CHEMISTRY 135 SEMESTER 01-2006
THERMOCHEMISTRY

1) Given the following heats of reaction:

$I_2(s) + Cl_2(g) \rightarrow 2ICl(g) \quad \Delta H = +35\text{ kJ}$

$N_2(g) \rightarrow 2N(g) \quad \Delta H = +946\text{ kJ}$

$Ag^+(aq) + 2NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq) \quad \Delta H = -111\text{ kJ}$

$H^+(aq) + HC_2O_4^-(aq) \rightarrow H_2C_2O_4(aq) \quad \Delta H = +0.54\text{ kJ}$

$Si(s) + 2H_2(g) \rightarrow SiH_4(g) \quad \Delta H = -61.9\text{ kJ}$

a) Consider the two reactions which occur in solution. Imagine these are conducted in a thermally insulated vessel using the number of moles of reactant indicated in the equation. If the vessel contains 1000g of solution of specific heat capacity 4.18 $Jg^{-1}K^{-1}$, what would be the temperature change in each case? Give the correct sign for your answers.

b) Calculate the heat changes which would occur when each of the following mixtures is allowed to react to completion:
   - i) 0.1 mol of solid iodine and 0.1 mol of gaseous chlorine.
   - ii) 0.1 mol of solid iodine and 0.2 mol of gaseous chlorine.
   - iii) 12.7g of solid iodine and 7.1g of gaseous chlorine.
   - iv) 100 cm^3 of 0.1M silver nitrate solution and 100 cm^3 0.2M aqueous ammonia.
   - v) 100 cm^3 of 0.1M silver nitrate solution and 50 cm^3 of 0.4M aqueous ammonia.
   - vi) 2.8g of solid silicon and 0.4g of gaseous hydrogen.
   - vii) 2.8g of solid silicon and 4 dm^3 of gaseous hydrogen, measured at s.t.p.

c) Calculate the heat change involved in:
   - i) the complete decomposition of 4.50g of gaseous ICl to solid iodine and gaseous chlorine.
   - ii) the complete decomposition of 5 dm^3 of gaseous SiH_4 (measured at s.t.p.) to solid silicon and gaseous hydrogen.

2) Calculate the heat change involved when 40g sodium sulfate 10-water crystallizes from water, given the information:

$Na_2SO_4.10H_2O(s) + aq \rightarrow Na_2SO_4(aq) \quad \Delta H = +79\text{ kJ}$

3) When solid white phosphorus is burned in excess oxygen the following reaction occurs:

$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s) \quad \Delta H = -3005\text{ kJ}$

When gaseous phosphorus is burned in excess oxygen, at the same temperature as before, the reaction is:

$P_4(g) + 5O_2(g) \rightarrow P_4O_{10}(s) \quad \Delta H = -3018\text{ kJ}$

Calculate the heat change for the process:

$P_4(s) \rightarrow P_4(g)$

4) A gaseous mixture of 100g of oxygen and 100g of hydrogen is sparked to form water, according to the equation:

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

a) What mass of water is formed?

b) How many kilojoules of heat would be evolved?

Use the following data:

$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \quad \Delta H = -485\text{ kJ}$

$H_2O(g) \rightarrow H_2O(l) \quad \Delta H = -44\text{ kJ}$

5) Calculate ΔH for the process

$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

given that

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \quad \Delta H = -92.2\text{ kJ}$

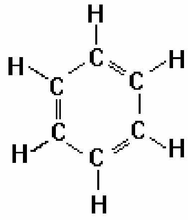
$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \quad \Delta H = -484\text{ kJ}$

$N_2(g) + O_2(g) \rightarrow 2NO(g) \quad \Delta H = +180.2\text{ kJ}$

6) The standard heats of formation of ethyne gas (C_2H_2), carbon dioxide gas, and water vapour are respectively +226, -393, and -243 kJ mol^{-1}. Calculate the heat change involved when 0.1 mol of gaseous ethyne is completely burned to CO_2 and water vapour. What use is made of this reaction in industry?

