CHEMICAL REACTION

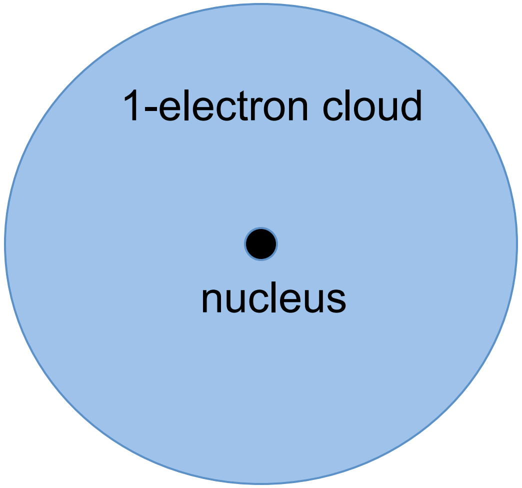
- I am teaching Engineering Thermodynamics to a class of 75 undergraduate students.
- I plan to go through these slides in one 90-minute lecture.

Zhigang Suo, Harvard University

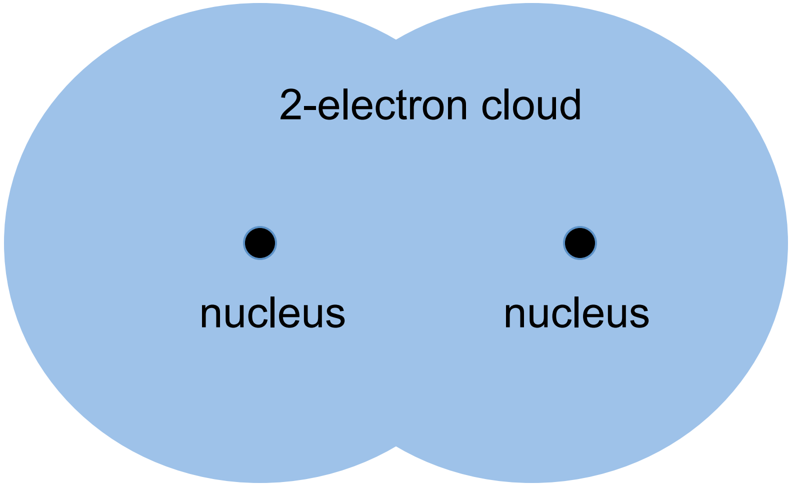
Before coming to class, please watch these videos on **fuel cells:**
Video 1: https://www.youtube.com/watch?v=Mon06rujCOM
Video 2: https://www.youtube.com/watch?v=R15R54oZAdA&list=PLZbRNoceG6UmxLgueFB1XBc_HDwY6_HpD&index=2

Atom, molecule, and chemical bond

hydrogen atom, H
nucleus
electron



hydrogen molecule, H_2
molecule
chemical bond

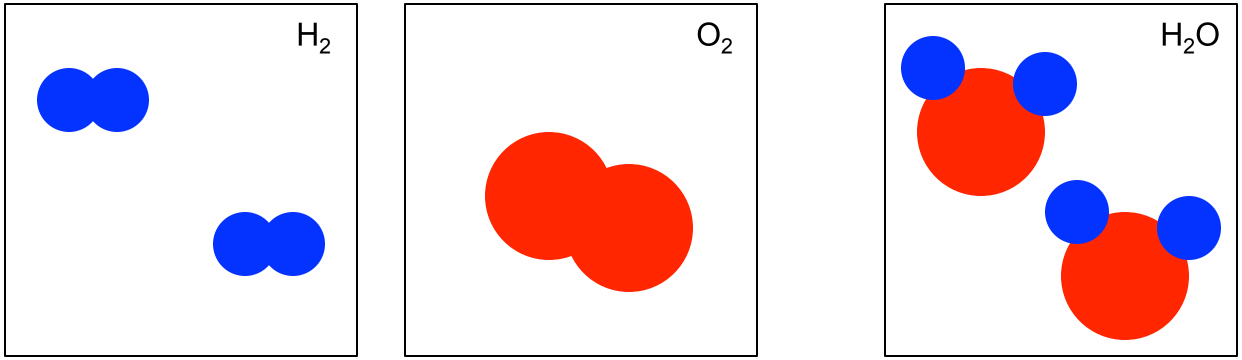


Chemical reaction

beaks and reforms **chemical bonds**

destroys and creates **molecules**

conserves the number of **atoms** in each species



$$2H_2 + O_2 \rightarrow 2H_2O$$

$$(\text{reactant 1}) + (\text{reactant 2}) + \ldots \rightarrow (\text{product 1}) + (\text{product 2}) + \ldots$$

