

Chem 300A: Chemistry in Modern Society



The World of Chemistry



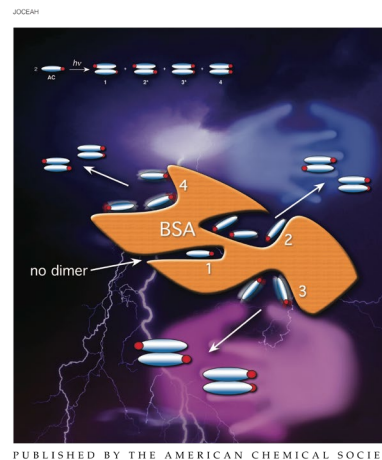
Chemical and Engineering News (C&EN) (2009) 87 (24), 7.



C&EN (2009) 87 (14), 10.



C&EN (2009) Latest news March 10



Nishijima et al. (2007)
J. Org. Chem. 72, 2707.

The World of Chemistry

PERIODIC TABLE
Atomic Properties of the Elements

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

Physcis Laboratory
physics.nist.gov

Standard Reference Data Group
www.nist.gov/srd

Frequently used fundamental physical constants

For the most accurate values of these and other constants, visit physics.nist.gov/constants
1 second = 9 192 631 770 periods of radiation corresponding to the transition between the two hyperfine levels of the ground state of ¹³³Cs

speed of light in vacuum	<i>c</i>	299 792 458 m s ⁻¹ (exact)
Planck constant	<i>h</i>	6.6261 × 10 ⁻³⁴ J s (<i>h</i> = <i>h</i> /2π)
elementary charge	<i>e</i>	1.6022 × 10 ⁻¹⁹ C
electron mass	<i>m_e</i>	9.1094 × 10 ⁻³¹ kg
	<i>m_ec²</i>	0.5110 MeV
proton mass	<i>m_p</i>	1.6726 × 10 ⁻²⁷ kg
fine-structure constant	<i>α</i>	1/137.036
Rydberg constant	<i>R_∞</i>	10 973 732 m ⁻¹
	<i>R_∞c</i>	3.289 842 × 10 ¹⁵ Hz
	<i>R_∞hc</i>	13.6057 eV
Boltzmann constant	<i>k</i>	1.3807 × 10 ⁻²³ J K ⁻¹

