How do we access chemical energy?

Carry out chemical transformations which change the types (and strengths of) chemical bonds

Why do combustion reactions give off energy?

X-O bonds tend to be stronger than X-X and O-O bonds

Order wood, Coal, Natural Gas (methane), gasoline (C₈H₁₈), and ethanol in terms of energy content (per gram) using Table 4.3

CH₄> gasoline>coal~ethanol>wood

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Table 4.3	Energy Conten	t of Fuels			
So	urce	kJ/g			
Ну	drogen	140			
Me	ethane	56			
Pro	opane	51			
Ga	soline	48			
Co	al (hard)	31			
Eth	nanol	30			
Wo	ood (oak)	14			

What are the major energy-related issues/challenges facing us today? Issues/Challenges:

- 1. Global Climate change (CO₂)
- 2. Peak Oil
- 3. Energy Security
- 4. Growing demand
- 5. Impact on Economy
- 6. Air & water pollution

What are the pluses & minuses of coal?

- +Abundant
- +Spread out over the globe
- -A solid
- -Lower energy content than petroleum, more CO₂ emission per unit energy
- -difficult & dangerous to obtain
- -environmentally disruptive to obtain & utilize (remember SO₂ & NO₂)

What are the pluses & minuses of natural gas?

- +Relatively abundant (we have a lot)
- +"Clean" due to high energy content & less CO₂ emission per unit energy than oil
- -A gas (difficult to ship overseas)
- -Still does emit CO₂
- -Combustion still can generate NO₂

What are the pluses & minuses of oil/petroleum?

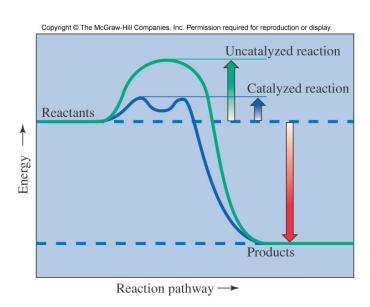
- +High energy content
- + a liquid (easy to pump, store, and transport)
- + we know how to use it
- We're running out of it
- It tends to be in places that aren't friendly
- It does emit CO₂
- -Combustion generates NO₂

What's involved in refining crude oil to gasoline?

Distillation
Catalytic cracking
Oligomerization
Reforming

What's a catalyst?

By providing an alternative reaction pathway, reaction can proceed with less energy input---catalyst is not transformed due to the reaction (catalyst is reused many times)



What are the pluses & minuses of wind power?

- + Wind is "free"
- + Wind is abundant (but localized)
- Have to build infrastructure (takes energy & \$\$\$)
- The wind doesn't blow all the time, have to have a load balance
- Wind isn't where people are have to transport the energy (with losses)
- Destroys views
- Covers land

What goes into a lifecycle cost analysis?

```
Energy for construction
Transportation to site
Operational phase energy use
Decommissioning
transport
energy
recycling
```

Biofuels

What are the two major biofuels?

Ethanol (from sugars)

Biodiesel (fatty acids)

How do we/do we want to produce ethanol?

Partial combustion/Fisher-Tropsch

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$$

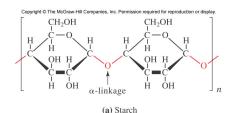
Synthesis/water gas

Water gas shift reaction:

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$

Fischer-Tropsch process:

$$nCO(g) + (2n+1)H_2(g) \rightarrow C_nH_{2n+2}(g,l) + nH_2O(g)$$

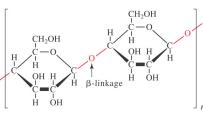


Sugar fermentation

$$C_6H_{12}O_6 \rightarrow 2C_2H_6O + 2CO_2$$

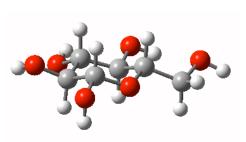
92 kJ/mol exothermic

As a fuel sugars have an energy content of 16 kJ/g Ethanol has an energy content of 30 kJ/g



(b) Cellulose

Cellulose degradation to sugars & then fermentation



What are the three major macronutrients?

Fats

Carbohydrates (sugars)

Proteins

Of the three major macronutrients (fats, carbohydrates & proteins) Which has the higher energy content?

