8.21 The Physics of Energy
Fall 2009

Introduction & apologies
A tour of internal energy
Asides: Enthalpies of formation &reaction

Case study I: Ethanol
II: Cement
III: The hydrogen economy

8.21 Lecture 7

Chemical (and Biological) Energy

September 23, 2009

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Chemical and Biological Energy

How can we analyze statements like

- "Burning ethanol produces less CO_2 than burning gasoline."

- "Why does cement manufacturing produce so much more CO_2 per Joule of energy consumption than other manufacturing?"

- "Hydrogen is the fuel of the future!"

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Chemical (and Biological) Energy

A course unto itself

SOURCES

- Fossil fuels
- Biofuels
- Wood, waste, etc.

TRANS FORMATION AND STORAGE

- Batteries   Chemical$\leftrightarrow$ Electrical
- Fuel Cells   Chemical$\leftrightarrow$ Electrical
- Engines $\left.\begin{array}{l}\text{Bio}\\ \text{Chemical}\end{array}\right\} \leftrightarrow$ Mechanical
- Working fluids   Mechanical$\leftrightarrow$ Heat
- Photosynthesis   Radiation$\leftrightarrow$ Biochemical

USES

- Heating & Cooling
- Transportation
- Manufacturing
- ...

- Emphasize physics issues, especially as they impact the rest of the course
- Almost all chemistry (apologies!)
- Review basic thermochemistry!

CO_2!

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Outline

- A tour of the internal energy of matter

  - Change of internal energy with temperature — heat capacities

  - Solid $\Leftrightarrow$ liquid $\Leftrightarrow$ gas — changes of phase or *latent heat*

  - Molecules $\Leftrightarrow$ atoms — heat of formation

  - Atoms $\Leftrightarrow$ electrons and nuclei — atomic binding

  - Nuclei $\Leftrightarrow$ protons and neutrons — nuclear binding

  - Matter $\Leftrightarrow$ Rest mass energy

- Case Studies

  - Energy content of ethanol versus gasoline or natural gas

  - Making cement

  - Hydrogen as a fuel or an energy storage system

- Thermodynamic asides

  - Internal energy — a state variable

  - Enthalpy — separating work from internal energy

- Thermodynamic aside

  - Enthalpies of reaction and combustion.

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A little thermodynamics

Looking back to Unit 4

And ahead to future work

- System — very large numbers of molecules ($\sim N_0 \sim 10^{24}$)

  Settle down.   Achieve equilibrium state.

- STATE VARIABLE: intrinsic characteristic of system in equilibrium

- State variables:
  $$\text{Pressure} \quad p$$
  $$\text{Density} \quad \rho = N/V$$
  $$\text{Temperature} \quad T$$

- For single phase systems (like a gas or a liquid) two of p, ρ, T specify the state of the system.

  Equation of state like $P = \frac{N}{V}k_B T = \rho k_B T$ determines the other.

- Work and heat not state variables

  Add work and extract heat and leave system in exactly the same state it began

- Internal energy — U — is a state variable

  $$dU = dQ - dW = dQ - pdV$$

  HEAT ADDED MINUS WORK DONE BY

- $U = U(T, \rho)$ or $U = U(T, p)$.

- Internal energy can be viewed the sum of thermal energy plus all the energy stored in the binding energy of molecules, atoms, and nuclei.

  Internal energy   =

  (1) Energy necessary to assemble material at $T = 0$: energy in nuclear, atomic, and chemical bonds,

  +

  (2) Thermal energy necessary to raise material to temperature T.

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I.   Internal energy

- Energy is conserved (First Law)

- What is the energy content of material?

- It depends on the context

Ice block images removed
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Consider a block of ICE

and add energy

THERMAL ENERGY I	Motions of molecules	WARM
THERMAL ENERGY II	Inter molecular binding energy	MELT/VAPORIZE
INTERATOMIC BINDING ENERGY	Binds atoms in H_2O	ELECTROLYZE
ATOMIC BINDING ENERGY	Binds electrons to H and O nuclei	IONIZE
NUCLEAR BINDING ENERGY	Binds protons and neutrons into nuclei	DISASSEMBLE INTO p AND n
RESTMASS ENERGY	The mass itself!	??

WARM	38.1 J/mol-K
MELT/VAPORIZE	6.01/40.7 kJ/mol
ELECTROLYZE	241 kJ/mol
IONIZE	199.8 MJ/mol
DISSASSEMBLE NUCLEI	3 TJ/mol
REST MASS	1.6 PJ/mol

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How to relate these energies to the atomic world and the world of electromagnetic radiation?

Energy per mole $\Rightarrow$ Energy per molecule (or atom, or nucleus)