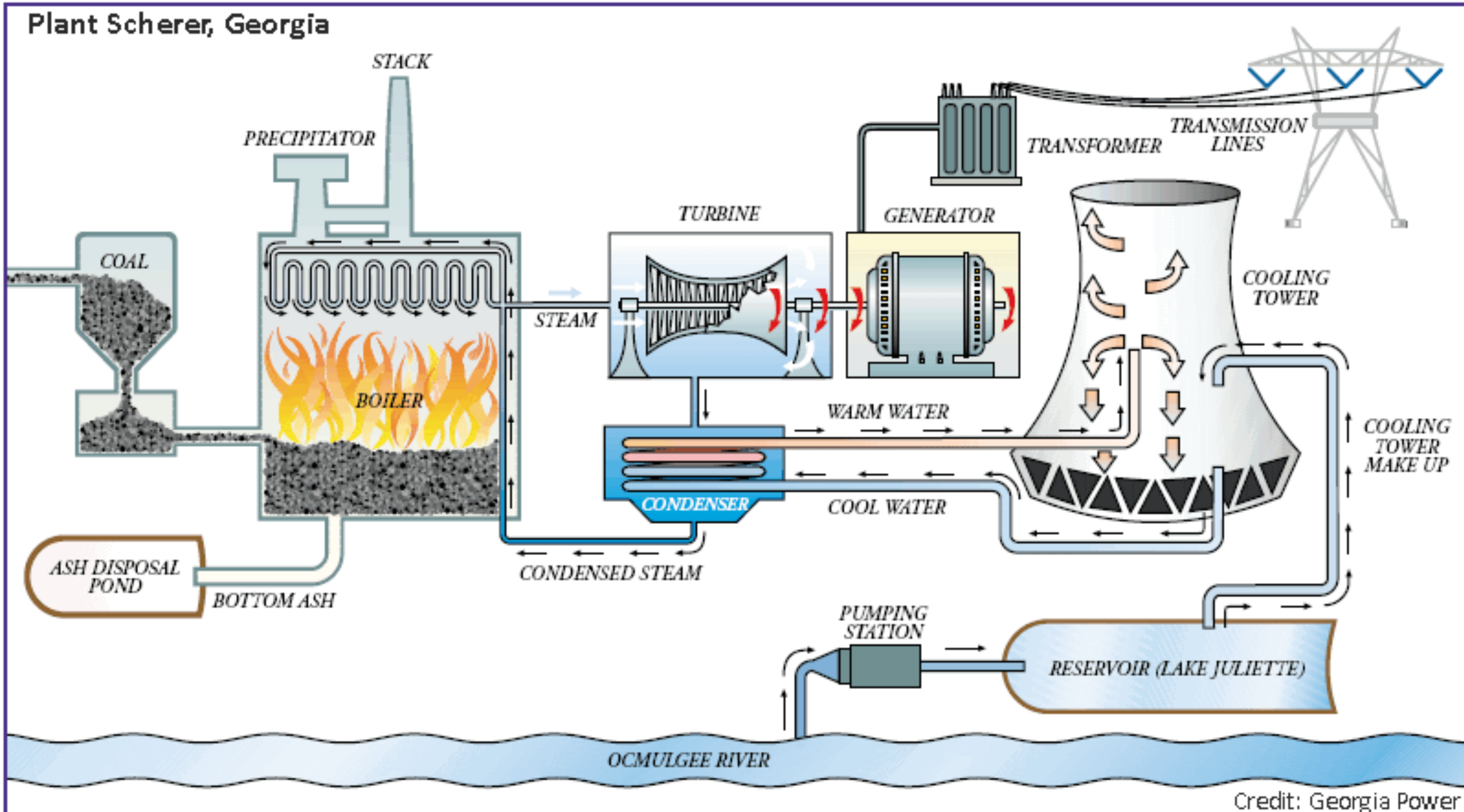
Plan

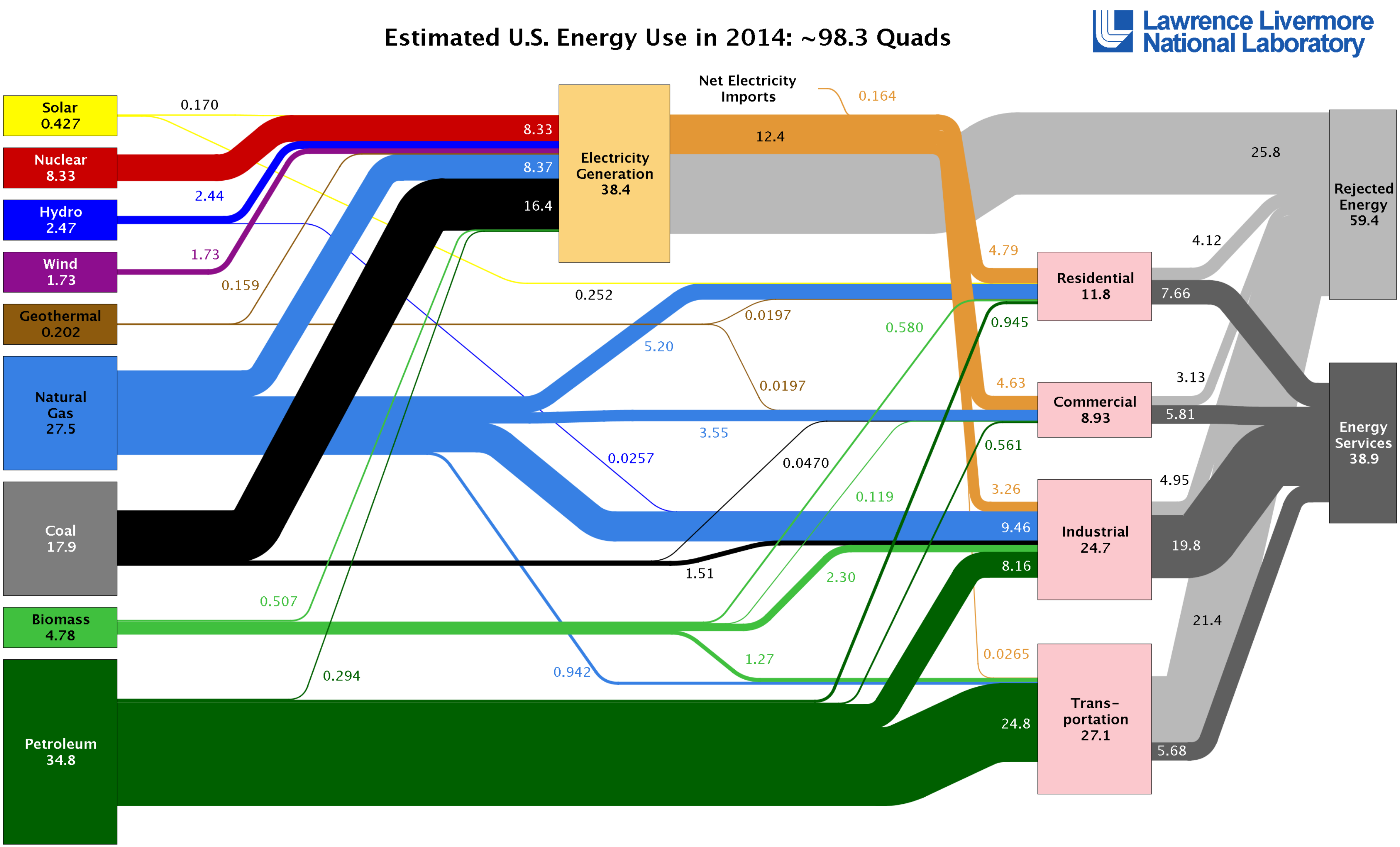
- Fossil-fueled civilization
- Conservation of mass
- Conservation of energy
- Generation of entropy

Combustion

A fuel and oxygen react, produce **other molecules**, and release energy by **heat**.

$C + O_2 \rightarrow CO_2$, heat out

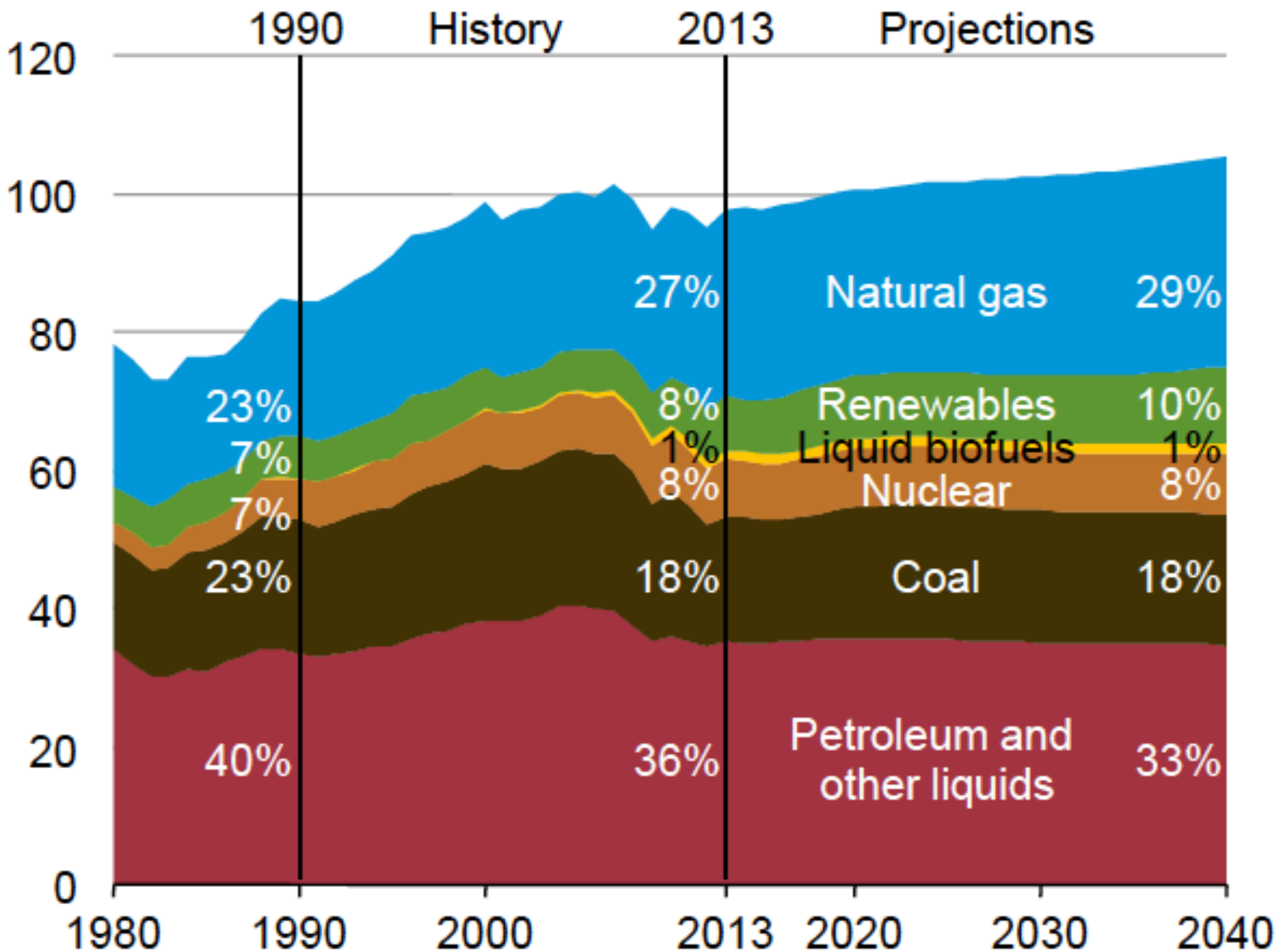




Source: LLNL 2015. Data is based on DOE/EIA-0035(2015-03), March, 2014. If this information or a reproduction of it is used, credit must be given to the Lawrence Livermore National Laboratory and the Department of Energy, under whose auspices the work was performed. Distributed electricity represents only retail electricity sales and does not include self-generation. EIA reports consumption of renewable resources (i.e., hydro, wind, geothermal and solar) for electricity in BTU-equivalent values by assuming a typical fossil fuel plant "heat rate." The efficiency of electricity production is calculated as the total retail electricity delivered divided by the primary energy input into electricity generation. End use efficiency is estimated as 65% for the residential and commercial sectors 80% for the industrial sector, and 21% for the transportation sector. Totals may not equal sum of components due to independent rounding. LLNL-MI-410527