- Solids
- Liquids
- Gases
- Artificially Prepared

Period	Group 1 IA		Group 2 IIA		Transition Metals										Main Group Elements						Noble Gases								
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18											
1	¹ H Hydrogen 1.00784 1s																		² He Helium 4.002602 1s										
2	³ Li Lithium 6.941 1s ² 2s	⁴ Be Beryllium 9.012182 1s ² 2s ²											⁵ B Boron 10.811 1s ² 2s ² 2p	⁶ C Carbon 12.0107 1s ² 2s ² 2p ²	⁷ N Nitrogen 14.0067 1s ² 2s ² 2p ³	⁸ O Oxygen 15.9994 1s ² 2s ² 2p ⁴	⁹ F Fluorine 18.9984032 1s ² 2s ² 2p ⁵	¹⁰ Ne Neon 20.1797 1s ² 2s ² 2p ⁶											
3	¹¹ Na Sodium 22.989770 [Ne]3s	¹² Mg Magnesium 24.3050 [Ne]3s ²										¹³ Al Aluminum 26.981538 [Ne]3s ² 3p	¹⁴ Si Silicon 28.0855 [Ne]3s ² 3p ²	¹⁵ P Phosphorus 30.973761 [Ne]3s ² 3p ³	¹⁶ S Sulfur 32.065 [Ne]3s ² 3p ⁴	¹⁷ Cl Chlorine 35.453 [Ne]3s ² 3p ⁵	¹⁸ Ar Argon 39.948 [Ne]3s ² 3p ⁶												
4	¹⁹ K Potassium 39.0983 [Ar]4s	²⁰ Ca Calcium 40.078 [Ar]4s ²	²¹ Sc Scandium 44.955910 [Ar]3d ¹ 4s ²	²² Ti Titanium 47.867 [Ar]3d ² 4s ²	²³ V Vanadium 50.9415 [Ar]3d ³ 4s ²	²⁴ Cr Chromium 51.9961 [Ar]3d ⁵ 4s	²⁵ Mn Manganese 54.938049 [Ar]3d ⁵ 4s ²	²⁶ Fe Iron 55.845 [Ar]3d ⁶ 4s ²	²⁷ Co Cobalt 58.933200 [Ar]3d ⁷ 4s ²	²⁸ Ni Nickel 58.6934 [Ar]3d ⁸ 4s ²	²⁹ Cu Copper 63.546 [Ar]3d ¹⁰ 4s	³⁰ Zn Zinc 65.409 [Ar]3d ¹⁰ 4s ²	³¹ Ga Gallium 69.723 [Ar]3d ¹⁰ 4s ² 4p	³² Ge Germanium 72.64 [Ar]3d ¹⁰ 4s ² 4p ²	³³ As Arsenic 74.92160 [Ar]3d ¹⁰ 4s ² 4p ³	³⁴ Se Selenium 78.96 [Ar]3d ¹⁰ 4s ² 4p ⁴	³⁵ Br Bromine 79.904 [Ar]3d ¹⁰ 4s ² 4p ⁵	³⁶ Kr Krypton 83.798 [Ar]3d ¹⁰ 4s ² 4p ⁶											
5	³⁷ Rb Rubidium 85.4678 [Kr]5s	³⁸ Sr Strontium 87.62 [Kr]5s ²	³⁹ Y Yttrium 88.90585 [Kr]4d ¹ 5s ²	⁴⁰ Zr Zirconium 91.224 [Kr]4d ² 5s ²	⁴¹ Nb Niobium 92.90638 [Kr]4d ⁴ 5s	⁴² Mo Molybdenum 95.94 [Kr]4d ⁵ 5s	⁴³ Tc Technetium (98) [Kr]4d ⁵ 5s ²	⁴⁴ Ru Ruthenium 101.07 [Kr]4d ⁷ 5s	⁴⁵ Rh Rhodium 102.90550 [Kr]4d ⁸ 5s	⁴⁶ Pd Palladium 106.42 [Kr]4d ¹⁰	⁴⁷ Ag Silver 107.8682 [Kr]4d ¹⁰ 5s	⁴⁸ Cd Cadmium 112.411 [Kr]4d ¹⁰ 5s ²	⁴⁹ In Indium 114.818 [Kr]4d ¹⁰ 5s ² 5p	⁵⁰ Sn Tin 118.710 [Kr]4d ¹⁰ 5s ² 5p ²	⁵¹ Sb Antimony 121.760 [Kr]4d ¹⁰ 5s ² 5p ³	⁵² Te Tellurium 127.60 [Kr]4d ¹⁰ 5s ² 5p ⁴	⁵³ I Iodine 126.90447 [Kr]4d ¹⁰ 5s ² 5p ⁵	⁵⁴ Xe Xenon 131.293 [Kr]4d ¹⁰ 5s ² 5p ⁶											
6	⁵⁵ Cs Cesium 132.90545 [Xe]6s	⁵⁶ Ba Barium 137.327 [Xe]6s ²	Lanthanides	⁷² Hf Hafnium 178.49 [Xe]4f ¹⁴ 5d ² 6s ²	⁷³ Ta Tantalum 180.9479 [Xe]4f ¹⁴ 5d ³ 6s ²	⁷⁴ W Tungsten 183.84 [Xe]4f ¹⁴ 5d ⁴ 6s ²	⁷⁵ Re Rhenium 186.207 [Xe]4f ¹⁴ 5d ⁵ 6s ²	⁷⁶ Os Osmium 192.22 [Xe]4f ¹⁴ 5d ⁶ 6s ²	⁷⁷ Ir Iridium 192.217 [Xe]4f ¹⁴ 5d ⁷ 6s ²	⁷⁸ Pt Platinum 195.078 [Xe]4f ¹⁴ 5d ⁹ 6s ¹	⁷⁹ Au Gold 196.96655 [Xe]4f ¹⁴ 5d ¹⁰ 6s ¹	⁸⁰ Hg Mercury 200.59 [Xe]4f ¹⁴ 5d ¹⁰ 6s ²	⁸¹ Tl Thallium 204.3833 [Hg]6p	⁸² Pb Lead 207.2 [Hg]6p ²	⁸³ Bi Bismuth 208.98038 [Hg]6p ³	⁸⁴ Po Polonium (209) [Hg]6p ⁴	⁸⁵ At Astatine (210) [Hg]6p ⁵	⁸⁶ Rn Radon (222) [Hg]6p ⁶											
7	⁸⁷ Fr Francium (223) [Rn]7s	⁸⁸ Ra Radium (226) [Rn]7s ²	Actinides	¹⁰⁴ Rf Rutherfordium (261) [Rn]5f ¹⁴ 6d ² 7s ²	¹⁰⁵ Db Dubnium (262) [Rn]5f ¹⁴ 6d ³ 7s ²	¹⁰⁶ Sg Seaborgium (266) [Rn]5f ¹⁴ 6d ⁴ 7s ²	¹⁰⁷ Bh Bohrium (264) [Rn]5f ¹⁴ 6d ⁵ 7s ²	¹⁰⁸ Hs Hassium (277) [Rn]5f ¹⁴ 6d ⁶ 7s ²	¹⁰⁹ Mt Meitnerium (268) [Rn]5f ¹⁴ 6d ⁷ 7s ²	¹¹⁰ Uun Ununnilium (281) [Rn]5f ¹⁴ 6d ⁸ 7s ²	¹¹¹ Uuu Unununium (272) [Rn]5f ¹⁴ 6d ⁹ 7s ²	¹¹² Uub Ununbium (285) [Rn]5f ¹⁴ 6d ¹⁰ 7s ²	Uuq Ununquadium (289) [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ¹	Uuh Ununhexium (292) [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ²	Uu Ununseptium (295) [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ³	Uuo Ununoctium (298) [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁴	Uu Ununnonium (301) [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁵	Uu Unundecium (304) [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁶											
	⁵⁸ Ce Cerium 140.116 [Xe]4f ¹ 5d ¹ 6s ²	⁵⁹ Pr Praseodymium 140.90765 [Xe]4f ³ 6s ²	⁶⁰ Nd Neodymium 144.24 [Xe]4f ⁴ 6s ²	⁶¹ Pm Promethium (145) [Xe]4f ⁵ 6s ²	⁶² Sm Samarium 150.36 [Xe]4f ⁶ 6s ²	⁶³ Eu Europium 151.964 [Xe]4f ⁷ 6s ²	⁶⁴ Gd Gadolinium 157.25 [Xe]4f ⁷ 6s ²	⁶⁵ Tb Terbium 158.92534 [Xe]4f ⁹ 6s ²	⁶⁶ Dy Dysprosium 162.500 [Xe]4f ¹⁰ 6s ²	⁶⁷ Ho Holmium 164.93032 [Xe]4f ¹¹ 6s ²	⁶⁸ Er Erbium 167.259 [Xe]4f ¹² 6s ²	⁶⁹ Tm Thulium 168.93421 [Xe]4f ¹³ 6s ²	⁷⁰ Yb Ytterbium 173.04 [Xe]4f ¹⁴ 6s ²	⁷¹ Lu Lutetium 174.967 [Xe]4f ¹⁴ 5d ¹ 6s ²	⁸⁹ Ac Actinium (227) [Rn]5f ⁷ 6s ²	⁹⁰ Th Thorium 232.0381 [Rn]5f ¹⁴ 6s ²	⁹¹ Pa Protactinium 231.03688 [Rn]5f ¹⁴ 6d ¹ 7s ²	⁹² U Uranium 238.02891 [Rn]5f ³ 6d ¹ 7s ²	⁹³ Np Neptunium (237) [Rn]5f ⁶ 6d ¹ 7s ²	⁹⁴ Pu Plutonium (244) [Rn]5f ⁷ 6d ¹ 7s ²	⁹⁵ Am Americium (243) [Rn]5f ⁷ 7s ²	⁹⁶ Cm Curium (247) [Rn]5f ⁷ 7s ²	⁹⁷ Bk Berkelium (247) [Rn]5f ⁹ 7s ²	⁹⁸ Cf Californium (251) [Rn]5f ¹⁰ 7s ²	⁹⁹ Es Einsteinium (252) [Rn]5f ¹¹ 7s ²	¹⁰⁰ Fm Fermium (257) [Rn]5f ¹² 7s ²	¹⁰¹ Md Mendelevium (258) [Rn]5f ¹³ 7s ²	¹⁰² No Nobelium (259) [Rn]5f ¹⁴ 7s ²	¹⁰³ Lr Lawrencium (262) [Rn]5f ¹⁴ 7s ² 7p ¹

[†]Based upon ¹²C. () indicates the mass number of the most stable isotope.