Conversion factor: 1 MJ/mole = 10.4 eV/molecule

Or: 1 eV/molecule = 96.5 KJ/mole

Shorter wavelength
⇕
Higher energy

Relate to type of electromagnetic radiation...
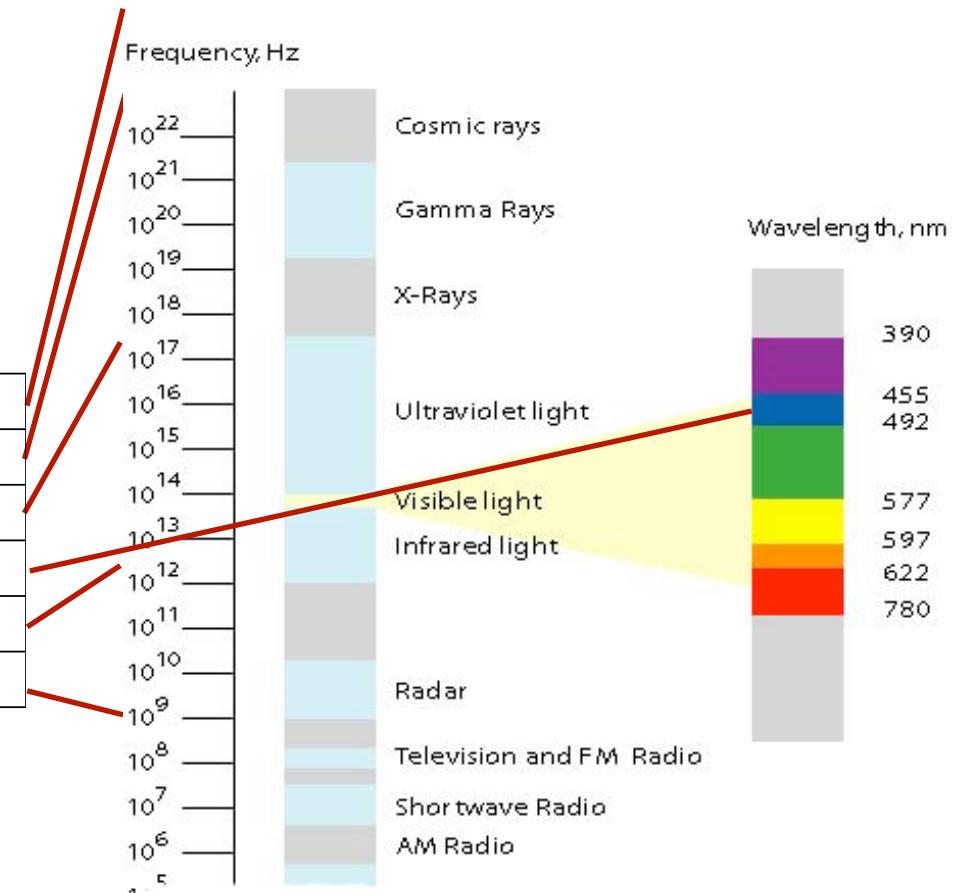
$$\lambda = c/\nu = 2\pi\hbar c/E$$

$$\nu = E/(2\pi\hbar)$$

1 MJ/mole $\Leftrightarrow$ 10.4 eV/atom $\Leftrightarrow$ $\lambda = 119$ nm
1 MJ/mole $\Leftrightarrow$ 2.5×10^{15} Hz

ANNIHILATE	1.6 PJ/mol	4 YHz
FUSE	3 TJ/mol	387.5 ZHz
IONIZE	199.8 MJ/mol	500 PHz
ELECTROLYZE	241 kJ/mol	.6 PHz $\Leftrightarrow$ 470 nm
MELT/VAPORIZE	6.01/40.7 kJ/mol	15 – 90 THz
WARM	38.1 J/mol-K	95 GHz

Frequency, Hz

10^{22}	Cosmic rays
10^{21}	
10^{20}	Gamma Rays
10^{19}	
10^{18}	X-Rays
10^{17}	
10^{16}	Ultraviolet light
10^{15}	
10^{14}	Visible light
10^{13}	Infrared light
10^{12}	
10^{11}	
10^{10}	
10^{9}	Radar
10^{8}	Television and FM Radio
10^{7}	Shortwave Radio
10^{6}	AM Radio

Wavelength, nm

	390
	455
	492
	577
	597
	622
	780

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THERMAL ENERGY — MOTION OF MOLECULES

Atoms vibration graph removed
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Gas molecules graph removed
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- Add energy to the system.
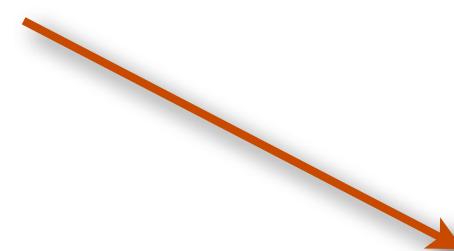
- $\Rightarrow$ Kinetic:
  - Liquid/gas: translational and rotational
  - Solid: vibration

- $\Rightarrow$ Potential
  - Solid: stretching of bonds
  - Liquid/gas: increasing average separation

Vibration of atoms in
a crystal lattice

Kinetic energy
of a gas

Proportionality between change in internal energy and
change in temperature defines

Heat capacity (as discussed in Lecture 4)

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A Little More Thermodynamics

As described in Unit 4 (on Heat)

Remember difference between *constant volume* and *constant pressure*.

Add heat at constant volume $dQ = dU$

Defines heat capacity at constant volume

$$\left.\frac{\partial Q}{\partial T}\right|_V = \left.\frac{\partial U}{\partial T}\right|_V \equiv C_V$$

Add heat at constant pressure $dQ = dU + pdV$

So heat added at constant pressure does not *all* go into increasing the internal energy of a system.
Some goes into *work* against the environment.

Remember enthalpy: $H \equiv U + pV$

Add heat at constant pressure $dQ = dH = dU + pdV$

Defines heat capacity at constant pressure

$$\left.\frac{\partial Q}{\partial T}\right|_P = \left.\frac{\partial H}{\partial T}\right|_P \equiv C_P$$

The distinction matters most for gases where volume changes can be significant!

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Some useful heat capacities

Substance	Specific Heat Capacity KJ/kg K	Molar Heat Capacity J/mol K
Ice	2.09	37
Water	4.19	75
Steam	2.01	34
Ethanol(l)	2.42	113
Copper	0.38	33
Liquid sodium	1.39	32
Air	0.73	21
Helium	3.125	12.5

Substance	Specific Heat Capacity KJ/kg K
Steel	0.51
Glass	0.78
Granite	0.80
Wood	1.67
Soil	1.05

Lots of stories here!
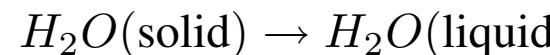
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MELT OR VAPORIZE— INTERMOLECULAR BINDING ENERGY

Energy derived from change of phase — breaking the "bonds" of intermolecular forces.