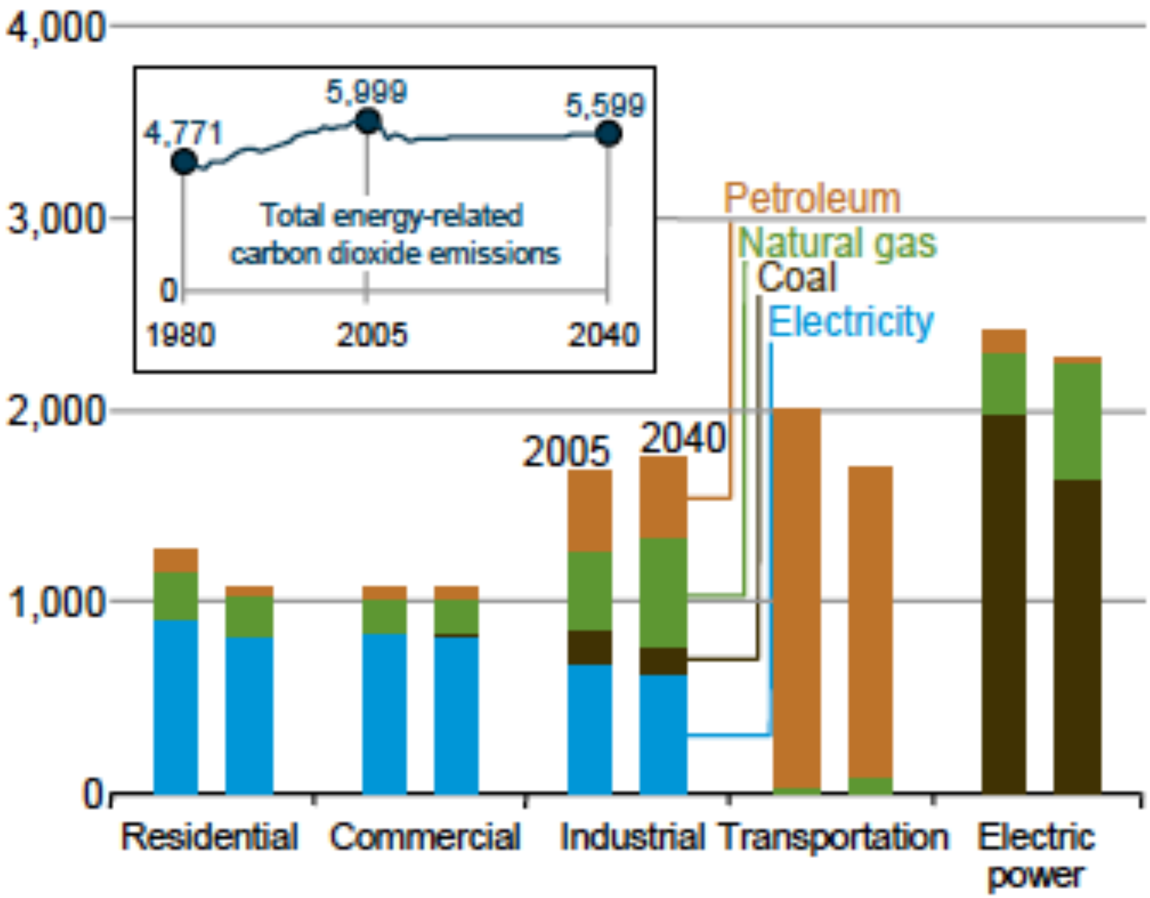
https://flowcharts.llnl.gov/

Figure 18. Primary energy consumption by fuel in the Reference case, 1980-2040 (quadrillion Btu)



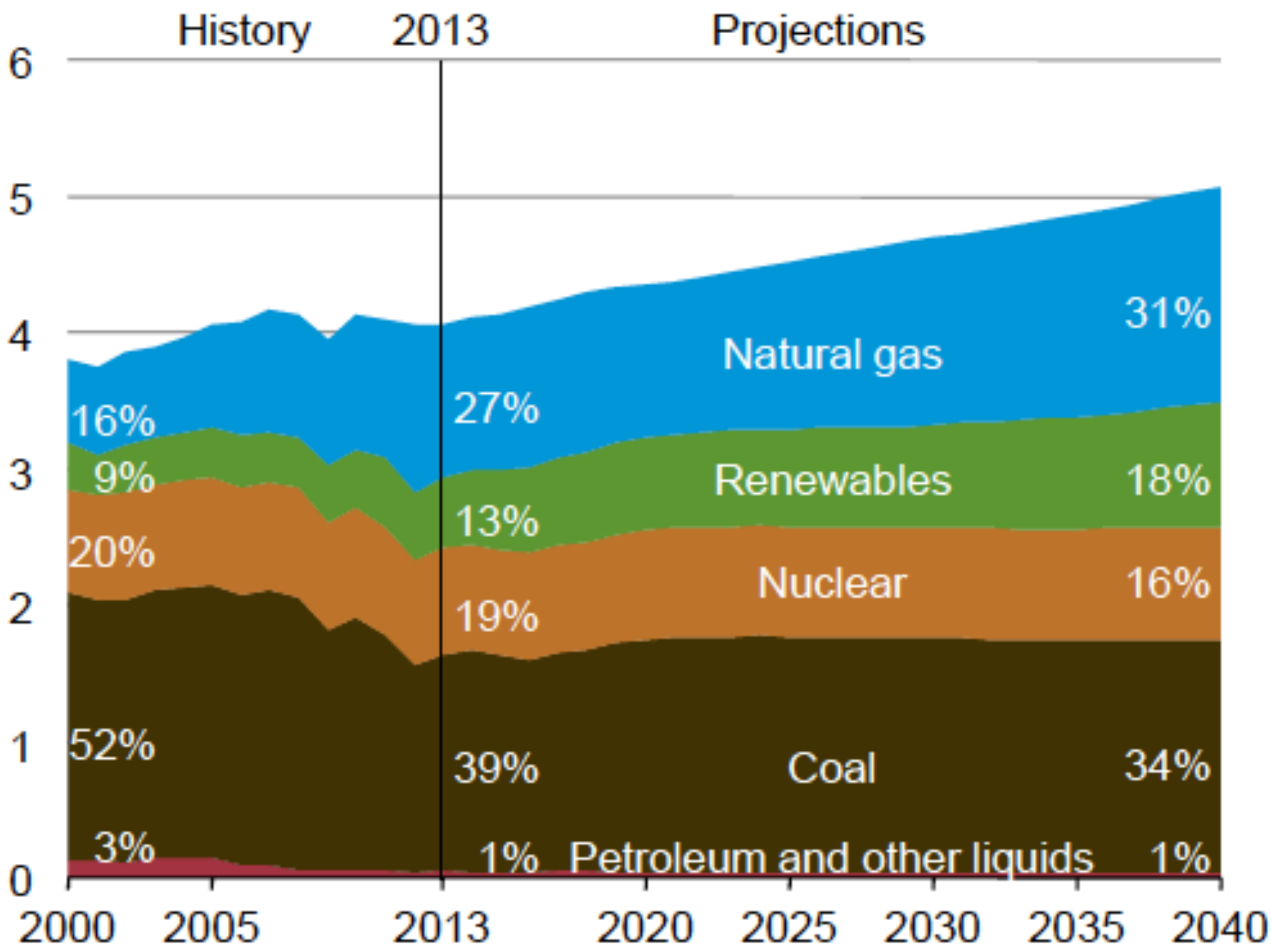
Annual Energy Outlook 2015, Prepared by US Energy Information Administration (EIA)

Figure MT-64. U.S. energy-related carbon dioxide emissions by sector and fuel in the Reference case, 2005 and 2040 (million metric tons)



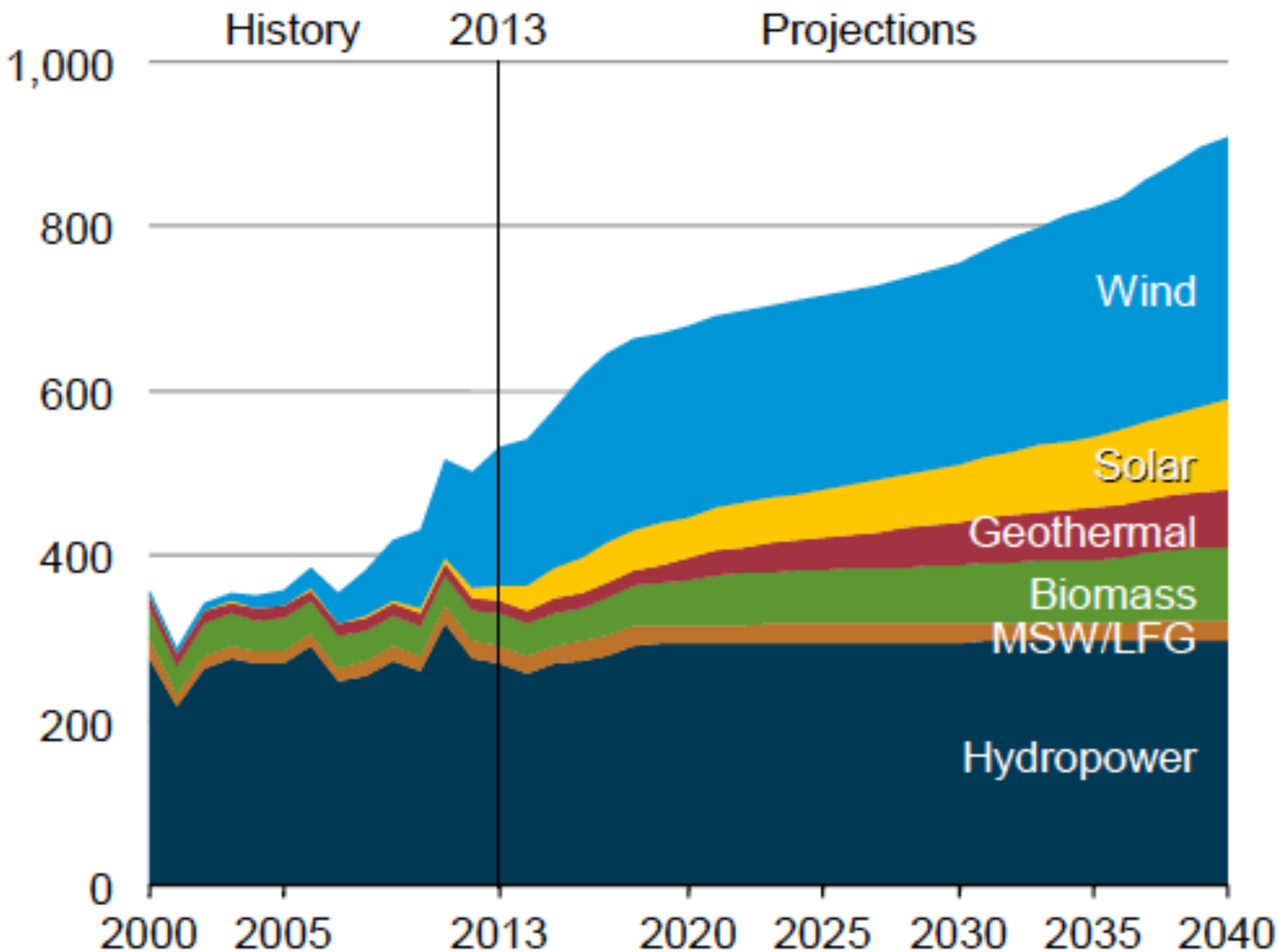
Annual Energy Outlook 2014, Prepared by US Energy Information Administration (EIA)

Figure 31. Electricity generation by fuel in the Reference case, 2000-2040 (trillion kilowatthours)



Annual Energy Outlook 2015, Prepared by US Energy Information Administration (EIA)

Figure 34. Renewable electricity generation by fuel type in the Reference case, 2000-2040 (billion kilowatthours)



Annual Energy Outlook 2015, Prepared by US Energy Information Administration (EIA)

On 18 November 2015, the UK energy secretary proposes to close all Britain's coal-fired power plants by 2025.

http://www.economist.com/news/britain/21678760-another-u-turn-electricity-will-not-solve-britains-power-crunch-not-boring-enough

The Stone Age did not end because humans ran out of stones. It ended because it was time for a re-think about how we live.

