In the U.S., fossil fuel combustion provides

- 70% of electricity
- 85% of total energy

Fossil fuels produce large amounts of CO_2

The supply of fossil fuels is finite, and may be running out (estimates vary)

- 150 years left for coal
- 50 years left for oil

Energy Transformations

First Law of Thermodynamics:

Energy is neither created nor destroyed

- Conservation of Energy
- Conservation of Mass

Energy **can** be converted from one form into another

Energy Transformation

Second Law of Thermodynamics

- **The entropy of the universe always increases during a spontaneous process**
- It is impossible to completely convert heat into work without making some other changes in the universe
- Organized energy is always being transformed into chaotic motion or heat energy

Randomness is decreased only through a **non-**spontaneous process (work must be performed)

Table 4.2 Bond Energies (in kJ/mol)

	H	C	N	O	S	F	Cl	Br	I
Single bonds									
H	436								
C	416	356							
N	391	285	160						
O	467	336	201	146					
S	347	272	—	—	226				
F	566	485	272	190	326	158			
Cl	431	327	193	205	255	255	242		
Br	366	285	—	234	213	—	217	193	
I	299	213	—	201	—	—	209	180	151

Multiple bonds

C=C	598	C=N	616	C=O	803 in CO_2
C≡C	813	C≡N	866	C≡O	1073
N=N	418	O=O	498		
N≡N	946				

Source: Data from Darrell D. Ebbing, *General Chemistry,* Fourth Edition, 1993 Houghton Mifflin Co. Data originally from *Inorganic Chemistry: Principles of Structure and Reactivity,* Third Edition by James E. Huheey, 1983, Addison Wesley Longman.

Formation of Water

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$ + energy

Reactants

- Hydrogen (2 molecules, each with 1 H-H bond)
- Oxygen (one O=O double bond)

