"A" students work
(without solutions manual)
~ 10 problems/night.

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Module #11
Thermochemistry

FITCH Rules

General
- G1: Suzuki is Success
- G2. Slow me down
- G3. Scientific Knowledge is Referential
- G4. Watch out for Red Herrings
- G5. Chemists are Lazy

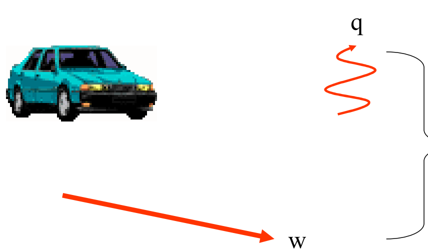
Chemistry
- C1. It's all about charge
- C2. Everybody wants to "be like Mike"
- C3. Size Matters
- C4. Still Waters Run Deep
- C5. Alpha Dogs eat first

$$E_{el} = k\left(\frac{q_1q_2}{r_1+r_2}\right) \quad or \quad = k\left(\frac{q_1q_2}{d}\right)$$

Energy: capacity to do work

$$w = (F)d$$

Or transfer heat, q



Energy
Consumed
Depends on
Both work
And heat

$$\Delta E = E_{final} - E_{initial} = q + w$$

Properties and Measurements

Property	Unit	Reference State
Size	m	size of earth
Volume	cm^3	m
Weight	gram	mass of 1 cm^3 water at specified Temp (and Pressure)
Temperature	^{o}C, K	boiling, freezing of water (specified Pressure)
1.66053873x10^{-24}g	amu	(mass of 1C-12 atom)/12
quantity	mole	atomic mass of an element in grams
Pressure	atm, mm Hg	earth's atmosphere at sea level
Energy, General		
Animal	hp	horse on tread mill
heat	BTU	1 lb water 1 ^{o}F
	calorie	1 g water 1 ^{o}C
Kinetic	J	m, kg, s
Electrostatic		1 electrical charge against 1 V
electronic states in atom		Energy of electron in vacuum
Electronegativity	F	

Heat flow measurements — Reference state?

To set a "heat flow" scale

1. Defined conditions: how experiment is performed open flask, closed flask, pressure

2. **Define the direction of heat flow by giving a positive or negative number**

Does the "system (earth)" gain energy?

+ heat
- heat?

For image above
system (earth) gains heat
from surroundings (sun)

To set a "heat flow" scale

1. Defined conditions: how experiment is performed open flask, closed flask, pressure

2. **Define the direction of heat flow by giving a positive or negative number**

We would get a different answer if we asked
"Does the "system (sun)" gain energy?"

+ heat
- heat?

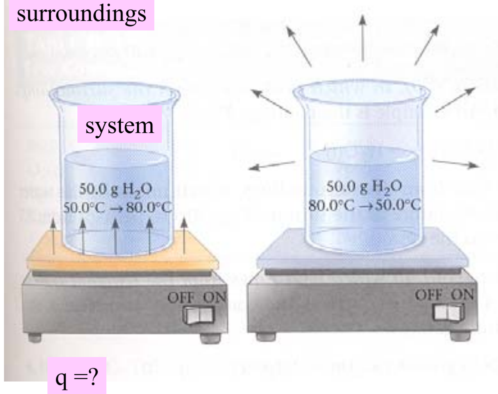
For this question: the
system (sun) loses heat
to the surroundings (earth)

First Law of Thermodynamics: Energy is conserved

No universal change in energy
Just a transfer of energy

surroundings

system



q =?

q>0 system

q<0 system

E = constant when System AND surroundings considered!

To set a "heat flow" scale

1. Defined conditions: how experiment is performed open flask, closed flask, pressure

2. Define the direction of **heat flow (q)** by giving a positive or negative number

q is + when heat flows into the system from the surroundings

q is - when heat flows out of the system into the surroundings

3. **Chemical process in the "system" is defined by heat flow**

endothermic q>0
exothermic q<0

Properties and Measurements

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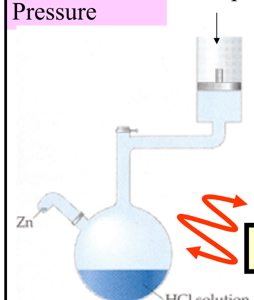
$1.66053873 \times 10^{-24}$g	amu	(mass of 1C-12 atom)/12
quantity	mole	atomic mass of an element in grams
Pressure	atm, mm Hg	earth's atmosphere at sea level
Energy: Thermal	BTU	1 lb water 1 °F
	calorie	1 g water 1 °C
Kinetic	J	2kg mass moving at 1m/s
Energy, of electrons		energy of electron in a vacuum
Electronegativity		F
Heat Flow		into system = +

Chemical reactions involve
1. **heat exchange**

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

Heat exchange At constant Pressure

Constant Atm.pressure



$q_P = \Delta H$

Subscript Reminds us that Pressure is constant

As a review:

who is oxidized?
who is reduced?
what is the oxidation number on H_2?
Who is an oxidizing agent?

H = enthalpy

Greek: *thalpein* – to heat
en - in
H for (?) *heat*

1 atm pressure = constant pressure

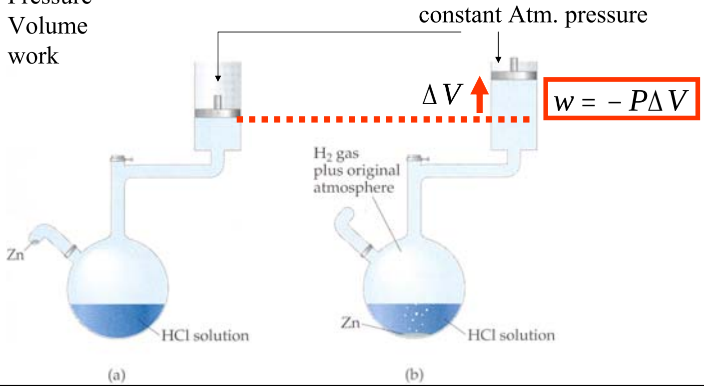
This means heat flow, q, is **enthalpy change**

Chemical reactions involve

1. **heat exchange**
2. **work**

$$Zn(s) + 2H^{+}(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

Pressure-Volume work



$$\Delta E = E_{final} - E_{initial} = q + w$$

$$\Delta E_P = q_P + (-P\Delta V)$$

$$\Delta E_P = \Delta H + (-P\Delta V)$$

$$\Delta E_P = \Delta H - P\Delta V$$

This is a form of Rule G3

Science is referential

Generally final - initial

Change in volume is typically small for Most reactions

$$\Delta E_P \approx \Delta H$$

This means we can measure the energy change of A chemical reaction by measuring the heat exchange At constant pressure

five Navy Avengers disappeared in the Bermuda Triangle on Dec. 5, 194

First example problem will involve methane

We will prove to ourselves that the Pressure-Volume work is a Small contribution to the total energy change

3 to 8 standard cubic feet of biogas per pound of manure. The biogas usually contains 60 to 70% methane.