For a description of the data, visit physics.nist.gov/data

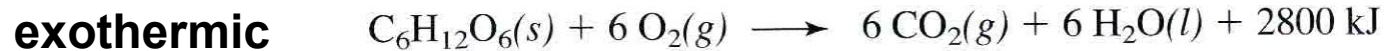
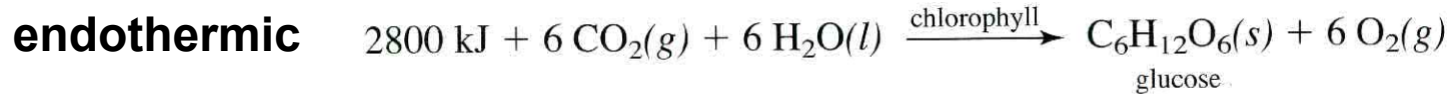
NIST SP 966 (September 2003)

Energy – Costs and Requirements

Dragonfly accelerating to 50 km/h	2×10^{-7} kJ
Good MLB fastball (95 mph)	1.3×10^{-1} kJ
Car accelerating from 0-90 km/h	$\sim 10^2$ kJ
Burning 1kg wood	1.4×10^4 kJ
Burning 1kg coal	3×10^4 kJ
Burning 1kg gasoline	5×10^4 kJ
Burning 1kg natural gas	5.5×10^4 kJ
Flying a 747 jet at 640 mph	13×10^7 kJ
Nuclear fission 1kg ^{235}U	8×10^{10} kJ
Nuclear fusion 1kg ^2H	34×10^{11} kJ
US daily energy consumption	3×10^{14} kJ
World daily energy consumption	1×10^{15} kJ
Daily solar output	3×10^{28} kJ

Energy

Uphill energetically



Downhill energetically

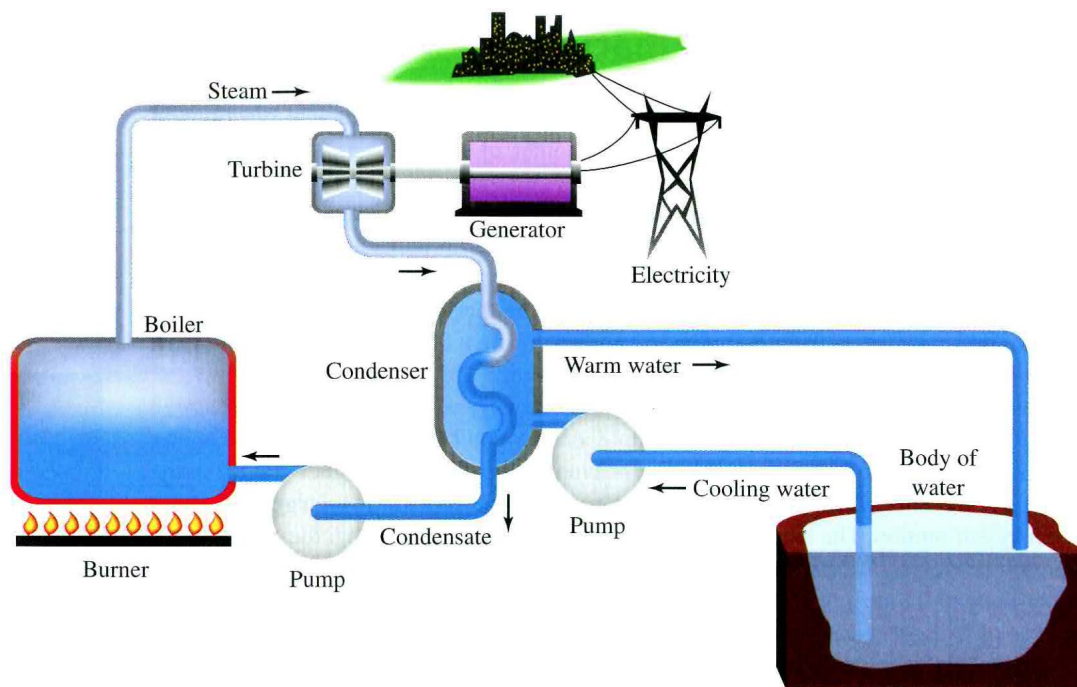
Glucose is the energy currency here

NOTE: one 'food' calorie = 1 kcal = 4.18 kJ

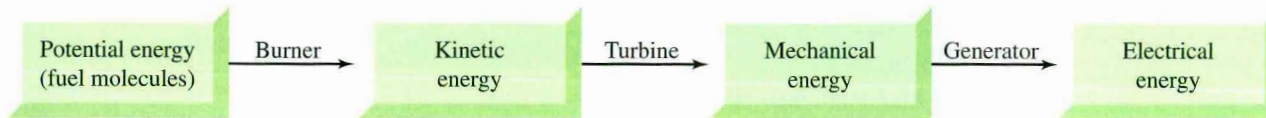
Energy - Petroleum

Energy = Potential energy + kinetic energy

Energy is conserved



**Losses
occur at
each step**



Chemistry in Context 6th Edition, ACS, McGraw-Hill

Table 4.2

Bond Energies (in kJ/mol)

	H	C	N	O	S	F	Cl	Br	I
<i>Single Bonds</i>									
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
<i>Multiple Bonds</i>									
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.