William McDonough

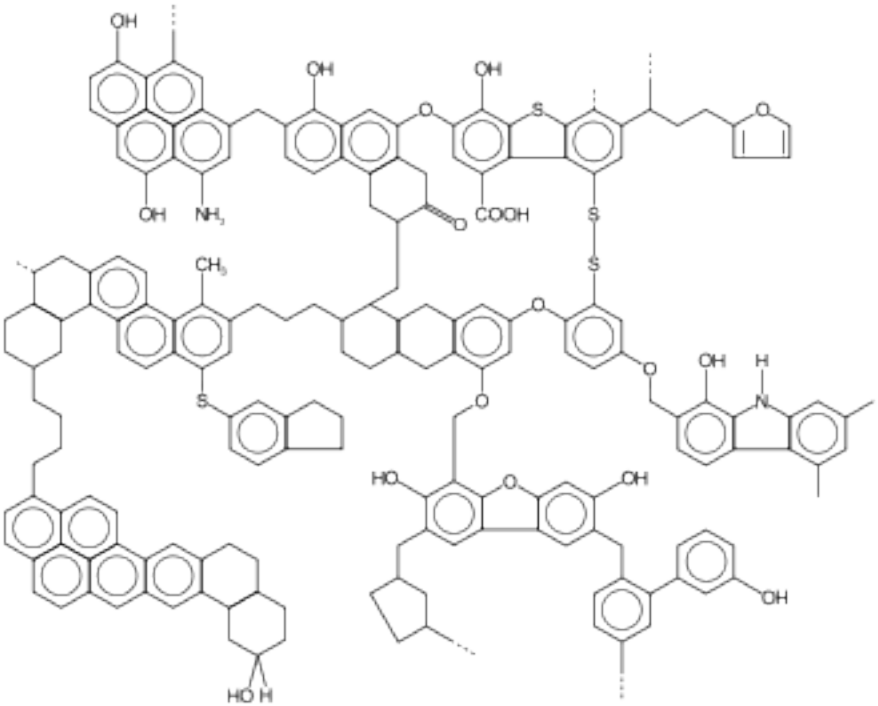
Plan

- Fossil-fueled civilization
- Conservation of mass
- Conservation of energy
- Generation of entropy

Coal

Earliest recognized use: China 4000 BC
Industrial Revolution
Pollution

Composition
carbon
hydrogen
sulfur
oxygen
nitrogen



https://en.wikipedia.org/wiki/Coal

Petroleum

ships, cars, airplanes
Rockefeller, Middle East

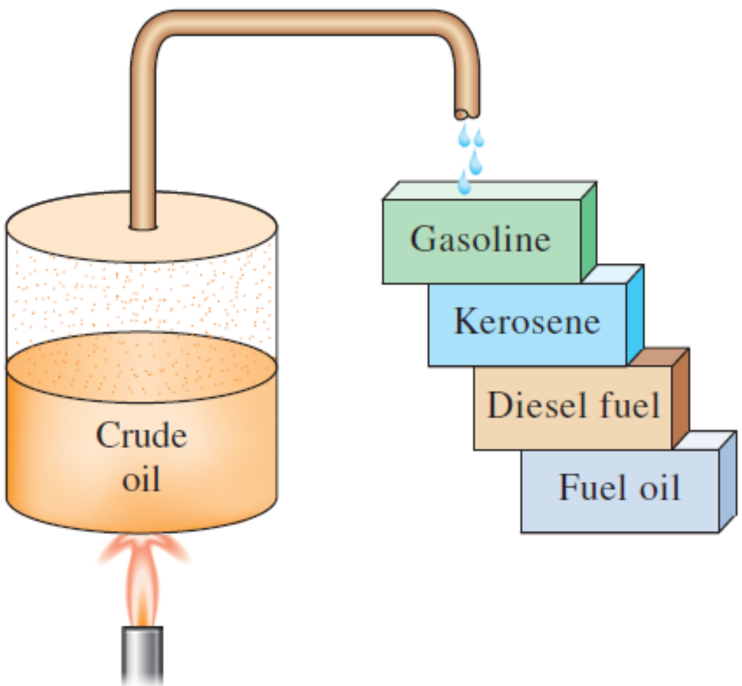


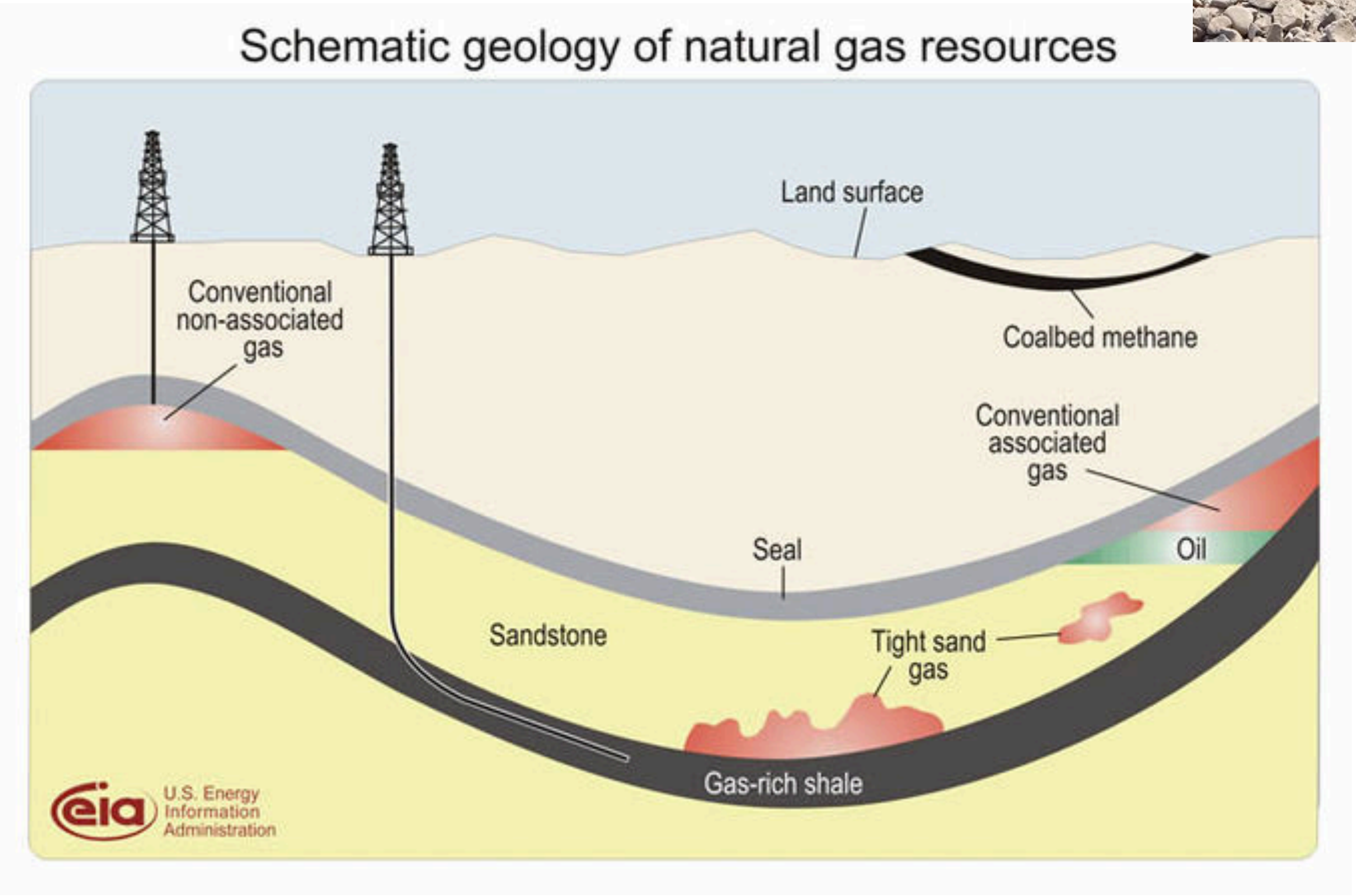
FIGURE 15–1
Most liquid hydrocarbon fuels are obtained from crude oil by distillation.

fuel	molecule	formula
gasoline	octane	C_8H_{18}
diesel fuel	dodecane	$C_{12}H_{26}$

Yergin, The Prize, 1991

Natural gas

primarily methane, CH_4



https://en.wikipedia.org/wiki/Natural_gas

Dry air

gas	formula	molar mass, kg/kmol	number fraction
nitrogen	N_2	28.02	0.7809
oxygen	O_2	32.00	0.2095
argon	Ar	39.94	0.0933
carbon dioxide	CO_2	44.01	0.0003

- In analyzing combustion, we approximate dry air as 0.21 O_2 and 0.79 N_2 by number fraction.
- 0.79/0.21 = 3.76
- (1 kmol of O_2) + (3.76 kmol of N_2) = (4.76 kmol of air)
- Oxygen participates in combustion.
- Nitrogen does not participates in combustion.