Methane Gas Recovery At landfills

Consider the contribution of volume of **gas phase molecules**

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$$

$$PV = nRT$$

At constant T:

$$P(\Delta V) = (\Delta n)RT$$

$$P(\Delta V) = \left(n_{gas\ final} - n_{gas\ initial}\right)RT$$

$$P(\Delta V) = (1 - 3moles)\left(0.0821\frac{L \cdot atm}{mol \cdot K}\right)298K$$

$$P(\Delta V) = -48.9316 L \cdot atm$$

%&$*! Conversions – if Interested see slide after next

$$P(\Delta V) = (-48.9316 L \cdot atm)\left(\frac{0.1013kJ}{L \cdot atm}\right) = -4.9kJ$$

2mole change

Consider the contribution of volume change **for water** in this reaction

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$$

$$\left[2mole H_2O_{(l)}\right] * \left[\frac{18g}{mol}\right] * \left[\frac{1cm^3 water}{1g water}\right] * \left[\frac{1L}{10^3 cm^3}\right] = 0.036L$$

%&$*! Conversions – if Interested see next slide

$$PV = [1atm][0.036L]\frac{0.1013kJ}{L - atm} = 0.0036kJ$$

	Energy in kJ	
Most reactions total (q):	~ 1000	kJ
PV 1 mole gas	~ 2.5	kJ
PV 2mole liquid water	~ 0.0036	kJ

By the end of This module We will see this Is "true"

Sig fig tells us that PV energy small compared to q

Optional Slide: conversion

$$(atm)\left(\frac{1.01325x10^5\ Pa}{atm}\right)\left(\frac{\left(\frac{kg}{m \cdot s^2}\right)}{Pa}\right)(L)\left(\frac{10^3 cm^3}{L}\right)\left(\frac{1m}{10^2 cm}\right)^3\left(\frac{J}{\left(\frac{kg \cdot m^2}{s^2}\right)}\right)\left(\frac{kJ}{10^3 J}\right) = 0.101325kJ$$

$$\left(\frac{0.101325kJ}{(atm)(L)}\right) = \left\{\left(\frac{1.01325x10^5\ Pa}{atm}\right)\left(\frac{\left(\frac{kg}{m \cdot s^2}\right)}{Pa}\right)\left(\frac{10^3 cm^3}{L}\right)\left(\frac{1m}{10^2 cm}\right)^3\left(\frac{J}{\left(\frac{kg \cdot m^2}{s^2}\right)}\right)\left(\frac{kJ}{10^3 J}\right)\right\}$$

To set a "heat flow" scale

1. **Defined conditions: how experiment is performed Constant Pressure**
2. **But not on the path taken (state property)**

Heat flow depends the conditions

H= **enthalpy**

$$q_{reaction}\Big|_{cons\tan t\,pressure} = \Delta H = H_{products} - H_{reac\tan ts}$$

Enthalpy is a state property

(measured under constant pressure, but how measured under that constant pressure is not important)

$$q = \Delta H > 0$$

endothermic

$$H_{products} > H_{reactants}$$

$$H_2O_{(s)} + heat \longrightarrow H_2O$$ Think of heat as a reactant

$$q = \Delta H < 0$$

exothermic

$$H_{products} < H_{reactants}$$

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + H_2O_{(l)} + heat$$ Think of heat as a product

---

Enthalpy is an "extensive" property

Depends upon the amount present

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)} \qquad \Delta H = -890kJ$$

890kJ of heat is released when 1 mole of methane Reacts with oxygen

$$\frac{-890kJ}{1moleCH_{4(g)}}$$

$$\left(\frac{-890kJ}{1moleCH_{4(g)}}\right)\left(2moleCH_{4(g)}\right) = -1780kJ$$

Properties and Measurements

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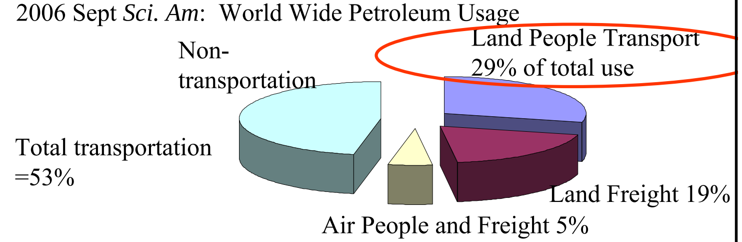
Kinetic	J	m, kg, s
Electrostatic		1 electrical charge against 1 V
electronic states in atom		Energy of electron in vacuum
Electronegativity F		
Heat flow measurements		constant pressure, define system vs surroundi[ngs] per mole basis (intensive)

Context for the next example problem

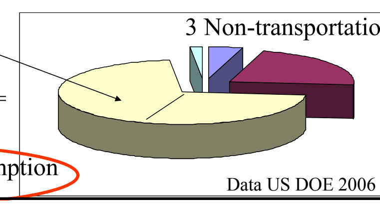
2006 Sept *Sci. Am*: World Wide Petroleum Usage

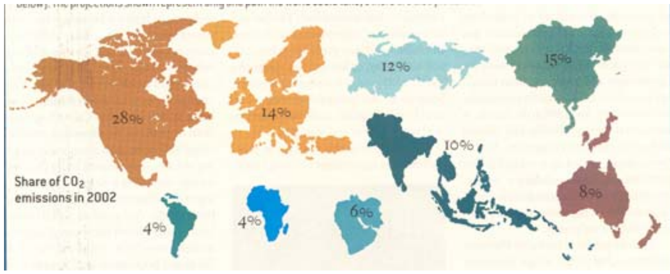


U.S. differs from world in distribution of petroleum use

Transportation = 71.8%

57.8% of Transportation= Personal land transport = 41.5% of total U.S. consumption





Example: If you drove an automobile 1.50×10^2 miles at 17.5 miles/gal you consume a certain number of gallons of gasoline. If you burn that number of gallons of gasoline at constant pressure how much heat would be released? Assume the gasoline is pure octane with a density of the octane 0.690 g/mL?

$$\Delta H = -1.09x10^4\,kJ \qquad 2C_8H_{18} + 25O_2 \rightarrow 16CO_{2(g)} + 18H_2O_{(g)}$$

Strategy: need moles of octane consumed (Golden Bridge)

$$\text{miles} \xrightarrow{\text{mpg}} \text{gallons} \xrightarrow{\text{density}} \text{grams} \xrightarrow{\text{Molar mass}} \text{moles} \xrightarrow{\Delta H} \text{heat}$$

$$(150.mi)\left(\frac{1gal}{17.5mi}\right)\left(\frac{3.7852L}{gal}\right)\left(\frac{10^3 mL}{L}\right)\left(\frac{0.690gC_8H_8}{mLC_8H_8}\right)\left(\frac{1moleC_8H_8}{114gC_8H_8}\right)\left(\frac{-1.09x10^4\,kJ}{2moleC_8H_8}\right) =$$

$$\Delta H = -1{,}070{,}243.955kJ$$

$$\Delta H = -1.07x10^6\,kJ \quad \text{3 sig fig}$$

We will use part of this problem Again:

$$\left(\frac{3.7852L}{gal}\right)\left(\frac{10^3 mL}{L}\right)\left(\frac{0.690gC_8H_8}{mLC_8H_8}\right)\left(\frac{1moleC_8H_8}{114gC_8H_8}\right)\left(\frac{-1.09x10^4\,kJ}{2moleC_8H_8}\right) = \frac{-124{,}861kJ}{gal}$$