Latent heat of melting or vaporization

Solid   Liquid   Gas

MELT

$$H_2O(\text{solid}) \rightarrow H_2O(\text{liquid})$$
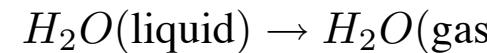
6.01 kJ/mol at 0° C and 1 atm

$$\Delta H \approx \Delta U = + \text{ 6.01 kJ/mol}$$

Even though measurement was made at constant pressure, the volume change is so small that the result is very nearly ΔU. Not so for liquid $\leftrightarrow$ vapor

VAPORIZE

$$H_2O(\text{liquid}) \rightarrow H_2O(\text{gas})$$
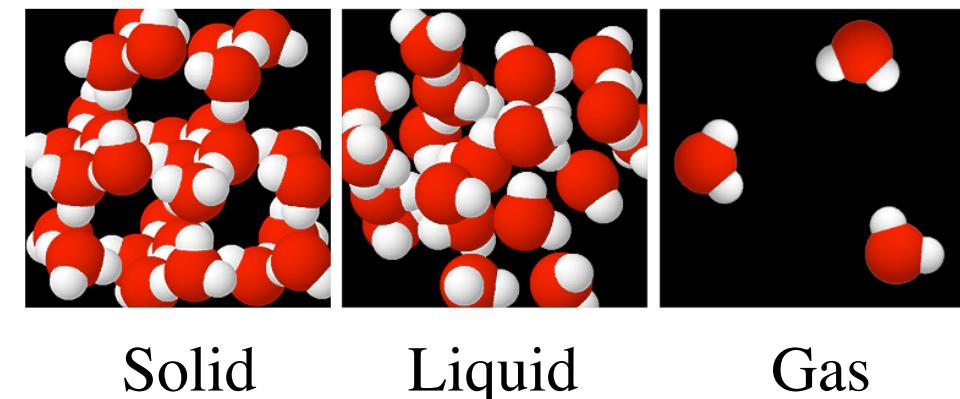
40.7 kJ/mol at 100° C and 1 atm

$$\Delta H = + \text{ 40.7 kJ/mol}$$

Changing liquid to gas creates
$\Delta V_{\text{gas}} \sim 22\,\text{L} = 0.022\,\text{m}^3$

$$\begin{aligned}\Delta H &= \Delta U + p\Delta V_{\text{gas}} \\ &= \Delta U + RT\Delta n_{\text{gas}}\end{aligned}$$

$$\Delta n_{\text{gas}}RT = 1\,\text{mole} \times 8.31\,\text{Jmol}^{-1}\text{K}^{-1} \times 373\,\text{K} = 3.10\,\text{kJ}$$

$$\Delta U = 40.7\,\text{kJ/mol - 3.1 kJ/mol} = 37.6\,\text{kJ/mol}$$

- Latent heat of vaporization is much larger than melting.

- $\Delta H \approx \Delta U$

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Phase diagrams --- recording information about important substances

Phase diagram of water

Image from http://commons.wikimedia.org/wiki/File:Phase-diag.svg

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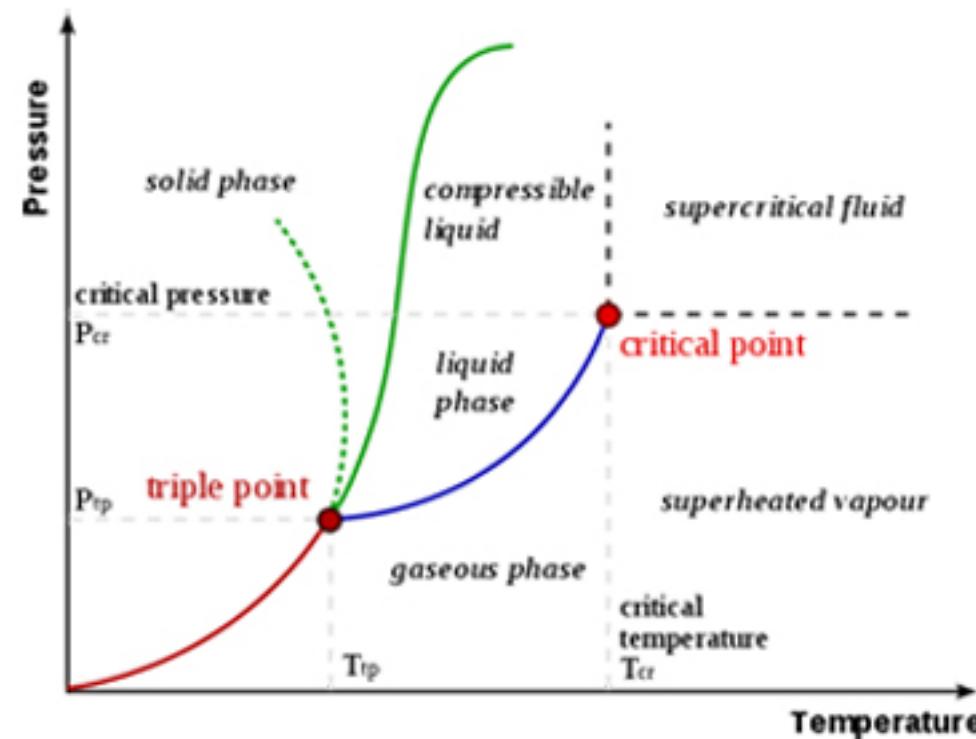
Phase diagram of carbon dioxide

No liquid phase
at atmospheric
pressure (dry ice)
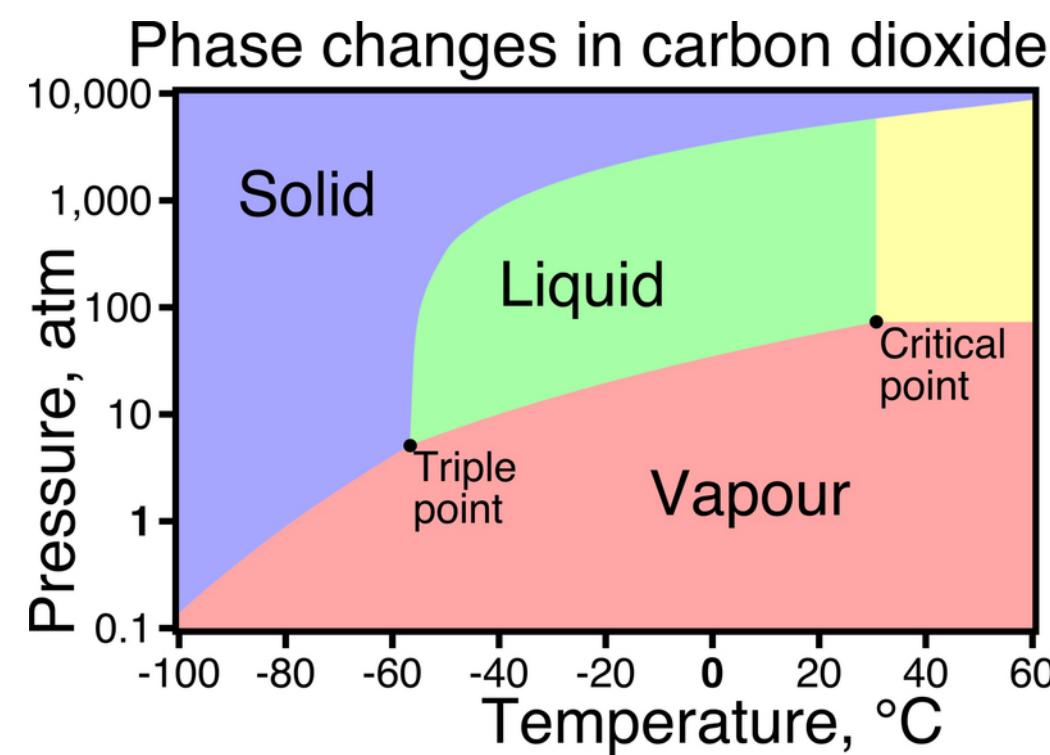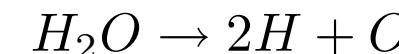
Diagram from public domain.