Complete combustion

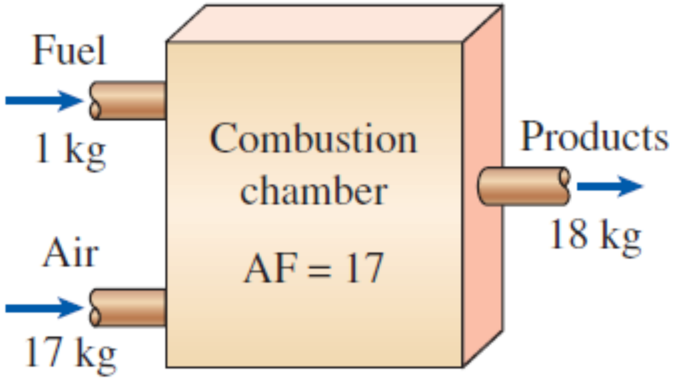
- All the carbon in the fuel burns to CO_2
- All the hydrogen burns to H_2O
- All the sulfur (if any) burns to SO_2.

Air-fuel ratio

$$\left(\text{Air-fuel ratio}\right) = \frac{\left(\text{mass of air}\right)}{\left(\text{mass of fuel}\right)}$$

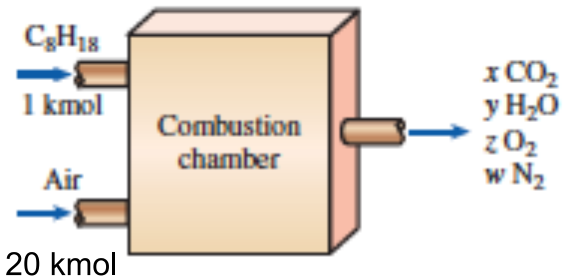
$$AF = \frac{m_{\text{air}}}{m_{\text{fuel}}}$$

m = nM
m = mass
n = number of moles
M = molar mass



Stoichiometry

Chemical reaction conserves the number of atoms in each species.



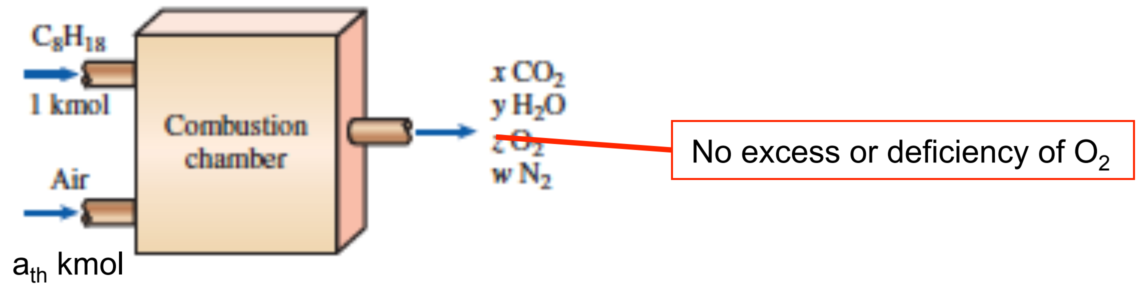
$$C_8H_{18} + 20(O_2 + 3.76N_2) \rightarrow xCO_2 + yH_2O + zO_2 + 20(3.76N_2)$$

C:	8 = x	x = 8
H:	18 = 2y	y = 9
O:	40 = 2x + y + 2z	z = 7.5

$$C_8H_{18} + 20(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O + 7.5O_2 + 20(3.76N_2)$$

Theoretical air

Air containing just right amount of oxygen to complete combustion



$$C_8H_{18} + a_{th}\left(O_2 + 3.76N_2\right) \rightarrow xCO_2 + yH_2O + a_{th}\left(3.76N_2\right)$$

C:	$8 = x$	$x = 8$
H:	$18 = 2y$	$y = 9$
O:	$2a_{th} = 2x + y$	$a_{th} = 12.5$

$$C_8H_{18} + 12.5\left(O_2 + 3.76N_2\right) \rightarrow 8CO_2 + 9H_2O + 12.5\left(3.76N_2\right)$$

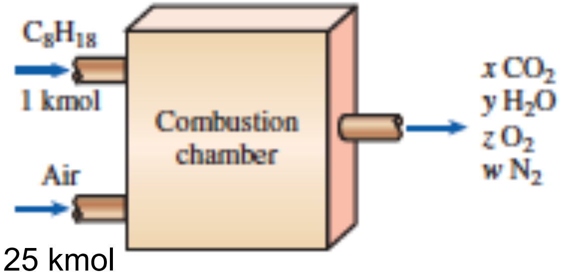
Excess air

Example: 100% excess air = 200% theoretical air

Combustion in theoretical air: $C_8H_{18} + 12.5(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O + 12.5(3.76N_2)$

Theoretical air: $a_{th} = 12.5$

Combustion in 100% excess air: $a = (200\%)a_{th} = 25$



Combustion in excess air $C_8H_{18} + 25(O_2 + 3.76N_2) \rightarrow xCO_2 + yH_2O + zO_2 + 25(3.76N_2)$

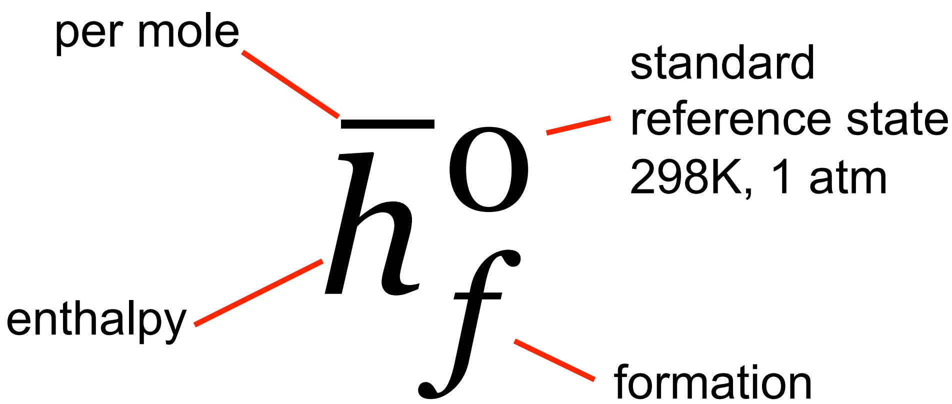
C:	8 = x	x = 8
H:	18 = 2y	y = 9
O:	50 = 2x + y + 2z	z = 12.5

$$C_8H_{18} + 25(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O + 12.5O_2 + 25(3.76N_2)$$

Plan

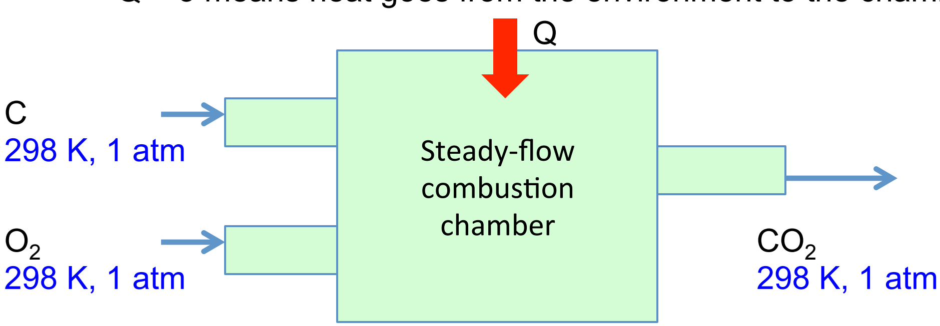
- Fossil-fueled civilization
- Conservation of mass
- Conservation of energy
- Generation of entropy