Rules

1. Enthalpy is an extensive property (depends upon number of moles)
2. Enthalpy change for a reaction is equal in magnitude, but opposite in sign, to the enthalpy for the reverse reaction

$$\Delta H = -1.09x10^4\,kJ \qquad 2C_8H_{18} + 25O_2 \rightarrow 16CO_{2(g)} + 18H_2O_{(g)}$$

$$\Delta H = +1.09x10^4\,kJ \qquad 16CO_{2(g)} + 18H_2O_{(g)} \rightarrow 2C_8H_{18} + 25O_2$$

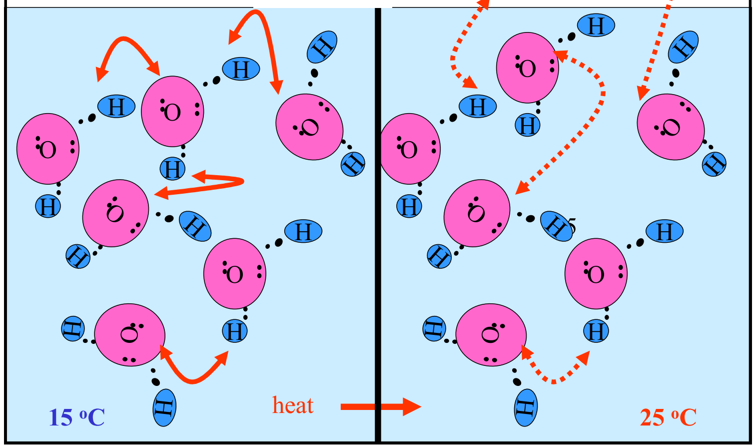
3. Enthalpy change depends upon the state of the reactant and products

$$\Delta H = +44kJ \qquad H_2O_{(l)} \rightarrow H_2O_{(g)}$$

ENERGY measurement
- a) change in temperature
- b) some function specific to the material and how it is organized (bonds)

ENERGY change is a function of
a) temperature
b) material

$E_{el} = k\left(\frac{q_1 q_2}{d}\right)$



ENERGY measurement

a) change in temperature

b) some function specific to the material and how it is organized (bonds)

$q = C(t_{final} - t_{initial})$

$q = C\Delta t$

Pure material

$q = m \cdot c \cdot \Delta t$

m = mass

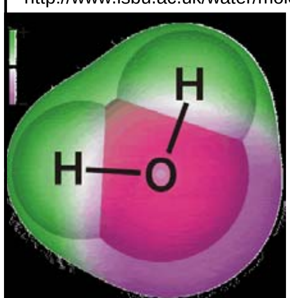
c = **specific heat** of a pure substance

C = heat capacity = heat required to raise the temperature of the system 1°C

units: J/°C

http://www.lsbu.ac.uk/water/molecule.html

$charge\ density \approx \frac{q}{r}$



Shape and charge distribution On water

Electron density of water

Electrons on Oxygen sit "out there" causing large Electrostatic potential Oriented on the electrons

$C_{(liquid H2O)}$=4.18J/g-°C

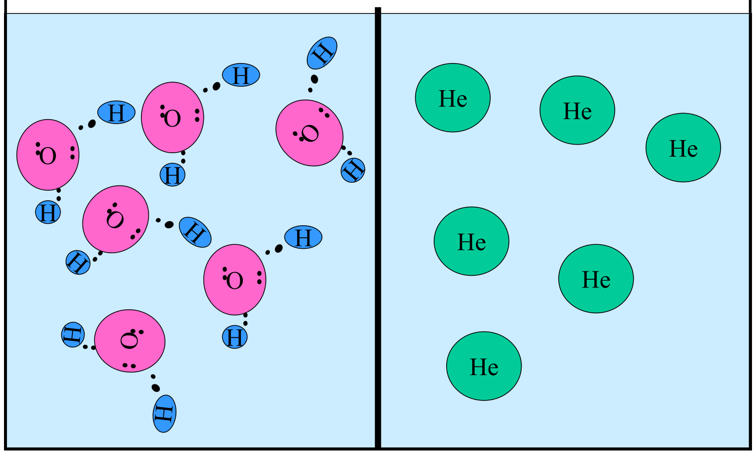
Liquid water is very strongly organized due to the **polarity** of the molecule, so it has a high **specific heat**

Specific heats, c, of various substances in various physical states

Material	Specific Heats c, (J/g-K)
Pb(s)	0.12803
Pb(l)	0.16317
Cu(s)	0.382
Fe(s)	0.446
Cl_2(g)	0.478
C(s)	0.71
CO_2(g)	0.843
NaCl(s)	0.866
Al(s)	0.89
C_6H_6(l)	1.72
H_2O(g)	1.87
C_2H_5OH(l)	2.43
H_2O(l)	4.18

Ability to store heat in a substance is variable.

For the same amount of energy, easier to break electrostatic attraction of He compared to water with it's localized charge



Example: 1.00 cup of water is heated from 25.0 °C to 100.0 °C. How many joules were used to heat the water?

$$q = m \cdot c \cdot \Delta t$$

Mass of water:

$$[1.00cup]\left[\frac{1qt}{4cups}\right]\left[\frac{1L}{1.057qt}\right]\left[\frac{10^3 mL}{L}\right]\left[\frac{1g}{1mL}\right] = 236.51g$$

$$\Delta t = T_{final} - T_{initial} \qquad \Delta t = 100^o C - 25^o C$$

$$\Delta t = 75^o C \qquad \Delta t = 75K$$

$$q = 236.51g\left[\frac{4.18J}{gK}\right]75K \qquad q = 7.41x10^4 J$$

$$q = 74148.53 \qquad q = 74.1kJ$$

Example 2: 1 cup of dry soil (specific heat, c = 0.800 J/gK; density =1.28 g/cm³). Calculate the Joules required to raise the temperature of the dry soil from 25°C to 100 °C.

$$[1.00cup]\left[\frac{1qt}{4cups}\right]\left[\frac{1L}{1.057qt}\right]\left[\frac{10^3 mL}{L}\right]\left[\frac{1.28g}{1mL}\right] = (236.51g)1.28 = 302.7g$$

$$q = 302.7g\left[\frac{0.8J}{gK}\right]75K$$

$$q_{dry\ soil} = 18{,}164J = 18.1kJ$$

$$q_{water} = 74.1kJ$$

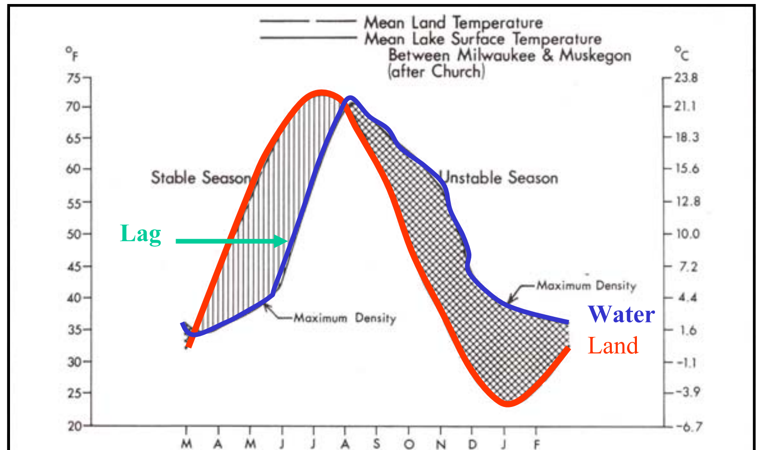


Figure 27 Mean Land Temperatures versus Mean Surface Lake Temperatures in Southern Lake Michigan Area