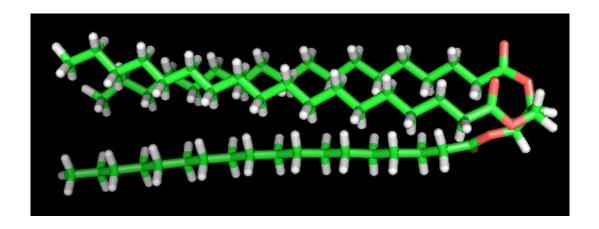
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Table 11.5

Average Energy Content of Macronutrients

Fats 9 Cal/g 38 kJ/g
Carbohydrates 4 Cal/g
Proteins 4 Cal/g 4 Cal/g

How is biodiesel made?



When comparing a renewable energy source such as corn ethanol What factors need to be considered on the biofuel side?

Energy to grow the plants (fertilizer, tilling, etc.)

Energy to transport the raw material to the refinery

Energy to refine the raw material

Energy to transport the fuel (ethanol, biodiesel)

Competition with food

Animal feed as side product

Energy to build to biorefinery

Energy to build the farm machinery

When comparing a renewable energy source such as corn ethanol What factors need to be considered on the petroleum side?

The chemical content of the oil

Energy to recover the petroleum

Energy to transport the petroleum to the refinery

Energy to refine the petroleum

Energy to transport the fuel (gasoline, diesel)

Energy to build new off-shore rigs

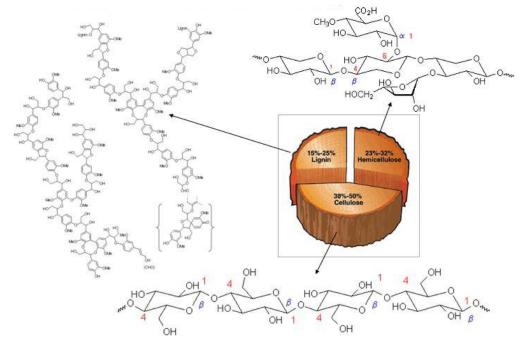
Energy to build/maintain refineries

How much energy can reasonably be recovered from biofuels?

$$1.3x10^9 \text{ ton} \times \frac{900 \text{kg}}{\text{ton}} \times \frac{1000 \text{g}}{\text{kg}} \times \frac{1.4x10^4 \text{J}}{\text{e}} = 1.6x10^{19} \text{J} = 16 \text{ EJ}$$

What is in wood?

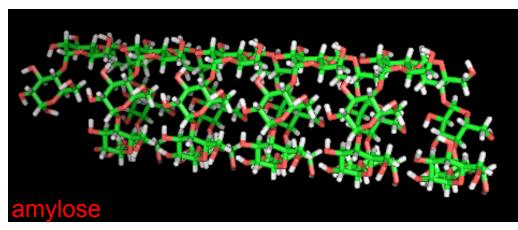
Cellulose & lignin

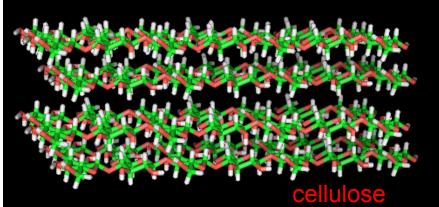


Is lignin a better energy source than cellulose?

Lignin has an energy content of 33 kJ/g Sugars have an energy content of 17 kJ/g Why can't "we" eat cellulose?

Curved versus linear (rod-like) structure



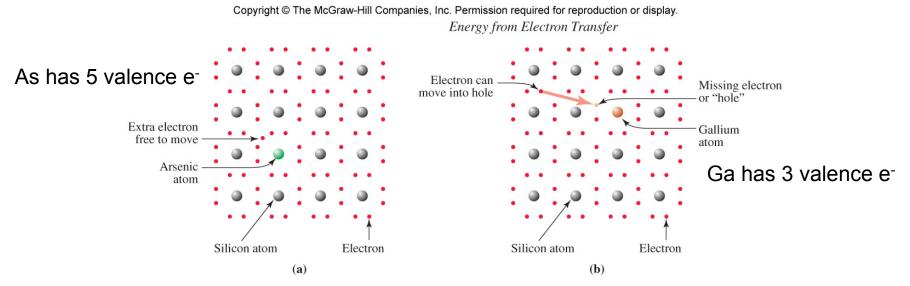


What are the pluses & minuses of Solar Thermal & PV?

