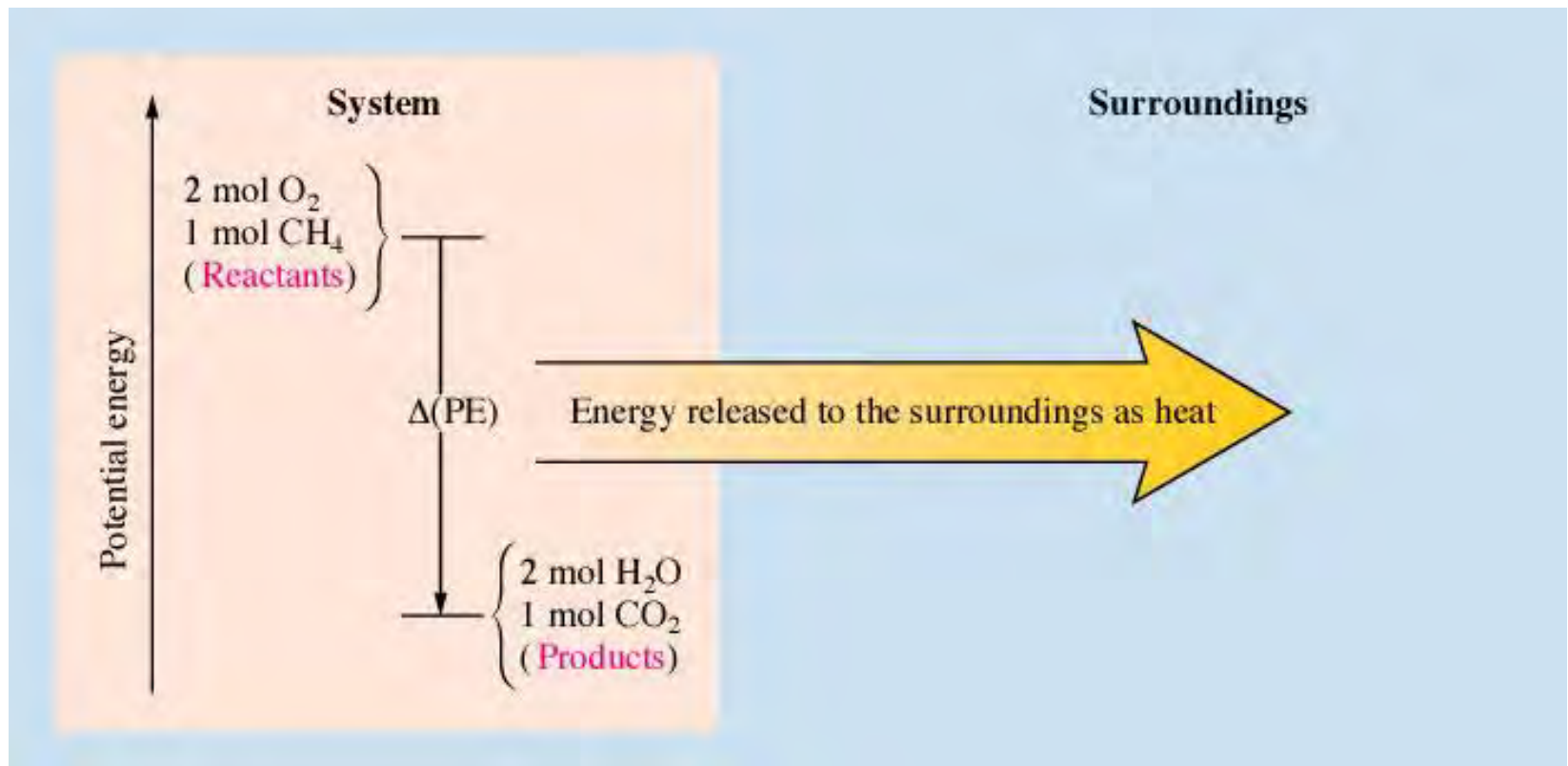
Depending on the level of investigation, the microscopic view of energy including

- Sensible energy (temperature)
- Latent energy (phase change)
- Chemical energy (bond breaking/generation)
- Nuclear energy (sub-atomic level)

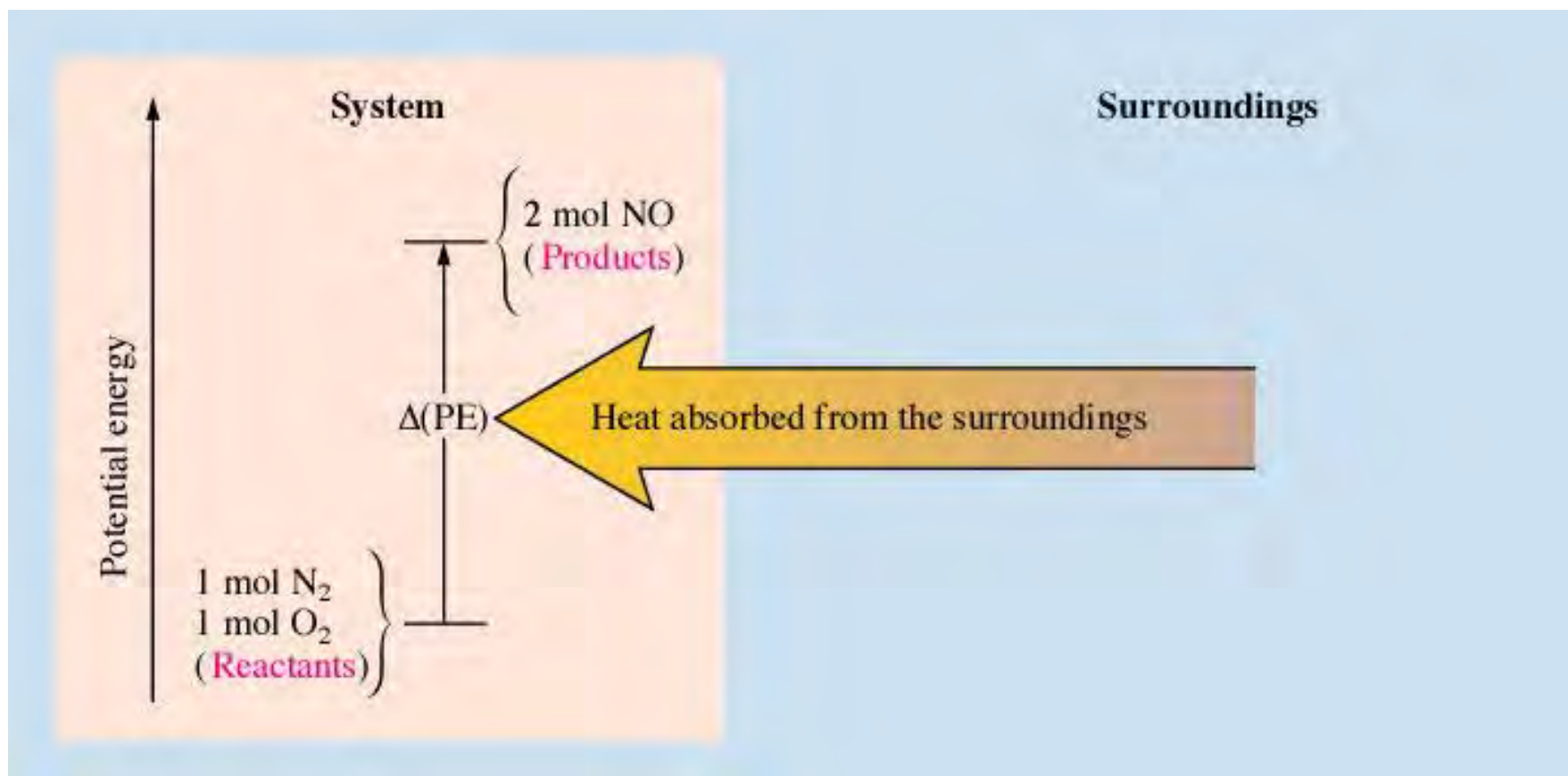


During combustion process, chemical bonds may break and form new bonds. It is necessary to define a **Standard reference state (25°C, 1atm)**

Consider methane combustion (exothermic)



Or oxygen and nitrogen generate nitric oxide (NO) reaction (endothermic)



The **Standard Reference State** is defined as  
Temperature

$$T_{ref} = 25^{\circ}\text{C} \equiv 298.15\text{ K}$$

Pressure

$$p_{ref} = p^0 = 1\text{ atm} = 101.325\text{ kPa}$$

Consistent with Chemkin and NASA

# Standardised Enthalpy and Enthalpy of Formation

Standardised enthalpy is the sum of an enthalpy that takes into account the energy associated with chemical bonds, the **enthalpy of formation**,  $h_f$ , and the enthalpy that associated with temperature, the **sensible enthalpy change**,  $\Delta h_s$

$$\bar{h}_i(T) = \bar{h}_{f,i}^0(T_{ref}) + \Delta \bar{h}_{s,i}(T)$$

Standardised  
enthalpy at  
temperature  $T$

Enthalpy of formation  
at standard reference  
state ( $T_{ref}, p^0$ )

Sensible enthalpy  
change in going from  
 $T_{ref}$  to  $T$



For the elements in their **naturally occurring state** at the reference state temperature and pressure, enthalpies of formation are zero. For instance

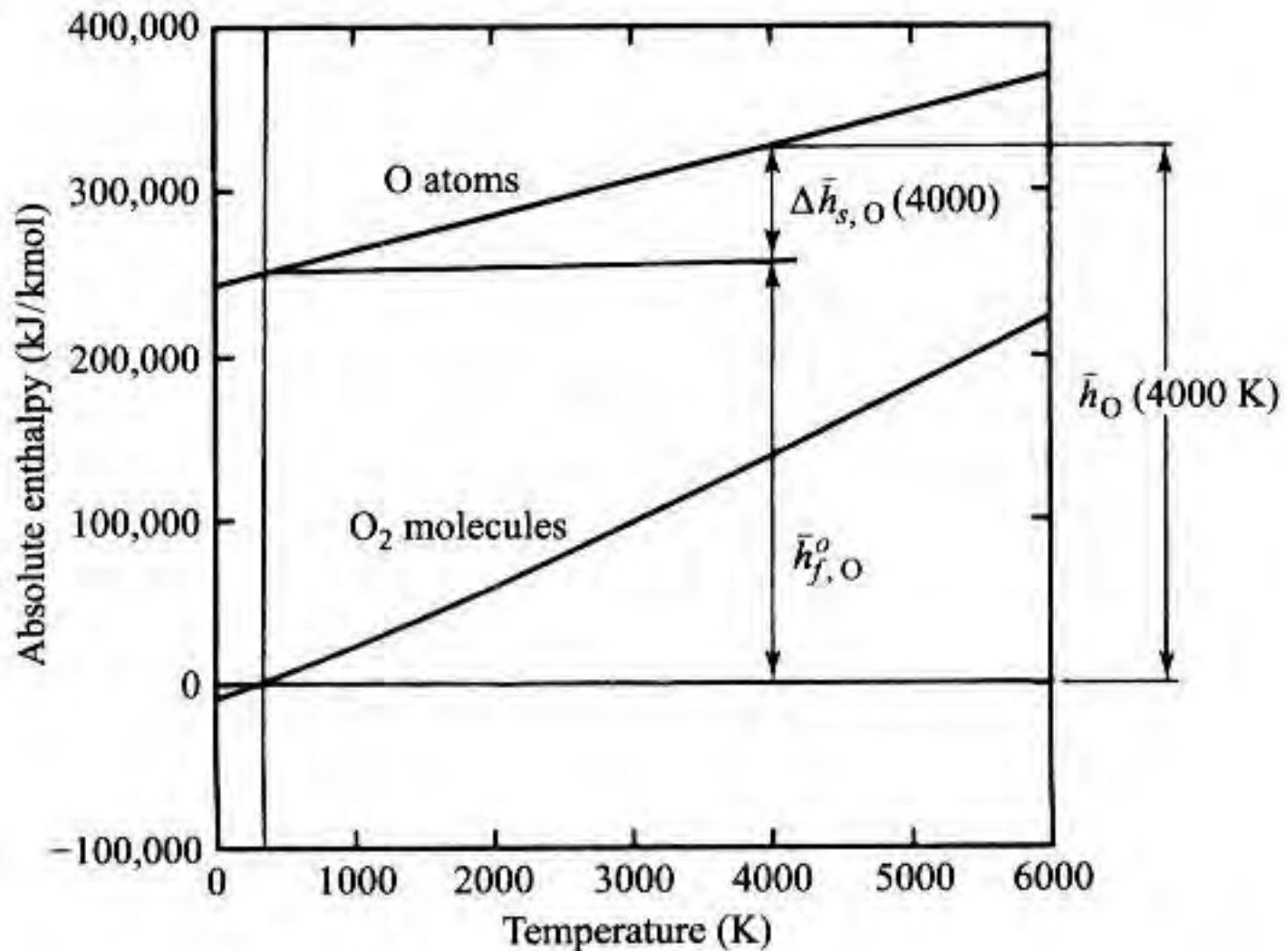
$$(\bar{h}_{f,O_2}^0)_{298} = 0$$

Net change in enthalpy associated with breaking the chemical bonds of the standard-state elements and forming new bonds to create the compound of interest. For example, 498,390 kJ/kmol energy is request to break the bond of O<sub>2</sub> and generate two O atoms, therefore

