Thermochemistry

Thermochemistry and Energy and Temperature

Thermochemistry is study of changes in energy (heat) associated with physical or chemical changes.

Force = push F= m a (mass x acceleration) force units: N (newton) = kg m s^{-2}
Work = force x distance W = F d energy units: J (joule) = kg m^2 s^{-2}

Energy is the capacity to do work

Forms of energy are electrical, mechanical, chemical, nuclear, etc.
Conservation of energy means **energy is never created or destroyed but always changed from one form to another**

Units and conversion factors

joule (J)	J = kgm^2s^{-2}	J and kJ are SI (metric) units
calorie (cal)	1 cal = 4.184 J	
kilocalorie (kcal)	kcal = 4184 J	
kilojoule (kJ)	kJ = 1000 J	
diet calorie (Cal)	Cal= 1000 cal = 4184J	

Values for water fp and bp below:

Temperature	Freezing Point	Boiling Point
^oF Fahrenheit	32	212
^oC Celsius	0	100
K Kelvin	273	373

and scales to convert temperature are

$^oF = 1.8(C) + 32$
$^oC = (^oF – 32)/1.8$
$K = {}^oC + 273$

For **T in equation always use K** T=273K but only 0^oC
For **ΔT in equation can use K or ^{o}C** (will be the same ΔT change)

Example: if T=273K then T= 0^oC however if ΔT=10K then ΔT=10^oC

Note on R and R

Gas constant R can be written as
R = 0.08206 L atm/mol K which is used to calc **amounts** such as P,V,or n from PV=nRT

and
R = 8.31 J/mol K which is used for to calc **energy** (J) from RT or nRT

Make sure units work correctly in any calculation you do.

Temperature and Heat

Temperature is the degree of hotness
Heat is the amount of energy associated with thermal motion

Small metal foil at 100°C has less heat energy than large block of metal at 100°C even though temperatures are the same.

Energy
Potential Energy = position energy (chemical bonds)
Kinetic Energy = motion energy (heat)

First Law of Thermodynamics

First Law is conservation of energy.
or Energy of universe is constant.

Heat flow exothermic (heat out of system) (-)
and endothermic (heat into system) (+)

System is whatever we are studying or measuring. So universe is divided into system and surroundings.

First Law of Thermodynamics says that total energy change is sum of changes of heat and work going into or out of system.

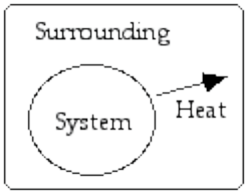
$\Delta U = q + w$ or $\Delta E = q + w$ different books use U or E for internal energy
ΔU or ΔE = change in internal energy
q = heat (random motion)
w = work (organized motion)

Heat changes

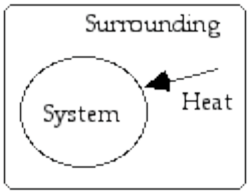
First Law of Thermodynamics means (conservation of energy)
or (energy of universe is constant)

so notice below if heat leaves system
then it goes to surroundings and therefore energy of universe is constant
same true if heat goes into system from surroundings

Exothermic



Endothermic



(http://www.miramar.sdccd.cc.ca.us/faculty/fgarces/ChemComon/HandoutAcitity/handout_20O/Thermoho_f/Thermoho.htm\)