Enthalpy of formation



$$\bar{h}_f^o = Q = -393{,}520\,\mathrm{kJ/kmol}$$

Sign convention
Q > o means heat goes from the environment to the chamber



C + O_2 → CO_2, heat out

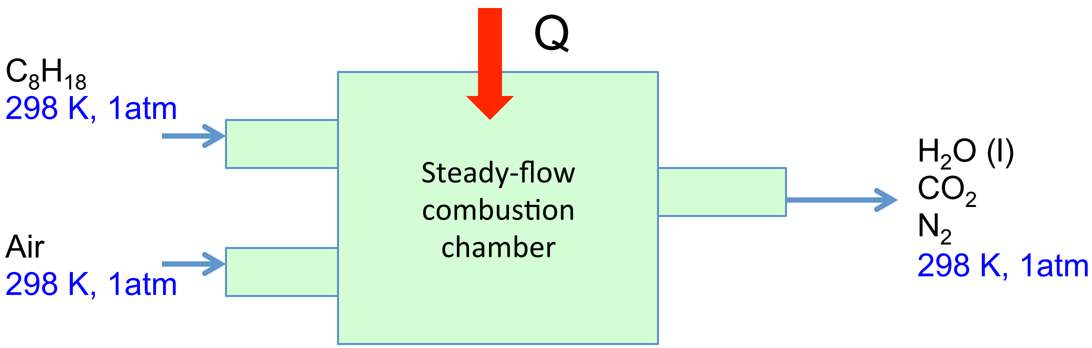
TABLE A–26

Enthalpy of formation, Gibbs function of formation
25°C, 1 atm

Substance	Formula	$\bar{h}_f^o$ kJ/kmol
Carbon	$C(s)$	0
Hydrogen	$H_2(g)$	0
Nitrogen	$N_2(g)$	0
Oxygen	$O_2(g)$	0
Carbon monoxide	$CO(g)$	−110,530
Carbon dioxide	$CO_2(g)$	−393,520
Water vapor	$H_2O(g)$	−241,820
Water	$H_2O(\ell)$	−285,830
Hydrogen peroxide	$H_2O_2(g)$	−136,310
Ammonia	$NH_3(g)$	−46,190
Methane	$CH_4(g)$	−74,850
Acetylene	$C_2H_2(g)$	+226,730
Ethylene	$C_2H_4(g)$	+52,280
Ethane	$C_2H_6(g)$	−84,680
Propylene	$C_3H_6(g)$	+20,410
Propane	$C_3H_8(g)$	−103,850
n-Butane	$C_4H_{10}(g)$	−126,150
n-Octane	$C_8H_{18}(g)$	−208,450
n-Octane	$C_8H_{18}(\ell)$	−249,950
n-Dodecane	$C_{12}H_{26}(g)$	−291,010
Benzene	$C_6H_6(g)$	+82,930
Methyl alcohol	$CH_3OH(g)$	−200,670
Methyl alcohol	$CH_3OH(\ell)$	−238,660
Ethyl alcohol	$C_2H_5OH(g)$	−235,310
Ethyl alcohol	$C_2H_5OH(\ell)$	−277,690
Oxygen	$O(g)$	+249,190
Hydrogen	$H(g)$	+218,000
Nitrogen	$N(g)$	+472,650
Hydroxyl	$OH(g)$	+39,460

Enthalpy of combustion

$$\bar{h}_C = Q = \sum\left(n\bar{h}_f^o\right)_p - \sum\left(n\bar{h}_f^o\right)_r$$



$$C_8H_{18}(l) + a_{th}(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O(l) + a_{th}(3.76N_2)$$

$$\begin{aligned}
\bar{h}_C &= \sum\left(n\bar{h}_f^o\right)_p - \sum\left(n\bar{h}_f^o\right)_r \\
&= \left(n\bar{h}_f^o\right)_{CO_2} + \left(n\bar{h}_f^o\right)_{H_2O(l)} - \left(n\bar{h}_f^o\right)_{C_8H_{18}} \\
&= (8\text{kmol})(-393.520\text{kJ/kmol}) \\
&\quad + (9\text{kmol})(-285{,}830\text{kJ/kmol}) \\
&\quad - (1\text{kmol})(-249{,}950\text{kJ/kmol}) \\
&= -5{,}470{,}680\text{kJ/kmol } C_8H_{18}
\end{aligned}$$

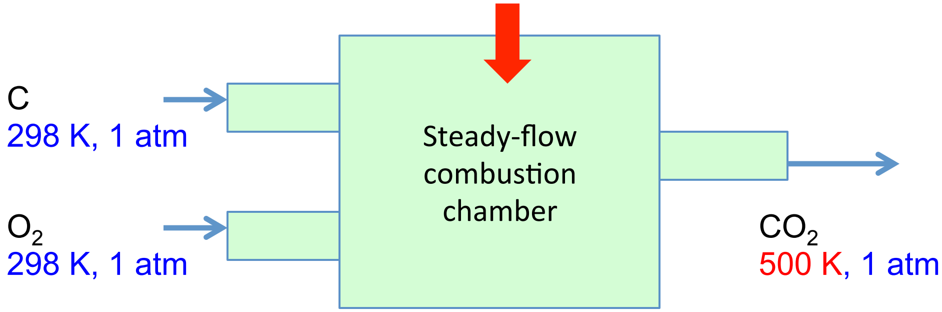
TABLE A–26

Enthalpy of formation, Gibbs function of formation
25°C, 1 atm

Substance	Formula	$\bar{h}_f^o$ kJ/kmol
Carbon	$C(s)$	0
Hydrogen	$H_2(g)$	0
Nitrogen	$N_2(g)$	0
Oxygen	$O_2(g)$	0
Carbon monoxide	$CO(g)$	−110,530
Carbon dioxide	$CO_2(g)$	−393,520
Water vapor	$H_2O(g)$	−241,820
Water	$H_2O(\ell)$	−285,830
Hydrogen peroxide	$H_2O_2(g)$	−136,310
Ammonia	$NH_3(g)$	−46,190
Methane	$CH_4(g)$	−74,850
Acetylene	$C_2H_2(g)$	+226,730
Ethylene	$C_2H_4(g)$	+52,280
Ethane	$C_2H_6(g)$	−84,680
Propylene	$C_3H_6(g)$	+20,410
Propane	$C_3H_8(g)$	−103,850
n-Butane	$C_4H_{10}(g)$	−126,150
n-Octane	$C_8H_{18}(g)$	−208,450
n-Octane	$C_8H_{18}(\ell)$	−249,950
n-Dodecane	$C_{12}H_{26}(g)$	−291,010
Benzene	$C_6H_6(g)$	+82,930
Methyl alcohol	$CH_3OH(g)$	−200,670
Methyl alcohol	$CH_3OH(\ell)$	−238,660
Ethyl alcohol	$C_2H_5OH(g)$	−235,310
Ethyl alcohol	$C_2H_5OH(\ell)$	−277,690
Oxygen	$O(g)$	+249,190
Hydrogen	$H(g)$	+218,000
Nitrogen	$N(g)$	+472,650
Hydroxyl	$OH(g)$	+39,460

Enthalpy

$$H = n\left(\bar{h}_f^o + \bar{h} - \bar{h}^o\right)$$



$$C + O_2 \rightarrow CO_2$$

$$H_{CO_2} = n_{CO_2}\left(\bar{h}_f^o + \bar{h}_{500} - \bar{h}_{298}\right)_{CO_2}$$

$$= (1\,\text{kmol})(-393{,}520 + 17{,}678 - 9{,}364)\,\text{kJ/kmol}$$

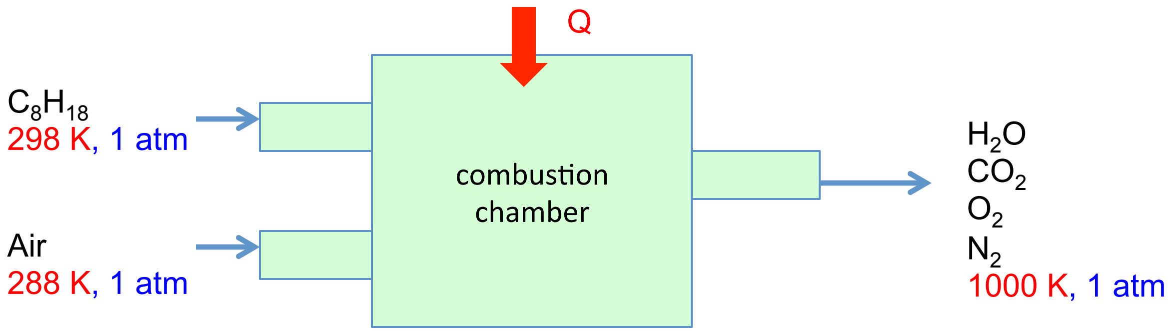
TABLE A–20

Ideal-gas properties of carbon dioxide, CO_2

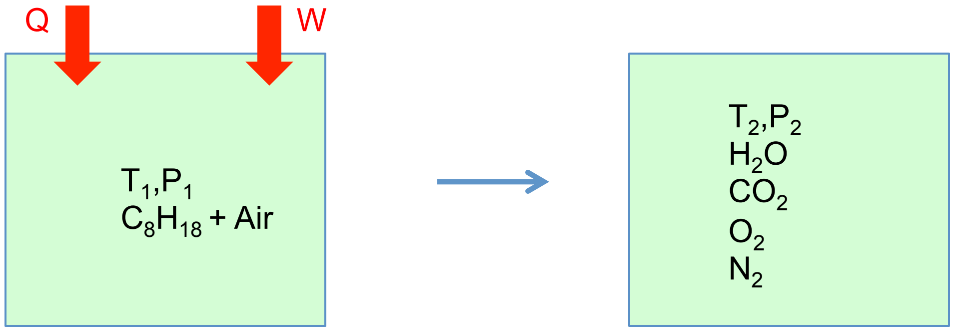
T K	$\bar{h}$ kJ/kmol	$\bar{u}$ kJ/kmol	$\bar{s}^o$ kJ/kmol·K
0	0	0	0
220	6,601	4,772	202.966
230	6,938	5,026	204.464
240	7,280	5,285	205.920
250	7,627	5,548	207.337
260	7,979	5,817	208.717
270	8,335	6,091	210.062
280	8,697	6,369	211.376
290	9,063	6,651	212.660
298	9,364	6,885	213.685
300	9,431	6,939	213.915
310	9,807	7,230	215.146
320	10,186	7,526	216.351
330	10,570	7,826	217.534
340	10,959	8,131	218.694
350	11,351	8,439	219.831
360	11,748	8,752	220.948
370	12,148	9,068	222.044
380	12,552	9,392	223.122
390	12,960	9,718	224.182
400	13,372	10,046	225.225
410	13,787	10,378	226.250
420	14,206	10,714	227.258
430	14,628	11,053	228.252
440	15,054	11,393	229.230
450	15,483	11,742	230.194
460	15,916	12,091	231.144
470	16,351	12,444	232.080
480	16,791	12,800	233.004
490	17,232	13,158	233.916
500	17,678	13,521	234.814
510	18,126	13,885	235.700
520	18,576	14,253	236.575
530	19,029	14,622	237.439
540	19,485	14,996	238.292
550	19,945	15,372	239.135
560	20,407	15,751	239.962
570	20,870	16,131	240.789
580	21,337	16,515	241.602
590	21,807	16,902	242.405