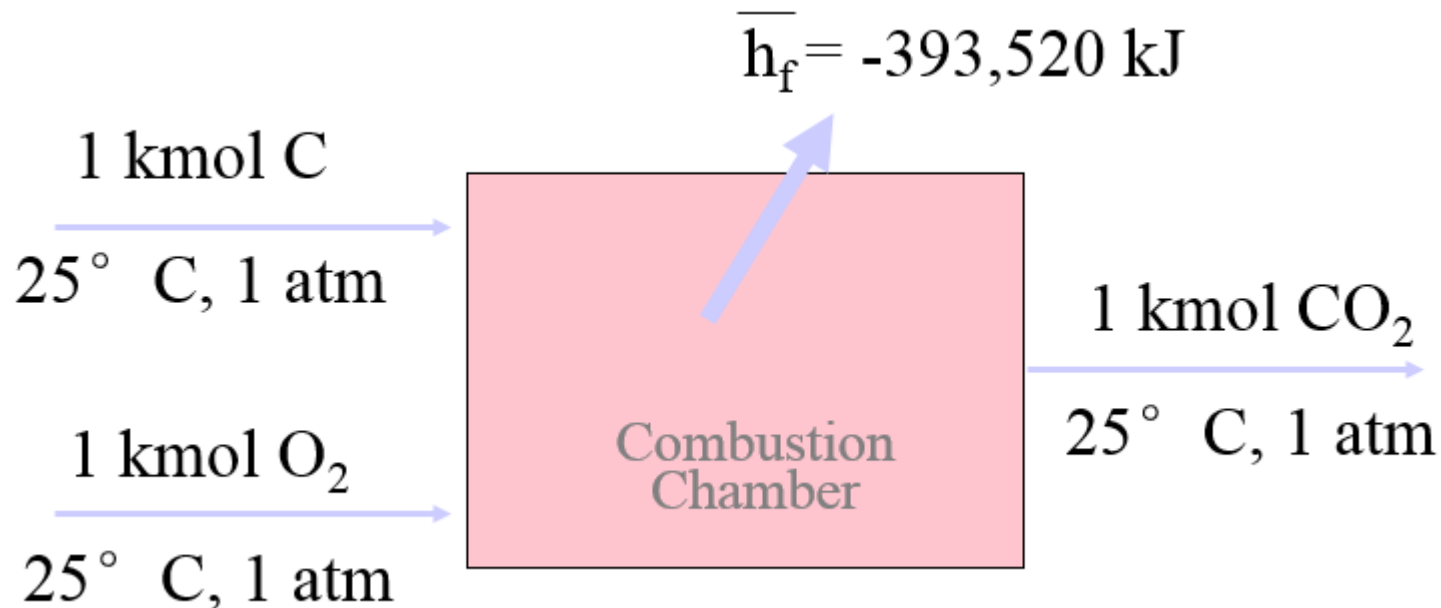
$$(\bar{h}_{f,O}^0) = 249,195 \text{ kJ} / \text{kmol}_O$$

# Enthalpy of formation

Graphic interpretation of standardised enthalpy, enthalpy of formation and sensible enthalpy

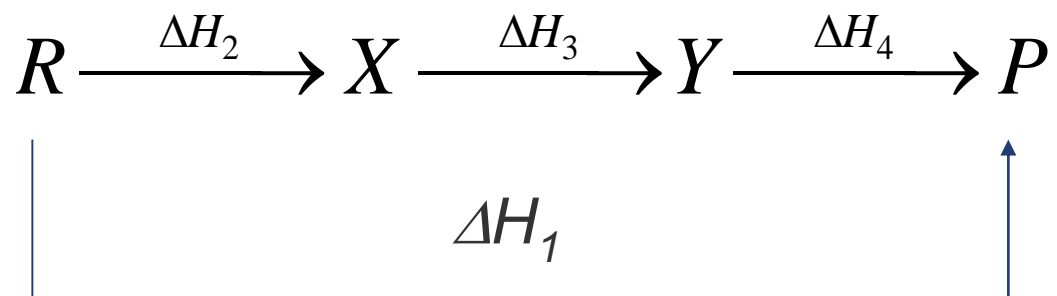


A fundamental parameter related to a reference state  
Independent of reaction path



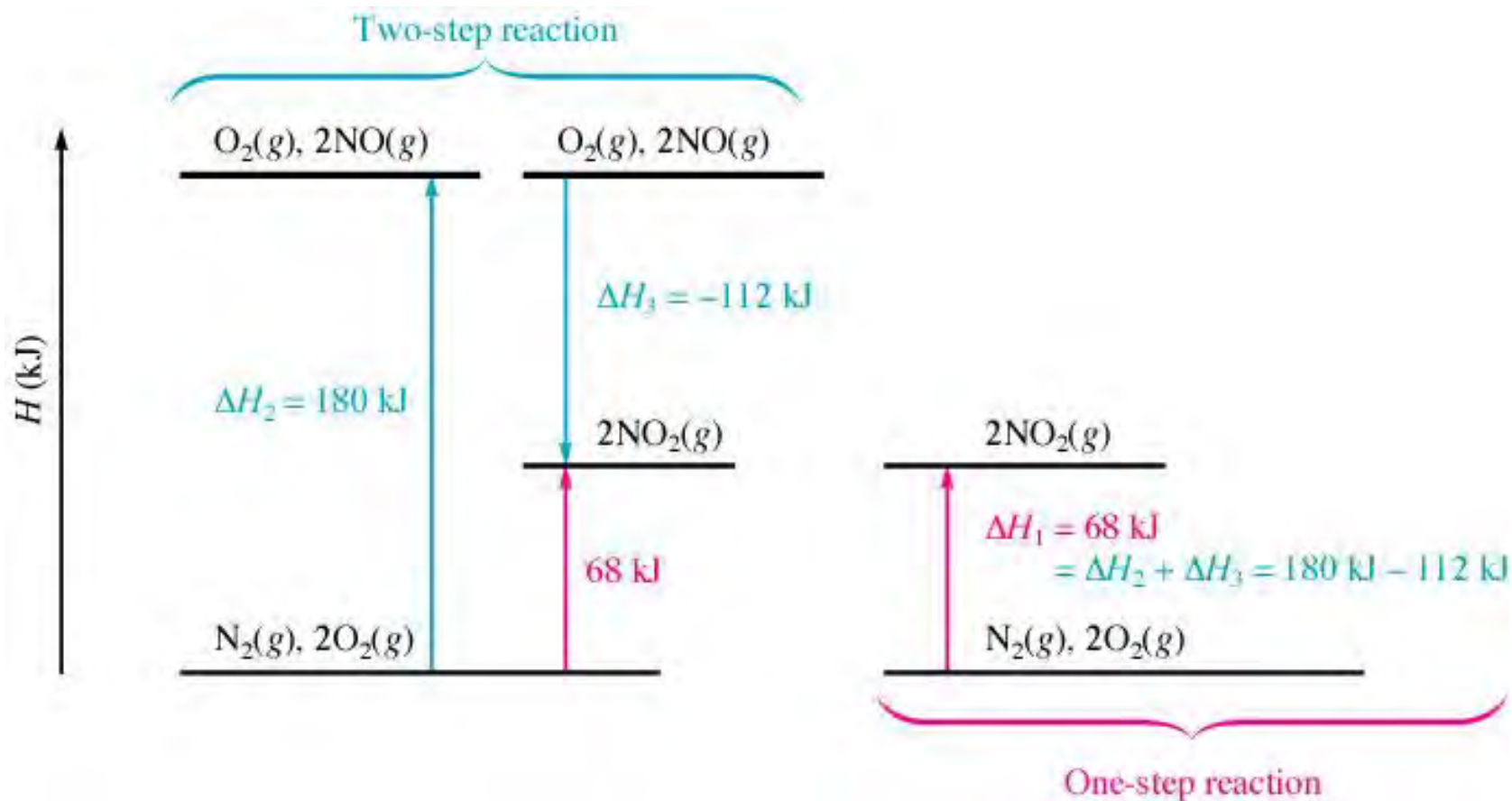
Note: negative enthalpy of formation means energy is released-exothermic,  
positive means energy is requested (absorbed) - endothermic.

The enthalpy of formation is only decided by the reactants and products, independent of the process (i.e. one step reaction or multi-step reaction have the same enthalpy of formation)



$$\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$$

# Hess's Law

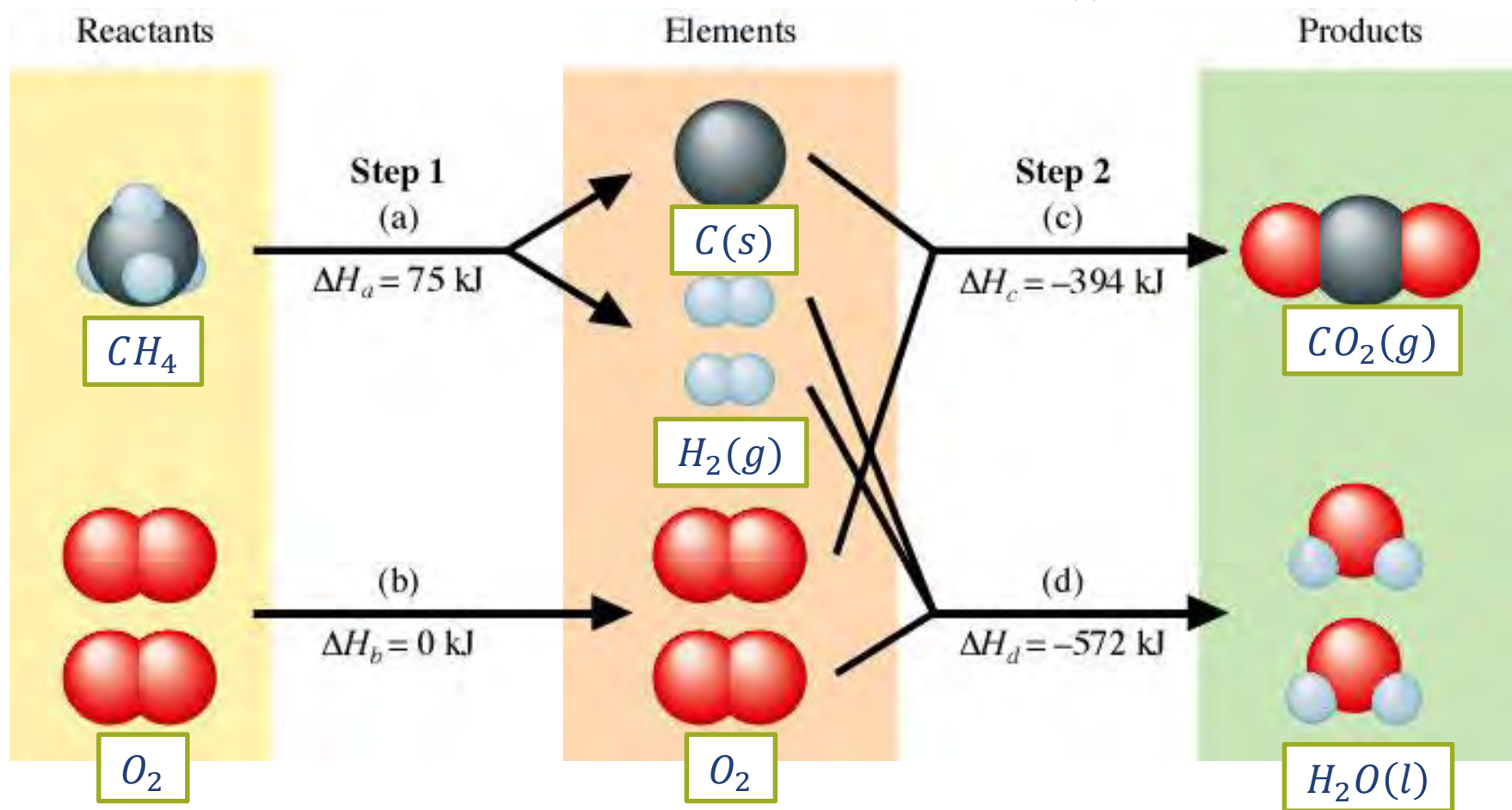


If reaction is reversible,  $\Delta H$  is also reversible



If reaction is multiplied,  $\Delta H$  is too







A gas stream at 1 atm contains a mixture of CO, CO<sub>2</sub> and N<sub>2</sub> in which the CO mole fraction is 0.10 and the CO<sub>2</sub> mole fraction is 0.20. the gas-stream temperature is 1200 K.  
Determine the standardised enthalpy of the mixture on both a mole basis (kJ/kmol) and a mass basis (kJ/kg).