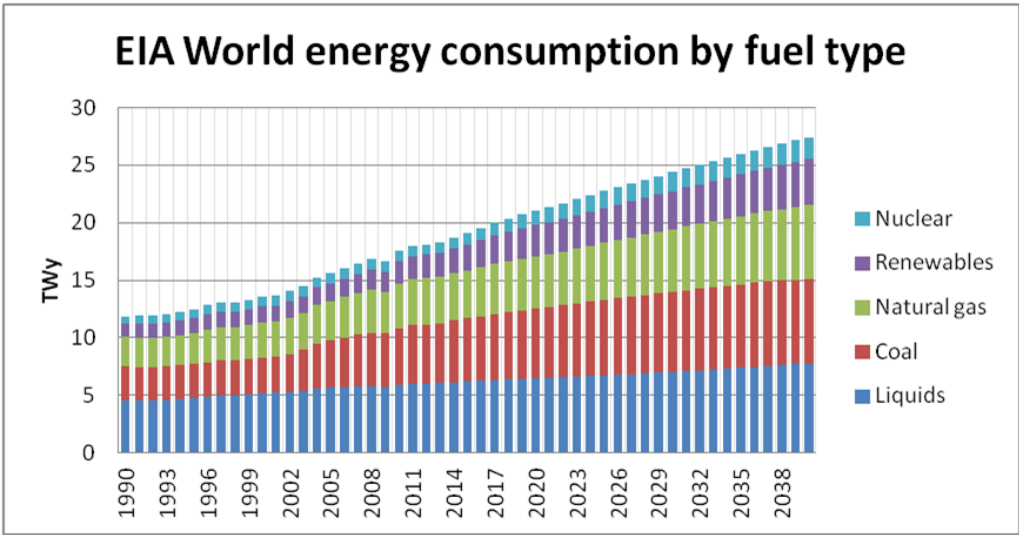


Energy balance = Energy of C – (Energy of A + Energy of B)

Energy balance < 0 corresponds to a favorable reaction – **exothermic**

Energy balance > 0 corresponds to an unfavorable reaction - **endothermic**

Potential energy is stored in the bonds of molecules



Projected world energy needs

US is about 1/3 of world total

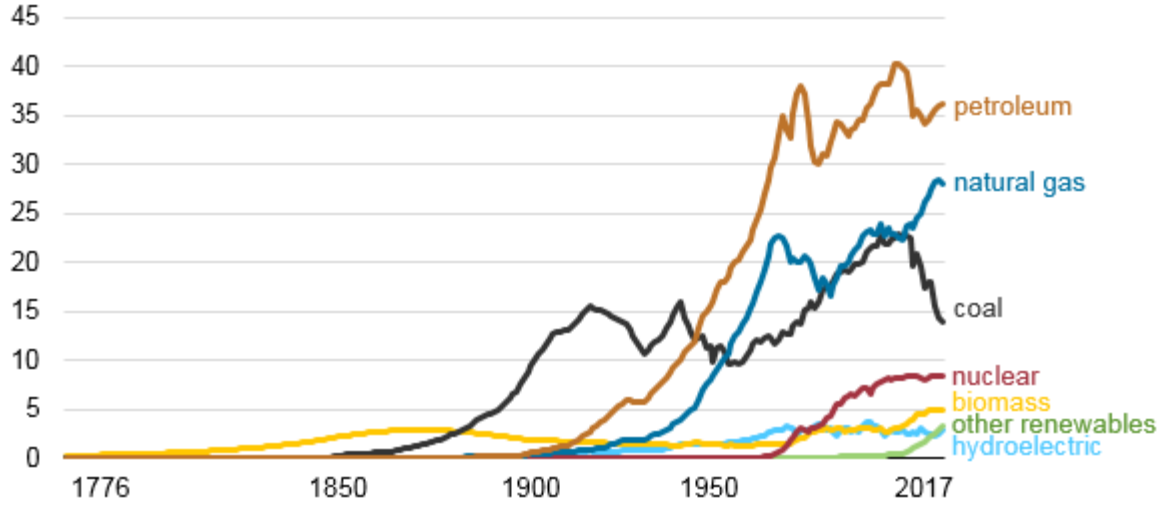
Euanmearns.com

US EIA

US energy consumption:

Canada is the highest consumer of energy per capita on the planet

Energy consumption in the United States (1776-2017)
quadrillion British thermal units



