Ch 6 Thermochemistry

Energy - ability to do work or produce heat

Law of Conservation of Energy?

Energy

Potential	**Kinetic**
- Energy that could become kinetic	- Energy in motion
Ex:	Ex:

Where does energy go when an object stops moving on its own?

Ways to transfer energy:

A) Work - force attracting over a distance

B) Heat - Transfer of energy due to different Temp.

C) Pathway - way work and heat transfer, total E stays the same

State Function and State Property:

- Property of a system that depends only on its current state (not how it got to that state)

A) Energy of a compound = state function

B) Work = NOT a state function (amount of work depends on mechanism used)

A System and its Energy:

A) System - Part we are focusing on

B) Surroundings - Everything else around our system

EX: Methane + Oxygen ---> Carbon dioxide + water + heat

System:

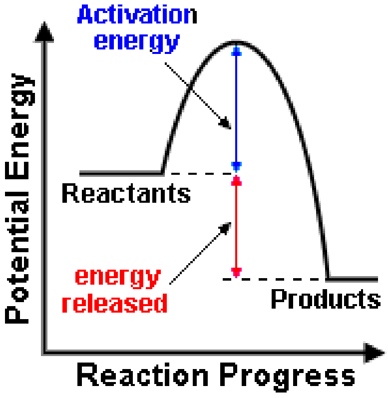
Surroundings:

C) Endothermic - rxn or phase change absorbs heat (▲H = +, energy is a reactant)

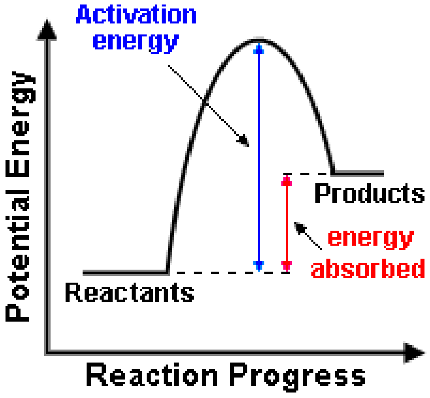
D) Exothermic - rxn or phase change produces heat (▲H = -, energy is a product)

E) ***NOTE: Energy gained/lost by system = energy lost/gained by surroundings***

F)



Exothermic reaction



Endothermic reaction

1st Law of Thermodynamics - energy of universe is constant

Internal energy (▲ E) - Sum of Kinetic + potential energy in a system

$\boxed{\blacktriangle E = q + w}$

q = heat
  +q = endothermic
  -q = exothermic

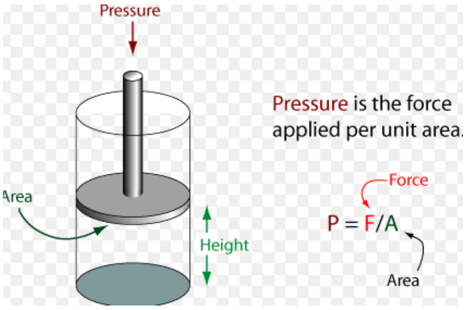
w = work
  +w = work in, surroundings do work on system
  -w = work out, does work on surroundings

Ex: Find ▲ E for an endothermic system, 15.6 kJ of heat flows and 1.4 kJ of work is done on the system.

Ex: Calculate the change in energy of a system if 38.9 J of work is done by the system with an associated loss of heat of 16.2 J.

Energy and work on a car engine:

- heat from combustion of gasoline expands the gases in the cylinder, pushing back the piston, and then transferred into motion of the car



- *Since the gas is expanding and doing work on the surroundings, w = (-)*

$w = -P\Delta V$ (w = work, P = pressure, V = volume)

- *If compression were occurring, work = (+) due to work flowing into system*

Ex: Find work for a gas expansion from 46 L to 64 L at a constant external pressure of 15 atm

Ex: A balloon is inflated from 4.00×10^6 L to 4.50×10^6 L. Energy was added in the amount of 1.3×10^8 J as heat. The constant pressure of the atmosphere is 1.00 atm. Calculate ΔE. (Note 1 L* atm = 101.3 J)

Ex: A piston is compressed from a volume of 8.3 L to 2.8 L against a constant pressure of 1.9 atm. In the process there is a heat gain by the system of 350 J. Calculate the change in energy of the system.