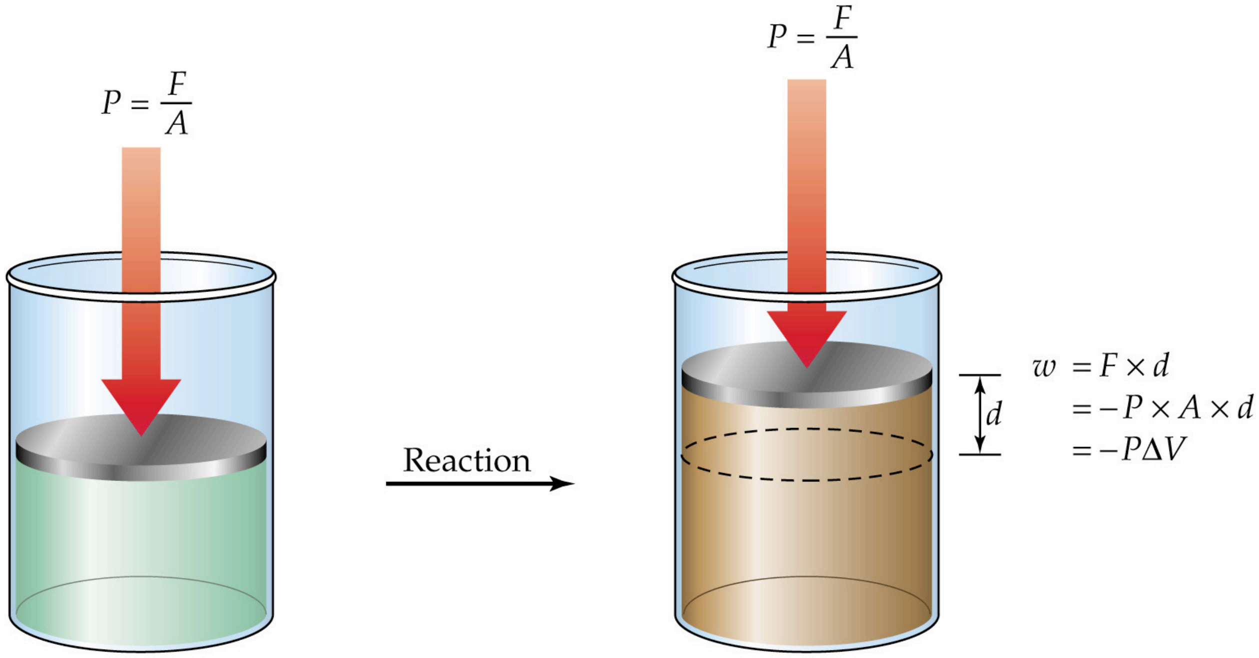
Signs: + into system → system energy increases endothermic (energy in)
– out of system → system energy decreases exothermic (energy out)

Work gas expansion (generally we are more interested in heat)

Imagine a piston moving in a cylinder then to calculate work (w) of surroundings recall

$w = (\text{force})(\text{distance}) = F(\Delta d)$
and can multiple by (A/A) where A= area of top of cylinder
$w = F(\Delta d)(A/A)$
and regroup terms
$w = (F/A)(A\,\Delta d)$
and recall that pressure is defined as force/area so $P=F/A$
and the change in $A\,\Delta d$ is same as change in volume ΔV
so therefore the work of gas expansion is given by
$w = P(\Delta V)$

and work of system (gas in cylinder is opposite sign)
$w = -P(\Delta V)$



Before reaction
(initial state)

After reaction
(final state)

(http://wps.prenhall.com/wps/media/objects/602/616516/Chapter_08.html)

Units: atm = force/area, Pascal = N/m^2, 101325 Pa = 1 atm

Work of expanding gas useful conversion 101 J = 1 L atm

Pressure conversion: 1 atm = 1.01×10^5 Pa = 760 torr

Example
What is the work of the gas that expands by 10.0L against an external pressure of exactly 5.5 atmosphere?
convert atm to N/m^2

$w = - P\, \Delta V$

$P = 5.5\text{atm} (1.01 \times 10^5\ N/m^2\ /\text{atm})$ because pascal Pa = N/m^2
$P = 5.56 \times 10^5\ N/m^2$

$\Delta V = 10.0L (1\ m^3\ /1000L)$ because there are 1000 liters in 1 cubic meter
$\Delta V = 1.0 \times 10^{-2}\ m^3$

so $w = -(5.56\text{x}10^5\ \text{N/m}^2)(1.0\text{x}10^{-2}\ \text{m}^3)$
$w = -5.56\text{x}10^3\ \text{Nm} = -5.56\text{x}10^3\ \text{J}$

or –5.56 kJ since a (newton)(meter) = joule and 1000J = 1 kJ

or using conversion that 101 J = 1 atm L then
$w = -P\,\Delta V$
$w = -(5.5\ \text{atm})(+10\ \text{L})(101\ \text{J/atmL}) = -5.56\text{x}10^3\ \text{J}$ (same result)

Calorimetry (measuring heat changes)

$q = C\,\Delta T$
q = heat (J)
C = heat capacity (J/^{o}C)
ΔT = temp change (^{o}C)

Heat capacity = heat required to raise temp by 1^{o}C
Specific heat = heat capacity of 1g of substance

	(heat capacity)	(mass)	(specific heat, can be per gram or per mol)
Symbol	(C)	(m)	(s)
Units	(J/^{o}C)	(g)	(J/g^{o}C)
	(J/K)	(g)	(J/ g K)
or if per mole	(J/K)	mol	(J/mol K)