Because water has a high heat capacity it takes longer than air or soil to warm up and longer to cool down

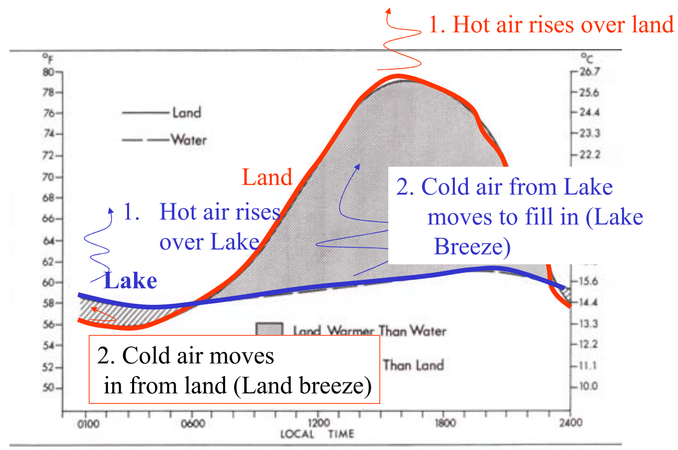
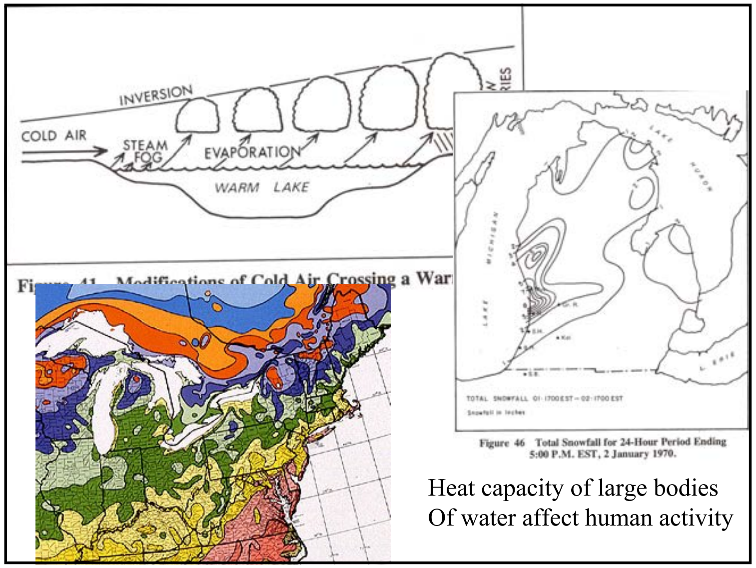


Figure 36 Diurnal Temperatures, Land versus Water, Typical of the Great Lakes in the Early Summer

The temperature change in 24 hours in summer for water is not much leading to big differences between lake and land and thus a lake breeze



Heat capacity of large bodies
Of water affect human activity

Example 3: Heat capacity of the metal block of a car combustion engine. Assume that a Prius … der 176.6 kg engine block is made of iron. The specific heat of iron is 440 J/kg-C. If I drive 8 miles twice a day (to work and back) at an average 42 mpg, what fraction of the total available enthalpy in 1 gallon of octane is consumed in heating the engine block from 25°C to 100°C?

$$q = m \cdot c \cdot \Delta t$$

$$q = (200kg)\left(\frac{440J}{kg \cdot C}\right)(100 - 25C) = 5{,}828kJ$$

$$\left(\frac{42miles}{1gal}\right)\left(\frac{trip}{8miles}\right)\left(\frac{5{,}828kJ\ engine\ heating}{1trip}\right) = \left(\frac{27{,}730kJ\ heating}{gal}\right)$$

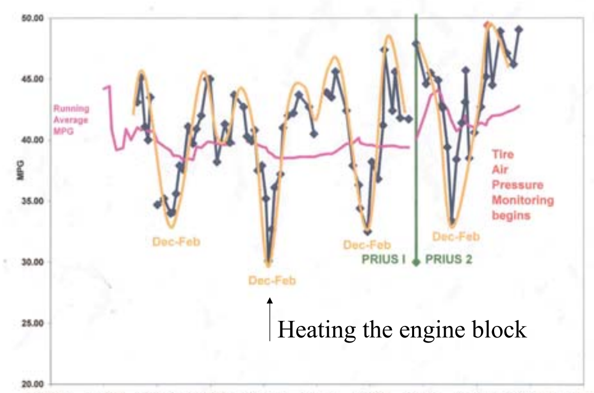
Compare to heat available from combustion of 1 gallon of octane (from before

$$\Delta H = -1.09x10^4\ kJ \qquad 2C_8H_{18} + 25O_2 \rightarrow 16CO_{2(g)} + 18H_2O_{(g)}$$

$$\left(\frac{3.7852L}{gal}\right)\left(\frac{10^3 mL}{L}\right)\left(\frac{0.690gC_8H_8}{mLC_8H_8}\right)\left(\frac{1moleC_8H_8}{114gC_8H_8}\right)\left(\frac{-1.09x10^4\ kJ}{2moleC_8H_8}\right) = \frac{-124{,}861kJ}{gal}$$

$$\left(\frac{5{,}828kJ}{124{,}861kJ}\right)100 = 22.2\%$$

Let's compare to what I measure



Prius 1

$$\left(\frac{39 - 31mpg}{39mpg}\right)100 = 20.5\%$$

Prius 2

$$\left(\frac{43 - 34mpg}{43mpg}\right)100 = 20\%$$

Properties and Measurements

Property		Unit	Reference State
Size		m	size of earth
Volume		cm^3	m
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Temperature		^oC, K	boiling, freezing of water (specified Pressure)
$1.66053873 \times 10^{-24}$g		amu	(mass of 1C-12 atom)/12
quantity	mole		atomic mass of an element in grams
Pressure		atm, mm Hg	earth's atmosphere at sea level
Energy, General			
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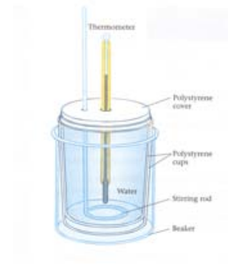
	Kinetic	J	m, kg, s
	Electrostatic		1 electrical charge against 1 V
	electronic states in atom		Energy of electron in vacuum
	Electronegativity F		

Heat flow measurements — constant pressure, define system vs surroundin
per mole basis (intensive) **Calorimetry**



Relate reaction heat
To the calorimeter heat

$$q_{reaction} = -q_{calorimeter}$$

If the temperature of the water rises (heat flow into water)
then heat must have been lost from the reaction