Energy content of fuels

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

Coal = 2 x heat of wood

- approximate formula $C_{135}H_{96}O_9NS$

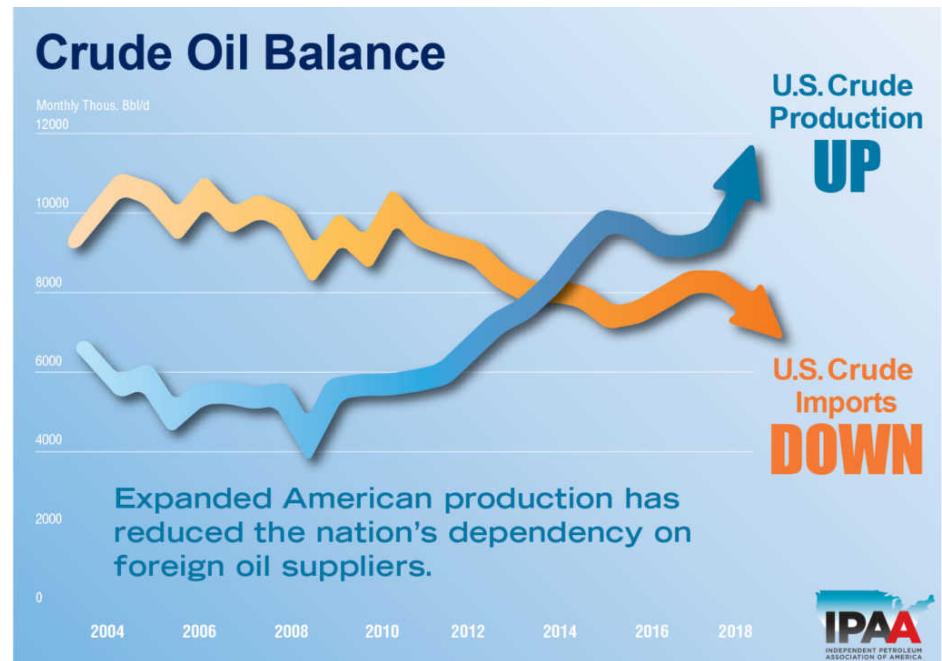
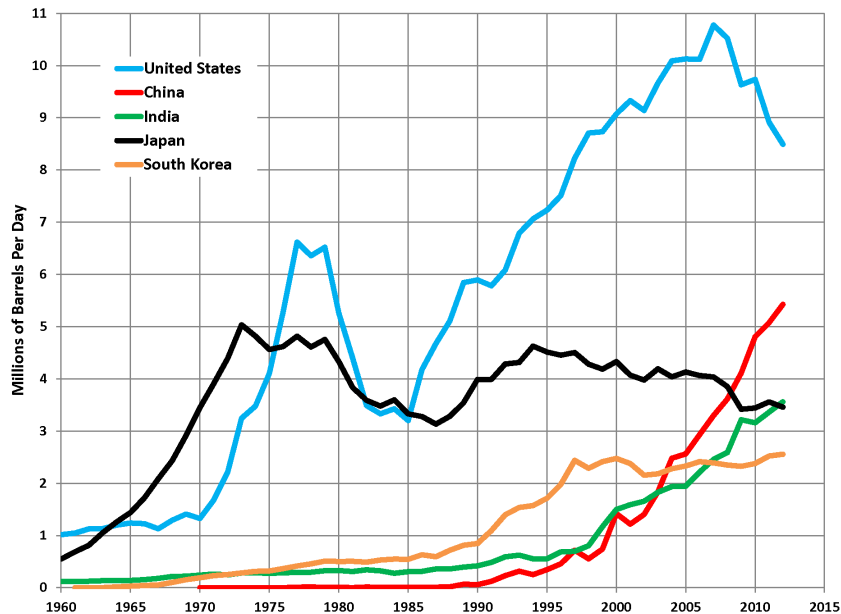
- also contains small amounts of Si, Na, Ca, Al, Ni, Cu, Zn, As, Pb, Hg

Petroleum

More concentrated source of energy – 40-60% more energy per gram than coal

Canada is a net exporter

US production – was a net importer

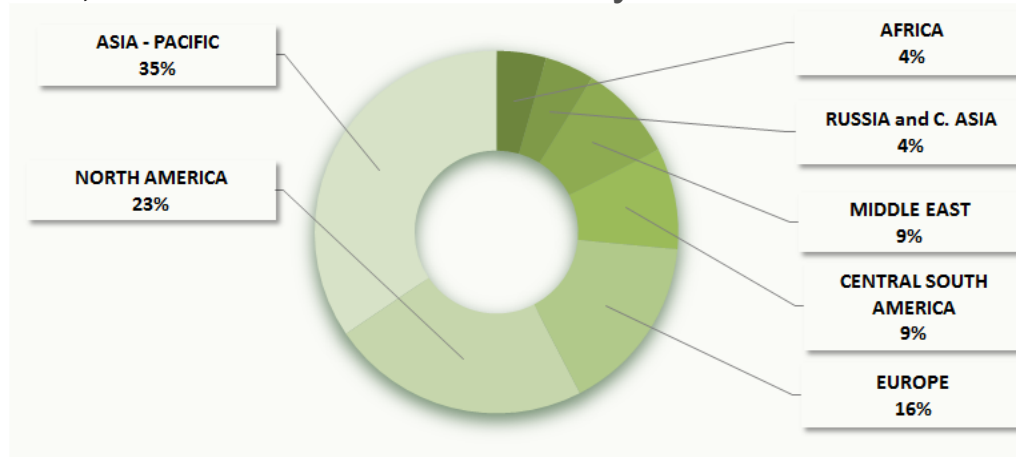


Recent reversal of this trend due to rapidly increasing shale oil production

Petroleum

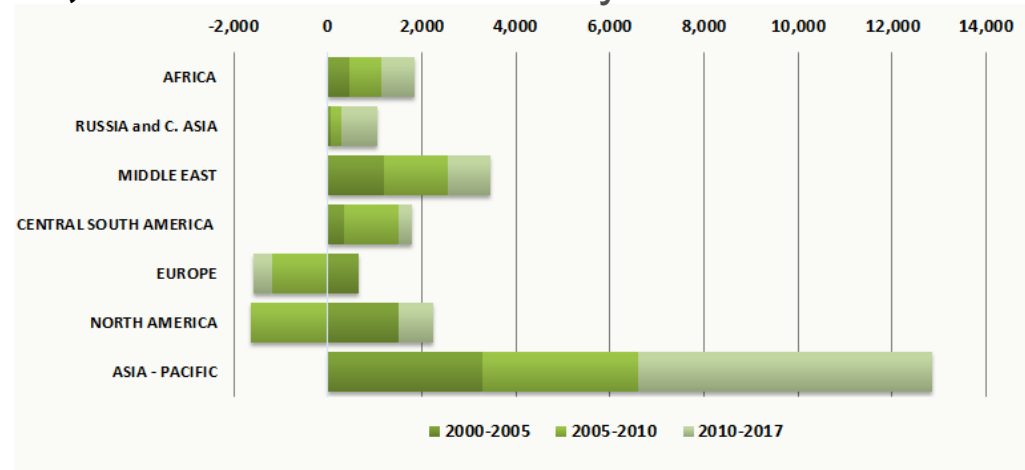
World Oil Consumption (2017)