C = m s

Water (liquid) specific heat is 1.00 cal/g ^{o}C or 4.18 J/g ^{o}C

Or per mol specific heat = (18g/mol)(4.18 J/g^{o}C) = 75.2 J/mol ^{o}C

Combining equations $q = C\,\Delta T$ and $C = m\,s$ we get

$q = m\,s\,\Delta T$ heat = (mass)(specific heat) (change in temperature)

or if done in moles then
$q = (\text{mol})(s_{\text{mol}})\,\Delta T$ heat = (moles) (heat per mol) (change in temperature)

Change is always the difference of (final value – initial value)
Δ = final – initial

Example
How much heat is put into 100. g of water to raise temperature from 25 to 75 degrees Celsius? The specific heat of water is 4.184 J/ g ^{o}C

100. g of Water with temp change $25 \rightarrow 75^{o}$C

$q = m\ s\ (\Delta T) = C\ (T_2 - T_1)$ where $C = m\ s$
$q = (100g)(4.184\ J/g\ ^{o}C)(75.0\ ^{o}C - 25.0\ ^{o}C)$
$q = 20920\ J = 20.9\ kJ$ endothermic Heat goes into water (the system)

Suppose same water cools $75 \rightarrow 25^{o}$C then
$q = -20.9\ kJ$ exothermic Heat leaves water (the system) to go to surroundings)

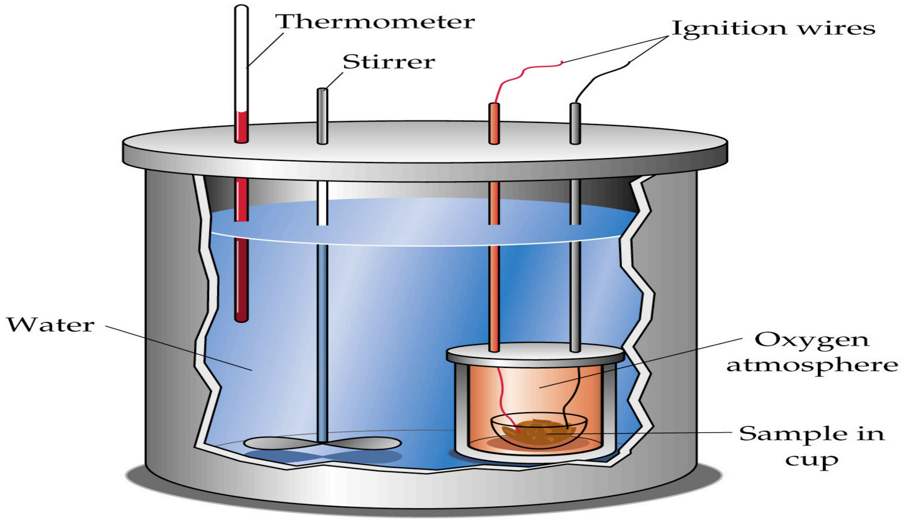
Example using per mole
How much heat is put into 100. g of water to raise temperature from 25 to 75 degrees Celsius? The molar heat capacity of water is 75.31 J/mol ^{o}C

moles = 100. g (mol/18.0 g) = 5.556 mol
$q = m\ s\ (\Delta T) = C\ (T_2 - T_1)$ where $C = m\ s$
$q = (5.556\ mol)\ (75.31\ J/g\ ^{o}C)\ (75.0\ ^{o}C - 25.0\ ^{o}C) = 20920$ or 20.9kJ

notice final answer in problems above should be 3 sig fig 2.09×10^4 J or 20.9kJ

Calorimeter device to measure changes in heat

Bomb Calorimeter shown below



(http://wps.prenhall.com/wps/media/objects/602/616516/Chapter_08.html)

Calorimeter is used to measure C and ΔT and thus find q for a reaction
A “bomb” calorimeter is one that uses a metal chamber to rapidly burn a sample in an oxygen atmosphere

Example:
3.00g of glucose was burned in an excess of oxygen in bomb calorimeter with metal holder (“bomb”) heat capacity of 2.21 kJ/^{o}C. and 1.2kg of water where water has a specific heat capacity of 4.184 kJ/kg^{o}C. The temp change upon combustion of glucose and oxygen was 19.0→25.5^{o}C

Question– what is the heat evolved from the combustion of 1.00 mol of glucose?