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ELECTROLYZE − INTERATOMIC BINDING ENERGY
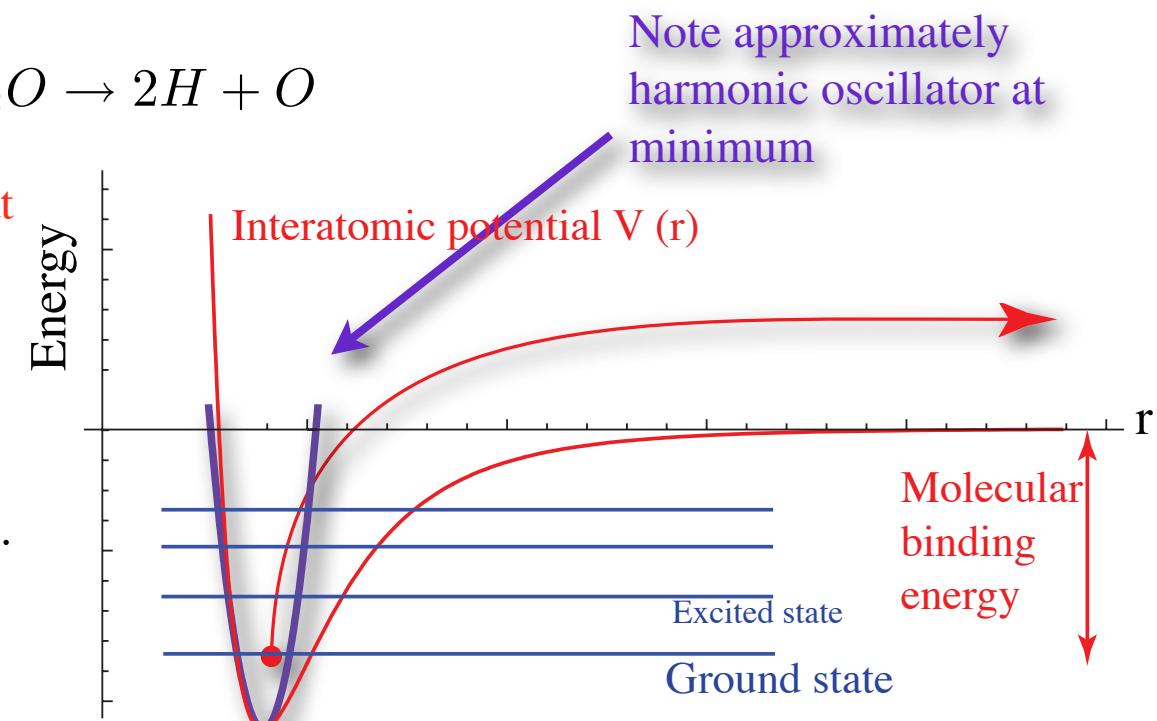
Now that the ice has been vaporized, further addition of energy raises the temperature until the bonds that hold the water molecule together begin to break. Corresponding to the reaction

$$H_2O \rightarrow 2H + O$$

- Interatomic forces are typically attractive at long distances and repulsive at short distances.

- Range of bond types from *ionic* when one atom transfers an electron to another to complete an atomic shell — *e.g.* Na$^+$–Cl$^-$. To *covalent* when atoms share electrons. Typical potential is Lennard-Jones,

$$V(r) = \frac{a}{r^{12}} - \frac{b}{r^6}$$

- Formation or disassociation of molecules involves breaking bonds, or exciting atoms out of the potential well.


Note approximately harmonic oscillator at minimum

Interatomic potential V (r)

Energy

Molecular binding energy

Excited state

Ground state

r
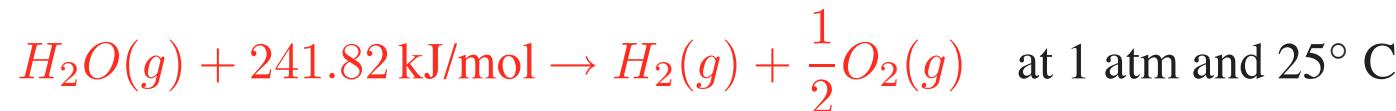
Ionic bonding graph removed due to copyright restrictions.

Polar covalent bond graph removed due to copyright restrictions.

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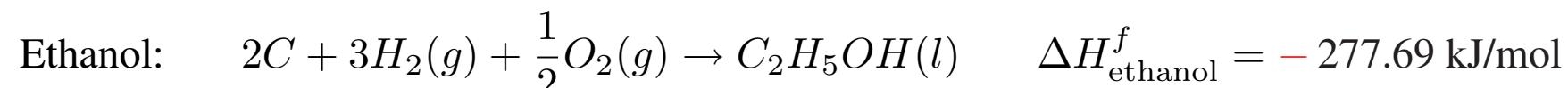
Enthalpies of formation

Instead of quoting changes in internal energy to break molecules up into constituent atoms, it is more useful to

- Quote enthalpy since reactions usually occur at constant pressure.