97,815 thousand barrels/day



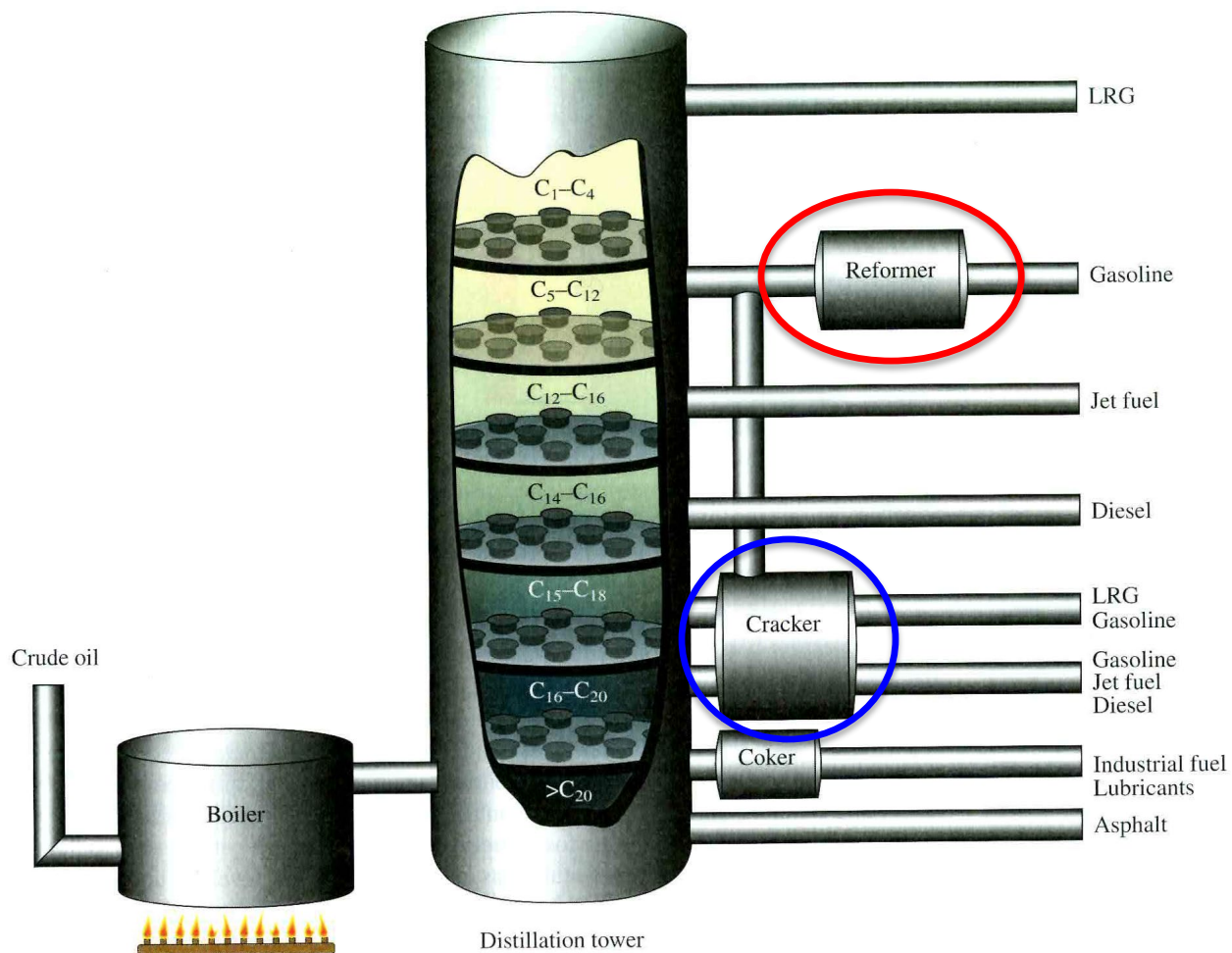
World Oil Consumption Growth (2000-2017)

20,676 thousand barrels/day



From: World Oil and Gas Review 2018, Vol. 1

Petroleum Refining: fractional distillation



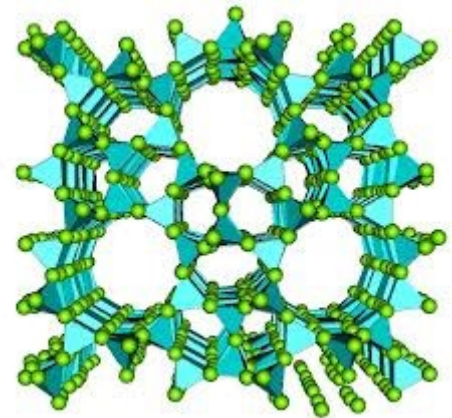
LRG = liquefied refinery gas

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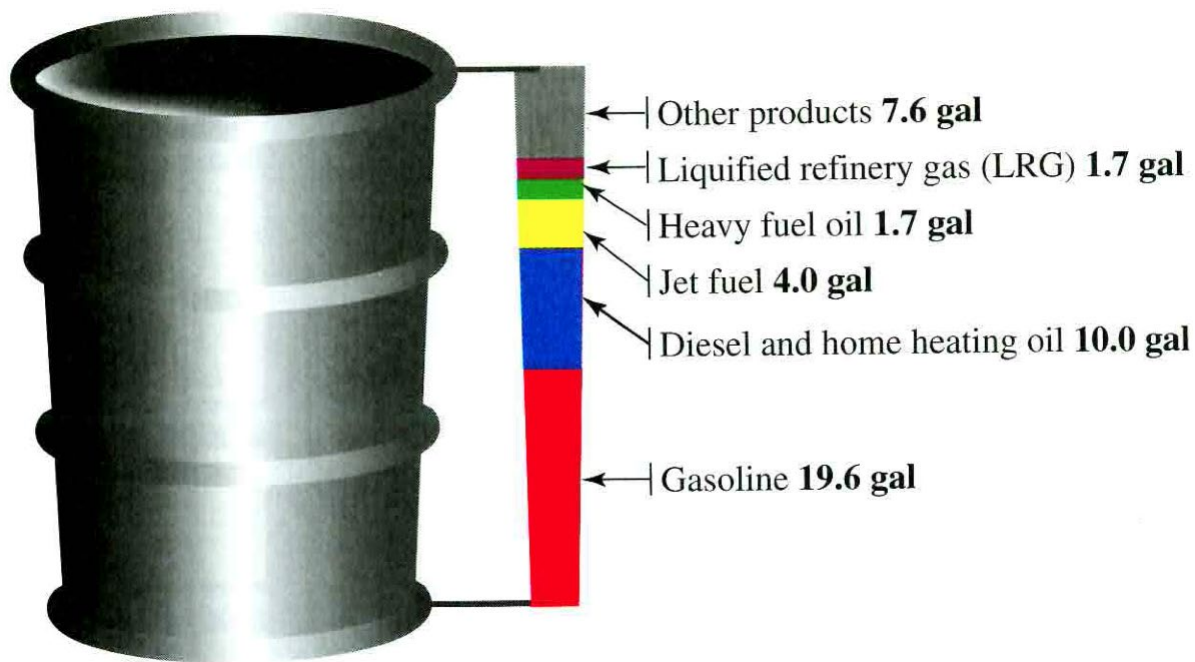
Petroleum fractions and cracking