Total heat capacity
$C_{total} = C_{cal} + C_{H2O}$
$= (2.21\ kJ/^oC + 1.2kg(4.18kJ/kg^oC))$
$= (7.23\ kJ/^oC)$

Heat absorbed by calorimeter and water
$q = C_{total}\ (\Delta T)$
$q = 7.23\ kJ/^oC\ (\ 25.5\ -19^oC)$
q = +47.0 kJ absorbed by water calorimeter

so therefore q= -47.0 kJ for heat released from combustion of glucose

and per mole
Heat evolved = (-47.0 kJ/ 3.00g glucose)(180g/1mol)
$\Delta U = -\ 2.82 \times 10^3$ kJ/mol of glucose

Reaction
$C_6H_{12}O_6\ (s) + 6O_2\ (g) \rightarrow 6CO_2\ (g) + 6H_2O\ (l)$
$\Delta U = -2.82 \times 10^3$ kJ/mol

Next section will show that if the same amount of gas is on reactant and product side then ΔU = ΔH so for above $\Delta H = -2.82 \times 10^3$ kJ/mol

Remember ΔU or ΔE for is used for internal energy.
Some books use ΔU and some use ΔE for change in internal energy

Connection between Internal Energy and Enthalpy

Internal Energy (ΔE or ΔU) = q_V constant volume heat change

Enthalpy $\Delta H = q_P$ constant pressure heat change

Often ignore the difference because it is small

However, if need to calculate exactly
$\Delta U = q + w$
and heat is $q = \Delta H$ and work is $w = -\Delta(PV)$
so $\Delta U = \Delta H - \Delta(PV)$
$\mathbf{\Delta H = (\Delta U) + \Delta\ (PV)}$

and it is the gas produced or used up that causes change in PV so

$\Delta\ (PV) = \Delta\ (nRT) = RT(\Delta n_{gas})$
and therefore

$\mathbf{\Delta H = \Delta U + RT(\Delta n_{gas})}$ **where** $\mathbf{\Delta n_{gas} = \Sigma n_{gas}(prod) - \Sigma n_{gas}(react)}$
where n_{gas} is moles of gas on product or reactant side of chemical equation

For Example:
If in a reaction among other things happening 4 mol gas → 5 mol gas
then

$\Delta n_{gas} = \Sigma n_{gas}(prod) - \Sigma n_{gas}(react)$
$\Delta n_{gas} = 5 - 4$
$\Delta n_{gas} = +1$ mol

and
$RT(\Delta n_{gas}) = (8.31\ J/molK)(298K)(+\ 1\ mol) = 2476\ J = 2.5\ kJ$

so then $\Delta H = \Delta U + 2.5kJ$ this could be a small difference if ΔH is hundreds of kJ

Usually the difference between ΔH and ΔU is small

$\Delta H = \Delta U$ if only liquid and solid – that is no gas among reactants or products
or if same moles of gas on product and reactant sides so $\Delta n_{gas} = 0$

Bomb Calorimetry (in closed container) gives us ΔU but
Usually we are interested in enthalpy (ΔH)

Reaction in a beaker open to room is at constant pressure but volume may change if gas produced or used up so in a beaker heat change is ΔH

so to repeat
Internal Energy $\Delta U = q_v$ (constant volume) heat change

Enthalpy $\Delta H = q_p$ (constant pressure) heat change

$\boldsymbol{\Delta H = (\Delta U) + \Delta (PV)}$
but if no increase or decrease in gas then $\Delta(PV) = 0$ and $\Delta H = \Delta U$

Thermochemical Equations
Enthalpy is the heat content (H)

Enthalpy change is $\Delta H = H_{products} - H_{reactants}$

So ΔH is the heat change for chemical reactions

$\Delta H = (-)$ is exothermic heat given off (feels hot)
$\Delta H = (+)$ is endothermic heat taken in (feels cool)

Examples:

For $H_2 (g) + (1/2)O_2 (g) \rightarrow H_2O (g) + 286$ kJ
we say for reaction above $\Delta H = -286$ kJ since heat given off

for the reverse or opposite reaction
$H_2O (g) + 286 \text{ kJ} \rightarrow H_2 (g) + (1/2)O_2 (g)$
we say $\Delta H = +286$ kJ since heat was put into reaction

Remember heat in (reactant side) $\Delta H = +$ heat out (product side) $\Delta H = -$

Applications:
Our society runs on exothermic reactions – we burn coal, oil, natural gas (methane, CH_4), and gasoline (a mixture of different hydrocarbons) to heat our homes, run our cars, and produce electricity. Our society would collapse without exothermic reactions!