Enthalpy and Calorimetry:

Enthalpy (ΔH) - is a state function

Thus: ΔH does NOT depend on pathway between 2 states

$H = E + P * V$

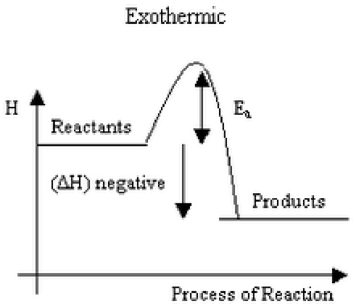
H = enthalpy
E = energy
V = Volume
P = pressure

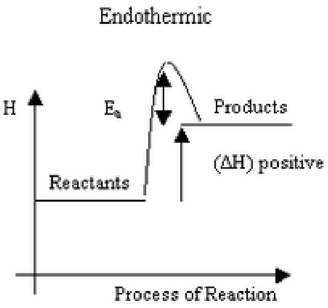
Note: At constant pressure, the ΔH = energy flow as heat

$\Delta H = H_{products} - H_{reactants}$

$\Delta H = q_p$

ΔH = - (exothermic) ΔH = + (endothermic)





Ex: When 1 mole of CH_4 is burned at constant P, 890 kJ of energy is released as heat. Calculate ΔH for a process when 5.8 g of methane is burned at constant P.

Ex: When solid potassium hydroxide pellets are added to water, the following happens:

$$NaOH_{(s)} \longrightarrow NaOH_{(aq)}$$

For this reaction at constant P, ΔH = -43 kJ/mol. Answer the following regarding the addition of 14.0 g of NaOH to water.

a) Does the beaker get warmer or colder?
b.) Is the reation exo- or endothermic?
c.) What is the enthalpy change for the dissolution?

Calorimetry:

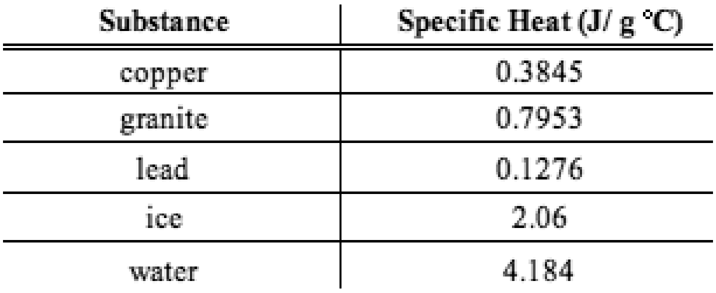
Calorimetry - science of measuring heat

Calorimeter - device used to measure heat of a chemical reaction

Heat capacity (C) - ratio of heat absorbed per increase in temperature

Specific Heat Capacity (C_p) - amt of heat needed to raise 1 gram of substance by 1 C

Molar Heat Capacity - Heat capacity per mole (J/C or K * mole)



Substance	Specific Heat (J/ g °C)
copper	0.3845
granite	0.7953
lead	0.1276
ice	2.06
water	4.184

Notes about Cp values: The higher the value, the more heat needed/gram to increase temp by 1 C

Would a high or low Cp value make a good insulator?

Would a high or low Cp value make a good conductor?