- Use molecular form for elements that are found as molecules in nature: H_2, O_2, Cl_2, *etc.*

- Specify state (solid, liquid, gas), temperature, and pressure of reactants.

$$H_2O(g) + 241.82\,\text{kJ/mol} \rightarrow H_2(g) + \frac{1}{2}O_2(g) \quad \text{at 1 atm and } 25° \text{ C}$$

- Inverse process (building up molecules) yields *"Heat" or Enthalpy of Formation*

Water: $\quad H_2(g) + \dfrac{1}{2}O_2(g) \rightarrow H_2O(g)$ $\qquad\qquad \Delta H^f_{\text{water}} = -241.82\,\text{kJ/mol}$

Ethanol: $\quad 2C + 3H_2(g) + \dfrac{1}{2}O_2(g) \rightarrow C_2H_5OH(l)$ $\quad \Delta H^f_{\text{ethanol}} = -277.69 \text{ kJ/mol}$

Sucrose: $\quad 6C + 6H_2(g) + 3O_2(g) \rightarrow C_6H_{12}O_6(s)$ $\quad \Delta H^f_{\text{sucrose}} = -1268 \text{ kJ/mol}$

Note the $-$ sign: The internal energy of H_2O is less than that of $H_2 + \frac{1}{2}O_2$, so energy is given off to the environment

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A word about signs

Internal energy and enthalpy are properties of a substance, so the sign of ΔU and ΔH are chosen so
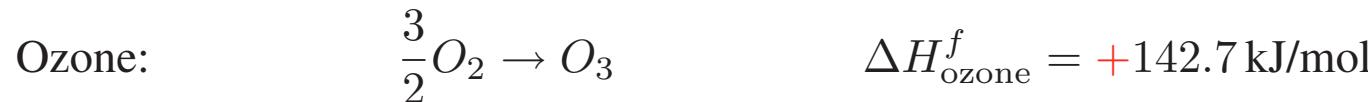
- A minus sign corresponds to a reduction in the internal energy or enthalpy of the substance, and a corresponding increase in the energy of the environment.

  An exothermic process.   Used for heating, work

- A plus sign is the opposite: an increase in the internal energy or enthalpy of the substance. Energy is removed from the environment.

  The process is endothermic.   Used for energy storage
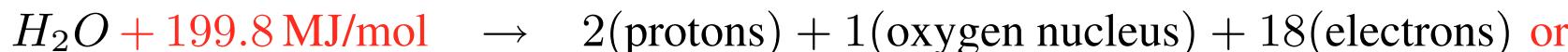
A positive enthalpy of formation is a sign of instability and high energy content, for example,

$$\text{Ozone:} \qquad \frac{3}{2}O_2 \to O_3 \qquad \Delta H^f_{\text{ozone}} = +142.7\,\text{kJ/mol}$$

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IONIZE − ATOMIC BINDING ENERGY
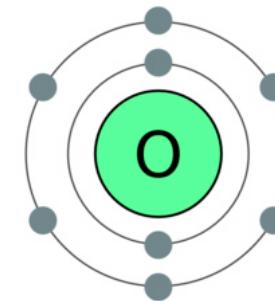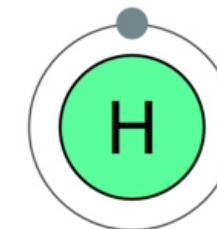
Energy necessary to completely remove all electrons from atoms. Electrons are bound by electrostatic (Coulomb) forces that are stronger than interatomic forces, so *ionization energies* are generally larger than heats of formation.

$$H_2O + 199.8\,\text{MJ/mol} \quad \rightarrow \quad 2(\text{protons}) + 1(\text{oxygen nucleus}) + 18(\text{electrons}) \text{ or}$$

$$H_2O \quad \rightarrow \quad 2(\text{protons}) + 1(\text{oxygen nucleus}) + 18(\text{electrons}) - 199.8\,\text{MJ/mol}$$

Note that it requires more energy to remove each successive electron. The innermost electron is bound by

$$E_0 = Z^2 \times 13.6 \text{ eV}$$

For heavy nuclei these energies get large.

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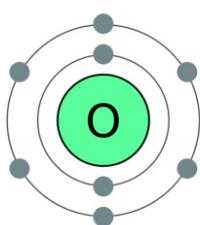
Hydrogen ionisation enthalpy 1312 kJ mol^{-1} Almost the same as hydrogen. Why?

- Conversion factor: 96.5 kJ/mole = 1 eV/atom,

- So ionization enthalpy of hydrogen is 1312/96.5 = 13.6 ev/atom

Oxygen ionisation enthalpy

1st	2nd	3rd	4th	5th	6th	7th	8th
1313.9	3388.3	5300.5	7469.2	10989.5	13326.5	71330	84078.0

Ionization enthalpies of oxygen graph
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64 times greater than ionization energy of hydrogen

$\approx 1 \text{ keV}$ an X-ray!

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Nuclear Binding Energy and Rest Mass Energy

These are really outside the scope of this chemistry/biology energy lecture

And will be covered later in the course

But a few slides are included for anyone who wants to look ahead

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FUSE — NUCLEAR BINDING

Nuclear interactions allow nuclei to fuse and fission
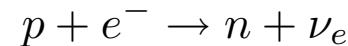
Weak interactions allow protons to turn into neutrons plus electrons and antineutrinos and vica versa

$$n \rightarrow p + e^- + \bar{\nu}_e \qquad\qquad \beta \text{ decay}$$

$$p \rightarrow n + e^+ + \nu_e \qquad\qquad \beta^+ \text{ decay}$$

$$p + e^- \rightarrow n + \nu_e \qquad\qquad \text{electron capture}$$

These processes allow less stable nuclei to react to form ones that have more binding energy (in stars, in nuclear reactors, and in nuclear bombs)

^{56}Fe (26 protons and 30 neutrons) is the most tightly bound nucleus, so everything tends toward iron.

28 H_2O atoms have the same number of protons, neutrons and electrons as ^{56}Fe

$$28\,(H_2O) + 46\,e^- \rightarrow 9\,(^{56}Fe) + 46\,\nu_e$$

Nuclear binding energies are typically ~ 8 MeV/nucleon, so nuclear reactions liberate much more energy than atomic interactions

This reaction goes from weaker to stronger binding, so it's *exothermic*, it liberates energy,

$$3 \times 10^6 \text{ MJ/mol}(H_2O)$$

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ANNIHILATE − RESTMASS ENERGY

Mass itself represents incredible reserves of stored internal energy, but it must be annihilated to be made available

$$H_2O + \overline{H_2O} \rightarrow \text{ENERGY} = 3.2 \times 10^{15} \text{ J/mol}(H_2O)$$

Calculation:

$$
\begin{aligned}
mc^2 &= (1 + 1 + 16) \times 10^{-3} \text{ kg mol}^{-1} \times \left(3 \times 10^8 \text{ m s}^{-1}\right)^2 \\
&= 18 \times 9 \times 10^{13} \text{ J} = 1.6 \times 10^{15} \text{ J}
\end{aligned}
$$

So half that energy is associated with the rest mass of H_2O.