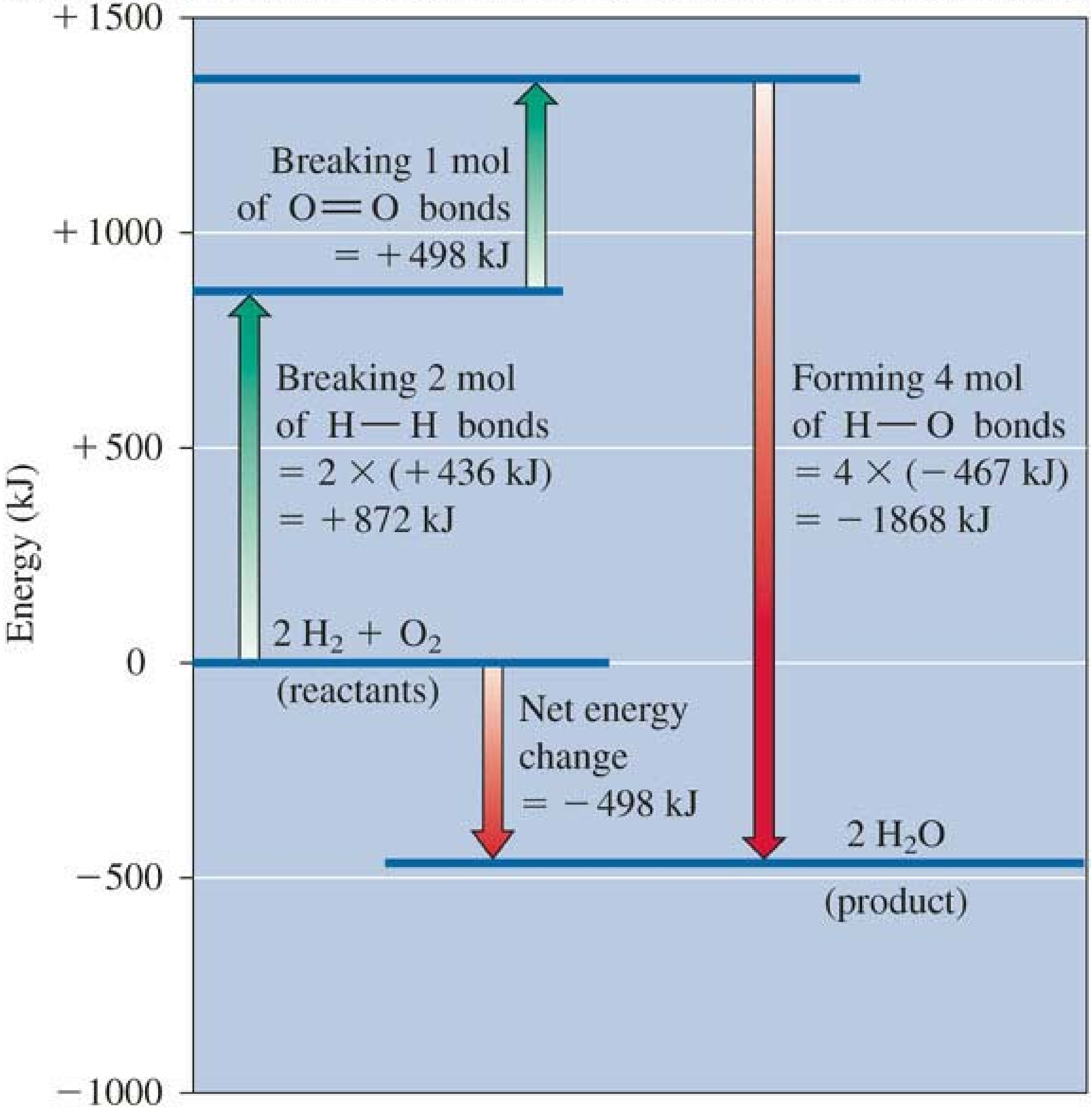
Products

- Water (2 molecules, each with 2 H-O bonds)

Molecule	Bonds per molecule	Moles	Total Number of Bonds	Bond Process	Energy per bond	Total Energy
H—H	1	2	1 × 2 = 2	breaking	+436 kJ	2 × (+436) = +872 kJ
O═O	1	1	1 × 1 = 1	breaking	+498 kJ	1 × (+498) = +498 kJ
H—O—H	2	2	2 × 2 = 4	making	−467 kJ	4 × (−467) = −1868 kJ

Energy is **released** because there is energy left over

- 872 kJ + 498 kJ – 1868 kJ = – 498 kJ (exothermic)


+1500
+1000
+500
0
−500
−1000
Energy (kJ)
Breaking 1 mol of O═O bonds = +498 kJ
Breaking 2 mol of H—H bonds = 2 × (+436 kJ) = +872 kJ
Forming 4 mol of H—O bonds = 4 × (−467 kJ) = −1868 kJ
2 H2 + O2 (reactants)
Net energy change = −498 kJ
2 H2O (product)

Formation of Water

- The overall energy change in breaking bonds and forming new ones is – 498 kJ
- The release of heat corresponds to a decrease in the energy of a chemical system
- This explains why the energy change is negative

Combustion of Methane

Molecule	Bonds per molecule	Moles	Total Number of Bonds	Bond Process	Energy per bond	Total Energy
CH_4	4	1	$4 \times 1 = 4$	breaking	+416 kJ	$4 \times (+416) = +1664$ kJ
O_2	1	2	$1 \times 2 = 2$	breaking	+498 kJ	$2 \times (+498) = +996$ kJ
CO_2	2	1	$2 \times 1 = 2$	making	−803 kJ	$2 \times (-803) = -1606$ kJ
H_2O	2	2	$2 \times 2 = 4$	making	−467 kJ	$4 \times (-467) = -1868$ kJ

