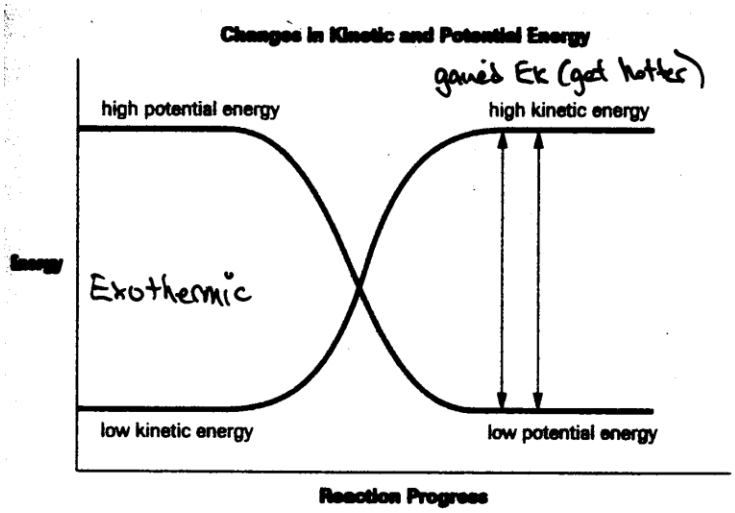
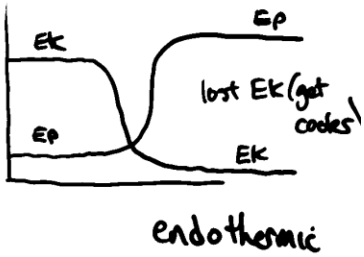
HEAT OF REACTION

- Recall that enthalpy is a measure of the total energy in a system
    - ie) it is the sum of all kinetic and potential energies within the system
    - total Ek = moving electrons, vibration of atoms within the molecules, rotation and translation of molecules
    - total Ep = nuclear potential energy of protons and neutrons and the energy stored in chemical bonds
- scientists have not been able to measure all of these energies so enthalpy serves no useful purpose in chemistry
- instead, we will concern ourselves with the change in enthalpy (/\H)
    - ie) how much energy was gained or lost by the system
    - when burning a fossil fuel, we don't care how much energy the fossil fuel had before burning or even after burning; what we are interested in is how much energy will be released when we burn the fuel

- most things react naturally to lower its potential energy
- since the law of conservation of energy states that energy cannot be created or destroyed, the loss of potential energy is seen as a gain in kinetic energy (seen as a release of heat); this is seen in an exothermic reaction
- in an endothermic reaction, the products gain potential energy through the transformation of kinetic energy into potential energy (loss of Ek = absorbed heat)





- any change in energy is usually the result of a transfer of heat or work
    - $\Delta H = Q + W$, where Q = heat and W = work

- if we can ensure that any change in energy is seen only as a change in temperature (heat) at a constant pressure, we call it the heat of reaction:

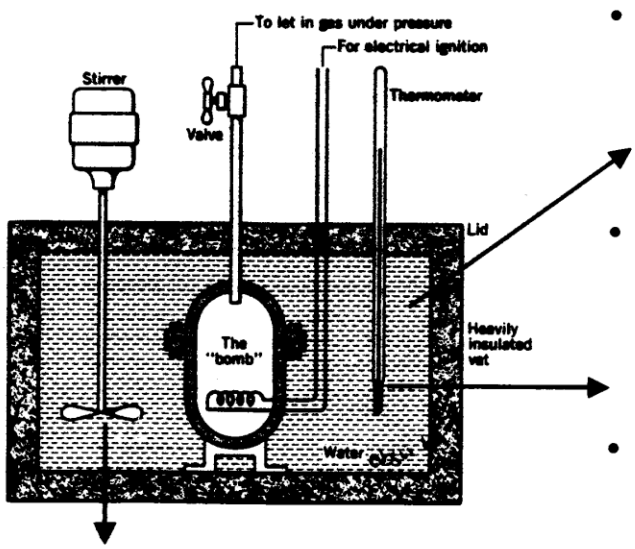
$$\Delta H = Q$$

    - if the system gains energy (endothermic), the surroundings released the energy into the system ($Q_{system} = +$, $Q_{surroundings} = -$)