**Table A.1** Carbon monoxide (CO), MW = 28.010, enthalpy of formation @ 298 K (kJ/kmol) = -110,541

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
1,500	35.178	38,847	-115,225	248.332	-243,674
1,600	35.451	42,379	-115,925	250.611	-252,214
1,700	35.694	45,937	-116,644	252.768	-260,711
1,800	35.910	49,517	-117,380	254.814	-269,164
1,900	36.101	53,118	-118,132	256.761	-277,576
2,000	36.271	56,737	-118,902	258.617	-285,948
2,100	36.421	60,371	-119,687	260.391	-294,281
2,200	36.553	64,020	-120,488	262.088	-302,576
2,300	36.670	67,682	-121,305	263.715	-310,835
2,400	36.774	71,354	-122,137	265.278	-319,057
2,500	36.867	75,036	-122,984	266.781	-327,245
2,600	36.950	78,727	-123,847	268.229	-335,399
2,700	37.025	82,426	-124,724	269.625	-343,519
2,800	37.093	86,132	-125,616	270.973	-351,606
2,900	37.155	89,844	-126,523	272.275	-359,661
3,000	37.213	93,562	-127,446	273.536	-367,684
3,100	37.268	97,287	-128,383	274.757	-375,677
3,200	37.321	101,016	-129,335	275.941	-383,639
3,300	37.372	104,751	-130,303	277.090	-391,571
3,400	37.422	108,490	-131,285	278.207	-399,474
3,500	37.471	112,235	-132,283	279.292	-407,347
3,600	37.521	115,985	-133,295	280.349	-415,192
3,700	37.570	119,739	-134,323	281.377	-423,008
3,800	37.619	123,499	-135,366	282.380	-430,796
3,900	37.667	127,263	-136,424	283.358	-438,557
4,000	37.716	131,032	-137,497	284.312	-446,291
4,100	37.764	134,806	-138,585	285.244	-453,997
4,200	37.810	138,585	-139,687	286.154	-461,677
4,300	37.855	142,368	-140,804	287.045	-469,330
4,400	37.897	146,156	-141,935	287.915	-476,957
4,500	37.936	149,948	-143,079	288.768	-484,558
4,600	37.970	153,743	-144,236	289.602	-492,134
4,700	37.998	157,541	-145,407	290.419	-499,684

**Table A.2** Carbon dioxide (CO<sub>2</sub>), MW = 44.011, enthalpy of formation @ 298 K (kJ/kmol) = -393,546

T(K)	$\bar{c}_p$ (kJ/kmol-K)	$(\bar{h}^o(T) - \bar{h}_f^o(298))$ (kJ/kmol)	$\bar{h}_f^o(T)$ (kJ/kmol)	$\bar{s}^o(T)$ (kJ/kmol-K)	$\bar{g}_f^o(T)$ (kJ/kmol)
200	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	355.725	-393,004
4,200	63.474	228,287	-406,499	358.253	-392,683
4,300	63.575	234,640	-407,135	359.748	-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

**Table A.7** Nitrogen (N<sub>2</sub>), MW = 28.013, enthalpy of formation @ 298 K (kJ/kmol) = 0

T(K)	$\bar{c}_p$ (kJ/kmol-K)	$(\bar{h}^o(T) - \bar{h}_f^o(298))$ (kJ/kmol)	$\bar{h}_f^o(T)$ (kJ/kmol)	$\bar{s}^o(T)$ (kJ/kmol-K)	$\bar{g}_f^o(T)$ (kJ/kmol)
200	28.793	-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
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

**Table A.6** Water (H<sub>2</sub>O), 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)	$(\bar{h}^o(T) - \bar{h}_f^o(298))$ (kJ/kmol)	$\bar{h}_f^o(T)$ (kJ/kmol)	$\bar{s}^o(T)$ (kJ/kmol-K)	$\bar{g}_f^o(T)$ (kJ/kmol)
200	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
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

$$x_{N_2} = 1 - x_{CO_2} - x_{CO} = 0.7$$

$$\begin{aligned} \bar{h}_{mix} = \sum x_i \bar{h}_i = & x_{CO} \left[ \bar{h}_{f,CO}^0 + \left( \bar{h}(T) - \bar{h}_{f,298}^0 \right)_{CO} \right] \\ & + x_{CO_2} \left[ \bar{h}_{f,CO_2}^0 + \left( \bar{h}(T) - \bar{h}_{f,298}^0 \right)_{CO_2} \right] \\ & + x_{N_2} \left[ \bar{h}_{f,N_2}^0 + \left( \bar{h}(T) - \bar{h}_{f,298}^0 \right)_{N_2} \right] \end{aligned}$$

Substitute values from Appendix A

$$\begin{aligned} h_{mix} = & 0.1[-110,540 + 28,440] \\ & + 0.2[-393,546 + 44,488] \\ & + 0.7[0 + 28,118] \\ = & -58,339.1 \text{ kJ/kmol}_{mix} \end{aligned}$$

To find  $h_{mix}$ , we need to determine the molecular weight of the mixture:

$$M_{\text{mix}} = \sum x_i M_i = 0.1(28.01) + 0.20(44.01) + 0.7(28.013) = 31.212$$

Then,

$$h_{\text{mix}} = \frac{\bar{h}_{\text{mix}}}{M_{\text{mix}}} = \frac{-55,339.1 (\text{kJ/kmol})}{31.212 (\text{kg/kmol})} = -1869.12 \text{ kJ/kg}_{\text{mix}}$$

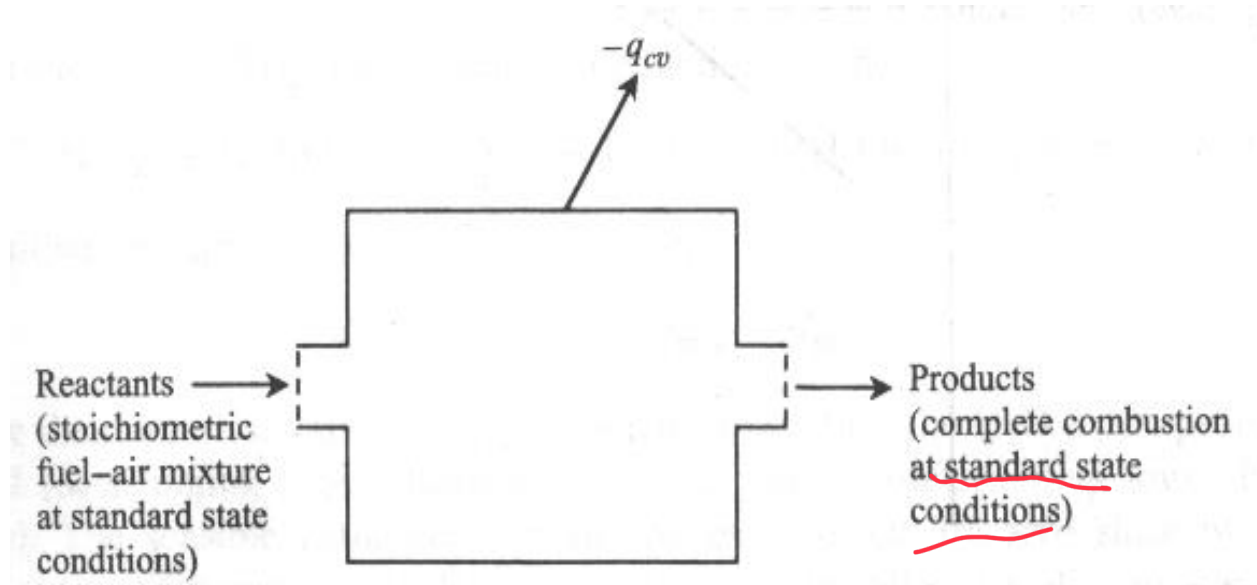
$$Y_{\text{CO}} = 0.10 \frac{28.01}{31.212} = 0.0897$$

$$Y_{\text{CO}_2} = 0.20 \frac{44.01}{31.212} = 0.2820$$

$$Y_{\text{N}_2} = 0.70 \frac{28.013}{31.212} = 0.6282$$

$$\text{Check: } 0.0897 + 0.2820 + 0.6282 = 1$$

For a steady state combustor, the complete combustion means



Based on the First Law, we have

$$q_{cv} = h_0 - h_i = h_{prod} - h_{reac}$$

With a complete reaction, at a certain state, the enthalpy difference between the products and reactants is called the **enthalpy of reaction,  $h_R$**

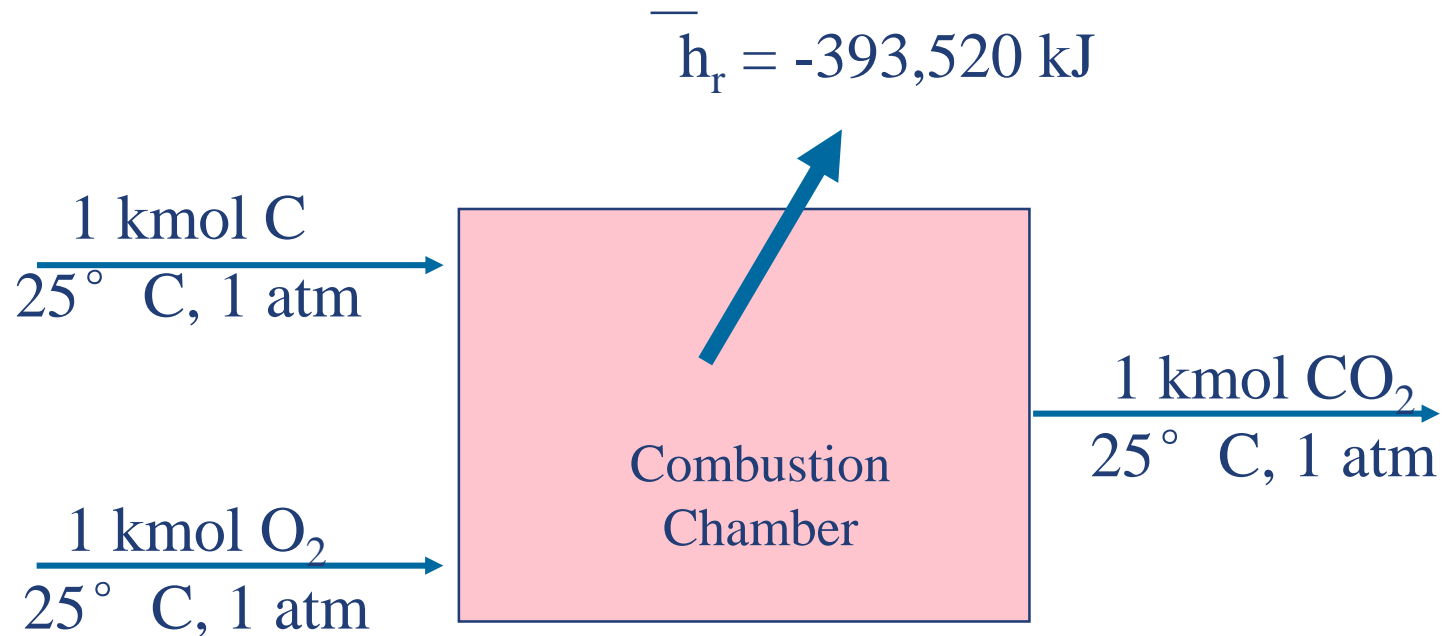
During combustion process, we call it **enthalpy of combustion,  $h_c$**  (kJ/kg or kJ/kmol)