- Total energy change in breaking bonds

  1664 kJ + 996 kJ = + 2660 kJ
- Total energy change in forming bonds

  - 1606 kJ + (-1868 kJ) = - 3474 kJ
- Net energy change

  2660 kJ + (-3474 kJ) = - 814 kJ

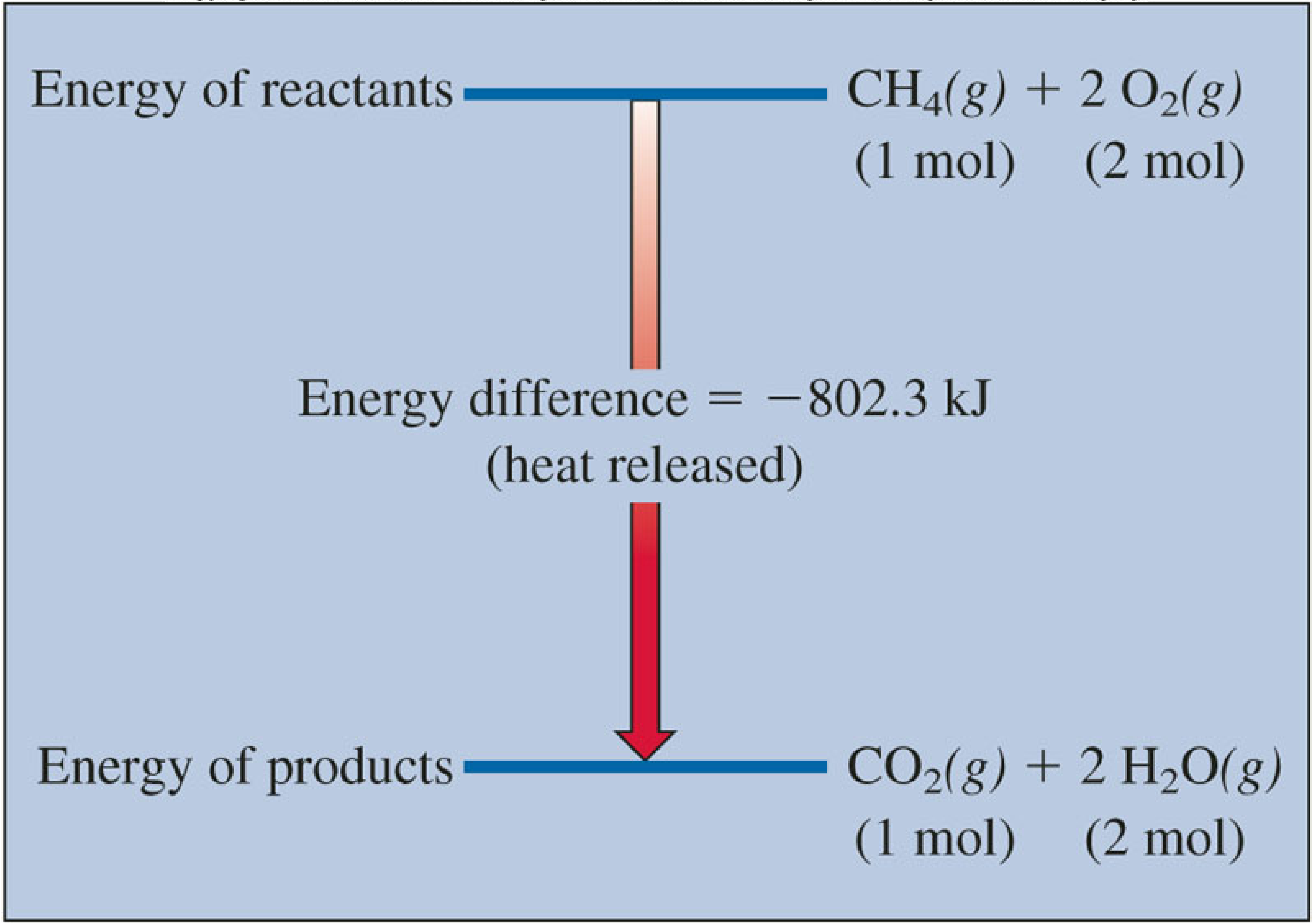
From Fuel Sources to Chemical Bonds

This theoretical value (- 814 kJ) compares very favorably with the experimental value (- 802.3 kJ). But it's not the same. Why not?

- In real chemical reactions, not all the bonds are broken – just the pertinent ones
- In real molecules, not all bonds the same type are energetically equal
  - The O-H bond in water is not the same strength as the O-H bonds in hydrogen peroxide, H_2O_2
- But we can calculate the energy of any reaction **as if** these assumptions were true, and get pretty close to the real answer