- if the system releases energy (exothermic), the surroundings gained the energy from the system (Q_{system} = -, $Q_{surroundings}$ = +)

- therefore, ΔH is negative for exothermic reactions and positive for endothermic reactions

- if this condition is met, how do we measure ΔH for a given reaction?
- We use a CALORIMETER to measure the amount of heat released or absorbed by the system by directly measuring the transfer of energy from the system to the surroundings via a temperature change



- The liquid in the calorimeter (water) will absorb any heat released by the reaction or will release any heat that is needed by the reaction
- By taking the temperature of the liquid, we can calculate how much heat was gained or released by the liquid/ surrounding using the formula:
- Q = mΔTc, m = mass of the liquid, $\Delta T = T_2 - T_1$ and c = specific heat capacity c for H_2O = 4.184 J/°C

- **It is important to stir the water so any heat released during the reaction is distributed evenly throughout the "water"**
  - **If not, the "water" nearer the "bomb" would be hotter than the water closer to the edges of the calorimeter**
- Likewise for an endothermic reaction, any heat needed by the reaction should be taken from all of the "water", not just the "water" in contact with the "bomb"
  - Otherwise, the "water" near the "bomb" would be colder than the water closer to the edges of the calorimeter

- When using Q = mΔTc, we are finding (in an exothermic reaction) the heat ABSORBED by the water therefore Q will be +
- When we refer back to the reaction itself, we must indicate that the reaction RELEASED energy so $Q_{Rx} = -Q_{calorimeter}$

Answer the following questions.

1. If the same amount of heat were added to individual 1 g samples of water, methanol and aluminium, which substance would undergo the greatest temperature change? Explain. (Look at their specific heat capacities)

2. There is 1.5 kg of water in a kettle. Calculate the quantity of heat that flows into the water when it is heated from 18°C to 98.7°C.

3. On a mountaineering expedition, a climber heats water from 0°C to 50°C. Calculate the mass of water that could be warmed by the addition of 8.00 kJ of heat.

4. Aqueous ethylene glycol is commonly used in car radiators as an antifreeze and coolant. A 50% ethylene glycol solution in a radiator has a specific heat capacity of 3.5J/g°C. What temperature change would be observed in a solution of 4 kg of ethylene glycol if it absorbs 250 kJ of heat?

5. Solar energy can preheat cold water for domestic hot water tanks.
    a. What quantity of heat is obtained from solar energy if 100 kg of water is preheated from 10°C to 45°C?
    b. If natural gas costs 0.351¢/MJ, calculate the money saved if the volume of water in part a is heated 1500 times per year.

6. The solar heated water in the previous question might be heated to the final temperature in a natural gas water heater.
    a. What quantity of heat flows into 100L (100 kg) of water heated from 45°C to 71°C?
    b. At 0.351¢/MJ, what is the cost of heating 100 kg of water by this amount, 1500 times per year?

MOLAR ENTHALPIES

- How much heat is released if 1 g of carbon is burned in excess oxygen. The heat gained by this reaction heated the 100 g of water found in the calorimeter from 20°C to 32.7°C. The specific heat capacity of water is 4.184 J/g°C.