$$\Delta h_R \equiv q_{cv} = h_{prod} - h_{reac}$$

Or

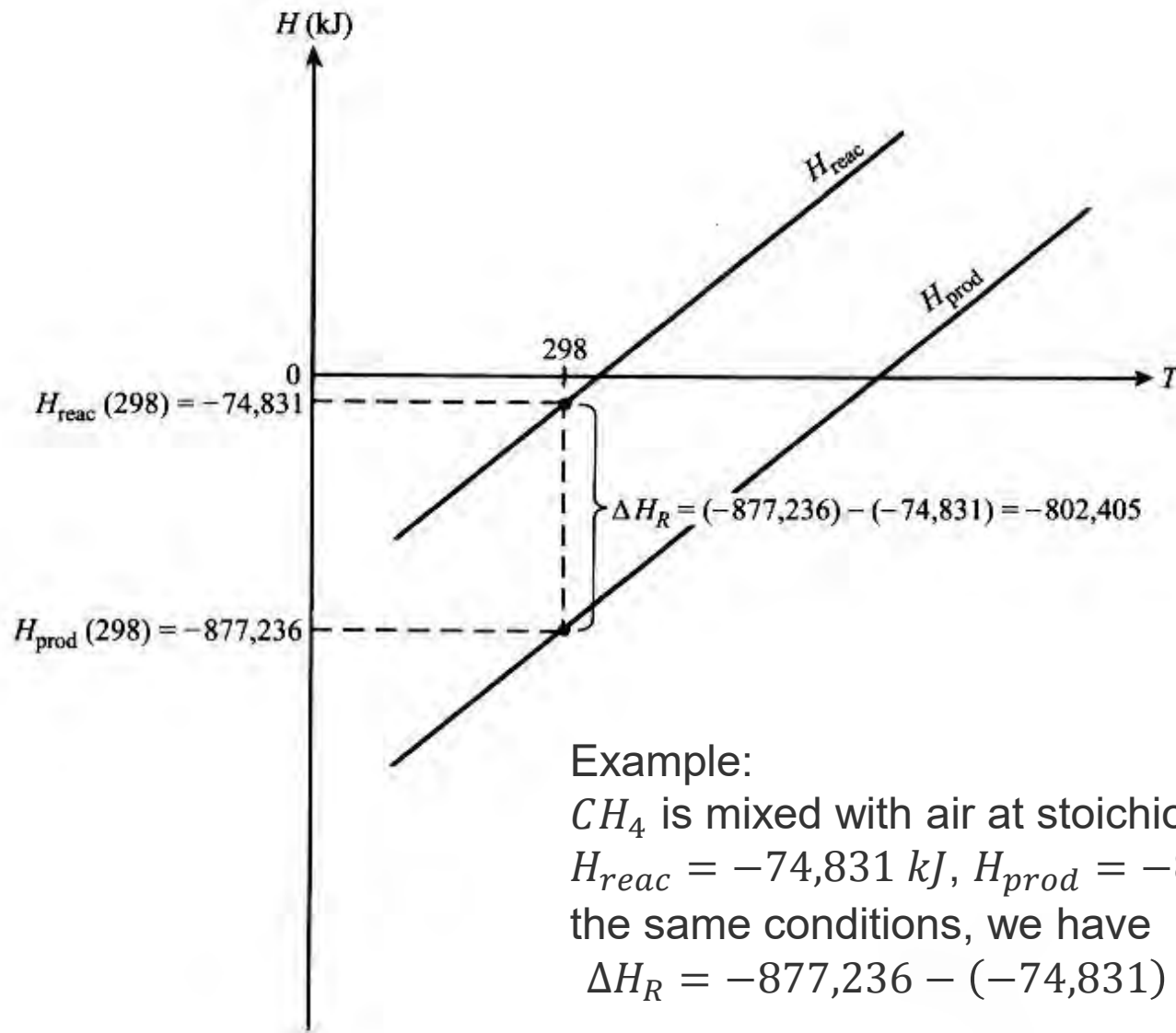
$$\Delta H_R = H_{prod} - H_{reac}$$





The enthalpy of reaction (enthalpy of combustion) is **negative** because the enthalpy of the products is less than the enthalpy of the reactants, i.e. the reaction is **exothermic**

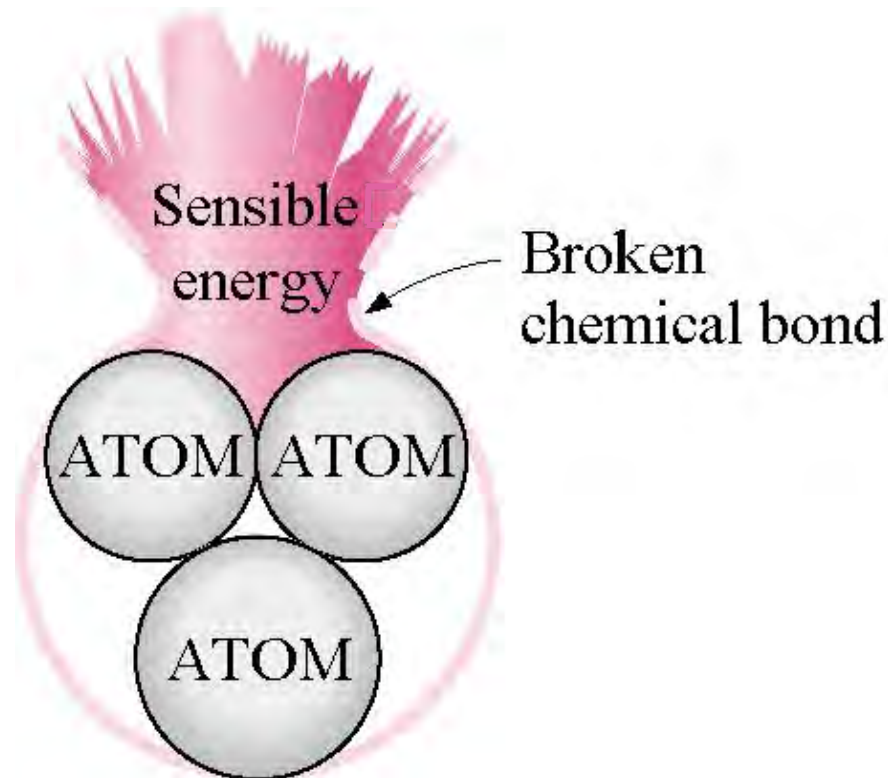
# Enthalpy of combustion



# Enthalpy of combustion

A microscopic view

When existing chemical bonds are broken and new bonds are formed, usually a large amount of sensible heat is released, i.e. combustion process



## Enthalpy of reaction

### Enthalpy of reaction by unit mass of fuel

$$\Delta h_R \left( \frac{kJ}{kg_{fuel}} \right) = \Delta H_R / M_{Fuel}$$

$$\Delta h_R \left( \frac{kJ}{kg_{CH_4}} \right) = \left( -\frac{801,405}{16.043} \right) = -50,016$$

### Enthalpy of reaction by unit mass of mixture

$$\Delta h_R \left( \frac{kJ}{kg_{mix}} \right) = \Delta h_R \left( \frac{kJ}{kg_{fuel}} \right) \frac{m_{fuel}}{m_{mix}}$$

**NOTE: Enthalpy of reaction is related to temperature**

Where

$$\frac{m_{fuel}}{m_{mix}} = \frac{m_{fuel}}{m_{air} + m_{fuel}} = \frac{1}{(A/F) + 1}$$

For methane (stoichiometric A/F ratio 17.11)

$$\Delta h \left( \frac{kJ}{kg_{mix}} \right) = \frac{-50,016}{17.11 + 1} = -2761.8$$

**Heat of combustion**,  $\Delta h_c$  (a.k.a. the **heating value**), is numerically equal to the enthalpy of reaction but with opposite sign (positive).

**Upper or Higher heating value:**  $H_2O$  is condensed to a liquid

**Lower heating value:**  $H_2O$  is condensed to a gas/vapour

$$\text{HHV} = \text{LHV} + \text{Latent Heat of Vaporization (25}^\circ\text{C)}$$

- A. Determine the upper and lower heating values at 298 K of gaseous n-decane,  $C_{10}H_{22}$ , per kilomole of fuel and per kilogram of fuel. The molecular weight of n-decane is 142.284 kg/kmol.
- B. If the enthalpy of vaporisation of n-decane is  $359 \text{ kJ/kg}_{fuel}$ , what are the upper and lower heating values of liquid n-decane?

# Fuel properties

**Table B.1** Selected properties of hydrocarbon fuels: enthalpy of formation,<sup>a</sup> Gibbs function of formation,<sup>a</sup> entropy,<sup>a</sup> and higher and lower heating values all at 298.15 K and 1 atm; boiling points<sup>b</sup> and latent heat of vaporization<sup>c</sup> at 1 atm; constant-pressure adiabatic flame temperature at 1 atm;<sup>d</sup> liquid density<sup>e</sup>

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



A. For 1 mole of  $C_{10}H_{22}$ , the combustion equation can be written as



For either the upper or lower heating value

$$\Delta H_C = -\Delta H_R = H_{\text{reac}} - H_{\text{prod}}$$

The **sensible** enthalpies for all species are zero at 298 K (reference state), the enthalpies of formation of  $O_2$  and  $N_2$  are also zero at 298 K.

Recognising that

$$H_{\text{reac}} = \sum_{\text{reac}} N_i \bar{h}_i \quad \text{and} \quad H_{\text{prod}} = \sum_{\text{prod}} N_i \bar{h}_i$$

We have

$$\Delta H_{C, H_2O(l)} = HHV = (1)\bar{h}_{f, C_{10}H_{22}}^0 - [10\bar{h}_{f, CO_2}^0 + 11\bar{h}_{f, H_2O(l)}^0]$$

?

Continue...

Enthalpy of formation for liquid water from enthalpy of formation for gaseous water and enthalpy of vaporisation (values from table)

$$\bar{h}_{f,H_2O(l)}^0 = \bar{h}_{f,H_2O(g)}^0 - \bar{h}_{fg} = -241,847 - 44,010 = -285,857 \text{ kJ / kmol}$$

Therefore, we obtain the HHV:

$$\begin{aligned} \Delta H_{C,H_2O(l)} &= (1)(-249,659 \frac{\text{kJ}}{\text{kmol}}) \\ &\quad - \left[ 10 \left( -393,546 \frac{\text{kJ}}{\text{kmol}} \right) + 11 \left( -285,857 \frac{\text{kJ}}{\text{kmol}} \right) \right] \\ &= 6,830,096 \text{ kJ} \end{aligned}$$

And 
$$\Delta \bar{h}_c = \frac{\Delta H_c}{N_{C_{10}H_{22}}} = \frac{6,830,096 \text{ kJ}}{1 \text{ kmol}} = 6,830,096 \text{ kJ / kmol}_{C_{10}H_{22}}$$

Or 
$$\Delta h_c = \frac{\Delta \bar{h}_c}{M_{C_{10}H_{22}}} = \frac{6,830,096 \text{ kJ / kmol}}{142.284 \text{ kg / kmol}} = 48,003 \text{ kJ / kg}_{C_{10}H_{22}}$$

Continue...