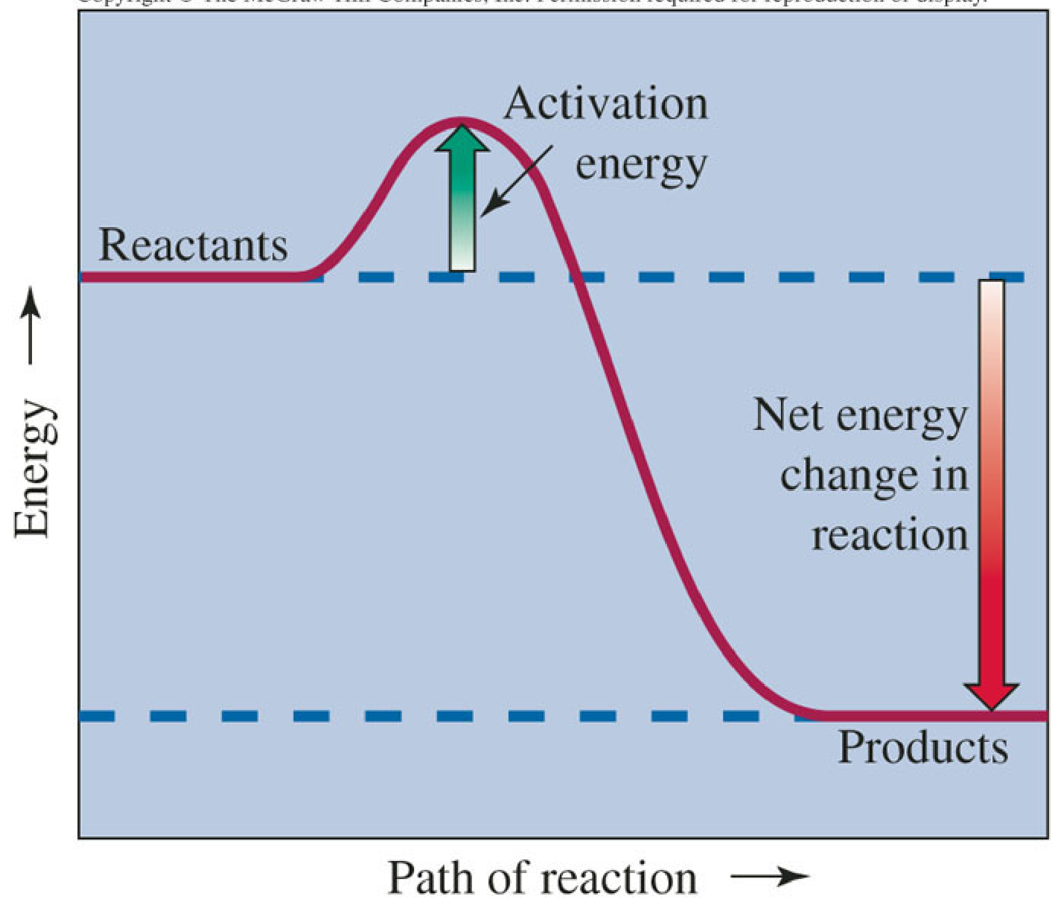
From Fuel Sources to Chemical Bonds

- Combustion of Propane, C_3H_8
  - -2024 kJ/mol
- Combustion of Ethanol, C_2H_5OH
  - -1281 kJ/mol


Energy of reactants
$CH_4(g) + 2\ O_2(g)$
(1 mol) (2 mol)
Energy difference = −802.3 kJ
(heat released)
Energy of products
$CO_2(g) + 2\ H_2O(g)$
(1 mol) (2 mol)