$C(s) + O_2(g) \rightarrow CO_2(g) + \text{energy}$

$m_{HA} = 100$ g
T1 = 20°C
T2 = 32.7°C
ΔT = 12.7°C
c = 4.184 J/g°C

Qcal = mΔTc
= (100)(12.7)(4.184)
= 5313.7 J
$Q_{Rx} = -5313$ J

- the calculation just completed gives us the heat released for the reaction using a specific amount of carbon
- obviously if we used more carbon, more heat would be generated
- if we want to express the amount of heat released/absorbed for the reaction in general terms (independent of the amount used), we need to use molar heat of reaction (molar enthalpy)
  - see page 306 for some examples
- $\Delta H = Q_{Rx}/n$

- going back to the example just completed;

$C(s) + O_2(g) \rightarrow CO_2(g) + \text{energy}$

m = 1 g
M = 12 g/mol

n = m/M
= 1/12
= 0.083 mol

$m_{HA} = 100$ g
T1 = 20°C
T2 = 32.7°C
ΔT = 12.7°C
c = 4.184 J/g°C

Qcal = mΔTc
= (100)(12.7)(4.184)
= 5313.7 J
$Q_{Rx} = -5313$ J

$\Delta H = Q_{Rx}/n$
= (-5.313 kJ)/(0.083)
= -64 kJ/mol

$C(s) + O_2(g) \rightarrow CO_2(g) + 64$ kJ

- Calculate the molar heat of reaction when hydrogen gas reacts with oxygen gas to produce water. The 1 L of hydrogen gas was at 21°C and at 400 kPa. At the completion of the reaction, the temperature was 31°C. The reaction took place in 1 kg of water.

$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) + \text{energy}$

V = 1L
P = 400 kPa
T = 21+273 = 294 K

PV=nRT
(400)(1) = n(8.314)(294)
n = 0.164 mol

m = 1 kg
c = 4.184 kJ/kg°C
T1 = 21°C
T2 = 31°C
ΔT = 10°C

Qcal = mΔTc
= (1)(10)(4.184)
= 41.84 kJ
Q_{Rx} = -41.84 kJ

ΔH = Q_{Rx}/n
= (-41.84)/(0.164)
= -255.1 kJ/mol

$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) + 2(255.1)kJ$

Answer these questions.

1. In a chemistry experiment to investigate the properties of a fertilizer, 10.0 g of urea, $NH_2CONH_2(s)$, is dissolved in 150 mL of water in a simple calorimeter. A temperature change from 20.4°C to 16.7°C is observed. Calculate the molar enthalpy of solution (energy needed to dissolve it) for the fertilizer urea.

2. In a 10.0 g sample of liquid gallium metal, at its melting point, is added to 50.0 g of water in a polystyrene calorimeter. The temperature of the water changes from 24.0°C to 27.8°C as the gallium solidifies. Calculate the molar enthalpy of solidification (energy needed to freeze) for gallium.

3. The energy involved in the process $H_2O(g) \rightarrow H_2O(l)$ could be described as the molar enthalpy of condensation. Describe the type of molar enthalpy that would be associated with each of the following reactions:
   a. $Br_2(l) \rightarrow Br_2(g)$
   b. $CO_2(g) \rightarrow CO_2(s)$
   c. $LiBr(s) \rightarrow Li^{+1}(aq) + Br^{-1}(aq)$
   d. $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$
   e. $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

4. In a laboratory investigation into the reaction:
   $Ba(NO_3)_2(s) + K_2SO_4(aq) \rightarrow BaSO_4(s) + 2KNO_3(aq)$, a researcher adds 261 g sample of barium nitrate to 2.0 L of potassium sulphate solution in a polystyrene calorimeter. As the barium nitrate dissolves, a precipitate is immediately formed. T_1 = 26.0°C and T_2 = 29.1°C. Calculate the molar enthalpy of the reaction of barium nitrate.

5. If the molar enthalpy of combustion of ethane is -1.56 MJ/mol, how much heat is produced in the burning of:
   a. 5.0 mol of ethane?
   b. 40.0 g of ethane?

6. The molar enthalpy of solution of ammonium chloride is +14.8 kJ/mol. What would be the final temperature of a solution in which 40.0 g of ammonium chloride is addes to 200.0 mL of water, initially at 25°C?