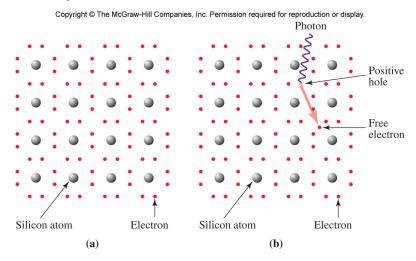
- +Sunlight is "free"
- + Sunlight is abundant (some places)
- Have to build infrastructure (takes energy & \$\$\$)
- The sun doesn't shine all the time, have to have a load balance
- Sunlight isn't where people are have to transport the energy (with losses)
- Destroys views
- Covers land
- Solar thermal uses water to drive turbines

Chemically, what do you need for a PV device?

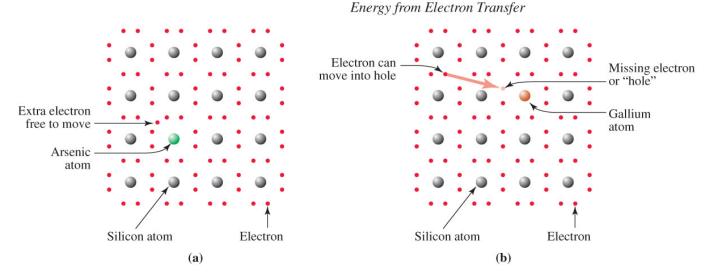
Doped:



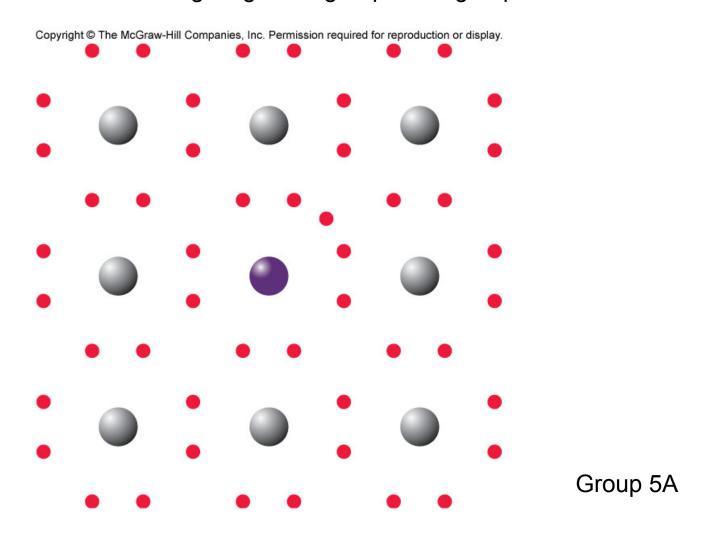
In a Si solar photovoltaic device, what types of elements can serve as dopants? Group 5A and Group 3A



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Is the purple atom in the following diagram a group 3A or group 5A element?



CO₂ emissions

kJ fuel→Grams fuel→moles fuel→moles CO₂→grams CO₂

1 kJ of energy derived from ethanol would release how many grams of CO₂?

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Fuel	g CO2		
natural gas	0.049		
gasoline	0.066		
sub-B coal	0.130		
anth coal	0.100		
wood	0.086		

Table 4.3 E	nergy Content of Fuels	
Source		kJ/g
Hydrog	gen	140
Methar	ne	56
Propan	e	51
Gasolin	ne	48
Coal (h	ard)	31
Ethano	1	30
Wood	(oak)	14

Nuclear

How much mass is converted to energy in the following nuclear decay process?

$$^{218}_{84} Po \rightarrow ^{214}_{82} Pb + ^{4}_{2} He$$

²¹⁸₈₄Po: 218.009

²¹⁴₈₂Pb: **214.000** 214.000+4.003-218.009=-0.006

⁴₂He: 4.003

Fill in the blank in the following nuclear decay process

How does radioactivity impact us and other living matter?