Energy as a Barrier to Reaction

- Activation energy – the energy necessary to initiate a reaction

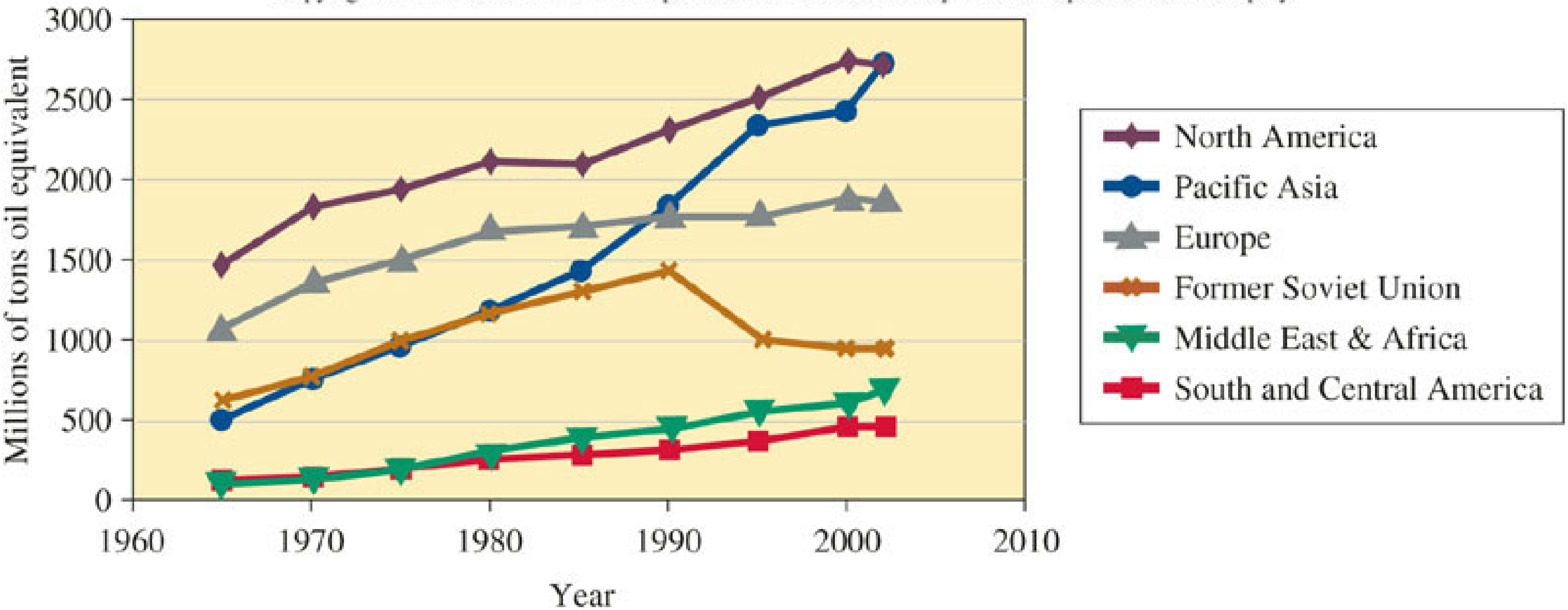


Energy as a Barrier to Reaction

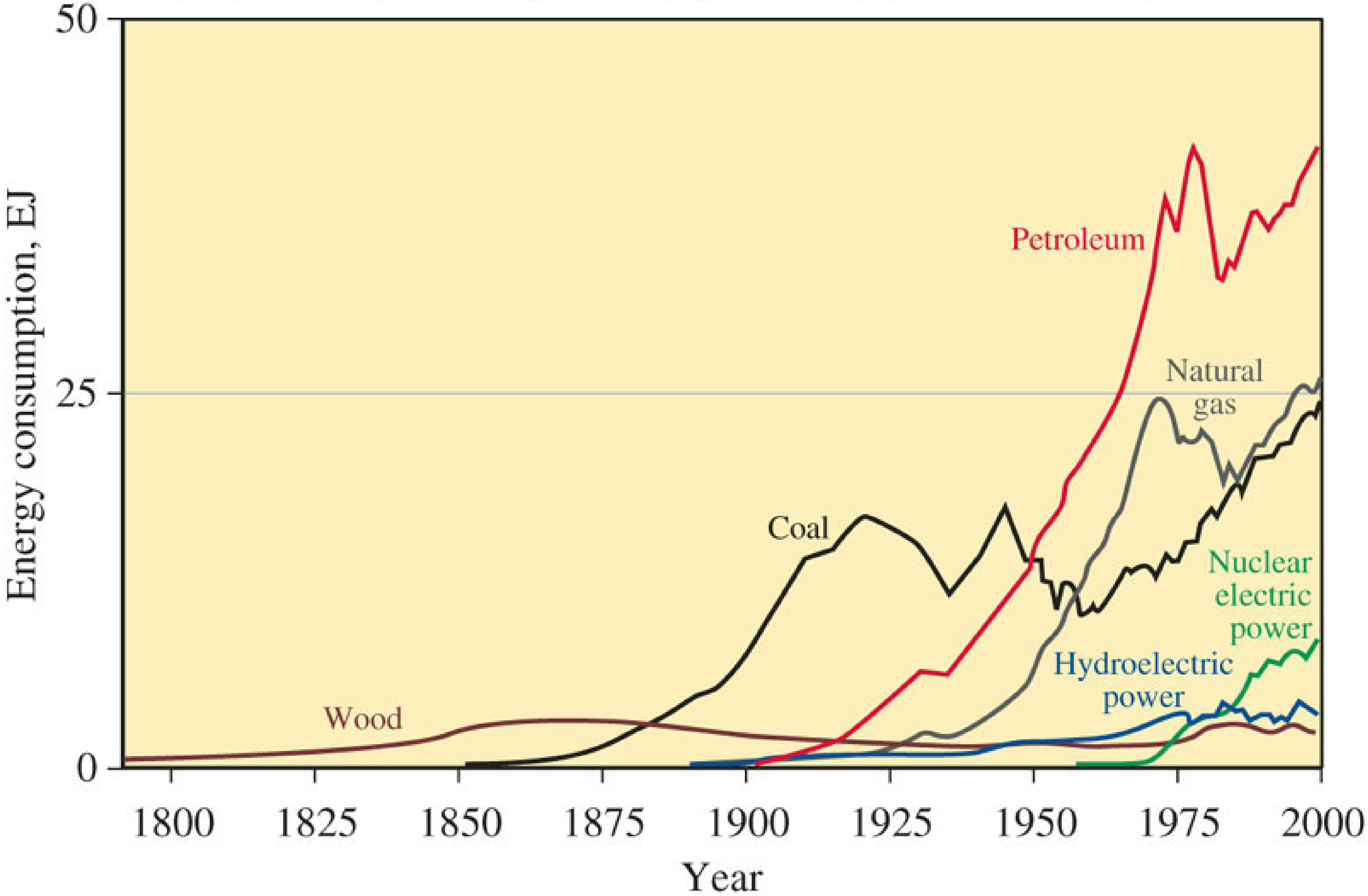
- Low activation energies – fast reaction rates
- High activation energies – slow reaction rates
- Useful fuels react at rates that are neither too fast nor too slow
- Smaller ‘bits’ react faster than large ‘bits’
- Increased temperatures help reactants to get over activation energy barrier