7. The molar enthalpy of combustion of decane ($C_{10}H_{22}$) is -6.78 MJ/mol. What mass of decane would have to be burned to raise the temperature of 500.0 mL of water from 20.0°C to 55.0°C?

8. In a laboratory investigation into the neutralization reaction, $HNO_3(aq) + KOH(aq) \rightarrow KNO_3(aq) + H_2O(l)$, a researcher adds solid potassium hydroxide to nitric acid in a polystyrene calorimeter. Calculate the molar enthalpy of neutralization of potassium hydroxide if 5.2 g of the substance was dissolved in 200 mL of nitric acid and its

temperature changed from 21.0°C to 28.1°C.

REPRESENTING ENTHALPY CHANGES

- there are four ways in which we can show energy in a chemical equation:

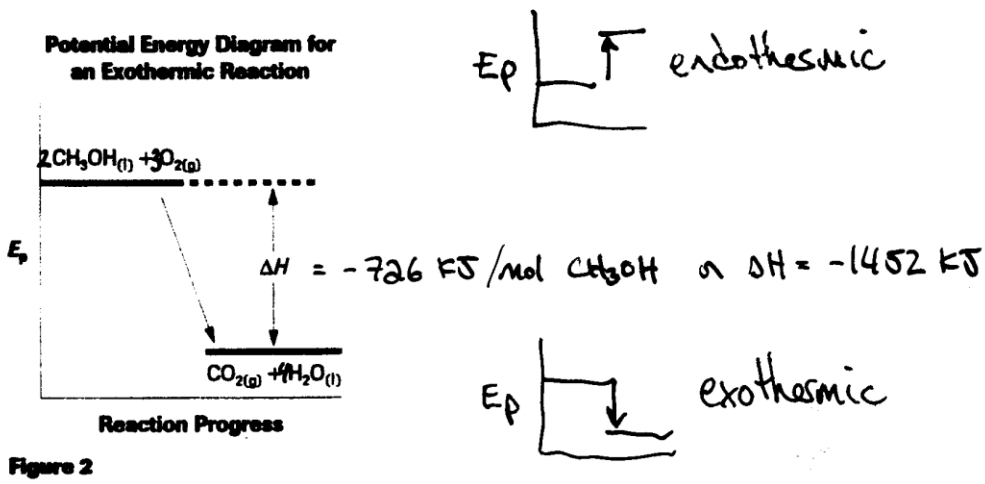
1. Include the energy change in a thermochemical equation
   eg) $2CH_3OH + 3O_2 \rightarrow 4H_2O + CO_2 + 1452$ kJ

2. State the change in enthalpy as a ΔH value for a specific reaction
   eg) $2CH_3OH + 3O_2 \rightarrow 4H_2O + CO_2$ $\Delta H = -1452$ kJ

3. State the molar enthalpy for a specific reaction
   eg) $2CH_3OH + 3O_2 \rightarrow 4H_2O + CO_2$ $\Delta H = -726$ kJ/mol of CH_3OH

4. Drawing a potential energy diagram to represent the change in energy
   eg)

eg)



- If 35 g of magnesium is reacted with an excess amount of oxygen in a bomb calorimeter, the 500 g of water has its temperature rise from 20°C to 45°C. Find the molar heat of reaction and express the change in energy in all 4 forms.

NET IONIC EQUATION

ONLY APPLIES TO IONIC SUBSTANCES THAT ARE DISSOLVED IN WATER!!!!!!

- consider the dissolving of table salt in water,
  $NaCl(s) \rightarrow Na^{+1}(aq) + Cl^{-1}(aq)$

What is the ΔH of this dissolving process?