For lower heating value, we use  $\bar{h}_{f,H_2O(g)}^0 = -241,847 \text{ kJ} / \text{kmol}$  in place of  $\bar{h}_{f,H_2O(l)}^0 = -285,857 \text{ kJ} / \text{kmol}$

We obtain:  $\Delta \bar{h}_C = 6,345,986 \text{ kJ} / \text{kmol}_{C_{10}H_{22}}$

Or  $\Delta h_C = 44,601 \text{ kJ} / \text{kg}_{C_{10}H_{22}}$

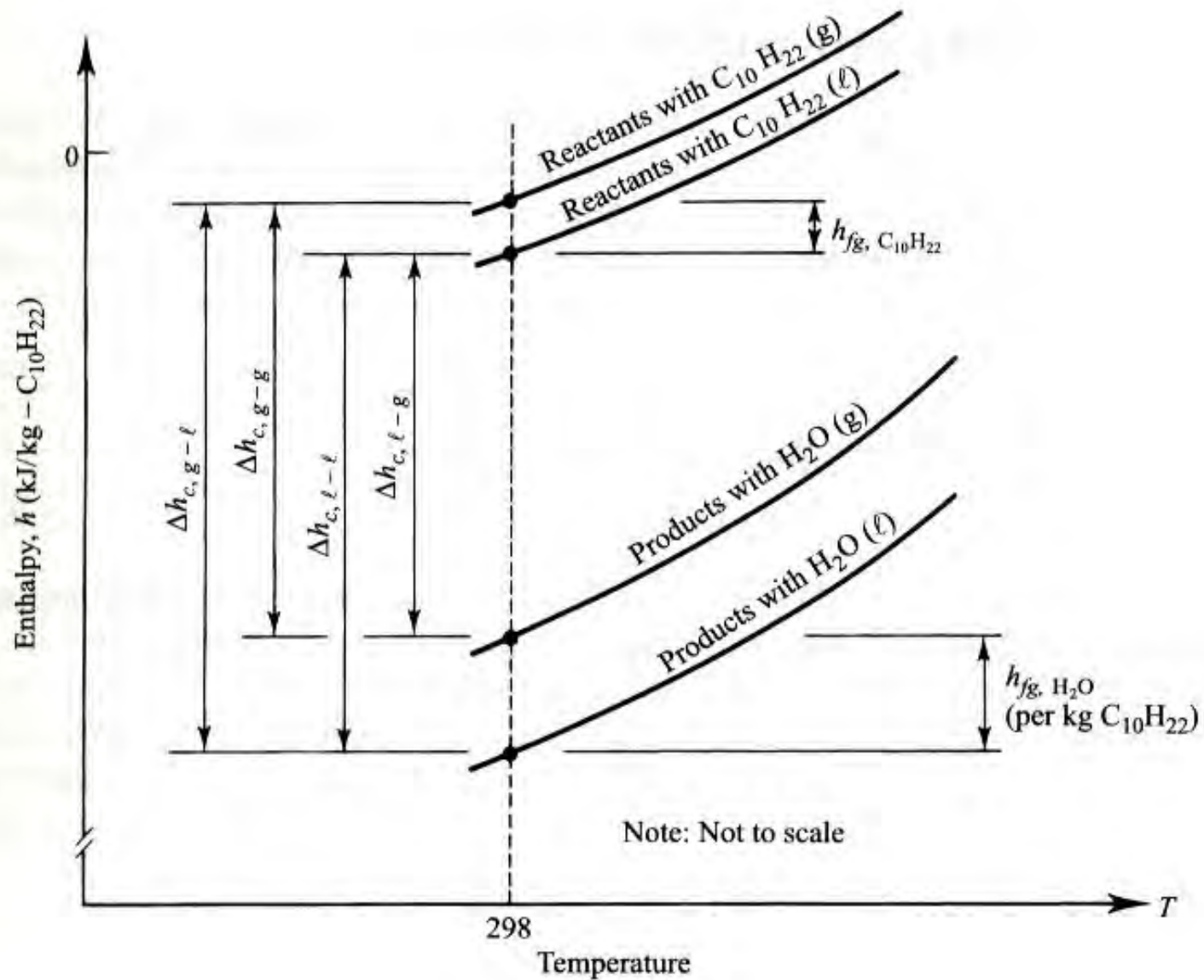
B. For liquid  $C_{10}H_{22}$

$$H_{\text{reac}} = (1)(\bar{h}_{f,C_{10}H_{22}(g)}^0 - \bar{h}_{fg}),$$

Or  $\Delta h_C (\text{liquid fuel}) = \Delta h_C (\text{gaseous fuel}) - h_{fg}$

Thus  $\Delta h_C (\text{higher}) = 48,003 - 359$   
 $= 47,644 \text{ kJ/kg}_{C_{10}H_{22}}$

$\Delta h_C (\text{lower}) = 44,601 - 359$   
 $= 44,242 \text{ kJ/kg}_{C_{10}H_{22}}$



# Adiabatic Flame Temperatures

We define two adiabatic flame temperatures: one for ~~constant-pressure~~ combustion and one for constant-volume.

Based on the First Law, for constant pressure adiabatic combustion temperature

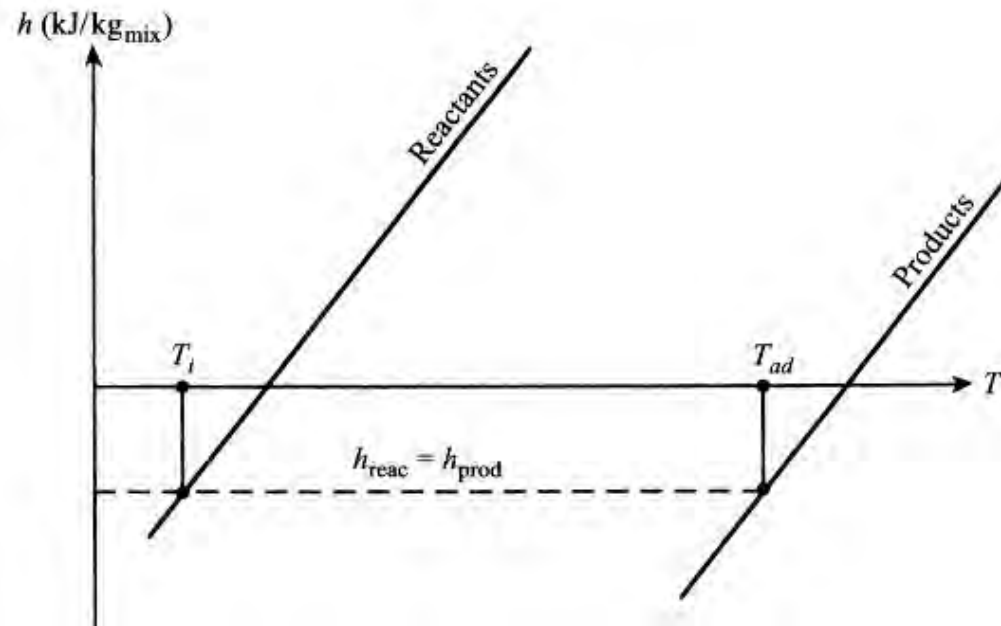
$$H_{\text{reac}}(T_i, P) = H_{\text{prod}}(T_{\text{ad}}, P)$$

*why heat constant  
why not work or internal energy*

Or

$$h_{\text{reac}}(T_i, P) = h_{\text{prod}}(T_{\text{ad}}, P)$$

Typical flame temperatures are several thousand Kelvins.



# Adiabatic Flame Temperatures

## Example

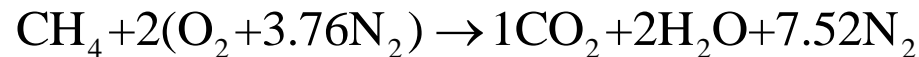
Estimate the constant pressure adiabatic flame temperature for the combustion of a stoichiometric  $\text{CH}_4$ -air mixture. The pressure is 1 atm and the initial temperature is 298 K.

Assume complete combustion, i.e. the product mixture consists of only  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{N}_2$ . and the product mixture enthalpy is estimated using constant specific heat evaluated at 1200 K ( $\approx 0.5 (T_i + T_{\text{ad}})$ ), where  $T_{\text{ad}}$  is guessed to be about 2100 K)

difference of  $H_c$   
and  $H_r$

<i>Species</i>	<i>Enthalpy of Formation @298K</i>	<i>Specific Heat @1200K</i>
<i><math>h_{f,i}^0</math> (kJ/kmol)</i>	<i><math>c_{P,i}</math> (kJ/kmol-K)</i>	
<b><math>\text{CH}_4</math></b>	-74,831	-----
<b><math>\text{CO}_2</math></b>	-393,546	56.21
<b><math>\text{H}_2\text{O}</math></b>	-241,845	43.87
<b><math>\text{N}_2</math></b>	0	33.71
<b><math>\text{O}_2</math></b>	0	----

Mixture composition:



$$N_{\text{CO}_2} = 1, \quad N_{\text{H}_2\text{O}} = 2, \quad N_{\text{N}_2} = 7.52$$

First Law:  $H_{\text{react}} = \sum_{\text{react}} N_i \bar{h}_i = H_{\text{prod}} = \sum_{\text{prod}} N_i \bar{h}_i$

$$H_{\text{react}} = (1)(-74,831) + 2(0) + 7.52(0) = -74,831 \text{ kJ}$$

$$\begin{aligned} H_{\text{prod}} &= \sum N_i [\bar{h}_{f,i}^0 + \bar{c}_{p,i} (T_{ad} - 298)] \\ &= (1)[-393,546 + 56.21(T_{ad} - 298)] \\ &\quad + (2)[-241,845 + 43.87(T_{ad} - 298)] \\ &\quad + (7.52)[0 + 33.71(T_{ad} - 298)] \end{aligned}$$

Equating  $H_{\text{react}}$  to  $H_{\text{prod}}$  and solving for  $T_{ad}$  yields

$$T_{ad} = 2318 \text{ K}$$

## Constant volume adiabatic combustion temperature

By the First Law

$$U_{reac}(T_{init}, p_{init}) = U_{prod}(T_{ad}, p_f)$$

Where  $U$  is the internal energy. Or in another form (as  $U + pV = H$ )

$$H_{reac} - H_{prod} - V(p_{init} - p_f) = 0$$

For an ideal gas

$$p_{init}V = \sum_{reac} n_i R_0 T_{init} = n_{reac} R_0 T_{init}$$

$$p_f V = \sum_{prod} n_i R_0 T_{ad} = n_{prod} R_0 T_{ad}$$

Thus

$$H_{reac} - H_{prod} - R_0(n_{reac}T_{init} - n_{prod}T_{ad}) = 0$$



For specific values

For reactants

$$\frac{m_{mix}}{n_{reac}} \equiv M_{reac}$$

For products

$$\frac{m_{mix}}{n_{prod}} \equiv M_{prod}$$

Thus we obtain (as mass is conserved)

$$h_{reac} - h_{prod} - R_0 \left( \frac{T_{init}}{M_{reac}} - \frac{T_{ad}}{M_{prod}} \right) = 0$$

Estimate the constant volume adiabatic flame temperature for the combustion of a stoichiometric  $\text{CH}_4$ -air mixture. The pressure is 1 atm and the initial temperature is 298 K.

Note: the estimated temperature would be higher than the last example (constant pressure, why?) but we use the same specific heat.

We have:  $H_{reac} - H_{prod} - R_0(n_{reac}T_{init} - n_{prod}T_{ad}) = 0$

Or

$$\sum_{reac} n_i \bar{h}_i - \sum_{prod} n_i \bar{h}_i - R_0(n_{reac}T_{init} - n_{prod}T_{ad}) = 0$$

From the table  $H_{reac} = (1)(-74,831) + 2(0) + 7.52(0) = -74,831 \text{ kJ}$

$$\begin{aligned} H_{prod} &= (1)[-393,546 + 56.21(T_{ad} - 298)] \\ &\quad + (2)[-241,845 + 43.87(T_{ad} - 298)] \\ &\quad + (7.52)[0 + 33.71(T_{ad} - 298)] \\ &= -877,236 + 397.5(T_{ad} - 298) \text{ kJ} \end{aligned}$$

Continue..