Example: When 1.00 g of ammonium nitrate, NH_4NO_3, is added to 50.0 g of water in a coffee-cup calorimeter, it dissolves:

$$NH_4NO_{3(s)} \rightarrow NH^+_{4(aq)} + NO^-_{3(aq)}$$

and the temperature of the water drops from 25.00 to 23.32 ^oC. Assuming that all the heat absorbed by the reactions comes from the water, calculate q for the reaction system.

$$q_{calorimeter} = m \cdot c \cdot \Delta t$$

$$q_{calorimeter} = [50.0 g]\left[4.18 \frac{J}{gK}\right][23.32^oC - 25.00^oC]$$

$$q_{calorimeter} = \left[209 \frac{J}{K}\right][-1.68K]$$

$$q_{calorimeter} = -351.12 J$$

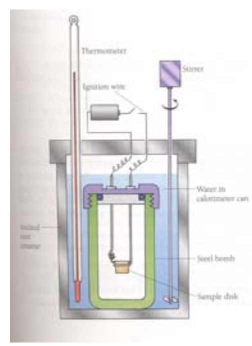
A 1 degree change in Celsus
Is a 1 degree change in Kelvin

$$q_{calorimeter} = -351 J$$

$$q_{reaction} = -q_{calorimeter}$$

$$q_{reaction} = -(-351 J)$$

$$q_{reaction} = 351 J$$



Not all calorimeters can be based on

$$q_{reaction} = -q_{calorimeter} = -m \cdot c \cdot \Delta t$$

Heat capacity of the calorimeter

$$q_{reaction} = -q_{reaction} = -\left\{\left[C_{cal}\right]\Delta t\right\}$$

In some problems
You will
Need to determine
This number
In one step and
Then go on

Example: The reaction between hydrogen and chlorine

$$H_{g(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$$

can be studied in a bomb calorimeter. It is found that when a 1 g sample of H_2 reacts completely, the temperature rises from 20.00 to 29.82 °C. Taking the heat capacity of the calorimeter to be 9.33 kJ/°C, calculate the amount of heat evolved in the reaction.

$$q_{reaction} = -[C_{cal}]\Delta t$$

Heat evolved? q

Calorimeter heat capacity = 9.33 kJ/°C

$T_{initial}$ = 20.00 °C

T_{final} = 29.82 °C

$$q_{reaction} = -\left[9.33 \frac{kJ}{^oC}\right]\left[29.82^oC - 20.00^oC\right]$$

$$q_{reaction} = -91.6kJ$$

Example: Salicyclic acid, $C_7H_6O_3$, is one of the starting materials in the manufacture of aspirin. When 1.00 g of salicylic acid burns in a bomb calorimeter, the temperature rises to 32.11°C from 28.91 °C. The temperature in the bomb calorimeter increases by 2.48°C when the calorimeter absorbs 9.37 kJ. How much heat is given off when one mole of salicylic acid is burned?

1.00 g of $C_7H_6O_3$

$T_{initial}$ 32.11°C

T_{final} 29.91°C

9.37kJ required to cause 2.48 °C change

$$q_{reaction} = -\left[\frac{9.37kJ}{2.48^oC}\right](32.11 - 29.91)$$

$$q_{reaction} = -8.3121kJ$$

$$q_{reaction} = -[C_{cal}]\Delta t$$

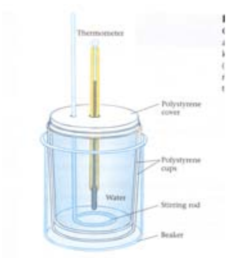
???

$$C_{cal} = \frac{9.37kJ}{2.48^oC}$$

$$(1moleC_7H_6O_3)\left(\frac{138gC_7H_6O_3}{1moleC_7H_6O_3}\right)\left(\frac{-8.3121kJ}{1gC_7H_6O_3}\right) = -315.8598kJ$$

$$= -316kJ$$

Combine



$$2C_8H_{18} + 25O_2 \rightarrow 16CO_{2(g)} + 18H_2O_{(g)}$$

calorimetry

Reaction stoichiometry

To get reaction enthalpies

Example 2 What is the enthalpy change for the reaction

ΔH

$$NH_4NO_{3(s)} \rightarrow NH^+_{4(aq)} + NO^-_{3(aq)}$$

If exactly 1 g of ammonium nitrate is reacted in a bomb calorimeter made with 50 g of water and the temperature of the water drops from 25.00 °C to 23.32 °C?

$$q_{reaction} = -q_{calorimeter} = -[50.0g]\left[4.18\frac{J}{g^oC}\right][23.32^oC - 25.00^oC]$$

$$q_{reaction} = \left[-209\frac{J}{^oC}\right][-1.68^oC]$$

1 g was reacted

2N=28.02
4H=4.04
3O=48.00
80.05

$$q_{reaction} = 351.12J$$

$$q_{reaction} = 351J$$

$$\left[\frac{351J}{1g}\right]\left[\frac{80.05g}{mol}\right] = \frac{28100J}{mol} = \frac{28.1kJ}{mol}$$

$$q_{reaction}\Big|_{constantpressure} = \Delta H = 351J$$

$$NH_4NO_{3(s)} \rightarrow NH^+_{4(aq)} + NO^-_{3(aq)} \qquad \Delta H = +28.1kJ$$

$NH_4NO_{3(s)} \rightarrow NH^+_{4(aq)} + NO^-_{3(aq)}$ $\Delta H = +28.1kJ$

Where did the per/mole go?

The reaction was written as a per/mole
Enthalpy is understood as a per/mole of reactant (or as the reaction is written)

$1NH_4NO_{3(s)} \rightarrow 1NH^+_{4(aq)} + 1NO^-_{3(aq)}$ $\Delta H = +28.1kJ$

Thermochemical Equation Rules

When there are no Coefficients it is understood that It is "1"

1. Value of)H applies when products and reactants are at same temperature, 25ºC unless otherwise specified.
2. Sign of)H indicates whether reaction, when carried out at constant pressure, is exothermic or endothermic
3. ΔH sign changes when reaction is reversed

$NH^+_{4(aq)} + NO^-_{3(aq)} \rightarrow NH_4NO_{3(s)}$ $\Delta H = -28.1kJ$

4. Stoichiometry is important
4. Phases of all species must be specified
5. Values of)H is same regardless of method used to calculate it (Hess's Law)

Example illustrating importance of phases

Using a coffee-cup calorimeter, it is found that when an ice cube weighing 24.6 g melts, it absorbs 8.19 kJ of heat. Calculate for the phase change represented by the thermochemical equation

$$H_2O_{(s)} \rightarrow H_2O_{(l)}$$

$$\left[\frac{8.19kJ}{24.6g_{ice}}\right]\left[\frac{18.02g_{H_2O}}{mole_{H_2O}}\right]\left[1mole_{H_2O}\right] = 6.00kJ$$

An example of several of the rules using Fuel Cells

Fuel cells use the reaction:

$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$$

Calculate the enthalpy for the equation above given that:

$\Delta H = +571.6kJ$ $2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)}$

Reverse reaction:

$\Delta H = -571.6kJ$ $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

scale

$\Delta H = \frac{-571.6kJ}{2} = -286kJ$ $H_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$

Here we got a number by coming "at it" from an odd direction

Hess's law

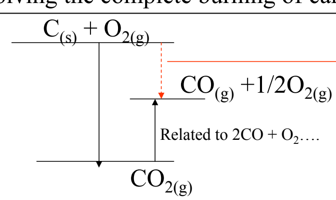
The value of ∆H for a reaction is the same whether it occurs in one step or in a series of steps (enthalpy (constant P, T) is a state function)

Germain Henri Hess
1802-1850
born in Geneva Switzerland
Professor of Chemistry
At St. Petersburg Technological Institute

Example of how Hess's law is useful

$$C_{(s)} + \tfrac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$$

It is difficult to measure the heat evolved for this reaction because it occurs as the partial burning of carbon in the presence of other reactions involving the complete burning of carbon



This is the
Number we want
But can't actually measure

Get to the number by an alternative Path (State function!)