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Summary

- **Internal energy** is the energy that is stored in the system as potential or kinetic (thermal) energy when a system is put together from its pieces.

- Only *changes in internal energy* are observable. (Usually we omit rest mass energy of protons and neutrons when considering internal energy of H_2O.)

- The kinds of internal energy we should consider are dictated by the circumstances — chemical binding for chemistry, nuclear binding for nuclear processes.

- **Enthalpy** $H = U + pV$ $\Delta H = \Delta U + p\Delta V$ is the energy that must be added to a mechanical system to change the internal energy. Includes energy needed to perform "pdV work".

- **Enthalphy of formation** is the energy necessary to form a chemical compound out of its (molecular) constituents, including pdV work.

- If enthalpy must be added to a system to enable a reaction (eg. ionization) the process is **endothermic**. If energy is given off (eg. condensation of a gas) the process is **exothermic**.

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Outline

- A tour of the internal energy of matter

  - Change of internal energy with temperature — heat capacities

  - Solid $\Leftrightarrow$ liquid $\Leftrightarrow$ gas — changes of phase or *latent heat*

  - Molecules $\Leftrightarrow$ atoms — heat of formation

  - Atoms $\Leftrightarrow$ electrons and nuclei — atomic binding

  - Nuclei $\Leftrightarrow$ protons and neutrons — nuclear binding

  - Matter $\Leftrightarrow$ Rest mass energy

- Case Studies

  - Energy content of ethanol versus gasoline or natural gas

  - Making cement

  - Hydrogen as a fuel or an energy storage system

- Thermodynamic asides

  - Internal energy — a state variable

  - Enthalpy — separating work from internal energy

- Thermodynamic aside

  - Enthalpies of reaction and combustion.

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Case Studies

(1) "Burning ethanol produces less CO_2 than burning gasoline."

Yes, it produces less CO_2 per kilogram of fuel, but it produces almost exactly the same amount of CO_2 per Joule of energy produced, which is what counts. Methane produces considerably less CO_2 per Joule of produced energy.

(2) "Cement manufacturing uses 1/2 % of all U. S. energy but generates 2 % of CO_2 emissions (even worse 5% of all CO_2 emissions worldwide)."

Cement manufacturing produces CO_2 both from burning hydrocarbon fuel *and* from the basic chemical reaction that makes cement out of limestone.

(3) "Hydrogen is the fuel of the future!"

Strictly speaking, hydrogen isn't a fuel at all! It is an energy storage system and should be considered in the same context as batteries, flywheels, super capacitors, etc.

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(1) "Burning ethanol produces less CO_2 than burning gasoline."

Need a diversion to introduce the ideas of

Enthalpy of Reaction and Combustion

- Need to know how much energy is liberated when a particular reaction takes place.

- Strategy: Combine Enthalpies of formation (ΔH^f) to obtain the reaction of interest:

- Want $\Delta H_{\text{reaction}}$ for $\quad A + B \rightarrow C + D$

- Again <u>note the sign</u>: $\Delta H_{\text{reaction}}$ is the change in the internal enthalpy of the products relative to the reactants, so $-\Delta H_{\text{reaction}}$ is the enthalpy given off to the environment.
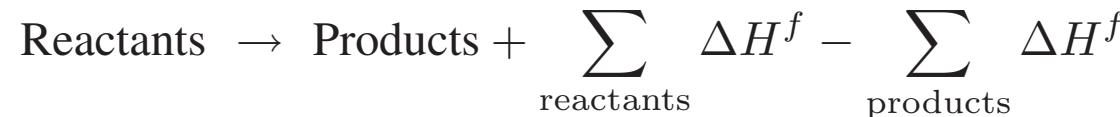
General Result: For a reaction Reactants $\rightarrow$ products

- In a reaction you are forming the products and unforming the reactants

- So (Hess's Law)

$$\Delta H(\text{Reaction}) = \sum_{\text{products}} \Delta H^f - \sum_{\text{reactants}} \Delta H^f$$

- And $-H(\text{reaction})$ is given off to the environment

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General Result: For a reaction Reactants → products

$$\text{Reactants} \rightarrow \text{Products} + \sum_{\text{reactants}} \Delta H^f - \sum_{\text{products}} \Delta H^f$$
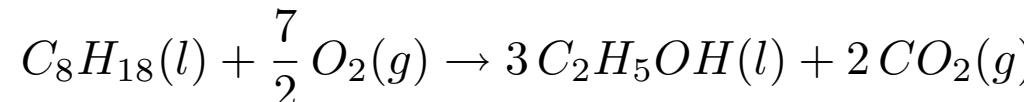
$$\Delta H(\text{Reaction}) = \sum_{\text{products}} \Delta H^f - \sum_{\text{reactants}} \Delta H^f$$

Some useful enthalpies of formation

Compound	Chemical Formula	Enthalpy of Formation
Diatomic gases	H_2, O_2, Cl_2,...	0 kJ/mol (by definition)
Methane	$CH_4(g)$	– 75 kJ/mol
Water vapor	$H_2O(g)$	– 242 kJ/mol
Octane	$C_8H_{18}(l)$	– 250 kJ/mol
Ethanol liquid	$C_2H_5OH(l)$	– 278 kJ/mol
Carbon dioxide	$CO_2(g)$	– 394 kJ/mol
Calcium oxide	CaO	– 635 kJ/mol
Iron Ore (Hematite)	Fe_2O_3	– 824 kJ/mol
Calcium carbonate	$CaCO_3$	– 1207 kJ/mol
Sucrose	$C_6H_{12}O_6$	– 1270 kJ/mol

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Example: Partial oxidation of octane to ethanol.   Balanced chemical reaction:

$$C_8H_{18}(l) + \frac{7}{2}\,O_2(g) \rightarrow 3\,C_2H_5OH(l) + 2\,CO_2(g)$$

$$\begin{aligned}
\Delta H_{\text{reaction}} &= 3\,\Delta H^f_{\text{ethanol}} + 2\,\Delta H^f_{CO_2} - \Delta H^f_{\text{octane}} \\
&= 3(-278\,\text{kJ/mol}) + 2(-394\,\text{kJ/mol}) - 1(-250\,\text{kJ/mol}) \\
&= -1372\,\text{kJ/mol}
\end{aligned}$$

Energy is given off, an exothermic reaction.