Gases	< 20 C	C1-C4 alkanes	synthesis gas additives
Petroleum ether	20-70 C	C5-C6 alkanes	gasoline ← cracking
Gasoline	70-180 C	C6-C10 alkanes	jet fuel
Kerosene	180-230 C	C11-C12 alkanes	diesel and furnace fuel
Light gas oil	230-305 C	C13-C17 alkanes	lube oil
Heavy gas oil	305-405 C	C18-C25 alkanes	grease, pet jelly
Lubricants	405-515 C	> C25 alkanes	roofing and road asphalt
Solids	> 515 C	PAH, high MW alkanes	

Catalytic cracking at high T and P over a catalyst (usually a *Zeolite*) breaks long chains down to shorter ones via **radicals** and/or **alkyl cations**:



Fractions of petroleum

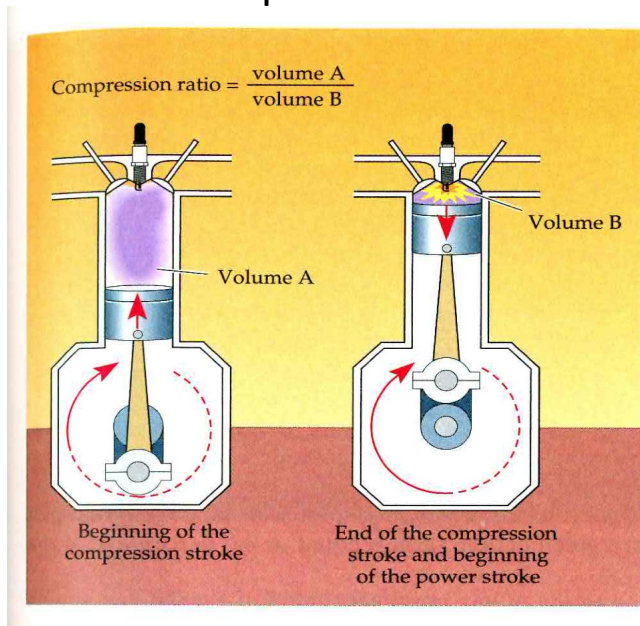


Natural gas = 87-96% methane + 2-6% ethane + other

Chemistry in Context 6th Edition, ACS, McGraw-Hill

Not all 'gasoline' fractions are created equal: the need for 'reforming'

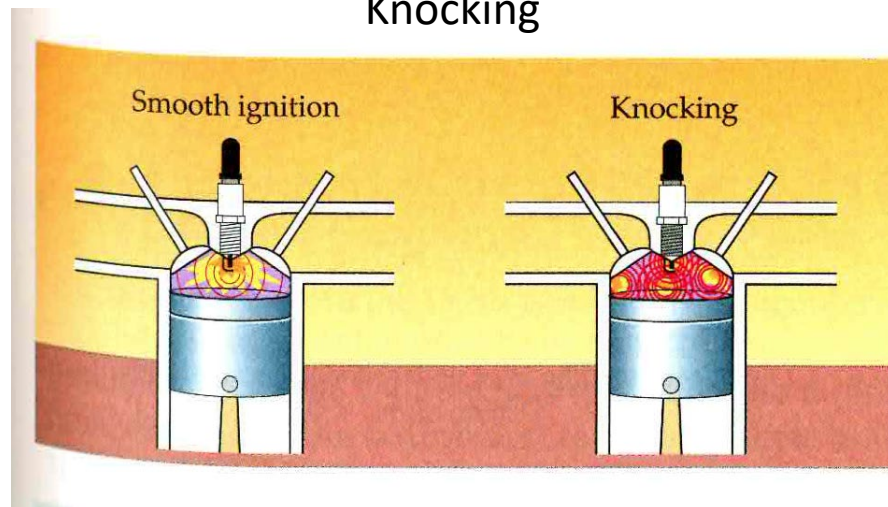
Compression



For optimal power output, we need **smooth combustion** at the very top of the piston stroke: **when spark plug fires**

Knocking is caused by **multiple ignition points** or **pre-ignition** and it depends on the **structure** of the hydrocarbon fuel

Knocking

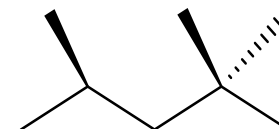


The Extraordinary Chemistry of Ordinary Things, 4th Ed.