- to figure this out, we must look at 2 components/steps of dissolving:

- the energy needed to pull the ions out of the crystal/solid which is an endothermic process is called **lattice energy**
  eg) $NaCl(s) \rightarrow Na^{+1} + Cl^{-1}$ $\Delta H = +766$ kJ/mol

- the energy released when polar water molecules are attracted to the ions (surrounding them) which is an exothermic process is called **salvation energy**
  eg) $Na^{+1} + Cl^{-1} \rightarrow Na^{+1}(aq) + Cl^{-1}(aq)$ $\Delta H = -770$ kJ/mol

$$\Delta H_{solution} = \Delta H_{lattice\ energy} + \Delta H_{solvation}$$

- consider reacting 2 solutions together: $AgNO_3$ + NaCl

  $Na^{+1}(aq) + Cl^{-1}(aq) + Ag^{+1}(aq) + NO_3^{-1}(aq) \rightarrow AgCl(s) + Na^{+1}(aq) + NO_3^{-1}(aq)$

- since the sodium and nitrate ions appear on both sides of the equation, they are called **spectator ions** (remain unchanged during the reaction)

- a net ionic equation just reports the reaction without the spectator ions
  N.I.E. = $Ag^{+1}(aq) + Cl^{-1}(aq) \rightarrow AgCl(s)$

Eg) Write out the net ionic equation between potassium hydroxide and sulfuric acid (water and a dissolved salt are formed)

STANDARD HEAT OF FORMATION (ΔH^o_f)

ΔH^o_f ° = standard conditions (P = 101.3 kPa and T = 25°C) & f = formation

- the ΔH^o_f for a compound is equal to the change in enthalpy from the synthesis of ONE mole of the compound formed from its ***ELEMENTS***
  - $H_2 + ½ O_2 \rightarrow H_2O + 242$ kJ
  - $Cu + N_2 + 3O_2 \rightarrow Cu(NO_3)_2 + 302.9$ kJ

- ΔH^o_f for any element = 0 because it doesn't require or release any energy to form an element from itself

HESS' LAW

HESS' LAW - for any reaction that can be written into steps, the ΔH^o is the same as the sum of all the ΔH^o_f found in each of the steps leading up to the overall reaction

- if we cannot find the ΔH experimentally, we can break the reaction down into steps that will allow us to calculate ΔH
- this can be done by:
  a) if the steps for a reaction are given, rearrange them so that when added together, they yield the overall reaction
     eg) Calculate the ΔH° for the following reaction:
     $HCl(g) + NaNO_2(s) \rightarrow HNO_2(l) + NaCl(s)$. Use the following thermochemical equations.
     $2NaCl(s) + H_2O(l) \rightarrow 2HCl(g) + Na_2O(s)$ ΔH°= +507.31 kJ
     $NO(g) + NO_2(g) + Na_2O(s) \rightarrow 2NaNO_2(s)$ ΔH° = -427.14 kJ
     $NO(g) + NO_2(g) \rightarrow N_2O(g) + O_2(g)$ ΔH° = -42.68 kJ
     $2HNO_2(l) \rightarrow N_2O(g) + O_2(g) + H_2O(l)$ ΔH° = +34.35 kJ

  b) write down the ΔH^o_f and corresponding expression that produces each reactant and product in the overall reaction; rearrange the equations making sure the compound is on the proper side of the arrow as in the original reaction; add up the equations, cancelling as necessary
     eg) Calculate the ΔH° for the combustion of propane

HW – Calculate the ΔH° for the following reactions. Write out the steps using the Ep form as well

$NaCl(s) + AgNO_3(s) \rightarrow AgCl(s) + NaNO_3(s)$ ΔH^o_f for sodium nitrate = -359.41 kJ/mol

$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(s) + H_2(g)$

$NaOH(s) + HCl(aq) \rightarrow H_2O(l) + NaCl(s)$

HESS' LAW (short form)

- Hess' law allows us to calculate ΔH° for a reaction without adding together the reaction steps
- All we need to do is … $\Delta H^\circ = \Sigma\ \Delta H^o_f$ products – $\Sigma\ \Delta H^o_f$ reactants

eg) Calculate the ΔH° for the reaction of ferric oxide powder reacting with carbon monoxide gas to produce iron and carbon dioxide gas.