A special reaction — Combustion: Complete oxidation

- Examples

    ⋆ Combustion of methane $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

    ⋆ Combustion of ethanol $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

    ⋆ Combustion of glycine $4C_2H_5NO_2 + 9O_2 \rightarrow 8CO_2 + 10H_2O + 2N_2$

- Reaction enthalpy for combustion is known as Enthalpy of Combustion

- Some conventions: Nitrogen is released as N_2 unless otherwise specified; water is assumed to be released as a liquid, CO_2 as a gas.

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Enthalpies of combustion for some important organic fuels

Compound	Chemical Formula	Enthalpy of Combustion
Methane gas	$CH_4(g)$	– 890 kJ/mol
Propane gas	$C_3H_8(g)$	– 2220 kJ/mol
Octane	$C_8H_{18}(l)$	– 5471 kJ/mol
Ethanol liquid	$C_2H_5OH(l)$	– 1368 kJ/mol
Sucrose	$C_6H_{12}O_6$	– 5645 kJ/mol

Enthalpy of combustion compared to CO_2 emssions

- Enthalpy of combustion — Gasoline : Ethanol = 4 : 1

- CO_2 produced — Gasoline : Ethanol = 4 : 1

- The same (to within accuracy of the calculation!)

- Enthalpy of combustion — Methane : Either = .65 : 1

- CO_2 produced – Methane : Either = .5 : 1

- CO_2 production per Joule from methane is .5/.65 = 77%.

- Choice between ethanol and gasoline depends on how they are obtained

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Compute actual CO_2 emissions per Joule of energy for octane, ethanol, methane

Alcohol	Ethanol	C_2H_5OH	46 gm/mol
Gasoline	Octane	C_8H_{18}	114 gm/mol
Natural Gas	Methane	CH_4	16 gm/mol

Combustion:

$$CH_4 + 2O_2 \rightarrow CO_2 + H_2O \qquad \Delta H = -890 \text{ kJ/mol}$$

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O \qquad \Delta H = -1368 \text{ kJ/mol}$$

$$C_8H_{18} + 12.5O_2 \rightarrow 8CO_2 + 9H_2O \qquad \Delta H = -5471 \text{ kJ/mol}$$

Mass of CO_2 (44 gm/mol) per kilogram of fuel:

Ethanol	2(44) gm (CO_2)/46 gm(ethanol)	1.91 gm CO_2/gm fuel
Octane	8(44) gm (CO_2)/114 gm(octane)	3.09 gm CO_2/gm fuel
Methane	44 gm (CO_2)/16 gm(methane)	2.75 gm CO_2/gm fuel

Mass of CO_2 per Joule of energy:

Ethanol	2(44) gm (CO_2) / mole(ethane)	÷ 1368 kJ/mole(ethanol)	.0643 gm CO_2 / kJ
Octane	8(44) gm (CO_2) / mole(octane)	÷ 5471 kJ/mole(octane)	.0643 gm CO_2 / kJ
Methane	44 gm (CO_2) / mole(methane)	÷ 890 kJ/mole(methane)	.049 gm CO_2 / kJ

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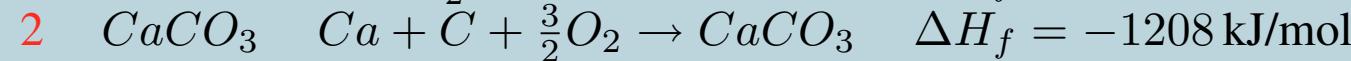
Why is concrete manufacturing so energy and especially CO_2 intensive?

Concrete consists of Portland Cement and aggregate. Portland Cement is 60-70% anhydrous calcium oxide — CaO plus other oxides ($\sim$ 25% SiO_2, small % Al_2O_3, Fe_2O_3,...

Drive CO_2 out of limestone with heat!

$$CaCO_3 \rightarrow CaO + CO_2 \qquad \Delta H(\text{reaction}) = 179\,\text{kJ/mol}$$

How to compute a heat of reaction from standard heats of formation.

1	CaO	$Ca + \frac{1}{2}O_2 \rightarrow CaO$	$\Delta H_f = -635\,\text{kJ/mol}$
2	$CaCO_3$	$Ca + C + \frac{3}{2}O_2 \rightarrow CaCO_3$	$\Delta H_f = -1208\,\text{kJ/mol}$
3	CO_2	$C + O_2 \rightarrow CO_2$	$\Delta H_f = -393.5\,\text{kJ/mol}$

$1 + 3 - 2 \qquad \Delta H(\text{reaction}) = \Delta H_f(1) + \Delta H_f(3) - \Delta H_f(2) = 179\,\text{kJ/mol}$
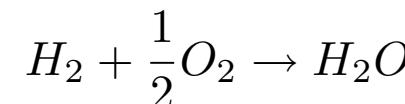
CO_2 budget: per kg of cement.

- Reaction CO_2: 1 kg cement $\rightarrow \sim$ .65 kg $CaO + \frac{44}{56} \times .65 = .51$ kg CO_2.

- Total CO_2 includes fuel for reactor. Need efficiency to compute. Result: 0.95 kg CO_2 per kg cement.

More than half from reaction.

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(3) "Hydrogen is the fuel of the future!"

- If what you mean by a fuel is something that provides primary energy input to human activities, the answer is NO!

  ⋆ It is not found on earth — there are no hydrogen mines!

  ⋆ It takes at least as much energy to create H_2 from other sources as it yields when the hydrogen is burned.

- Hydrogen is a energy storage system. And a good one — in principle

- Energy content of hydrogen

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

$\Delta H^f_{\text{water}}(l) = -285.83$ kJ/mole

- Enthalpy of H_2O liquid is 285.83 kJ/mole less than enthalpy of H_2 and (1/2) O_2, so burning hydrogen in oxygen is quite exothermic.