We eat food that our body metabolizes to produce energy and our brain needs a constant regular supply of glucose sugar molecules that are used for energy production. We would die without exothermic reactions!

ΔH tells us what the energy change will be but not how fast it will happen.
We will see later that:
Thermodynamics tell us what is likely to happen (where is equilibrium)
Kinetics tells us how fast it will happen (speed of reaction)

Enthalpies depend on amounts given for reaction as written and can depend on pressure and temperature.

If P=1.00 atm and T=25°C then at standard state and can indicate by ΔH^o
We will often just write ΔH instead of ΔH^o even if at standard state.

<u>How do you calculate ΔH for reaction?</u>
1. Law of Hess
2. Enthalpies of Formation
3. Bond Energies

<u>1. Law of Hess</u>
Change in enthalpy for reaction may be broken down into several steps so the way you get from reactants to products will give same overall ΔH

$A \rightarrow B \rightarrow C$ will have same ΔH as $A \rightarrow C$

Example:
If
$C\text{ (graphite)} + (1/2)\, O_2 \rightarrow CO$ $\Delta H = -110.5\text{kJ}$
$CO + (1/2)\, O_2 \rightarrow CO_2$ $\Delta H = -283.0\text{kJ}$
added together gives
$C\text{(graphite)} + O_2\text{ (g)} \rightarrow CO_2\text{(g)}$ and also $\Delta H = -393.5$

Rules:
ΔH is for reaction as written
a) If reverse reaction, change sign of ΔH (or can multiple value by –1)
b) If multiply or divide reaction by constant, do the same to ΔH

Example:
If $C + O_2\text{ (g)} \rightarrow CO_2\text{(g)}$ and $\Delta H = -393.5\text{kJ}$
then

reverse and get $CO_2\text{ (g)} \rightarrow C + O_2\text{ (g)}$ and $\Delta H = +393.5\text{ kJ}$
multiple this by 3 and get $3CO_2\text{ (g)} \rightarrow 3C + 3O_2\text{ (g)}$ and $\Delta H = 1180.5\text{ kJ}$

or another example
If
$A \rightarrow B$ $\Delta H = +5$ kJ
then
$B \rightarrow A$ $\Delta H = -5$ kJ
$3A \rightarrow 3B$ $\Delta H = +15$ kJ
$2B \rightarrow 2A$ $\Delta H = -10$ kJ

Formal Procedure to get ΔH:

In **Hess's Law** approach we use reactions with known ΔH values to find unknown ΔH for a reaction that is combination of known ones

Example:

Given		ΔH
(a)	$2CO \rightarrow 2C + O_2$	+221.0 kJ
(b)	$CO + (1/2)\, O_2 \rightarrow CO_2$	-283.0 kJ

Find
$C + O_2 \rightarrow CO_2$

–(a)	$2C + O_2 \rightarrow 2CO$	-221.0 kJ
–(a)/2	$C + (1/2)\, O_2 \rightarrow CO$	-110.5 kJ
(b)	$CO + (1/2)\, O_2 \rightarrow CO_2$	-283.0 kJ
–(a)/2 + (b)	$\mathbf{C + O_2 \rightarrow CO_2}$	

so then $\Delta H = -\Delta H_a/2 + \Delta H_b = -(+221.0)/2 + (-283.0) = -393.5$ kJ

Example combining reactions
Given:

	ΔH
(a) $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$	$\Delta H_a = -1531$ kJ
(b) $N_2O + H_2 \rightarrow N_2 + H_2O$	$\Delta H_b = -367$ kJ
(c) $H_2 + (1/2)\, O_2 \rightarrow H_2O$	$\Delta H_c = -286$ kJ

Then Find ΔH for the reaction:

$2NH_3 + 3N_2O \rightarrow 4N_2 + 3H_2O$ $\Delta H = ?$

Look for components found only in one reaction

NH_3 only in (a)
N_2O only in (b)