To solve rearrange equations to get CO on right hand side

$$\Delta H = -393.5kJ \qquad C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$

$$\Delta H = -566.0kJ \qquad 2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$$

$$\Delta H = -566.0kJ \qquad 2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$$

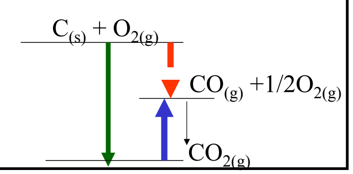
$$\Delta H = +566.0kJ \qquad 2CO_{2(g)} \rightarrow 2CO_{(g)} + O_{2(g)}$$

$$\Delta H = \frac{+566.0kJ}{2} \qquad CO_{2(g)} \rightarrow CO_{(g)} + \tfrac{1}{2}O_{2(g)}$$

$$\Delta H = +283.0kJ \qquad CO_{2(g)} \rightarrow CO_{(g)} + \tfrac{1}{2}O_{2(g)}$$

$$\Delta H = -393.5kJ \qquad C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$

$$\Delta H = -110.5kJ \qquad C_{(s)} + \tfrac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$$



Enthalpies of Formation

Invoke Rule G5: Chemists are Lazy

Rather than getting the enthalpy for each reaction from a bomb calorimeter use a smaller number of **standard** reactions from which Hess's law can be applied to get all the remainder reactions of interest

Enthalpy associated with standard reaction is

enthalpy of formation

which is the enthalpy change when one mole of compound is formed at constant pressure of 1 atm and a fixed temperature, ordinarily 25°C, from the elements in their stable states at that pressure and temperature. STP (Standard Temperature and Pressure)

This allows us to look at enthalpy of compounds not reactions which reduces total data which must Be acquired (Chemists are Lazy!!!)

---

1 is "understood"

$$\Delta H_f^O = -882kJ \qquad \tfrac{1}{2}N_{2(g,1atm,25C)} + O_{2(g,1atm,25C)} \rightarrow 1NO_{2(g,1atm,25C)}$$

Standard molar enthalpy of formation of a compound

From elements in their stable states at 1 atm pressure 25°C

Most ΔH_f^o are negative meaning that formation of the compound from the elements is ordinarily exothermic

Elements in their stable states at 1atm, 25°C have a standard molar enthalpy of 0

Why?

Elements in their stable states at 1atm, 25°C have a standard molar enthalpy of 0

$$Fe_s \rightarrow Fe_s$$

$$\Delta H^O_{Fe(s)} = \Delta H^O_{Fe(s)}\Big|_{1atm,25C} - \Delta H^O_{Fe(s)}\Big|_{1atm,25C} = 0$$

Products (standard state) - Reactants (standard state) = 0

$$\Delta H_f^O = -882kJ \qquad \tfrac{1}{2}N_{2(g,1atm,25C)} + O_{2(g,1atm,25C)} \rightarrow NO_{2(g,1atm,25C)}$$

Standard molar enthalpy of formation of a compound

From elements in their stable states at 1 atm pressure 25°C

Most ΔH_f^o are negative meaning that formation of the compound from the elements is ordinarily exothermic

For aqueous ions, the enthalpy is **scaled** relative to the proton

$$\Delta H_f^O H^+_{aq} = 0$$

Do we detect any patterns?

	ΔH_f^O kJ/mol		ΔH_f^O kJ/mol		kJ/mol ΔH_f^O
Al(s)	0	Fe(s)	0	Sc(s)	0
Ba(s)	0	Pb(s)	0	Si(s)	0
Be(s)	0	Li(s)	0	Na(s)	0
Br_2(g)	0	Mg(g)	0	S(s,rhombic)	0
Ca(s)	0	Mn(s)	0	Ti(s)	0
C(s,graphite)	0	Hg(l)	0	Zn(s)	0
Cs(s)	0	Ni(s)	0		
Cl_2(g)	0	N_2(g)	0		
Cr(s)	0	O_2(s)	0		
Cu(s)	0	P_4(s)	0		
F_2(g)	0	K(s)	0		
H_2(g)	0	Rb(s)	0		
H^+(aq)	0				
I_2(s)	0				

Common non-metals Have specific forms In which they Are standard

MOST metals are elemental solids (metal) in standard state

Group 17 with exception Of I_2 are gases in Stable, standard state

Properties and Measurements

Property	**Unit**	**Reference State**
Size	m	size of earth
Volume	cm^3	m
Weight	gram	mass of 1 cm^3 water at specified Temp (and Pressure)
Temperature	^oC, K	boiling, freezing of water (specified Pressure)
$1.66053873 \times 10^{-24}$g	amu	(mass of 1C-12 atom)/12
quantity	mole	atomic mass of an element in grams
Pressure	atm, mm Hg	earth's atmosphere at sea level
Energy, General		
	electronic states in atom	Energy of electron in vacuum
	Electronegativity	F
Heat flow measurements		constant pressure, define system vs surroundings per mole basis (intensive)

Standard Molar Enthalpy 25 ^oC, 1 atm, from stable state

) H_f^o H_{aq}^+ =0

Calculation of) H° **standard** enthalpy change of a reaction

$$\Delta H^O = \sum n\Delta H^o_{f,products} - \sum n\Delta H^o_{f,reactants}$$

1 atm pressure
25°C

1. The coefficients of products and reactants in the thermochemical equation must be taken into account

$$2Al_{(s)} + Fe_2O_{3(s)} \rightarrow 2Fe_{(s)} + Al_2O_{3(s)}$$

$$\Delta H^O = \{\Delta H^o_{f,Al_2O_3} + 2\Delta H^o_{f,Fe(s)}\} - \{\Delta H^o_{f,Fe_2O_{3s}} + 2\Delta H^o_{f,Al(s)}\}$$

$$\Delta H^O = \Delta H^o_{f,Al_2O_3} - \Delta H^o_{f,Fe_2O_{3s}}$$

2. Elements in standard states can be omitted because heats of formation are zero

OJO!

$$\Delta H^O = -1669.8 - (-822.16)$$

Appendix

$$\Delta H^O = -1669.8 + 822.16 = -847.65 kJ/mol$$

Calculation of) H° **standard** enthalpy change of hot and cold packs

$$\Delta H^O = \sum n\Delta H^o_{f,products} - \sum n\Delta H^o_{f,reactants}$$

1 atm pressure
25°C

$$NH_4NO_{3,s} \rightarrow NH^+_{4,aq} + NO^-_{3,aq}$$

$$\Delta H^O = \{\Delta H^o_{f,NH^+_{4,aq}} + \Delta H^o_{f,NO^-_{3,aq}}\} - \{\Delta H^o_{f,NH_4NO_{3,s}}\}$$

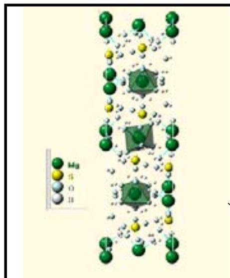
$$\Delta H^O = \{-132.5 + -205.0\} - \{-365.6\}$$

$$\Delta H^O = \{-337.5\} - \{-365.6\} = +28\frac{kJ}{mol}$$

Compares well to the calorimetry calc. (28.1kJ/mol)!