High energy particles/radiation destroys tissue and can cause

Molecular damage
$$H_2O \xrightarrow{\stackrel{0}{\circ} \gamma, x\text{-ray}} H_2O^{\bullet^+} + e^-$$
radical + a cation
will react with other molecules, including DNA

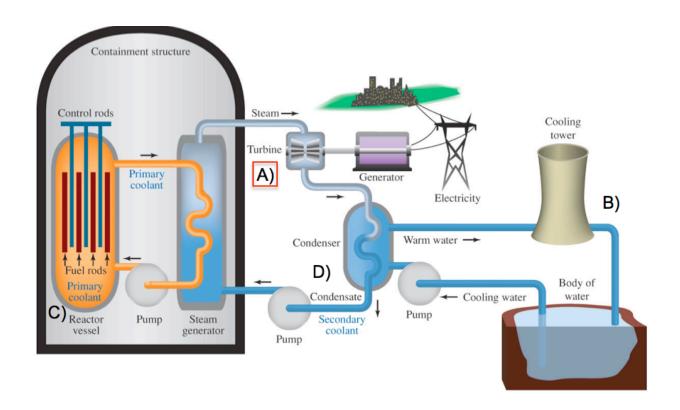
What types of cells are most impacted by radioactivity? rapidly dividing cells particularly susceptible (cancer treatment)

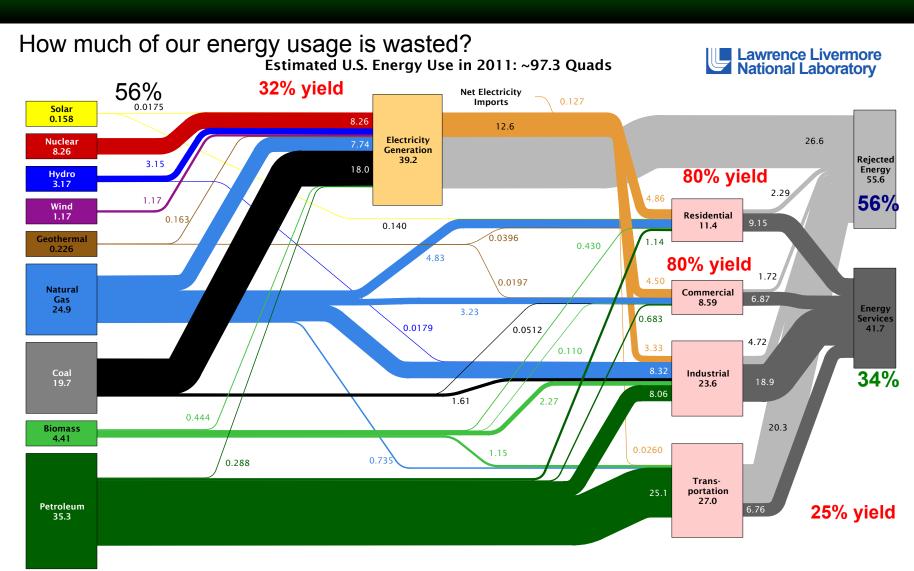
How long do we have to worry about radioactive decay?

Table 7.5	Fable 7.5 Half-Lives for Selected Radioisotopes					
Radioisotope	Half-life $(t_{1/2})$					
uranium-238	4.5×10^9 years					
potassium-40	1.3×10^9 years					
plutonium-239	24,110 years					
carbon-14	5715 years					
cesium-137	30.2 years					
strontium-90	29.1 years					
thorium-234	24.1 days					
iodine-131	8.04 days					
radon-222	3.82 days					
plutonium-231	8.5 minutes					
polonium-214	0.00016 seconds					

Energy Loss

In the following diagram, which labeled step in a nuclear fission power plant is only 30% efficient?





Source: LLNL 2012. Data is based on DOE/EIA-0384(2011), October, 2012. 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 flows for non-thermal resources (i.e., hydro, wind and solar) 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 80% for the residential, commercial and industrial sectors, and as 25% for the transportation sector. Totals may not equal sum of components due to independent rounding. LLNL-MI-410527

Losses mainly in the form of heat

What can we do to burn less gas?

Slow down

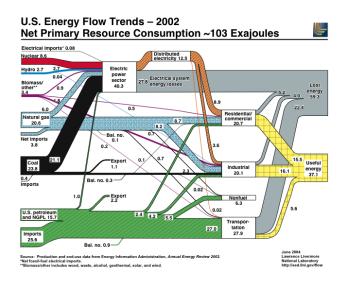
Use lighter cars (lighter materials, lighter batteries)

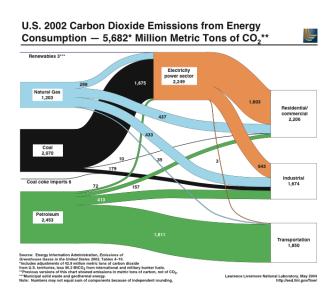
Drive less

If the fleet-average MPG increases from 18 MPG to 39 MPG what would this do for our annual usage of petroleum in EJ (the figure below will tell you what fraction of petroleum is used in transportation)? How does this number compare to the other "renewable" energy options?