And  $R_0(n_{reac}T_{init} - n_{prod}T_{ad}) = 8.315 \times 10.52 \times (298 - T_{ad})$

Note:  $n_{reac} = n_{prod} = 10.52 \text{ kmol}$  is not always true

Rearrange to find  $T_{ad}$

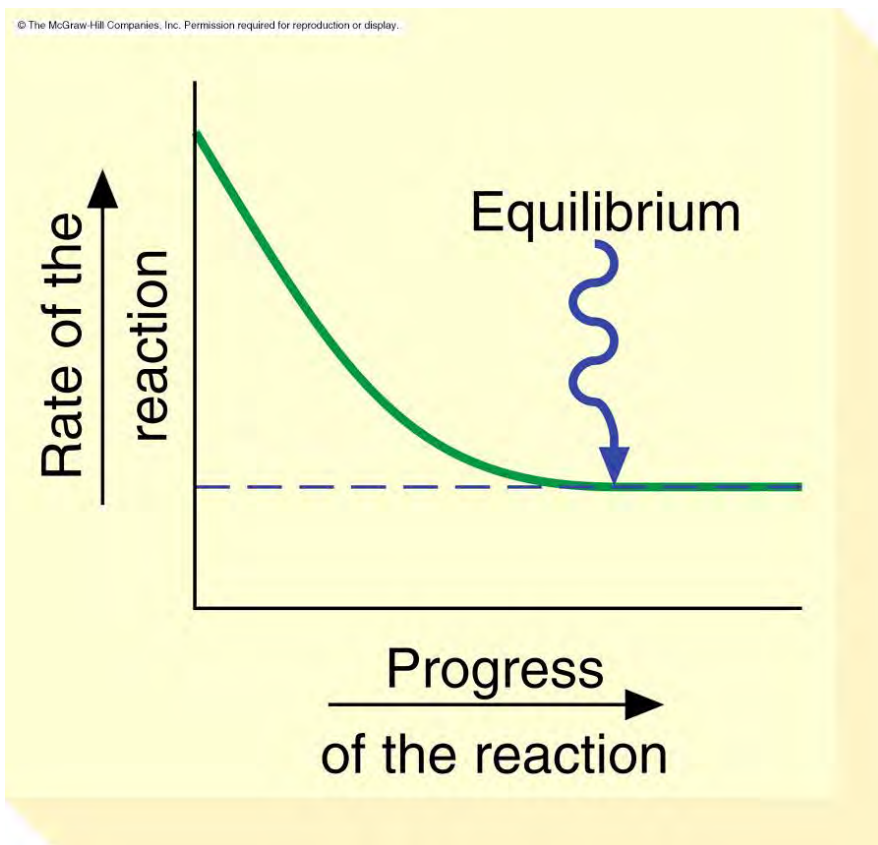
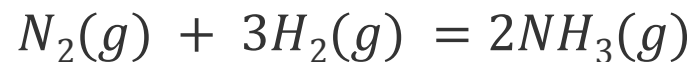
$$T_{ad} = 2889 \text{ K}$$

Note:  $T_{ad}$  for constant volume is higher than  $T_{ad}$  for constant pressure. What does this suggest **physically?**

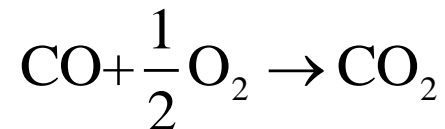
*fully combustion*

- So far we consider combustion (reaction) process in an ideal way that reactants react and form ideal products
- In real combustion process, the major species dissociate and produce a host of minor species.
- Example:
  - hydrocarbon complete combustion ideally produces  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{O}_2$ , and  $\text{N}_2$  (with excessive of air)
  - Dissociation yields  $\text{H}_2$ ,  $\text{OH}$ ,  $\text{CO}$ ,  $\text{H}$ ,  $\text{O}$ ,  $\text{N}$ ,  $\text{NO}$ , and possibly others.
- Question: how to decide the product species at a given temperature and pressure
- The calculation subject to the constraint of element/mass conservation (C, H, O, and N atom numbers will not change)

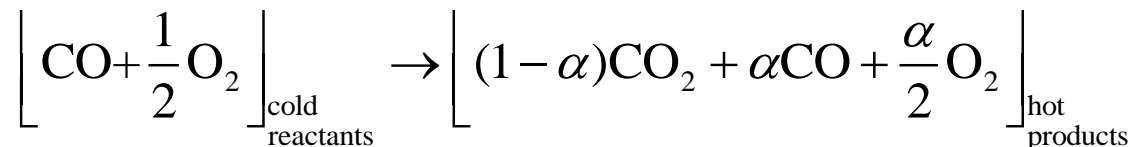
Consider the reaction of  $N_2$  and  $H_2$ .



- Chemical equilibrium (final state of a reaction) is governed by both the First and the Second Law of thermodynamics
- Consider the following combustion reaction



- At very high temperature,  $\text{CO}_2$  will dissociate. Assume the products are  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{O}_2$ , we have



where  $\alpha$  is the fraction of  $\text{CO}_2$  dissociated. When  $\alpha = 0$ , maximum amount of heat released and system achieves highest  $T$  and  $p$ ; when  $\alpha = 1$ , no heat released and everything ( $T$ ,  $p$ , ...) remains unchanged.

The entropy of the product mixture can be calculated by summing the product species entropies

$$S_{mix}(T_f, p) = \sum_{i=1}^3 n_i \bar{s}_i(T_f, p_i) = (1 - \alpha) \bar{s}_{CO_2} + \alpha \bar{s}_{CO} + \frac{\alpha}{2} \bar{s}_{O_2}$$

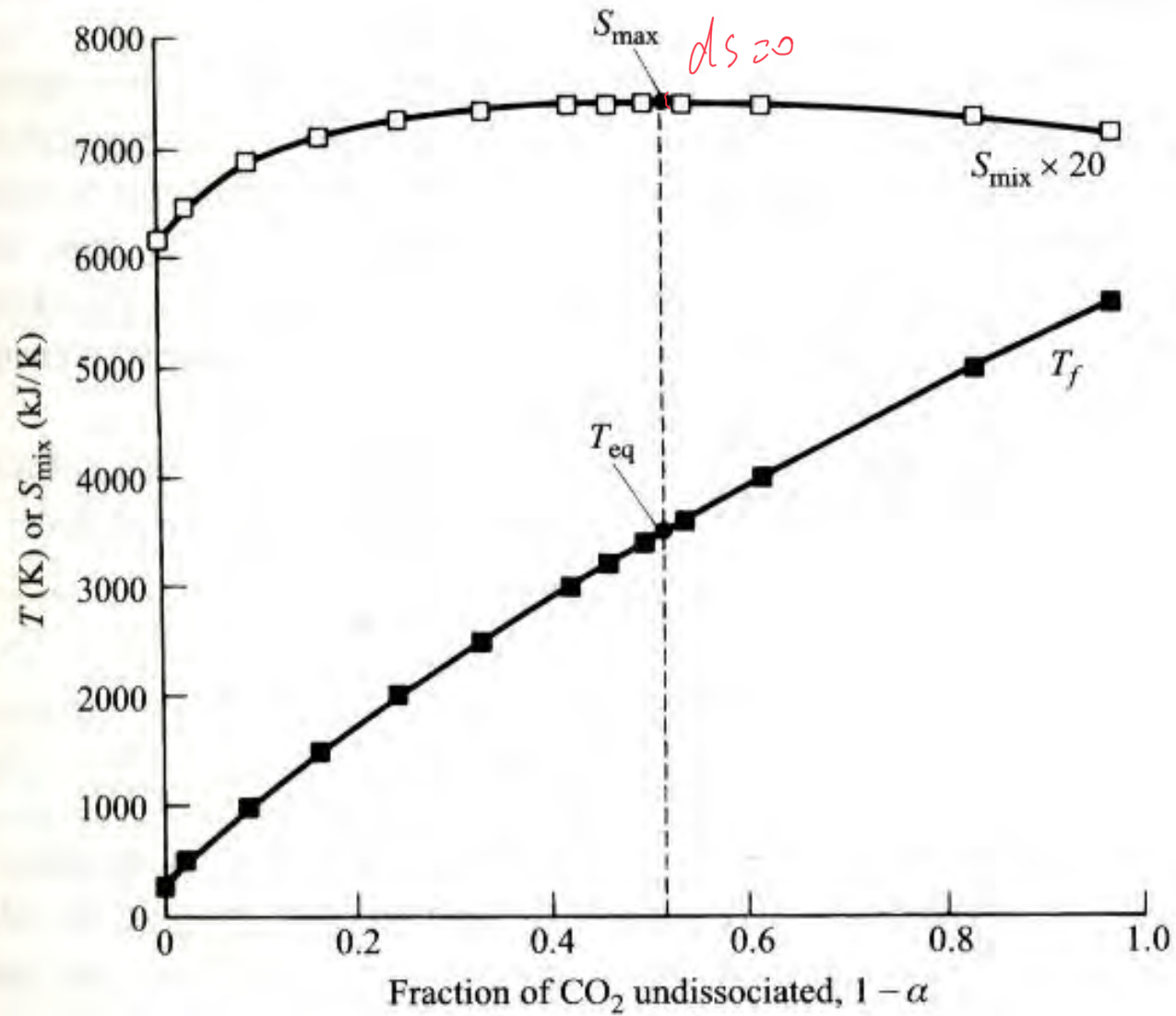
Where  $n_i$  is the mole number of species  $i$ .

The individual species entropies are obtained from:

$$\bar{s}_i = \bar{s}_i^0(T_{ref}) + \int_{T_{ref}}^{T_f} \bar{c}_{p,i} \frac{dT}{T} - R_0 \ln \frac{p_i}{p^0}$$

Note: ideal gas behaviour is assumed.





In the figure, for the reaction chosen,  $CO + \frac{1}{2} O_2 \rightarrow CO_2$ , the maximum entropy occurred near  $1 - \alpha = 0.5$

For the choice of conditions (constant  $U$ ,  $V$ ,  $m$ , no heat or work transfer) the Second Law requires that the entropy change internal to the system.

$$dS \geq 0$$

The composition of the system will spontaneously shift toward the maximum entropy point from either side, as  $dS$  is positive.

Formally, the condition for equilibrium can be written

$$(dS)_{U,V,m} = 0$$

②  $U, V, m$       ③  $I, I \Rightarrow S_{\max}$

To summarise, for an isolated system with fixed internal energy, volume and mass, with Second Law (entropy), First Law ( $U_{\text{reac}} = U_{\text{prod}}$ ) and state equations, the equilibrium  $T$ ,  $p$  and composition can be defined.

The previous conclusion is useful in illustrating the chemical equilibrium, the use of isolated (fixed energy) system of fixed mass and volume is not very useful for many real problems.

**Gibbs Free Energy,  $G$** , replaces the entropy  $G \equiv H - TS$

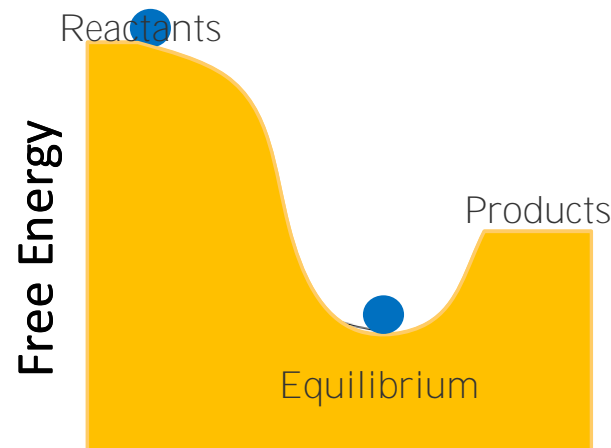
$$G \equiv H - TS = U + pV - TS$$

The Second Law can be expressed as

$$(dG)_{T,p,m} \leq 0$$

This is to say in a spontaneous process, towards its minimum value

$dG = 0$	Equilibrium
$dG < 0$	Spontaneous
$dG > 0$	Non spontaneous



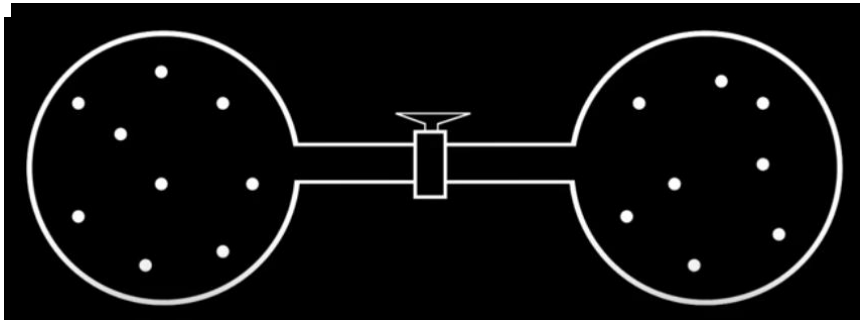
## Chemical reaction

Endothermic:  $\Delta H$  is positive

Exothermic:  $\Delta H$  is negative (spontaneous)

But not just  $\Delta H$

Consider the following spontaneous process,  $\Delta S$  plays a role



	$\Delta H^\circ < 0$	$\Delta H^\circ > 0$
$\Delta S^\circ > 0$	<p>Spontaneous</p> <p>Dissociation of unstable compounds</p>	<p>Spontaneous at high temps</p> <p>Dissociation of a strong compound</p>
$\Delta S^\circ < 0$	<p>Spontaneous at low temps</p> <p>Recombination reaction, e.g. <math>H. + H. \rightarrow H_2</math></p>	<p>Not Spontaneous</p> <p>Forming unstable compounds</p>

In equilibrium,

$$(dG)_{T,p,m} = 0$$

## Gibbs function and Gibbs function of formation

For a mixture of ideal gases, the Gibbs function of the *i*th species is

$$g = h + Ts$$

$$\bar{g}_{i,T} = \bar{g}_{i,T}^0 + R_0 T \ln\left(\frac{p_i}{p^0}\right)$$

Where  $\bar{g}_{i,T}^0$  is the Gibbs function of the pure species at the standard-state pressure  $p^0$  (1 atm) and  $p_i$  is the partial pressure.