Appendix

Compound	**ΔH_f^o, kJ/mol**
$NH_4NO_{3,s}$	-365.6
$NH_4^+{}_{,aq}$	-132.5
$NO_3^-{}_{aq}$	-205.0
$MgSO_{4,s}$	-1284.9
$Mg^{2+}{}_{aq}$	-466.8
$SO_4^{2-}{}_{aq}$	-909.3
Fe,s	0
$O_{2,g}$	0
$Fe_2O_{3,s}$	-1118.4



http://webmineral.com/data/Hexahydrite.shtml

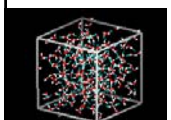
$$MgSO_{4,s} \xrightarrow{H_2O} Mg^{2+}_{aq} + SO^{2-}_{4,aq}$$

$$\Delta H^O = \left\{\Delta H^o_{f,Mg^{2+}_{aq}} + \Delta H^o_{f,SO^{2-}_{4aq}}\right\} - \left\{\Delta H^o_{f,MgSO_{4,s}}\right\}$$

$$\Delta H^O = \{-466.8 + -909.3\} - \{-1284.9\}$$

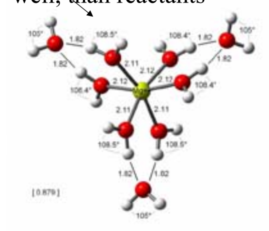
$$\Delta H^O = \{-1{,}376.1\} - \{-1284.9\} = -91.2\frac{kJ}{mol}$$

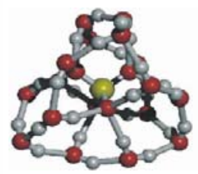
Products are more stable, lower in the energy well, than reactants



http://www.edinformatics.com/math_science/info_water.htm

Liquid water





http://www.lsbu.ac.uk/water/hofmeist.html

http://biochempress.com/Files/IECMD_2003/IECMD_2003_027.pdf

Example: Calculate the)H^o for the combustion of one mole of methane CH_4 according to the equation

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$$

Given the standard enthalpies of formation at 25°C, 1 atm from Appendix

	kJ/mol
$O_{2(g)}$	0
$CO_{2(g)}$	-393.5
$H_2O_{(g)}$	-241.8
$CH_{4(g)}$	-74.8

$$\Delta H^O = \sum n\Delta H^o_{f,products} - \sum n\Delta H^o_{f,reactants}$$

$$\Delta H^O = \left[(2molH_2O)\left(-241.8\frac{kJ}{molH_2O}\right) + (1molCO_2)\left(-393.5\frac{kJ}{molCO_2}\right)\right]$$

$$-\left[(2molO_2)\left(0\frac{kJ}{molO_2}\right) + (1molCH_4)\left(-74.8\frac{kJ}{molCH_{24}}\right)\right]$$

Example: Calculate the)H^o for the combustion of one mole of methane CH_4 according to the equation

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$$

$$\Delta H^O = \left[(2molH_2O)\left(-241.8\frac{kJ}{molH_2O}\right) + (1molCO_2)\left(-393.5\frac{kJ}{molCO_2}\right)\right]$$

$$-\left[(2molO_2)\left(0\frac{kJ}{molO_2}\right) + (1molCH_4)\left(-74.8\frac{kJ}{molCH_{24}}\right)\right]$$

$$\Delta H^O = [-877.10kJ] - [-74.8kJ] = -802.30kJ$$

Sig figs? $\Delta H^O = -802.3kJ$

Can also "reverse" the problem (inside out socks)

Example: Calculate the standard enthalpy of formation for octane

$\Delta H^o = -1.09x10^4 kJ$ $\quad 2C_8H_{18} + 25O_2 \rightarrow 16CO_{2(g)} + 18H_2O_{(g)}$

Given the standard enthalpies of formation at 25°C, 1 atm

	kJ/mol
$O_{2(g)}$	0
$CO_{2(g)}$	-393.5
$H_2O_{(g)}$	-241.8
$CH_{4(g)}$	-74.8

$$\Delta H^O = \sum \Delta H^o_{f,products} - \sum \Delta H^o_{f,reactants}$$

$$\Delta H^O = -1.09x10^4 kJ = \sum \Delta H^o_{f,products} - \sum \Delta H^o_{f,reactants}$$

$$-1.09x10^4 kJ = \left[(16molCO_{2(g)})\left(-393.5\frac{kJ}{molCO_{2(g)}}\right) + (18molH_2O_{(g)})\left(\frac{-241.8kJ}{molH_2O_{(g)}}\right)\right]$$

$$-\left[(2molC_8H_{18})\left(x\frac{kJ}{molC_8H_{18}}\right) + (25molO_2)\left(\frac{0kJ}{molO_2}\right)\right]$$

$$-1.09x10^4 kJ = [(-6296kJ) + (-4352.4kJ)] - [2x + 0]$$

$$2195.2kJ = -2x$$

$$-1.09x10^4 kJ = -8704.8kJ - 2x$$

$$x = -1.097x10^3 kJ$$

Bond Enthalpy

The change in enthalpy when 1 mole of bonds is broken in the gaseous State.

Rule G3: Science is referential!

$Br_{2(g)} \rightarrow 2Br_g \quad \Delta H = +193kJ$

$Cl_{2(g)} \rightarrow 2Cl_g \quad \Delta H = +243kJ$

Which has a stronger bond Enthalpy?

For covalent bonds, bond enthalpies depend on?

Bond length
Overall structure of the molecule

Bond length is nice, but it doesn't Really relate to the Periodic table AND it isn't the whole story

Electronegativities?
Can explain some trends

Bond	Bond Length pm	Pauling's ΔE.N.		Enthalpy Single Bond kJ/mol (Average)
Cl-Cl	199	0		243
Br-Br	228	0		193
I--I	267	0		151
H--F	92	1.8		568
H--Cl	127	1		432
H--Br	141	0.8		366
H--I	161	0.5		298
C--F	135	1.5		488
C--Cl	177	0.7		330
C--Br	194	0.5		288
C--I	214	0.2		216
C--F	135	1.5		488
C--O	143	1		360
C--N	147	0.5		308
C--C	154	0		348
H--H	74	0		436
H--O	96	1.3		366
H--N	101	0.8		391
H--C	109	0.3		413
H--H	74	0		436
H--C	109	0.3		413
H--N	101	0.8		391
H--O	96	1.3		366

Bond	Bond Length pm	Pauling's E.N.	atomic radii (pm)	Enthalpy Single Bond kJ/mol (Average)
H--H	74	2.2	37	436
C--C	154	2.5	77	348
Cl-Cl	199	3.2	99	243
S-S	205	2.6	104	226
Br-Br	228	3	114	193
N-N	145	3	70	159
I--I	267	2.7	133	151
O-O	148	3.5	66	145

??