$$\underset{-822.2}{Fe_2O_3(s)} + \underset{-110}{3CO(g)} \rightarrow \underset{0}{2Fe(s)} + \underset{-394}{3CO_2(g)}$$

$\Delta H^o = \Delta H^o_f$ products - ΔH^o_f reactants
= [0 + 3(-394)] – [-822.2 + 3(-110)]
= -1182 + 1152.2
= -29.8 kJ

eg) Calculate the ΔH° when ethene gas is reacted with water to produce ethanol.

$$\underset{+51.9}{C_2H_4(g)} + \underset{-286}{H_2O(l)} \rightarrow \underset{-278}{C_2H_5OH(l)}$$

$\Delta H^o = \Delta H^o_f$ products - ΔH^o_f reactants
= (-278) – [51.9 + (-286)]
= -278 – [-234.1]
= -43.9 kJ

eg) Calculate the change in enthalpy when sodium hydrogen carbonate decomposes into sodium carbonate, water vapour and carbon dioxide gas.

$$\underset{-947.7}{2NaHCO_3(s)} \rightarrow \underset{-1131}{Na_2CO_3(s)} + \underset{-242}{H_2O(g)} + \underset{-394}{CO_2(g)}$$

$\Delta H^o = \Delta H^o_f$ products - ΔH^o_f reactants
= [-1131 + (-242) + (-394)] - [(-947.7)2]
= -1767 – [-1895.4]
= +128.4 kJ

eg) Calculate the ΔH° when ethanol is burned.

$$\underset{-278}{C_2H_5OH(l)} + \underset{0}{3O_2(g)} \rightarrow \underset{-394}{2CO_2(g)} + \underset{-242}{3H_2O(g)}$$

$\Delta H^o = \Delta H^o_f$ products - ΔH^o_f reactants
= [2(-394) + 3(-242)] - [-278 + 3(0)]
= -1514 + 278
= -1236 kJ

eg) Calculate the ΔH° when nitrogen monoxide gas reacts with oxygen gas to make nitrogen dioxide gas.

$$\underset{+90.4}{2NO(g)} + \underset{0}{O_2(g)} \rightarrow \underset{+34}{2NO_2(g)}$$

$\Delta H^o = \Delta H^o_f$ products - ΔH^o_f reactants
= [2(34)] - [2(90.4) + 0]
= 68 - 180.8
= -112.8 kJ

Answer the following questions:

1. The enthalpy changes for the formation of aluminium oxide and iron (III) oxide from their elements are:
   $2Al(s) + 3/2O_2(g) \rightarrow Al_2O_3(s)$ ΔH° = -1675.1 kJ
   $2Fe(s) + 3/2O_2(g) \rightarrow Fe_2O_3(s)$ ΔH° = -824.2 kJ
   Calculate the enthalpy change for the following target reaction using the above reactions:
   $Fe_2O_3(s) + 2Al(s) \rightarrow Al_2O_3(s) + 2Fe(s)$ ΔH° = ?

2. Coal gasification converts coal into a combustile mixture of carbon monoxide and hydrogen, called coal gas, in a gasifier. $H_2O(g) + C(s) \rightarrow CO(g) + H_2(g)$ ΔH° = ?
   Calculate the standard enthalpy change for this reaction from the following chemical equations and enthalpy changes.
   $2C(s) + O_2(g) \rightarrow 2CO(g)$ ΔH° = -221.0 kJ
   $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ ΔH° = -483.6 kJ

3. The coal gas described in the previous question can be used as a fuel, for example, in a combustion turbine. $CO(g) + H_2(g) \rightarrow CO_2(g) + H_2O(g)$ ΔH° = ?
   Predict the change in enthalpy for this combustion reaction from the following information.
   $2C(s) + O_2(g) \rightarrow 2CO(g)$ ΔH° = -221.0 kJ
   $C(s) + O_2(g) \rightarrow CO_2(g)$ ΔH° = -393.5 kJ
   $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ ΔH° = -483.6 kJ