In dealing with reacting systems, a **Gibbs function of formation**,  $\bar{g}_{f,i}^0$  is:

$$\bar{g}_{f,i}^0(T) \equiv \bar{g}_i^0(T) - \sum_{j \text{ elements}} \nu'_j \bar{g}_j^0(T)$$

Where  $\nu'_j$  are the **stoichiometric coefficients** of the elements required to form one mole of the compound of interest. e.g.  $\nu'_{O_2} = \frac{1}{2}$ ,  $\nu'_C = 1$  for a mole of CO from O<sub>2</sub> and C.

Gibbs function of formation of the naturally occurring elements are assigned values of zero.

# Gibbs function for mixture

Assume ideal gases

$$G = H - TS$$

$$G_{mix} = \sum n_i \bar{g}_{i,T} = \sum n_i \left[ \bar{g}^0_{i,T} + R_0 T \ln \left( \frac{p_i}{p^0} \right) \right]$$

Where  $n_i$  is the number of moles of the  $i$ th species

$\Rightarrow dG \approx$

For fixed temperature and pressure, the equilibrium condition becomes

$$dG_{mix} = 0 \quad \text{or} \quad \sum dn_i \left[ \bar{g}^0_{i,T} + R_0 T \ln \left( \frac{p_i}{p^0} \right) \right] + \sum n_i d \left[ \bar{g}^0_{i,T} + R_0 T \ln \left( \frac{p_i}{p^0} \right) \right] = 0$$

Because all changes in the partial pressures must sum to zero as the total pressure is constant, therefore  $\sum dp_i = 0$ , and  $d(\ln p_i) = dp_i/p_i$   $d\bar{g}_{i,T}^0 \approx 0$

Thus

$$dG_{mix} = \sum dn_i \left[ \bar{g}^0_{i,T} + R_0 T \ln \left( \frac{p_i}{p^0} \right) \right] = 0$$

## Gibbs function for mixture

For a general system, where



The change in the number of moles of each species is proportional to its stoichiometric coefficient

$$dn_A = -\kappa a$$

$$dn_B = -\kappa b$$

...

$$dn_E = +\kappa e$$

$$dn_F = +\kappa f$$

...

Substituting into previous equation, and cancelling the constant  $\kappa$

$$\begin{aligned} & -a \left[ \bar{g}_{A,T}^0 + R_0 T \ln \left( \frac{p_A}{p^0} \right) \right] - b \left[ \bar{g}_{B,T}^0 + R_0 T \ln \left( \frac{p_B}{p^0} \right) \right] - \dots \\ & + e \left[ \bar{g}_{E,T}^0 + R_0 T \ln \left( \frac{p_E}{p^0} \right) \right] + f \left[ \bar{g}_{F,T}^0 + R_0 T \ln \left( \frac{p_F}{p^0} \right) \right] + \dots = 0 \end{aligned}$$



Rearrange and group the log terms

$$\begin{aligned}
 & - \left( e \bar{g}_{E,T}^0 + f \bar{g}_{F,T}^0 + \dots - a \bar{g}_{A,T}^0 - b \bar{g}_{B,T}^0 - \dots \right) \\
 & = R_0 T \ln \frac{\left( \frac{p_E}{p_0} \right)^e \left( \frac{p_F}{p_0} \right)^f \text{ etc}}{\left( \frac{p_A}{p_0} \right)^a \left( \frac{p_B}{p_0} \right)^b \text{ etc}} \quad \text{= } R_0 T \ln K_p
 \end{aligned}$$

We define standard-state Gibbs function change  $\Delta G_T^0$

$$\Delta G_T^0 = \left( e \bar{g}_{E,T}^0 + f \bar{g}_{F,T}^0 + \dots - a \bar{g}_{A,T}^0 - b \bar{g}_{B,T}^0 - \dots \right) \text{ or}$$

$$\Delta G_T^0 = \left( e \bar{g}_{f,E}^0 + f \bar{g}_{f,F}^0 + \dots - a \bar{g}_{f,A}^0 - b \bar{g}_{f,B}^0 - \dots \right)_T$$

And we also define the **equilibrium constant**  $K_p$  as

$$K_p = \frac{\left( \frac{p_E}{p_0} \right)^e \left( \frac{p_F}{p_0} \right)^f \text{ etc}}{\left( \frac{p_A}{p_0} \right)^a \left( \frac{p_B}{p_0} \right)^b \text{ etc}} \quad K_p = \frac{\left( \frac{p_E}{p_0} \right)^e \left( \frac{p_F}{p_0} \right)^f \text{ etc}}{\left( \frac{p_A}{p_0} \right)^a \left( \frac{p_B}{p_0} \right)^b \text{ etc}}$$

So we have

$$\Delta G_T^0 = -R_0 T \ln K_p$$

Or

$$K_p = e^{-\Delta G_T^0 / R_0 T}$$

From the relation of  $K_p$  and  $\Delta G_T^0$ , we obtain a quantitative indication of whether a reaction favours products or reactants.

$\Delta G_T^0 > 0$ ,  $\ln K_p < 0$ , reactants are favoured (no reaction)

$\Delta G_T^0 < 0$ ,  $\ln K_p > 0$ , products are favoured (reaction)

Because

$$\Delta G_T^0 = \Delta H^0 - T\Delta S^0$$

$$K_p = e^{-\Delta H^0 / R_0 T} \cdot e^{\Delta S^0 / R_0}$$

$$K_p = e^{-\frac{\Delta G_T^0}{R_0 T}} = e^{\frac{T\Delta S^0 - \Delta H^0}{R_0 T}} = e^{\frac{\Delta S^0}{R_0}} \cdot e^{-\frac{\Delta H^0}{R_0 T}}$$

For  $K_p$  greater than 1, enthalpy change should be negative, i.e. exothermic and system energy becomes lower; also positive change in entropy, indicating greater molecular chaos.

Consider the dissociation of  $\text{CO}_2$  as a function of temperature and pressure



Find the composition of the mixture, i.e. the mole fractions of  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{O}_2$ , that results from subjecting originally pure  $\text{CO}_2$  to various temperatures, ( $T=1500, 2000, 2500$  and  $3000$  K) and pressures ( $p=0.1, 1, 10$  and  $100$  atm).

To find the three unknown mole fractions, we need 3 equations

Equation 1: equilibrium expression

$$K_p = e^{\frac{-\Delta G_T^0}{R_0 T}}$$

$$K_p = e^{-\Delta G_T^0 / R_0 T} \quad (1)$$

Equation 2: element conservation

$$\frac{\text{No. of carbon atoms}}{\text{No. of oxygen atoms}} = \frac{1}{2} = \frac{\chi_{CO} + \chi_{CO_2}}{2\chi_{O_2} + 2\chi_{CO_2} + \chi_{CO}} \quad (2)$$

Equation 3: mole fraction sum to unity:

$$\chi_{CO_2} + \chi_{CO} + \chi_{O_2} = 1 \quad (3)$$

## Solution continue

First we have *Notice  $\bar{g}^\circ$  is different from  $\hat{f}^\circ$  (Product - Reactant)*

$$\begin{aligned}\Delta G_T^0 &= \left( e\bar{g}_{f,E}^0 + f\bar{g}_{f,F}^0 + \dots - a\bar{g}_{f,A}^0 - b\bar{g}_{f,B}^0 - \dots \right)_T \\ &= \left[ \left( \frac{1}{2} \right) \bar{g}_{f,O_2}^0 + (1)\bar{g}_{f,CO}^0 - (1)\bar{g}_{f,CO_2}^0 \right]_{T=2500} \\ &= \left( \frac{1}{2} \right) 0 + (1)(-327,245) - (-396,152) \\ &= 68,907 \text{ kJ/kmol}\end{aligned}$$

From the definition of  $K_p$

$$K_p = \frac{(p_{CO}/p^0)^1 (p_{O_2}/p^0)^{0.5}}{(p_{CO_2}/p^0)^1}$$

By recognising  $p_i = \chi_i p$

$$K_p = \frac{(p_{CO}/p^0)^1 (p_{O_2}/p^0)^{0.5}}{(p_{CO_2}/p^0)^1} = \frac{\chi_{CO} \chi_{O_2}^{0.5}}{\chi_{CO_2}} \left( \frac{p}{p^0} \right)^{0.5}$$

Then we have

$$\frac{\chi_{CO} \chi_{O_2}^{0.5}}{\chi_{CO_2}} \left( \frac{p}{p^0} \right)^{0.5} = \exp \left[ \frac{-\Delta G_T^0}{R_0 T} \right] = 0.03635 \quad (1)$$