Steady flow

$$\dot{Q} = \sum \dot{n}_p \left(\bar{h}_f^{\,o} + \bar{h} - \bar{h}^{o} \right)_p - \sum \dot{n}_r \left(\bar{h}_f^{\,o} + \bar{h} - \bar{h}^{o} \right)_r$$



Closed system



$$Q + W = \sum n_p \bar{u}_p - \sum n_r \bar{u}_r$$
$$= \sum n_p \left(\bar{h}_f^o + \bar{h} - \bar{h}^o - P\bar{v} \right)_p - \sum n_r \left(\bar{h}_f^o + \bar{h} - \bar{h}^o - P\bar{v} \right)_r$$

The *Pv* terms are negligible for solids and liquids, and can be replaced by $R_u T$ for gases that behave as an ideal gas.

Adiabatic flame temperature

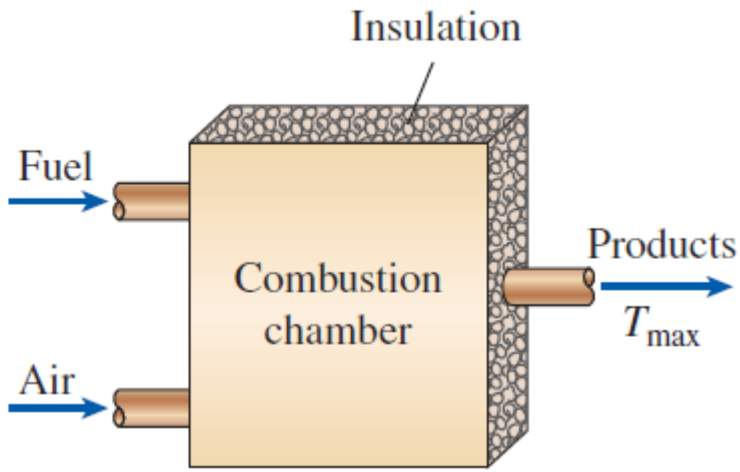


FIGURE 15–24
The temperature of a combustion chamber becomes maximum when combustion is complete and no heat is lost to the surroundings ($Q = 0$).

$$\sum\left(\dot{n}\bar{h}\right)_r = \sum\left(\dot{n}\bar{h}\right)_p$$

Calculating the adiabatic flame temperature by hand requires iteration.

Plan

- Fossil-fueled civilization
- Conservation of mass
- Conservation of energy
- Generation of entropy

Entropy is absolute

S = logΩ

TABLE A–26

Enthalpy of formation, Gibbs function of formation, and absolute entropy at 25°C, 1 atm

Substance	Formula	$\bar{h}_f^\circ$ kJ/kmol	$\bar{g}_f^\circ$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol·K
Carbon	C(*s*)	0	0	5.74
Hydrogen	$H_2(g)$	0	0	130.68
Nitrogen	$N_2(g)$	0	0	191.61
Oxygen	$O_2(g)$	0	0	205.04
Carbon monoxide	$CO(g)$	−110,530	−137,150	197.65
Carbon dioxide	$CO_2(g)$	−393,520	−394,360	213.80
Water vapor	$H_2O(g)$	−241,820	−228,590	188.83
Water	$H_2O(\ell)$	−285,830	−237,180	69.92
Hydrogen peroxide	$H_2O_2(g)$	−136,310	−105,600	232.63

TABLE A–18

Ideal-gas properties of nitrogen, N_2

T K	$\bar{h}$ kJ/kmol	$\bar{u}$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol·K
0	0	0	0
220	6,391	4,562	182.639
230	6,683	4,770	183.938
240	6,975	4,979	185.180
250	7,266	5,188	186.370

The entropy of a component of an ideal-gas mixture depends on the temperature and the **partial pressure** of the component.

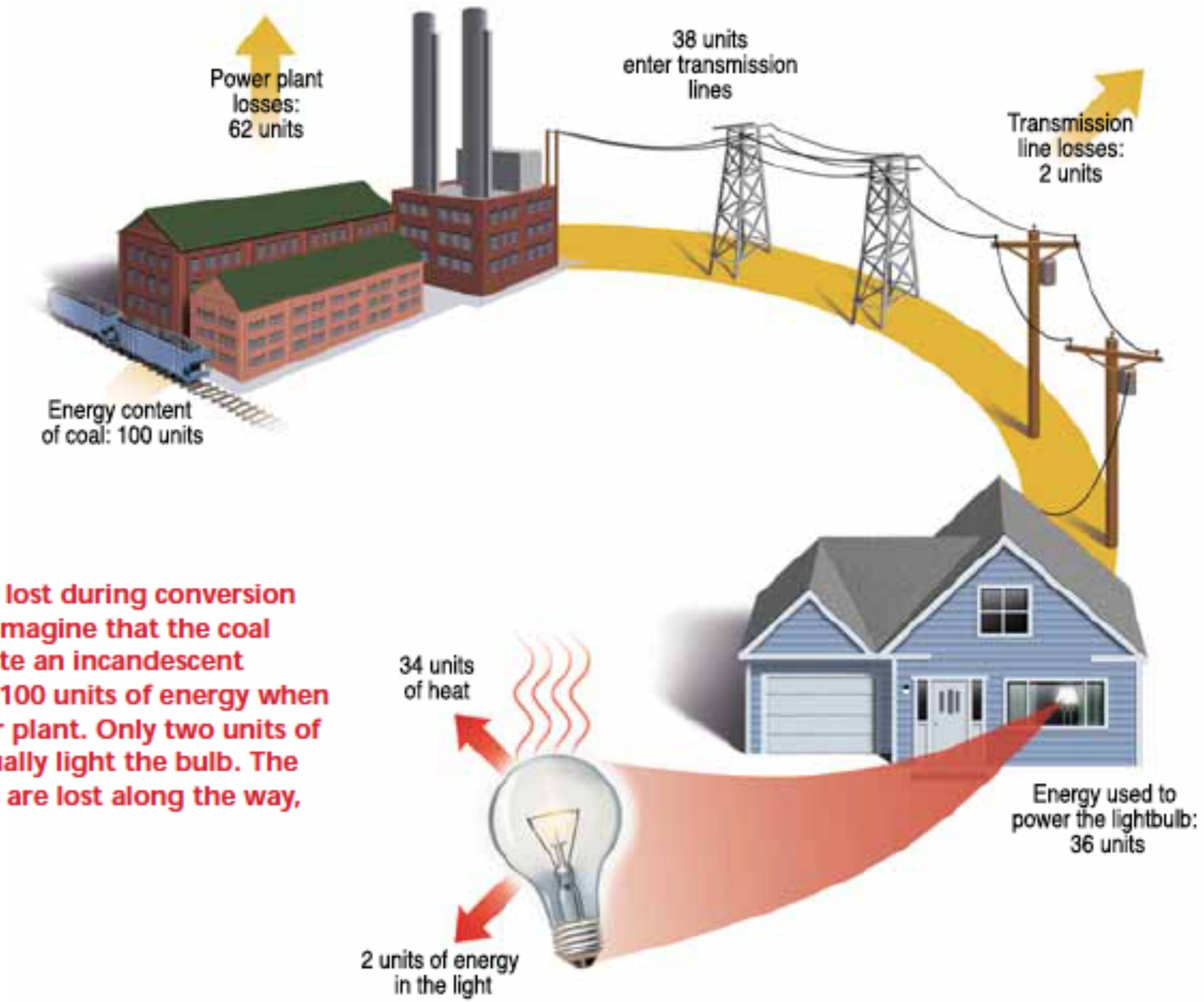
$$\bar{s}(T, P_i) = \bar{s}(T, P_o) - \bar{R}\log\frac{P_i}{P_o}$$

P_0 = 1 atm

P_i = $y_i P$, partial pressure

y_i number fraction

P total pressure of mixture.