- Energy density of hydrogen:

$$(286\,\text{kJ/mole}) \div (2\,\text{gm } H_2/\text{mole}) = 143\,\text{MJ/kg}$$

A very large number (because hydrogen is so light.)

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- Hydrogen: 143 MJ/kg

- Other energy storage systems:

  - ⋆ Methane: 56 MJ/kg
  - ⋆ Octane: 48 MJ/kg
  - ⋆ Ethanol: 31 MJ/kg

  - ⋆ Flywheel: ~ 0.5 MJ/kg
  - ⋆ NiMH Battery: ~ 0.22 MJ/kg
  - ⋆ Li Ion Battery: ~ 0.25 MJ/kg

- Hot water storage: H_2O at $100°C$ compared to $25°C$: 0.314 MJ/kg. Very much smaller, but water is very easy to heat and very cheap to gather and store!

Energetics of making hydrogen

Electrolysis:

It all depends on the original energy source

- Pass a current through a solution of an electrolyte in water, producing hydrogen gas and oxygen gas at the electrodes.

- Efficiency depends on source of electric current.

  - ⋆ Efficiency for conversion of original energy source (hydro, nuclear, solar, wind, coal?) to electricity, including transmission losses: η_1.
  - ⋆ Efficiency of electrolysis: η_2.
  - ⋆ Efficiency of infrastructure (recovery, compression, transport, storage): η_3.
  - ⋆ Efficiency for useful work from combustion of hydrogen (or fuel cell): η_4.
  - ⋆ Efficiency if original energy source were converted directly to useful work, $\eta^\star$.
  - ⋆ Typically $\eta^\star \gg \eta_1 \times \eta_2 \times \eta_3 \times \eta_4$
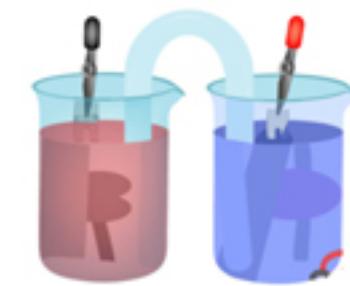
Figure by MIT OpenCourseWare.

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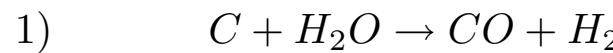
Right now the principal way to make hydrogen is from reaction
that start with hydrocarbons and/or coal

- A variety of processes

- Some ancient technologies: $C + H_2O \rightarrow H_2 + CO$
  produced "coal gas" throughout the world up through the
  middle of the 20th century

Coal factory image removed
due to copyright restrictions.

- Much research on new processes, but hydrocarbon based
  processes are either energy intensive or CO_2 emitting.

Commonly used reactions:

⋆ Syngas generation (the old gashouse!)
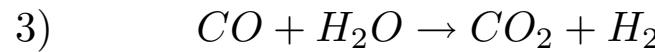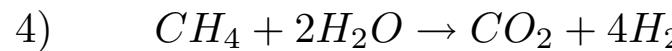
$$1) \qquad C + H_2O \rightarrow CO + H_2 \qquad \text{``Steam Reforming Coal''}$$
$$2) \qquad CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \text{``Steam Reforming Methane''}$$

Gas house image removed
due to copyright restrictions.

⋆ "Shift reaction"

$$3) \qquad CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{applied to CO from syngas}$$
$$4) \qquad CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \qquad \text{Steam reforming plus}$$

shift reaction on CH_4

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Analyze coal reforming (Reaction 1)

- Figure of merit, just burn the coal to heat water, generate electricity, etc.

  $\Delta H_{\text{carbon}}^{\text{combustion}} = -394\,\text{kJ/mole}$

- Make syngas by coal reforming,

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

  $\Delta H_{\text{reaction}} = +176\,\text{kJ/mole}$, so steam reforming coal is endothermic.

  Energy from combustion of produced hydrogen: 286 kJ/mole

  Energy from combustion of produced carbon monoxide: 283 kJ/mole

- Carbon monoxide is toxic and also poisons the catalysts used in today's hydrogen fuel cells.

- If the CO is not recovered and burned the hydrogen production cycle produces a net of 286-176 = 110 kJ/mole compared to direct combustion, which generates 394 kJ/mole.

- So what are the advantages of the "hydrogen economy"?

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And now, the advantages of hydrogen as an energy storage medium

- Low pollution: combustion yields water and small amounts of nitrogen oxides.

- Controllability: at ambient temperatures hydrogen combustion is very slow; catalysts allow for great reaction rate adjustment.

- Safety(!): lighter than air $\rightarrow$ disperses; auto-ignition temperature is much higher than gasoline (580°C versus 280°C); will not burn in concentrations less than 4% (limit for gasoline is 1%); hydrogen is not toxic.

- Very high specific energy density, 143 MJ/kg.

Big disadvantage: Hydrogen is very diffuse at p = 1 atm and T = 300 K.

- At NTP 1 kg is 22,400 L = 22.4 m^3, for a volumetric energy storage of

$$(143\,\text{MJ/kg}) \div (22.4\,\text{m}^3\text{/kg}) = 6.4\,\text{MJ/m}^3$$

- Compare octane (density $\approx$ .75 kg/L):

$$(48\,\text{MJ/kg}) \div (\approx 1.33 \times 10^{-3}\,\text{m}^3\text{/kg}) = 3.6\,\text{GJ/m}^3$$

- High pressure storage? (Materials)

- Liquify (Cryogenics)

- Adsorb hydrogen onto metals or advanced materials (Research)

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Summary

- Internal energy: Useful definition depends on context

- Ignore those processes that are frozen out (like nuclear energy in chemical processes)

- But don't forget them when they become active!

- Enthalpy: $H = U + PV$, energy input at constant pressure

- Heat capacity, latent heat of phase change, ionization...

- Enthalpies of formation, reaction, and combustion

- Energy balance in chemical reactions is easy

WARM	38.1 J/mol-K
MELT/VAPORIZE	6.01/40.7 kJ/mol
ELECTROLYZE	241 kJ/mol
IONIZE	199.8 MJ/mol
DISSASSEMBLE NUCLEI	3 TJ/mol
REST MASS	1.6 PJ/mol