Energy Consumption

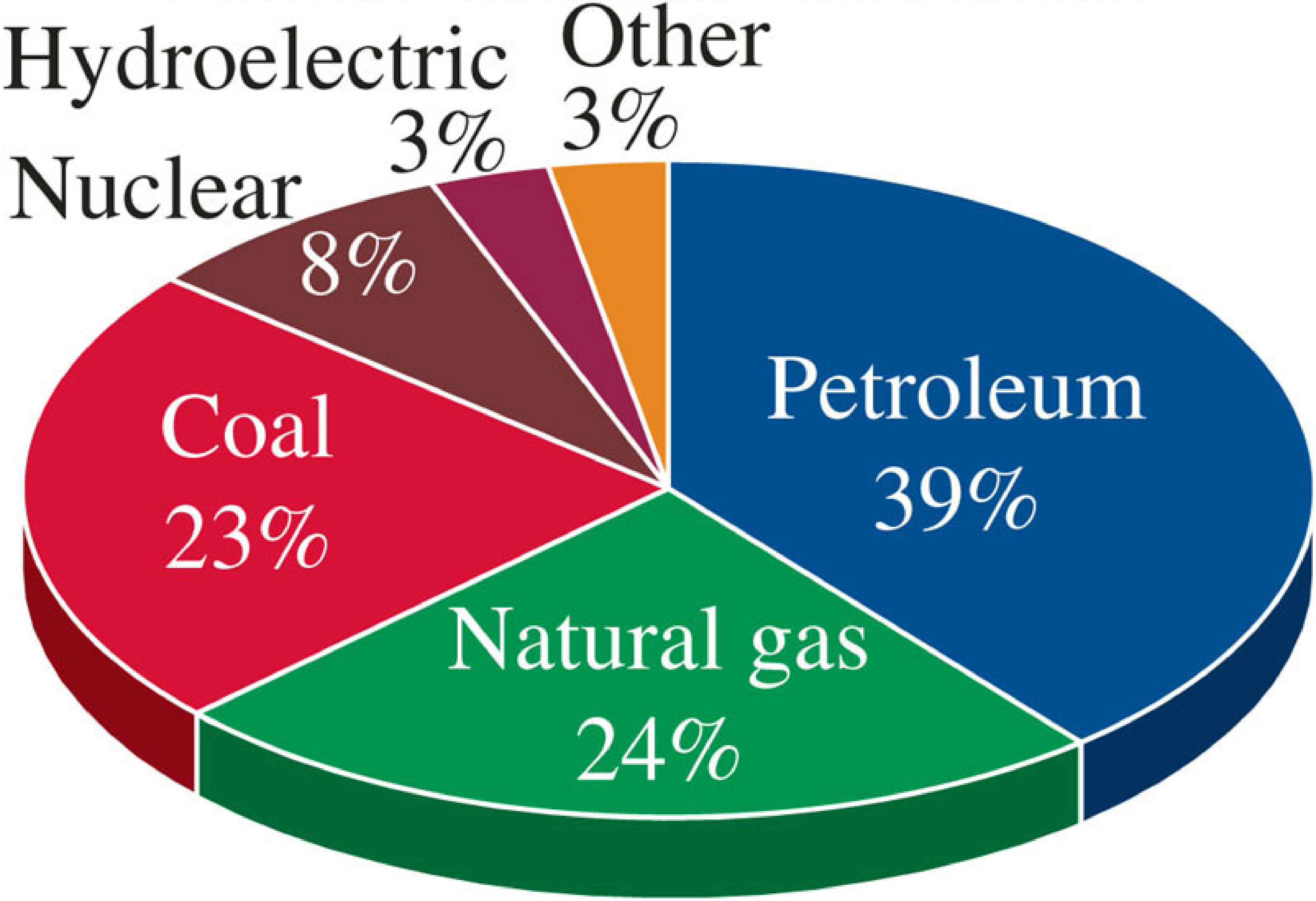
- Pre-Historic man had only body and food for fuel
  - Used ~2000 kcal/day of energy
- Currently, Americans have access to a lot more technology
  - Use 650,000 kcal/day of energy
  - 65 barrels of oil or 16 tons of coal per person per year