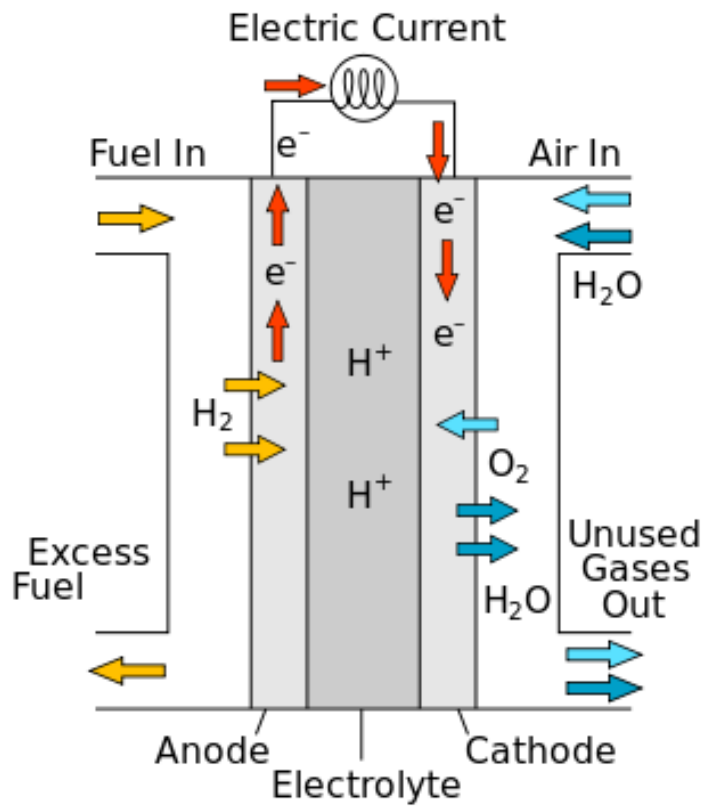
Example of energy lost during conversion and transmission. Imagine that the coal needed to illuminate an incandescent lightbulb contains 100 units of energy when it enters the power plant. Only two units of that energy eventually light the bulb. The remaining 98 units are lost along the way, primarily as heat.

What you need to know about energy, The National Academies.

Fuel cell

uses reaction to generate electricity directly, under **isothermal condition**.

Video 1: https://www.youtube.com/watch?v=Mon06rujCOM
Video 2: https://www.youtube.com/watch?v=R15R54oZAdA&list=PLZbRNoceG6UmxLgueFB1XBc_HDwY6_HpD&index=2

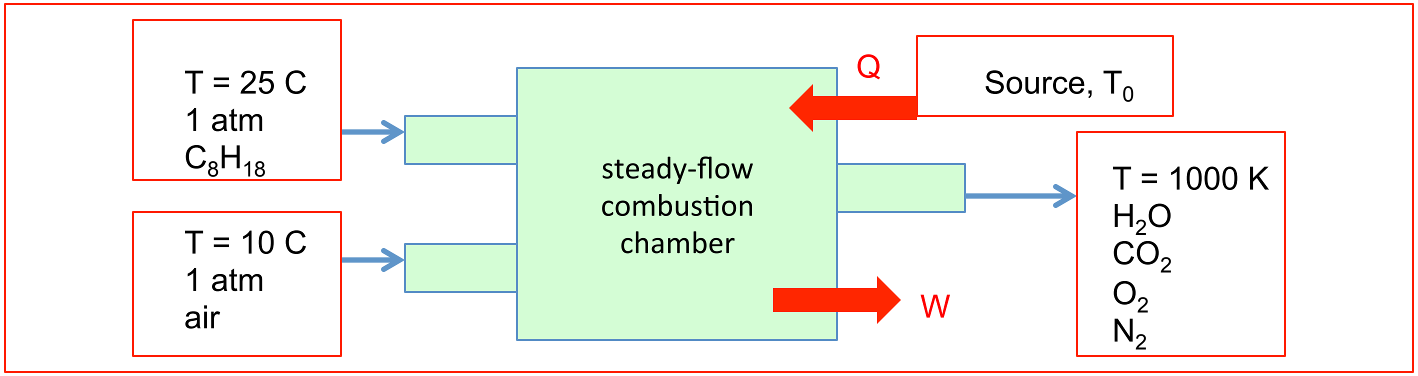


$$2H_2 \rightarrow 4H^+ + 4e^-$$

$$O_2 + 4e^- \rightarrow 2O^{-2}$$

$$2H_2 + O_2 \rightarrow 2H_2O$$

When confused, isolate



Energy is additive: $\dot{E}_{\mathrm{IS}} = \dot{Q} - \dot{W} + \sum\left(\dot{n}\bar{h}\right)_r - \sum\left(\dot{n}\bar{h}\right)_p$

Entropy is additive: $\dot{S}_{\mathrm{IS}} = \sum\left(\dot{n}\bar{s}\right)_r - \sum\left(\dot{n}\bar{s}\right)_p - \frac{\dot{Q}}{T_0}$

Isolated system conserves energy over time: $\dot{Q} - \dot{W} + \sum\left(\dot{n}\bar{h}\right)_r - \sum\left(\dot{n}\bar{h}\right)_p = 0$

Isolated system generates entropy over time: $\sum\left(\dot{n}\bar{s}\right)_r - \sum\left(\dot{n}\bar{s}\right)_p - \frac{\dot{Q}}{T_0} \geq 0$

Eliminate Q from the above two expressions: $\dot{W} \leq \sum \dot{n}_r\left(\bar{h} - T_0\bar{s}\right)_r - \sum \dot{n}_r\left(\bar{h} - T_0\bar{s}\right)_p$

Reversible process generates maximum work (constant P and T in reactants, products, and surroundings): $\dot{W}_{\mathrm{rev}} = \sum\left(\dot{n}\bar{g}\right)_r - \sum\left(\dot{n}\bar{g}\right)_p$

Reversible work

$$W_{\text{rev}} = \sum\left(n\bar{g}_f^o\right)_r - \sum\left(n\bar{g}_f^o\right)_p$$

$$2H_2 + O_2 \rightarrow 2H_2O$$

$$W_{\text{rev}} = (2\text{kmol})\bar{g}^o_{f,H_2} + (1\text{kmol})\bar{g}^o_{f,O_2} - (2\text{kmol})\bar{g}^o_{f,H_2O(l)}$$
$$= 0 + 0 - (2\text{kmol})(-237{,}180\text{kJ/kmol}) = 474{,}360\text{kJ/mole of } O_2$$

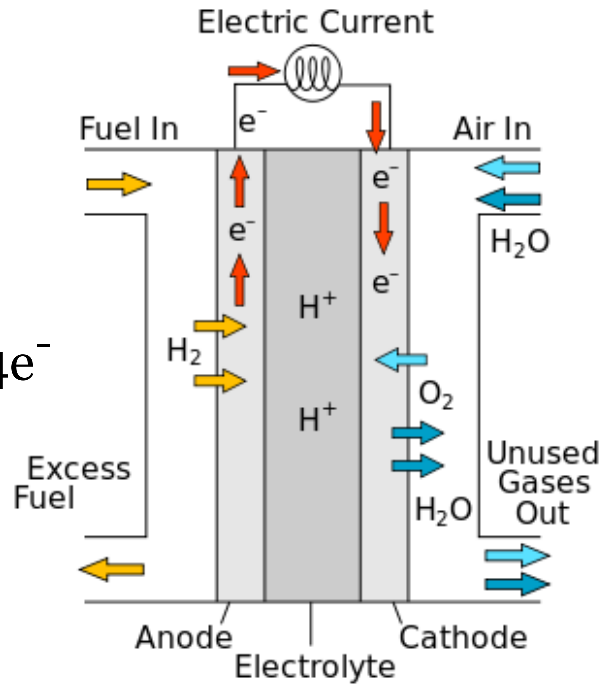
TABLE A–26

Enthalpy of formation, Gibbs function of formation, and absolute entropy at 25°C, 1 atm

Substance	Formula	$\bar{h}_f^\circ$ kJ/kmol	$\bar{g}_f^\circ$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol·K
Carbon	C(*s*)	0	0	5.74
Hydrogen	$H_2(g)$	0	0	130.68
Nitrogen	$N_2(g)$	0	0	191.61
Oxygen	$O_2(g)$	0	0	205.04
Carbon monoxide	$CO(g)$	−110,530	−137,150	197.65
Carbon dioxide	$CO_2(g)$	−393,520	−394,360	213.80
Water vapor	$H_2O(g)$	−241,820	−228,590	188.83
Water	$H_2O(\ell)$	−285,830	−237,180	69.92
Hydrogen peroxide	$H_2O_2(g)$	−136,310	−105,600	232.63

Electrochemistry: Open-circuit voltage

$$2H_2 \rightarrow 4H^+ + 4e^-$$



$$O_2 + 4e^- \rightarrow 2O^{-2}$$

$$2H_2 + O_2 \rightarrow 2H_2O$$

$$(\text{work}) = (\text{voltage})(\text{charge})$$

$$(\text{voltage}) = \frac{(\text{work})}{(\text{charge})} = \frac{474{,}360\text{kJ/mole of } O_2}{\left(1.60\times10^{-19}\text{coulomb/electron}\right)\left(4\times6.022\times10^{23}\text{electrons/mole of } O_2\right)} = 1.23\text{volt}$$

Summary

- Combustion of fossil fuel **may** dominate energy market for decades.
- **Conservation of mass**. Stoichiometry. Chemical reaction destroys and creases molecules, but conserves the number of atoms in each species.
- **Conservation of energy**. Enthalpy of formation.
- **Generation of entropy**. Absolute entropy. When confused, isolate.
- **Fuel cell** turns reaction directly into electricity, and is not limited by the Carnot efficiency. But fuel cell is governed by thermodynamics.