Wind 36 FJ

We would use 46% as much petroleum energy, so we would save/"create" 54% 0.54x44.7 EJ=24 EJ





Solar 38 EJ

Biofuels 16 EJ

28% of our energy use is transportation

32.6% of our CO₂ emissions come from transportation

```
1 calorie=4.184 J
1000 calories=1 Calorie
1 Calorie=1kcal
1 kcal=1.16 watt-hr
1 barrel (42 gallons) of crude oil=6.12x10<sup>9</sup>J
1 gallon gasoline=1.31x10<sup>8</sup>J
1 cubic ft natural gas=1.08x10<sup>6</sup>J
1 short ton coal=2.13x10<sup>10</sup>J
1 kilowatt-hour of electricity=3.60x10<sup>6</sup>J
1 EJ=1x10<sup>18</sup> J
1 Quad=1.055 EJ (a quadrillion BTU)
Gt=gigatonne (a billion metric tons (10<sup>9</sup>), 2200 billion pounds (2.2x10<sup>12</sup> lbs))
```

World Reserves	
Coal	20,200 EJ
Natural Gas	7,170 EJ
Oil	10,200 EJ
US use:	
Coal	20.8 EJ
Natural Gas	26.3 EJ
Oil	37.2 EJ
Nuclear	8.7 EJ
Biofuels	16.7 EJ
Wind	36 EJ
Solar	38 EJ
MPG	17.8

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Table 4.3 Energy Content	of Fuels		
Source	kJ/g		
Hydrogen	140		
Methane	56		
Propane	51		
Gasoline	48		
Coal (hard)	31		
Ethanol	30		
Wood (oak)	14		

Average Energy Content of Macronutrients

Fats	38 kJ/g
Carbohydrates	17 kJ/g
Proteins	17 kJ/g

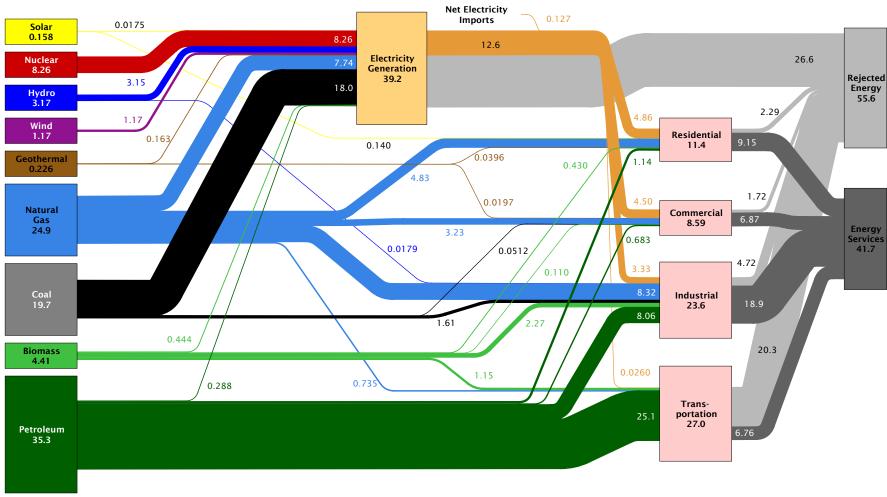
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Table 4.2 Bond Energies (in kJ/mol)									
	Н	C	N	0	S	F	Cl	Br	I
Single Bonds									
Н	436								
C	416	356							
N	391	285	160						
O	467	336	201	146					
S	347	272	-	_	226				
F	566	485	272	190	326	158			
Cl	431	327	193	205	255	255	242		
Br	366	285	_	234	213	_	217	193	
I	299	213	_	201		_	209	180	151
Multiple	Bonds .								
C=C	598			C=N	616		C=O	803 ii	n CO ₂
C≡C	813			$C \equiv N$	866		C≡O	1073	
N=N	418			0=0	498				
$N \equiv N$	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.

Estimated U.S. Energy Use in 2011: ~97.3 Quads





Source: LLNL 2012. Data is based on DOE/EIA-0384(2011), October, 2012. 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 flows for non-thermal resources (i.e., hydro, wind and solar) 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 80% for the residential, commercial and industrial sectors, and as 25% for the transportation sector. Totals may not equal sum of components due to independent rounding. LLNL-MI-410527