Try (a)/2 + 3(b) and combine to give:
$2NH_3 + 3/2O_2 + 3N_2O + 3H_2 \rightarrow N_2 + 3H_2O + 3N_2 + 3H_2O$

but need to get rid of
$3H_2 + (3/2)\ O_2 \rightarrow 3H_2O$
so
-3(c)
Therefore
(a)/2 + 3(b) – 3(c) gives the desired reaction
$\mathbf{2NH_3 + 3N_2O \rightarrow 4N_2 + 3H_2O}$
and
$\mathbf{\Delta H} = (-1531)/2 + 3(-367) - 3(-286) = \mathbf{-1009\ kJ}$

whatever you do to reactions do the same thing to the ΔH values

2. Enthalpies of Formation
Standard state of substance is 25°C and 1.00 atm

Standard enthalpy of formation ΔH_f^o

ΔH_f^o is change in heat when 1 mol of substance is made from elements in their standard states at 25°C at 1.00 atm

for example to make water need to combine hydrogen and oxygen
$H_2\ (g) + (1/2)\ O_2\ (g) \rightarrow H_2O\ (\ell)$ and find from experiment $\Delta H = -285.9$ kJ

or to make chloroform $CHCl_3$
$C\ (s) + (1/2)\ H_2\ (g) + 3/2Cl_2 \rightarrow CHCl_3\ (\ell)$ and measure that $\Delta H = -132$ kJ

ΔH_f^o for pure element always equals zero

Can use ΔH_f^o values to calculate ΔH for any reaction using
$\mathbf{\Delta H = \Sigma\Delta H_f^o\ (products) - \Sigma\Delta H_f^o\ (reactants)}$

where Σ means sum or add together all values

ΔH_f^o values are found in thermodynamic table(s) in your textbook
look up values for homework and values will be given for exam questions

Example:

$2NH_3\ (g) + 3Cl_2\ (g) \rightarrow N_2\ (g) + 6HCl\ (g)$

From table: -46.2 0 0 -92.3 kJ/mol

$\Delta H = [\ 1\ (0) + 6(-92.3)] - [2(-46.20\ ) + 3(0)]$ kJ

$= [-553.8] - [\ -92.4]$

$= -461.4$ kJ

Example calculate ΔH (enthalpy change) and also ΔE (internal energy change): for

$OF_2\ (g) + H_2O\ (g) \rightarrow O_2\ (g) + 2HF\ (g)$

where

ΔH_f^o 23 - 242 0 - 269 kJ/mol

Find ΔH

$\Delta H = [\ 1(0) + 2(-269)\ ] - [\ 1(23) + 1\ (-242)\ ]$

$\Delta H = [-538] - [\ -219]$

$\mathbf{\Delta H = -319\ kJ}$

and to find ΔU

recall that

$\mathbf{\Delta H = \Delta U + RT\Delta n_{gas}}$

Use this equation: $\Delta H = \Delta U + RT\Delta n_{gas}$

$(-319\text{ kJ}) = \Delta U + (3 - 2\text{ mol})(8.31\text{ J/molK})(298\text{ K})(\text{kJ}/ 1000\text{J})$

$(-319\text{ kJ}) = \Delta U + 2.5\text{ kJ}$

$-321.5\text{ kJ} = \Delta U$

So ΔH and ΔU are less than 1% difference

often we can ignore this small difference if ΔH is a large value
and not much gas is produced or used up.

3. Bond Energies

(not as accurate as above but used to see what is happening in a reaction and get approximate answer)

Bond dissociation energy is the energy required to break single bond or double bond or triple bond that holds two atoms together

BE = Bond energy (energy to break bond) and

$\Delta H = \Sigma$ BE (bond broken) + Σ BE(bonds formed)
Energy In (+) Energy Out (-)