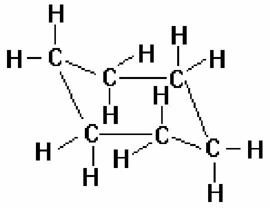
7) State Hess's law. Calculate the heat change for the direct synthesis of methanol from carbon monoxide and hydrogen given that the standard heats of combustion of methanol and carbon monoxide are -715 and -283 kJ mol^{-1} respectively, and the standard heat of formation of water is -286 kJ mol^{-1}. How is Hess's law used in your calculation?

8) The structures of benzene and cyclohexane may be represented as follows:



C_6H_6

Benzene



C_6H_{12}

Cyclohexane

Using mean bond energies from your textbook calculate the molar enthalpy of hydrogenation for benzene vapour, *i.e.* the enthalpy change for the reaction:

$C_6H_6(g) + 3H_2(g) \rightarrow C_6H_{12}(g)$

*In view of the fact that the molar enthalpy of hydrogenation of benzene vapour is in fact -205 kJ mol^{-1}, do you think that the benzene molecule is well represented by a structure including 3 C=C double bonds and 3 C–C single bonds? Is the benzene molecule more or less stable than is indicated by this structure?

9) Carefully explain the difference between the terms ***bond dissociation enthalpy*** and ***average bond enthalpy***.
Use average bond enthalpies and the bond dissociation enthalpy of oxygen, 498 kJ mol^{-1} ,to estimate the standard enthalpy change for the oxidation of ethanol to ethanal:

$CH_3CH_2OH(g) + \frac{1}{2}O_2(g) \rightarrow CH_3CHO(g) + H_2O(g)$

Why would this value not be very accurate?

10) a) Calculate the standard enthalpy of atomisation of chloromethane, $CH_3Cl(g)$, given that the standard enthalpy of formation of chloromethane is -82 kJ mol^{-1}, the standard enthalpy of sublimation of carbon is 717 kJ mol^{-1}, the standard enthalpy of atomisation of chlorine is 240 kJ mol^{-1} (per mole of chlorine molecules), and the equivalent value for hydrogen is 436 kJ mol^{-1}.

b) Given also that the mean bond enthalpy term for the C-H bond is 416 kJ mol^{-1}, estimate the mean bond enthalpy term for the C-Cl bond.

11) Give a detailed explanation of each of the following terms. Look up or calculate from listed values each of the following. Include a thermochemical equation in each case.
- a) Standard heat of combustion of butane.
- b) Standard heat of formation of sulfur dioxide.
- c) The C-C bond energy in ethane.
- d) The enthalpy of atomisation of chlorine.
- e) The enthalpy of sublimation of sodium.
- f) The enthalpy of first ionisation of aluminium.
- g) The second electron affinity of magnesium.
- h) The mean C-H bond enthalpy of methane.
- i) The lattice energy of magnesium chloride.

12) The calorific values of various food stuffs are often given in diet plans. They are obtained by burning specific amounts of the food in pure oxygen. What law makes it possible to apply these same values to the utilisation of the food in the human body? Describe the differences and similarities in the fate of the food in the two cases.

Answers

1) a) +26.6K, -0.13K b) i) +3.5 kJ ii) +3.5 kJ iii) +1.75 kJ
iv) -1.11 kJ v) -1.11 kJ vi) -6.19 kJ vii) -5.53 kJ
c) i) -0.485 kJ ii) +13.8 kJ 2) -9.81 kJ, 3) +13 kJ
4) a) +112.5g b) -1653 kJ 5) -907.2 kJ 6) -125.5 kJ
7) -217 kJ 8) ≃-380 kJ 9) -181 kJ mol^{-1}
10) +1573 kJ mol^{-1}, +325 kJ mol^{-1}