Constant Pressure calorimetry:

- Pressure never changes (Example - doing a calorimetry test in our classroom)

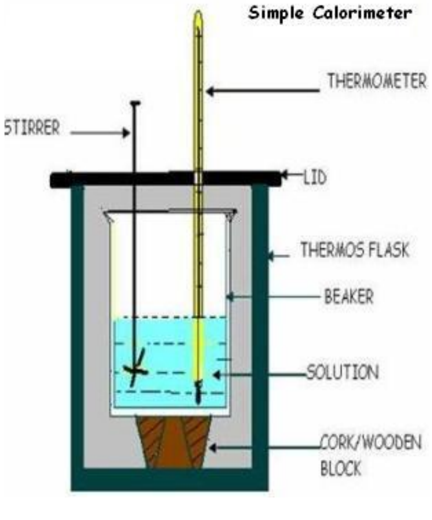
*At constant P ---> $\Delta H = q_p$

For a calorimetry system, $E_{\text{released by rxn}} = E_{\text{absorbed by solution}}$

$E = s \times m \times \Delta T$ or $q = m \times c \times \Delta T$

m = mass of water + solute
s or c = specific heat of water
ΔT = change in temp
** Assume Density of water = 1.0 g/mL

Ex: Add 50.0 mL of 1.0 M HCl to 50.0 mL of water. The original temp of each liquid was 25.0 C, and the final temp of the system is 31.9 C. Determine the amount of energy released. Then determine the ΔH per mole of H+ in reaction



Ex: 1.00 L of 1.00 M $Ba(NO_3)_2$ is added to 1.00 L of 1.00 M Na_2SO_4. The original temperatures of both solutions are 25.0 C and the final temp is 28.1 C of the mixture. Assume density of the final solution is 1.0 g/mL. Determine the ΔH of $BaSO_4$ ppt. formed.

Use of $q = m * c * \Delta T$ FOR A SYSTEM and SURROUNDINGS

Set: $q_{lost} = q_{gained}$ (Conservation of Energy Law)

Thus:
$$\underbrace{m * c * \Delta T}_{\text{System}} = \underbrace{m * c * \Delta T}_{\text{Surroundings}}$$

Ex: A 110. gram sample of Copper (Cp = 0.20 J/g*C) is heated to 82.4 C then placed into a container of water at 22.3 C. The final temp of the system is 24.9 C. What is the mass of the water in the calorimeter. Assume all heat lost = heat gained.

Ex: A 5.00 gram sample of Al pellets (Cp = 0.89 J/g*C) and a 10.00 g sample of Fe pellets (Cp = 0.45 J/g*C) are heated to 100.0 C then placed into a calorimeter of water. There is 97.3 g of water in the calorimeter and an initial temp of 22.0 C. Calculate the temperature of the water when all heat is transferred. Assume all heat lost = heat gained.

Constant Volume Calorimetry:

- If volume doesn't change, no work is done
- So a rigid chamber is used (V does not change)
and this IS A BOMB CALORIMETER

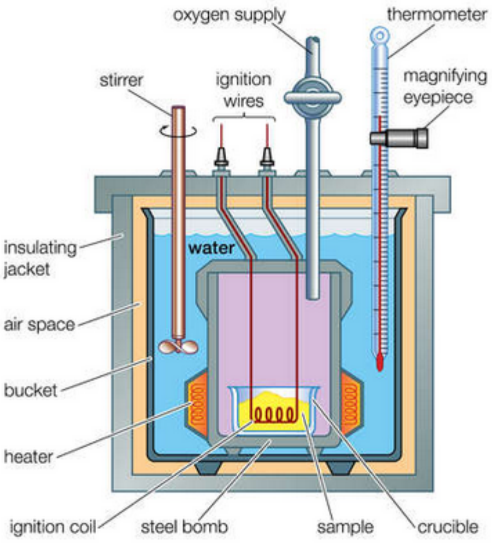
$\Delta E = \Delta T$ x heat capacity of the calorimeter

$\Delta E = q + w$ (but no work is done so $w = 0$)

$\Delta E = q$

Ex: It is suggested that hydrogen gas be used instead of natural gas. Find its energy of combustion (per gram) and compare to methane's value. We know from an experiment the following:

heat capacity of bomb calorimeter: 11.3 kJ/C
methane sample = 1.50 g sample, burned to produce a 7.3 C increase
Hydrogen sample = 1.15 g sample, burned to produce a 14.3 C increase



Hess's Law:

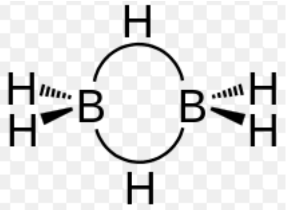
"Enthalpy is a state function, there for a change in enthalpy will be the same irregardless of # of steps in rxn"

Rules when using Hess's Law:
1.) If reaction is reversed, ΔH is reversed (+ to - or - to +)
2.) Magnitude of ΔH is proportional to reactants and products
    so 1/2 it, x2, x3 it based on reaction's coefficients
3.) Work backwards,
    a) if things need flipped, flip (+/-) enthalpy
    b) if things need multiplied, multiple rxn and enthalpy

Ex: Carbon is found in graphite and diamond. Determine ΔH for converting graphite ---> diamond based on the given enthalpy values.

graphite = ΔH = -394 kJ/mol   ($C_{graphite} + O_2 \text{ ---> } CO_2$)
diamond = ΔH = -396 kJ/mol   ($C_{diamond} + O_2 \text{ ---> } CO_2$)

Ex: Diborane (B_2H_6) is a highly reactive compound, once thought to be a good rocket fuel. Find ΔH for the synthesis of it if



$2\,B + 3H_2 \text{ ---> } B_2H_6$

Data Given:

$2\,B_{(s)} + 3/2\,O_{2(g)} \text{ ---> } B_2O_{3(s)}$ $\Delta H = -1273$
$B_2H_{6(g)} + 3O_{2(g)} \text{ ---> } B_2O_{3(s)} + 3H_2O_{(g)}$ $\Delta H = -2035$
$H_{2(g)} + 1/2O_{2(g)} \text{ ---> } H_2O_{(l)}$ $\Delta H = -286$
$H_2O_{(l)} \text{ ---> } H_2O_{(g)}$ $\Delta H = 44$

Standard Enthalpy of Formation- (ΔH_f^0) - Change in enthalpy for 1 mole of compound from its elements in their standard states

- sometimes too slow of a change to see experimentally, so we calculate it through standard enthalpy

NOTE: DO NOT CONFUSE STANDARD STATE WITH STP

Standard State:

^{0} - indicates process was carried out under standard conditions

Definitions of standard state:

Gases - at 1.00 atm (also use of 1 bar = 100,000 Pa)

(Both of these pressures are "Standard pressure")

Pure substance = s or l

Solution = 1.00 M

Element = its natural state at 1 atm and 25 C

Rules to use Standard State Enthalpy Calculations:

1) Reactants must be in standard state
2) Magnitude of ΔH gets adjusted due to coefficient difference (x by factor)
3) +/- ΔH is flipped if reaction is reversed
4) If no change occurs per an element $\Delta H_f^0 = 0$
5) Formula used with math:

$$H^0_{rxn} = \sum n_p \Delta H_f^0 \text{ (products)} - \sum n_r \Delta H_f^0 \text{ (reactants)} \qquad n = \text{moles}$$

Ex: Finding Enthalpies from ΔH_f^0

For the reaction: $4\ NH_{3(g)} + 7\ O_{2(g)} \rightarrow 4\ NO_{2(g)} + 6\ H_2O_{(l)}$

Ex #2: Another H_f^0 calculation - find the standard enthalpy change for this reaction:

$2Al_{(s)} + Fe_2O_{3(s)} \text{--->} Al_2O_{3(s)} + 2Fe_{(s)}$

Ex #3: Finding Enthalpies from Standard Enthalpies of Formation

Methanol was used as a fuel in racing cars until recently. Determine the standard enthalpy of combustion per gram of methanol with that per gram of gasoline.

Methanol combustion: $2CH_3OH_{(l)} + 3O_{2(g)} \text{--->} 2CO_{2(g)} + 4H_2O_{(g)}$

Gasoline combustion: $2C_8H_{18(l)} + 25O_{2(g)} \text{--->} 16CO_{2(g)} + 18H_2O_{(g)}$