Example given reaction $H_2 + (1/2)\ O_2 \rightarrow H_2O$
and BE values given

H–H	432 kJ/mol
O=O	495 kJ/mol
O–H	467 kJ/mol

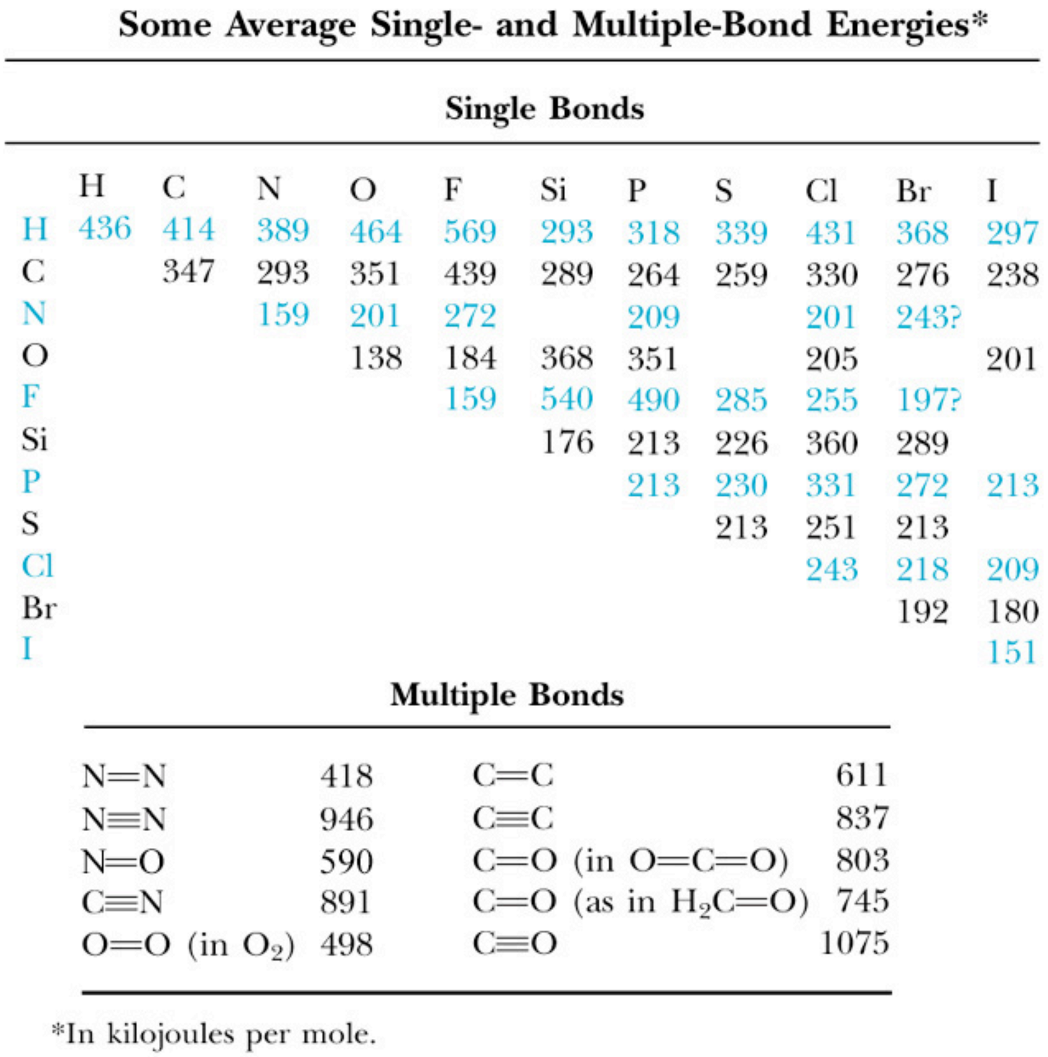
then for reaction
$\Delta H = 1(\text{H–H}) + (1/2)(\text{O=O}) + 2(\text{O–H})$
$\Delta H = 1(+432) + (1/2)(+495) + 2(-467)$ units are 2 mol(-467kJ/mol)
$\Delta H = (680) + (-934)$ kJ
$\Delta H = -254$ kJ for reaction as written

Chemical reactions break bonds and form bonds
so
Put energy in to break bond
Get energy out when form bond

and BE different for single,double, or triple because triple bond hardest to break
Diatomic Nitrogen:

Single bond	BE= 159 kJ/mol
Double bond	BE= 418 kJ/mol
Triple bond	BE= 941 kJ/mol

Tables shown below are available to find bond energy values



Some Average Single- and Multiple-Bond Energies*

Single Bonds

	H	C	N	O	F	Si	P	S	Cl	Br	I
H	436	414	389	464	569	293	318	339	431	368	297
C		347	293	351	439	289	264	259	330	276	238
N			159	201	272		209		201	243?	
O				138	184	368	351		205		201
F					159	540	490	285	255	197?	
Si						176	213	226	360	289	
P							213	230	331	272	213
S								213	251	213	
Cl									243	218	209
Br										192	180
I											151

Multiple Bonds

$N=N$	418	$C=C$	611
$N\equiv N$	946	$C\equiv C$	837
$N=O$	590	$C=O$ (in $O=C=O$)	803
$C\equiv N$	891	$C=O$ (as in $H_2C=O$)	745
$O=O$ (in O_2)	498	$C\equiv O$	1075