Bottom line –
atomic radii
ΔE.N. seem to "best" determine bond enthalpies

Bond	Bond Length pm	Pauling's ΔE.N.		Enthalpy Single Bond kJ/mol (Average)
Cl-Cl	199	0		243
Br-Br	228	0		193
I--I	267	0		151
H--F	92	1.8		568
H--Cl	127	1		432
H--Br	141	0.8		366
H--I	161	0.5		298
C--F	135	1.5		488
C--Cl	177	0.7		330
C--Br	194	0.5		288
C--I	214	0.2		216
C--F	135	1.5		488
C--O	143	1		360
C--N	147	0.5		308
C--C	154	0		348
H--H	74	0		436
H--O	96	1.3		366
H--N	101	0.8		391
H--C	109	0.3		413
H--H	74	0		436
H--C	109	0.3		413
H--N	101	0.8		391
H--O	96	1.3		366

Bond enthalpies increase Single <Double < Triple
But not by multiples of the single bond

Bond Enthalpy (kJ/mol)

	X-X	X=X	X≡X	
C-C	347	612	820	measured
		694	1041	calc.
N-N	159	418	941	measured
		318	477	calc.
C-N	293	615	890	measured
		586	879	calc.
C-O	351	715	1075	measured
		702	1053	calc.

http://chemviz.ncsa.uiuc.edu/content/doc-resources-bond.html

Your book's emphasis on bond enthalpies?

Relates to the energy
released
or
taken up
By a reaction

If Bonds of Reactants stronger than bonds products endothermic

We will take up the issue of bond enthalpy when discussing solids

Examples we have examined about energy so far

Hydrogen Fuel Cell

$\Delta H = -286kJ \qquad H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$

Fossil fuel burning (coal)

$\Delta H = -110.5kJ \qquad C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$

$\Delta H = -393.5kJ \qquad C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$

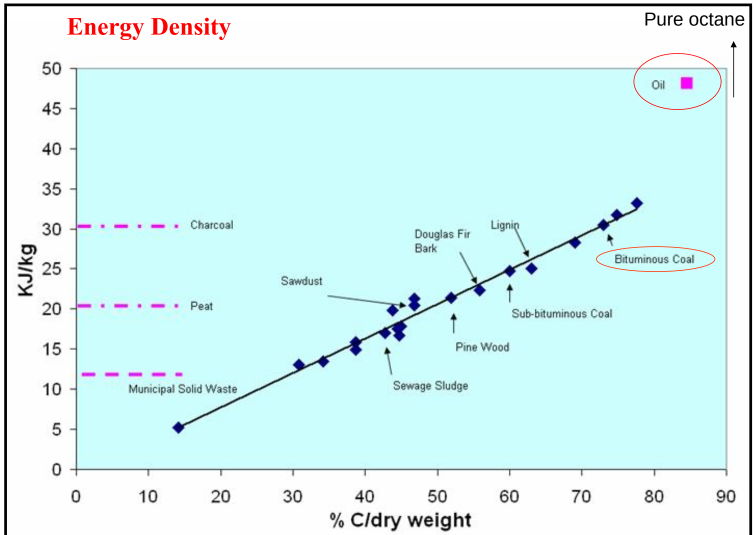
Fossil fuel burning (methane)

$\Delta H = -890kJ \qquad CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$

Fossil fuel burning (octane)

$\Delta H = -1.09x10^4 kJ \qquad 2C_8H_{18} + 25O_2 \rightarrow 16CO_{2(g)} + 18H_2O_{(g)}$

Energy Density



FITCH Rules

General

G1: Suzuki is Success
G2. Slow me down
G3. Scientific Knowledge is Referential
G4. Watch out for Red Herrings
G5. Chemists are Lazy

Chemistry

C1. It's all about charge
C2. Everybody wants to "be like Mike"
C3. Size Matters $\qquad E_{el} = k\left(\frac{q_1 q_2}{r_1 + r_2}\right)$
C4. Still Waters Run Deep
C5. Alpha Dogs eat first

"A" students work (without solutions manual) ~ 10 problems/night.

Alanah Fitch
Flanner Hall 402
508-3119
afitch@luc.edu

Office Hours W – F 2-3 pm

Summary Slides

$A + B + heat \to C$		$+q$	*endothermic*
heat	*to*	*system*	
$A + B \to heat + C$		$-q$	*exothermic*
heat	*to*	*surroundings*	

$$q = cm\left[t_{final} - t_{initial}\right] = cm\Delta t$$

c is a measure of the intermolecular interactions; very large for water = measure of the polarity of the water molecule

$$q|_{cons\tan tpressure} = \Delta H = enthalpychange = H_{products} - H_{reac\tan ts}$$

$\Delta H_{fusion,H_2O}$ $H_2O_{(s)} - H_2O_{(l)}$

$\Delta H_{vaporization,H_2O}$ $H_2O_{(l)} - H_2O_{(g)}$

Says something about intermolecular interactions (polarity!)

$$\Delta H = +571.6kJ \qquad 2H_2O_{(l)} \to 2H_{2(g)} + O_{2(g)}$$

$$\Delta H = -571.6kJ \qquad 2H_{2(g)} + O_{2(g)} \to 2H_2O_{(l)}$$

$$\Delta H = \frac{-571.6kJ}{2} = -286kJ \qquad H_{2(g)} + \tfrac{1}{2}O_{2(g)} \to H_2O_{(l)}$$

An example of Hess's Law

An example of a reaction of standard molar enthalpy of formation

$$\Delta H_f^O = -882kJ \qquad \tfrac{1}{2}N_{2(g,1atm,25C)} + O_{2(g,1atm,25C)} \to NO_{2(g,1atm,25C)}$$

$$\Delta H^O = \sum \Delta H^o_{f,products} - \sum \Delta H^o_{f,reac\tan ts}$$

$$\Delta H = \Delta E + \Delta(PV)$$

$$\Delta H = \Delta E + (PV)_{products} - (PV)_{reac\tan ts}$$

Properties and Measurements

Property	Unit	Reference State
Size	m	size of earth
Volume	cm^3	m
Weight	gram	mass of 1 cm^3 water at specified Temp (and Pressure)
Temperature	^oC, K	boiling, freezing of water (specified Pressure)
$1.66053873x10^{-24}$g	amu	(mass of 1C-12 atom)/12
quantity	mole	atomic mass of an element in grams
Pressure	atm, mm Hg	earth's atmosphere at sea level
Energy, General		
	electronic states in atom	Energy of electron in vacuum
	Electronegativity	F
Heat flow measurements		constant pressure, define system vs surroundings per mole basis (intensive)

Standard Molar Enthalpy 25 ^oC, 1 atm, from stable state

) H_f^o H_{aq}^+ =0

"A" students work
(without solutions manual)
~ 10 problems/night.

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