4. Ethyne gas may be reduced by reaction with hydrogen gas to form ethane gas in the following reduction reaction: $C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$.
   Predict the enthalpy change for the reduction of 200 g of ethyne, using the following information.
   $C_2H_2(g) + 5/2O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$ ΔH° = -1299 kJ
   $H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$ ΔH° = -286 kJ
   $C_2H_6(g) + 7/2O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ ΔH° = -1560 kJ

5. As an alternative to combustion of coal gas described earlier, coal gas can undergo a process called methanation.

   $3H_2(g) + CO(g) \rightarrow CH_4(g) + H_2O(g)$ $\Delta H° = ?$.

   Determine the enthalpy change involved in the reaction of 300 g of carbon monoxide gas in this methanation reaction, using the following reference equations and enthalpy changes:

   $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ $\Delta H° = -483.6$ kJ
   $2C(s) + O_2(g) \rightarrow 2CO(g)$ $\Delta H° = -221.0$ kJ
   $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ $\Delta H° = -802.7$ kJ
   $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H° = -393.5$ kJ

6. Use standard enthalpies of formation to calculate:
   a. The molar enthalpy of combustion for pentane (C_5H_{12}) to produce carbon dioxide gas and liquid water.
   b. The enthalpy change that accompanies the reaction between solid iron (III) oxide and carbon monoxide gas to produce solid iron metal and carbon dioxide gas.

7. The standard enthalpy of combustion of liquid cyclohexane to carbon dioxide and liquid water is -3824 kJ/mol. What is the <u>standard enthalpy of formation</u> of cyclohexane, $C_6H_{12}(l)$?

8. Methane, the major component of natural gas, is used as a source of hydrogen gas to produce ammonia. Ammonia is used as a fertilizer and a refrigerant, and is used to manufacture fertilizers, plastics, cleaning agents and prescription drugs. The following questions refer to some of the chemical reactions of these processes. For each of these equations, use standard enthalpies of formation to calculate $\Delta H°$.
   a. The first step in the production of ammonia is the reaction of methane with steam, using a nickel catalyst.

      $CH_4(g) + H_2O(g) + Ni(s) \rightarrow Ni(s) + CO(g) + 3H_2(g)$
   b. The second step of this process is the further reaction of water with carbon monoxide to produce more hydrogen. Both iron and zinc/copper catalysts are used.

      $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$
   c. After the carbon dioxide gas is removed by dissolving it in water, the hydrogen reacts with nitrogen in the air to form ammonia.

      $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

9. Nitric acid, required in the production of nitrate fertilizers, is produced from ammonia by the Ostwald process. Use standard enthalpies of formation to calculate the enthalpy changes in each of the following systems:
   a. $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$
   b. $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$
   c. $3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(l) + NO(g)$

10. Ammonium nitrate fertilizer is produced by the reaction of ammonia with nitric acid: $NH_3(g) + HNO_3(l) \rightarrow NH_4NO_3(s)$.
    a. Use standard enthalpies of formation to calculate the standard enthalpy change of the reaction used to produce ammonium nitrate.
    b. Sketch a potential energy diagram for the reaction of ammonia and nitric acid.
    c. Calculate the neat that would be produced or absorbed in the production of 50 tonnes of ammonium nitrate.

11. Coal is a major energy source for electricity, of which industry is the largest user. Anthracite coal is a high molar mass carbon compound with a composition of about 95% carbon by mass. A typical simplest-ratio formula for anthracite coal is $C_{52}H_{16}O(s)$. The standard enthalpy of formation of anthracite can be estimated at -396.4 kJ/mol. What is the quantity of energy available from burning 100.0 kg of anthracite coal in a thermal electric power plant, according to the following equation?

$$2C_{52}H_{16}O(s) + 111O_2(g) \rightarrow 104CO_2(g) + 16H_2O(g)$$