*In kilojoules per mole.

http://colossus.chem.umass.edu/genchem/whelan/111_Summer_2004_Daily.htm

Example:
Find ΔH for reaction given
$2NH_3 + Cl_2 \rightarrow N_2 + 6HCl$

and BE values

N-H	Cl-Cl	$N\equiv N$	H-Cl
389	243	941	431

and remember
ΔH = Σ BE (bond broken) + Σ BE(bonds formed)

Energy In (+)		Energy Out (-)		
reactant break 6	reactant break 3	product form 1	product form 6	
6(389)	3(243)	1(-941)	6(-431)	
+2334	+729	-941	-2586	Sum all values!

Result is $\Delta H = -464$ kJ
value is close but a little different than using heats of formation

Note that the BE Tables are average bond energy values

Consider H—O—H

Bond energy to break the first bond is 501 kJ/mol
Bond energy to break the second is 425 kJ/mol
Average = 463 kJ/mol
Easier to break the second bond and we use just average values

<u>Example of ΔH application</u>
U.S. Military uses Meals Ready to Eat (MRE)
Uses reaction of magnesium with water to heat food in meal.

Calculate enthalpy change for reaction below with ΔHf (kJ/mol) values given

$$Mg\ (s) + 2H_2O\ (l) \rightarrow Mg(OH)_2\ (s) + H_2\ (g) + \text{heat}$$

ΔH_f 0 -285.8 -924.5 0
so
$\Delta H = [\ 1(-924.5) + 1(0)] - [1(0) + 2(-285.8)] = -352.9$ kJ
$\Delta H = -352.9$ kJ for reaction as written.

<u>Another Example</u>
Given above how much magnesium is needed to heat 1.00L of water from 20.0 to 90.0 °C?

If specific heat of water is 4.184J/g K and water density is d=1.0g/mL then 1.00L of water is same as 1000mL or 1000g and then the heat q required to raise temp is

$q = m\ s\ \Delta T$
$q = (1000g)\ (4.184 J/g\ K)\ (90.0 - 20.0\ ^{o}C)$

q= 2.93×10^5 J or 293kJ

remember for °C or K the ΔT is same [90 -20] = 70°C

for K ΔT would be [(273 +90) - (273 +20)] or [363 -293] = 70 K

so 293kJ required as input but –353kJ given off by 1 mol of Mg so

(293kJ) /(353kJ/mol)= 0.830 mol or 0.830mol (24.3g/mol) = 20.2g of Mg to raise temp of water by 70°C

For more information on MRE see below from
Marshall Brain. *"How MREs Work"*. April 15, 2003
http://science.howstuffworks.com/mre.htm (January 21, 2007)

Flameless Heaters

"Most human beings much prefer a warm meal to a cold one, especially if they're in cold or wet conditions. Eating cold spaghetti or cold beef stew is definitely no fun. A hot meal, on the other hand, can lift a soldier's spirits.

Because of the importance of a hot meal, all military MREs come packaged with a **flameless heater**. The flameless heater uses a simple chemical reaction to provide sufficient heat to warm the food.

Chemical heating is actually a pretty widespread natural phenomenon. Everyone has seen iron rust. Rust is a natural process in which iron atoms combine with oxygen atoms to create reddish, crumbly iron oxide. The process is normally very slow, but we all know that wet iron rusts faster. Iron exposed to salty ocean water rusts the fastest.

When iron turns to rust, the oxidation process generates heat. But rust forms so slowly that the heat generated is unnoticeable. We are all familiar with much faster oxidation reactions as well. For example, when you "oxidize" the carbon atoms in a charcoal briquette, they get quite hot. We use the word **burning** to describe this high-speed sort of oxidation.

The idea behind a flameless heater is to use the oxidation of a metal to generate heat. Magnesium metal works better than iron because it rusts much more quickly. To make a flameless heater, magnesium dust is mixed with salt and a little iron dust in a thin, flexible pad about the size of a playing card. To activate the heater, a soldier adds a little water. Within seconds the flameless heater reaches the boiling point (of water) and is bubbling and steaming. To heat the meal, the soldier simply inserts the heater and the MRE pouch back in the box that the pouch came in. Ten minutes later, dinner is served!"
http://science.howstuffworks.com/mre4.htm