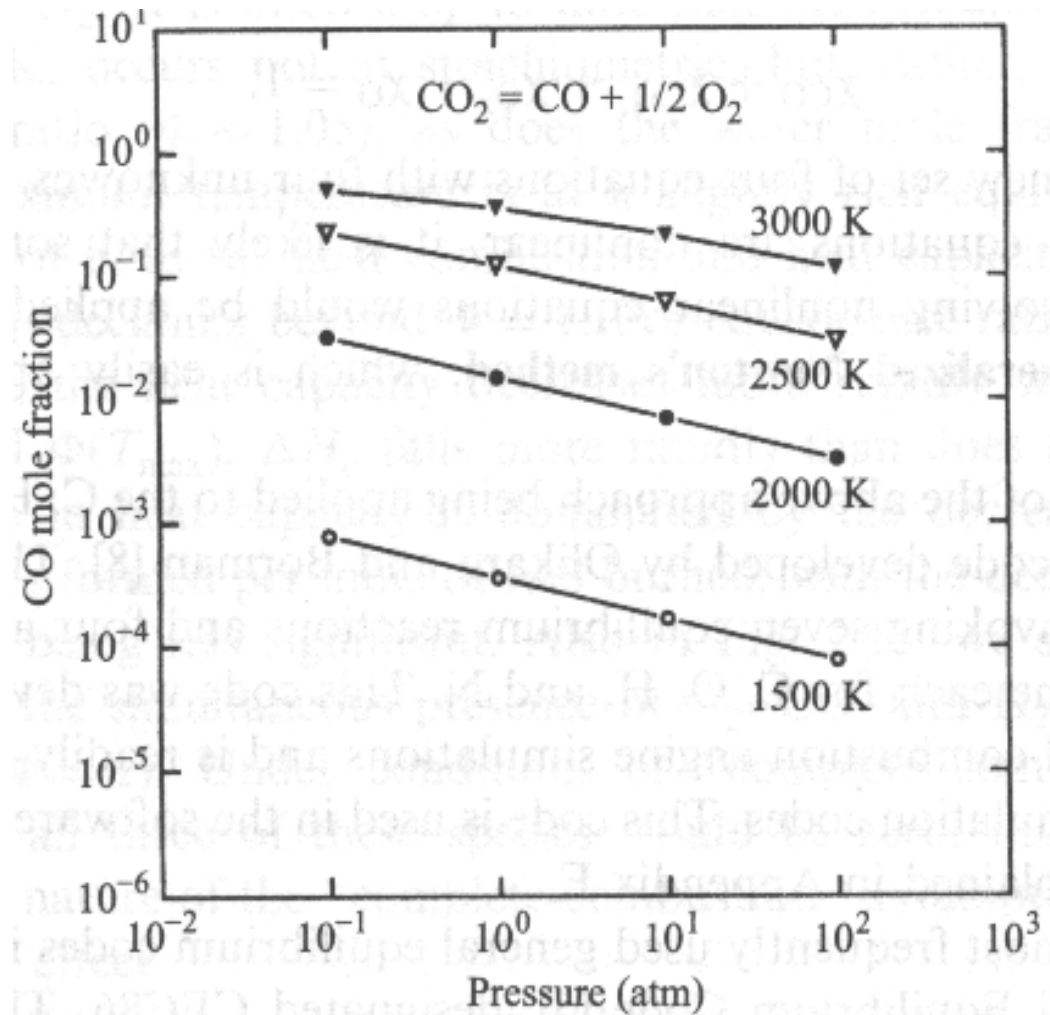
## Solution continue

We have 3 equations to solve 3 variables, requires iteration

	$P = 0.1 \text{ atm}$	$P = 1 \text{ atm}$	$P = 10 \text{ atm}$	$P = 100 \text{ atm}$
$T = 1500 \text{ K}, \Delta G_T^\circ = 1.5268 \cdot 10^8 \text{ J/kmol}$				
$\chi_{\text{CO}}$	$7.755 \cdot 10^{-4}$	$3.601 \cdot 10^{-4}$	$1.672 \cdot 10^{-4}$	$7.76 \cdot 10^{-5}$
$\chi_{\text{CO}_2}$	0.9988	0.9994	0.9997	0.9999
$\chi_{\text{O}_2}$	$3.877 \cdot 10^{-4}$	$1.801 \cdot 10^{-4}$	$8.357 \cdot 10^{-5}$	$3.88 \cdot 10^{-5}$
$T = 2000 \text{ K}, \Delta G_T^\circ = 1.10462 \cdot 10^8 \text{ J/kmol}$				
$\chi_{\text{CO}}$	0.0315	0.0149	$6.96 \cdot 10^{-3}$	$3.243 \cdot 10^{-3}$
$\chi_{\text{CO}_2}$	0.9527	0.9777	0.9895	0.9951
$\chi_{\text{O}_2}$	0.0158	0.0074	$3.48 \cdot 10^{-3}$	$1.622 \cdot 10^{-3}$
$T = 2500 \text{ K}, \Delta G_T^\circ = 6.8907 \cdot 10^7 \text{ J/kmol}$				
$\chi_{\text{CO}}$	0.2260	0.1210	0.0602	0.0289
$\chi_{\text{CO}_2}$	0.6610	0.8185	0.9096	0.9566
$\chi_{\text{O}_2}$	0.1130	0.0605	0.0301	0.0145
$T = 3000 \text{ K}, \Delta G_T^\circ = 2.7878 \cdot 10^7 \text{ J/kmol}$				
$\chi_{\text{CO}}$	0.5038	0.3581	0.2144	0.1138
$\chi_{\text{CO}_2}$	0.2443	0.4629	0.6783	0.8293
$\chi_{\text{O}_2}$	0.2519	0.1790	0.1072	0.0569

# Results

- At fixed temperature, increasing pressure suppresses the dissociation
- Increasing temperature at fixed pressure promotes the dissociation
- Any system initially in a state of equilibrium when subject to a change will shift in composition in such a way to minimise the change (**principle of Le Châtelier**)
  - Increasing pressure, shift to  $\text{CO}_2$  side
  - Increasing temperature, shift to  $\text{CO} + \text{O}_2$  side (endothermic reaction)



# Equilibrium products of combustion

Full equilibrium

Combine the **First Law**, the **complex chemical equilibrium** and **element conservation**,

Obtain:

**the adiabatic flame temperature** and **detailed composition of the products of combustion**

Example:

Propane ( $\text{C}_3\text{H}_8$ ) –air combustion at 1 atm, major products include  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{H}$ ,  $\text{OH}$ ,  $\text{O}_2$ ,  $\text{O}$ ,  $\text{NO}$ ,  $\text{N}_2$ , and  $\text{N}$

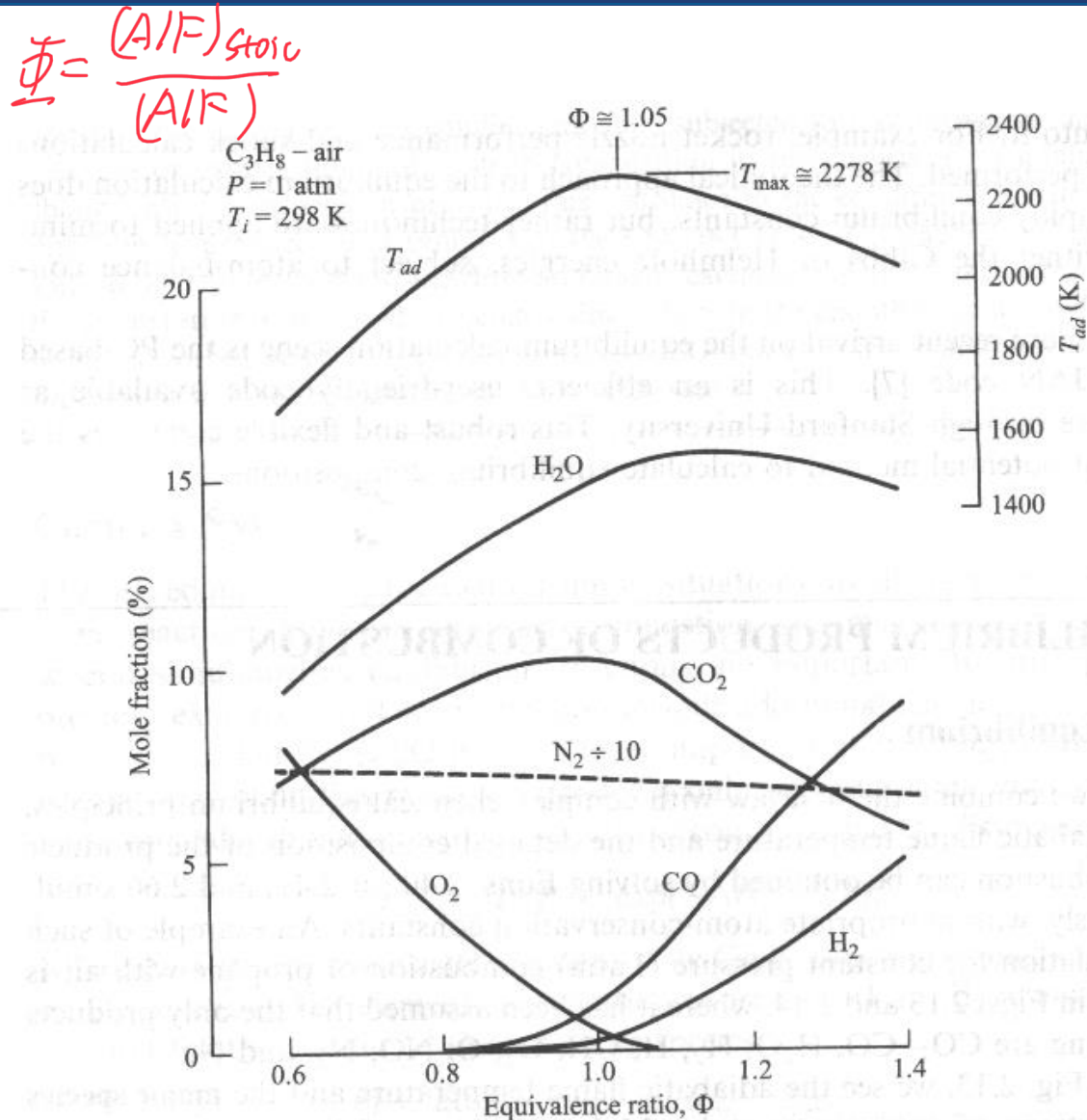
Lean combustion products:  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{O}_2$  and  $\text{N}_2$

Rich combustion products:  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2$ , and  $\text{N}_2$



# Propane combustion major products

- Maximum flame temperature 2278.4 K occurred at slightly rich ( $\Phi=1.05$ ), does the water mole fraction ( $\Phi=1.15$ )
- A consequence of both the heat of combustion and heat capacity of the products declining beyond  $\Phi=1$

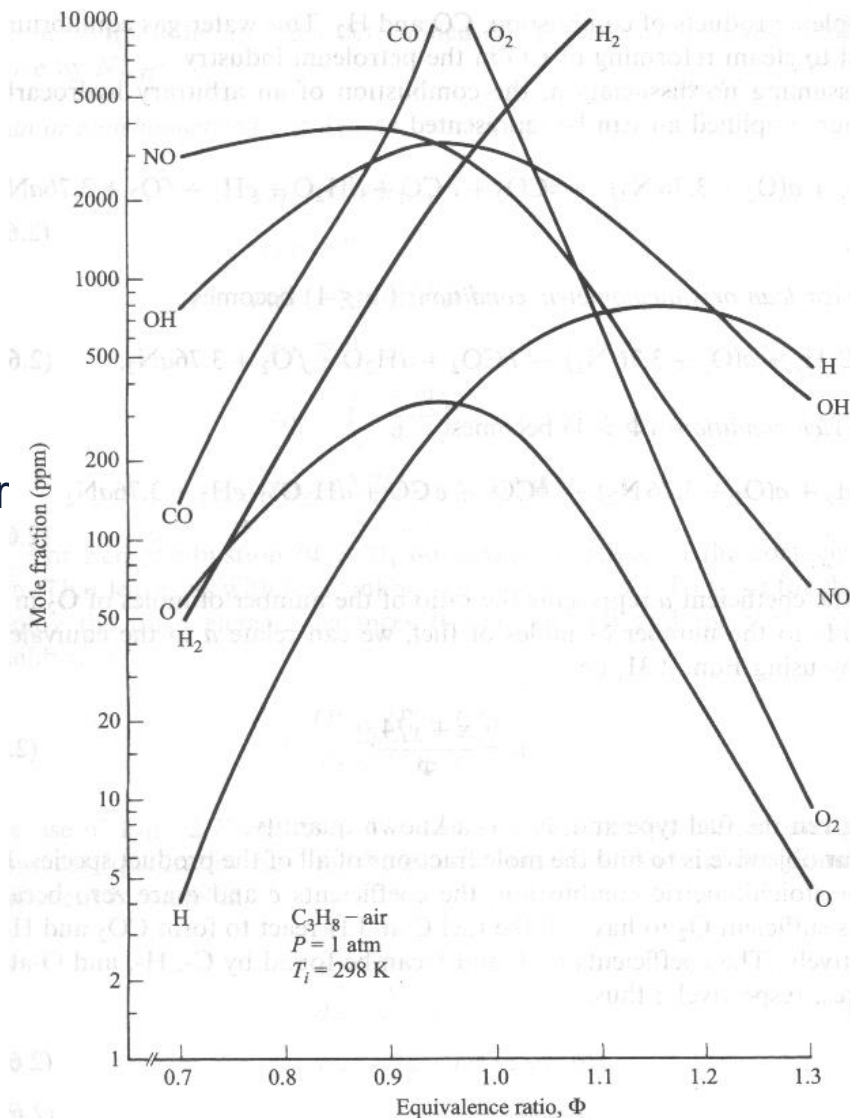


# Propane combustion minor products

Minor products O, H, OH and NO, all below 4000 ppm. CO is a minor product at lean combustion, O<sub>2</sub> is a minor product at rich combustion.

## Note:

- The level of the hydroxyl radical OH is more than an order of magnitude greater than the O atom.
- N atom is several orders of magnitude less than O atom.
- The lack of dissociation of the N<sub>2</sub> molecule is a result of the strong triple covalent bond.
- NO concentrations are flat and peak in lean region, falling rapidly in rich region. In most combustion system, NO concentration is below equilibrium (chemical kinetics).



- Stoichiometric reaction
- Enthalpy of formation
- Enthalpy of reaction and enthalpy of combustion, lower/higher heating values
- Adiabatic flame temperatures (constant pressure and constant volume)
- Chemical equilibrium
- Gibbs free energy and Gibbs function
- Gibbs function of formation and standard-state Gibbs function change