3000
2500
2000
1500
1000
500
0
Millions of tons oil equivalent
1960
1970
1980
1990
2000
2010
Year
North America
Pacific Asia
Europe
Former Soviet Union
Middle East & Africa
South and Central America



History of US energy consumption by source, 1 EJ = 10^{18} J



Annual US energy consumption by source, 2002. 'Other' includes wood, waste, alcohol, geothermal, wind and solar

Properties needed in a fuel

- Contain substantial energy content
- Plentiful
- Burn readily at just the right rate
- Others…

Energy Content

Table 4.3 Energy Content of Fuels

Source	kJ/g
Wood (oak)	14
Gasoline	48
Coal (hard)	31
Methane	56
Propane	51
Hydrogen	140
Ethanol	30

Fossil Fuels

- “You will die but the carbon will not; its career does not end with you…it will return to the soil, and there a plant may take it up again in time, sending it once more on a cycle of plant and animal life”
  - Jacob Bronowski in Biography of an Atom – And the Universe.

Organic matter (plants, animals) decays upon death, producing CO_2 and H_2O, just like in combustion

But in some cases, decaying matter doesn’t have enough O_2 around to complete the reaction

Other reactions take place deep in the earth at high temperatures and pressures, producing coal, petroleum and natural gas.

Fossil Fuels: Coal

- Was known in ancient times – used in funeral pyres as early as 3000 B.C.
- **Mining** for coal was not common until ~1300 A.D., in Britain
- During the Industrial Revolution (beginning in the 1700s), coal became the chief fuel source in Britain, and later the rest of the world
  - Fuel was needed in vast quantities to power the new Steam Engines
  - Wood was already in short supply

Fossil Fuels: Coal

- Coal is a better energy source than wood
  - Coal yields 30 kJ per gram
  - Wood yields 12 kJ per gram

- Coal has higher ratio of carbon (85% by mass)
  - Fuels with a higher carbon ratio produce more energy when they are burned
  - An **approximate** molecular formula for coal is $C_{135}H_{96}O_9NS$

Table 4.4 Fuel Value of Various U.S. Coals

Type of Coal	State of Origin	Heat Content (kJ/g)
Anthracite	Pennsylvania	30.5
Bituminous	Maryland	30.7
Subbituminous	Washington	24.0
Lignite (brown coal)	North Dakota	16.2
Peat	Mississippi	13.0
Wood	various	10.4–14.1

- As carbon content increases, so does the heat content
- The less oxygen a compound contains, the more energy per gram it will release on combustion
- “Better” coals have been exposed to higher pressures for longer times, losing more oxygen and becoming harder

Fossil Fuels: Coal

- Drawback #1: Difficult to obtain
  - Underground mining dangerous and expensive
  - Since 1900 more than 100,000 workers killed in **American** mine disasters – but how many worldwide? And how many have been made sick, or died from “black lung”?
- Drawback #2: Coal is a dirty fuel
  - Soot
  - Sulfur and nitrogen oxides
  - Mercury
  - Carbon dioxide

Fossil Fuels: Coal

- The benefit of coal: the global supply is large
  - 20-40 times greater than petroleum

- Because of this, coal is expected to become a much more important fuel in the next 100-150 years

- It will become important to find ways to better use coal – more cleanly, more safely