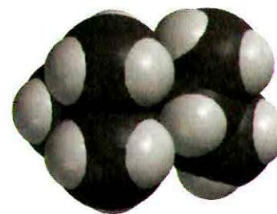
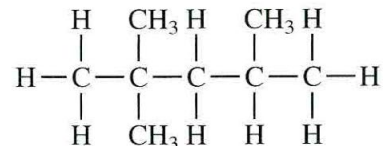
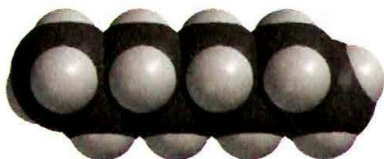
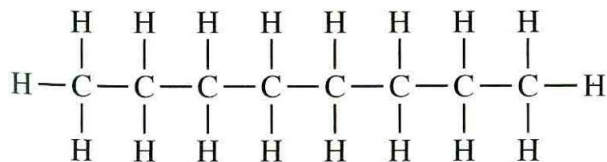
Octane number and structure

n-butane	C_4H_{10}	94 Octane number
n-pentane	C_5H_{12}	62
2-methylbutane		94
n-hexane	C_6H_{14}	25
2-methylpentane		73
2,2-dimethylbutane		92
n-heptane	C_7H_{16}	0
2-methylhexane		42
2,3-dimethylpentane		90
n-octane	C_8H_{18}	-20
2-methylheptane		22
2,3-dimethylhexane		71
2,2,4-trimethylpentane		100 (isooctane = the standard)
Benzene		106
Toluene		118
o-xylene		107
Ethanol		108
MTBE (methyl t-butyl ether)		116

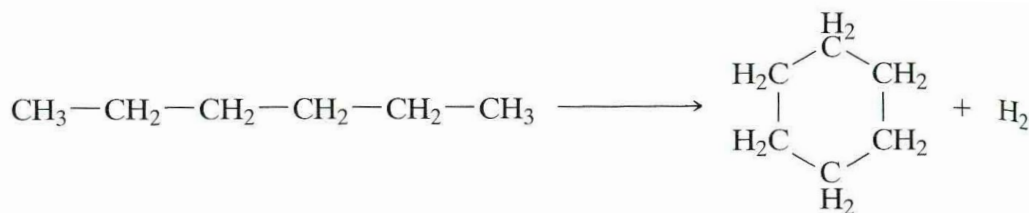
Arbitrarily set **isooctane at 100** and **n-heptane at 0**; all others rated against a *blend of the two*



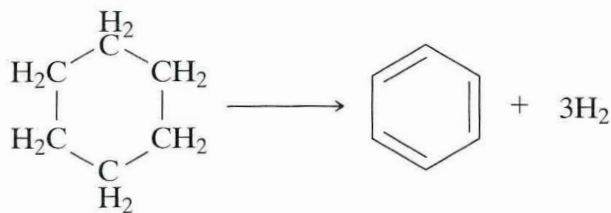
Reforming = rearranges the carbon backbone into more branched hydrocarbons



Chemistry in Context 6th Edition, ACS, McGraw-Hill



Typical catalysts are **Pt** or **Re** on SiO_2 or $\text{SiO}_2/\text{Al}_2\text{O}_3$

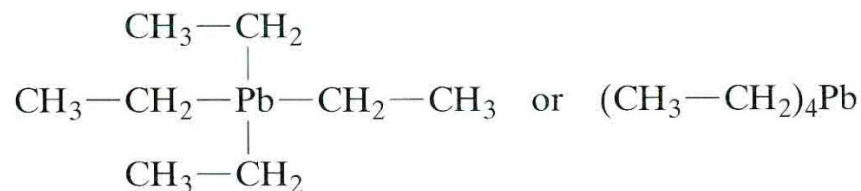


The Extraordinary Chemistry of Ordinary Things, 4th Ed.

Octane boosters: *gasoline anti-knock agents*

Tetraethyllead – raises octane ratings

(TEL) 1920's until late 70's



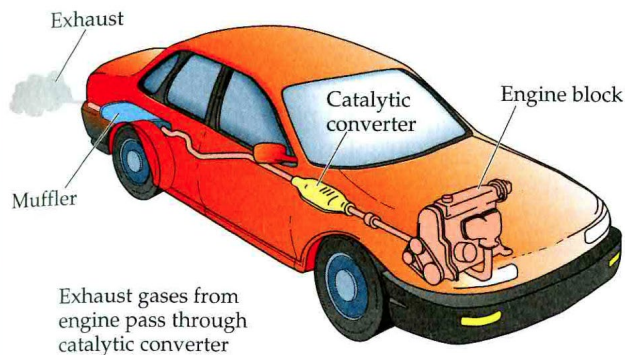
The Extraordinary Chemistry of Ordinary Things, 4th Ed.

Why it works: **Pb-C bond is weak** and breaks readily providing many ethyl radicals that enhance combustion

Issues: Pb is highly toxic and organoleads are readily absorbed and fat soluble

By mid-70's roadside levels were often found to be as high as **3 mg/g of soil** (about 200x background)

Phased out NOT because of acute toxicity effects of Pb but because **TEL killed the catalytic converters introduced to remove NO_x and SO_x byproducts** (that eventually oxidized to HNO₃ and H₂SO₄, forming acid rain)



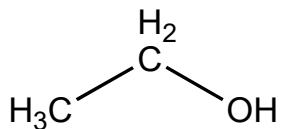
Catalytic converter: Pd and Pt



Other octane enhancers – **methyl-*tert*-butyl ether - MTBE**

Higher octane rating
Oxygenates CO to CO₂

Ethanol



E10 = gasoline with 10% ethanol

The Extraordinary Chemistry of Ordinary Things, 4th Ed.

Ethanol: renewable gasoline alternative or more trouble than its worth?

US government mandated use of ethanol blends E10, E15 and now up to E85

Many questions exist however:

lower fuel efficiency (up to 30% less)

massive subsidy to producers in US (51 cents per gallon in 2011)

severe corrosion problems in fuel lines and pumps

net zero or negative impact on CO₂ emissions

Substantial impact on world food sources:

***'The diversion of US maize into the production of biofuels, amid high energy prices, have pushed maize prices 84% higher year on year fueling rising global food prices, a report released by the World Bank Tuesday said.'* from Platts News Agency, 2011**

See also: <https://www.factcheck.org/2015/11/ethanol-higher-emissions-or-lower/>

Sources:

Eubanks, L.P., Middlecamp, C.H. Hetzel, C.E. and Keller, S.W. "Chemistry in Context: Applying Chemistry to Society" 6th edition (2009), A Project of the American Chemical Society, McGraw Hill Higher Education

Snyder, C.H. "The Extraordinary Chemistry of Ordinary Things" (2003), Wiley.

Platts News Agency, Singapore, Aug. 16, 2011

Sherman, A. and Sherman S.J. "Chemistry in Our Changing World", 3rd Ed. (1992), Prentice Hall