UNIVERSITY OF MALTA

DEPARTMENT OF CHEMISTRY

CH237 - Chemical Thermodynamics and Kinetics

Tutorial Sheet 2

1. (i) An average human produces about 10 MJ of heat each day through metabolic activity. If a human body were an isolated system of mass 65 kg with the heat capacity of water ($c_{p,m}$ [H20(l)] = 75 , what temperature rise would the body experience? Human bodies are actually open systems, and the main mechanism of heat loss is through the evaporation of water. What mass of water should be evaporated each day to maintain constant temperature?

NOTE: $c_{p,m}$ ($H_20_{(l)}$) = 75.3 JK^{-1} mol^{-1}, $\Delta_{vap}H^o$ ($H_20_{(l)}$) = 44.0 kJ mol^{-1}

(ii) The standard enthalpy of combustion of sucrose is -5645 kJ mol^{-1}. What is the advantage of complete oxidation (chem. eqn. 1) compared with anaerobic hydrolysis of sucrose to lactic acid (chem. eqn. 2)? Express your answer as energy per mole of energy released as heat, and as a percentage.

Chem. Eqn. 1: $C_{12}H_{22}O_{11} + 12O_2 \longrightarrow 12\ CO_2 + 11H_2O$

Chem. Eqn. 2: $C_{12}H_{22}O_{11} + H_2O \longrightarrow 4CH_3CH(OH)COOH$

(iii) How much sucrose would our average human require during a typical 24 hour period if we were to assume that our average human attains its energy through complete oxidation (95%) and anaerobic hydrolysis (5%) of sucrose.

2. (a) Calculate the heat required to melt 750 kg of sodium metal at 371 K.

(b) A sample of 1.00 mol $H_2O_{(g)}$ is condensed isothermally and reversibly to liquid water at 100°C. The standard enthalpy of vaporization of water at 100°C is 40.656 $kJmol^{-1}$. Find *q, w, ΔU,* and *ΔH.* for this process.

(c) 2.5 A 5.0 g block of solid carbon dioxide is allowed to evaporate in a vessel of volume 100 cm3 maintained at 25°C. Calculate the work done when the system expands (i) isothermally against a pressure of 1.0 atm, and, (ii) isothermally and reversibly to the same volume.

3. (a) (i) Calculate the standard enthalpy of formation of butane at 25°C from its standard enthalpy of combustion. (ii) The standard enthalpy of formation of ethyibenzene is -12.5 $kJmol^{-1}$ Calculate its standard enthalpy of combustion.

(b) Calculate the standard enthalpy of hydrogenation of 1-hexene to hexane given that the standard enthalpy of combustion of 1-hexene is -4003 $kJmol^{-1}$.

(c) (i) The standard enthalpy of combustion of cyclopropane is -2091 $kJmol^{-1}$ at 25°C. From this information and enthalpy of formation data for CO_2(g) and H_2O(g), calculate the enthalpy of formation of cyclopropane. (ii) The enthalpy of formation of propene is +20.42 $kJmol^{-1}$. Calculate the enthalpy of isomerization of cyclopropane to propene.

(d) Calculate the standard internal energy of formation of liquid methyl acetate from its standard enthalpy of formation, which is -442 $kJmol^{-1}$.

(e) Calculate the standard enthalpy of solution of AgCl(s) in water from the enthalpies of formation of the solid and the aqueous ions.

(f) The standard enthalpy of decomposition of the yellow complex H_3NS0_2 into NH_3 and SO_2 is +40$kJmol^{-1}$. Calculate the standard enthalpy of formation of H_3NS0_2.

(g) The mass of a typical sugar cube (sucrose) is 1.5 g. Calculate the energy released as heat when a cube is burned in air. To what height could a 65 kg person climb on the energy a cube provides assuming 25 per cent of the energy is available for work?

(h) The standard enthalpy of combustion of propane gas is -2220 kJmol-1 and the standard enthalpy of vaporization of propane liquid is +15 $kJmol^{-1}$. Calculate (i) the standard enthalpy and (ii) the standard internal energy of combustion of liquid propane.

(i) Use standard enthalpies of formation to calculate the standard enthalpies of the following reactions:

(i) $2NO_{2\,(g)} \longrightarrow N_2O_{4\,(g)}$

(ii) $NH_{3\,(g)} + HCl_{\,(g)} \longrightarrow NH_4Cl_{(s)}$

(j) Calculate the standard enthalpies of formation of

(i) $KClO_{3(s)}$ from the enthalpy of formation of KCl,

(ii) $NaHC0_{3(s)}$ from the enthalpies of formation of CO_2 and NaOH

together with the following information:

$2KCl0_{3(s)} \longrightarrow 2KCl_{(s)} + 3O_{2(g)}$ $\quad \Delta H = -89.4\ kJmol^{-1}$

$NaOH_{(s)} + C0_{2(g)} \longrightarrow NaCO_{3(s)}$ $\quad \Delta H = -127.5\ kJmol^{-1}$

(k) Set up a thermodynamic cycle for determining the enthalpy of hydration of Mg^{2+} ions using the following data:

Enthalpy of sublimation of $Mg_{\,(s)}$ = +167.2 $kJmol^{-1}$

First and second ionization enthalpies of $Mg_{\,(g)}$ = 7.646 eV and 15.035 eV

Dissociation enthalpy of $Cl_{2\,(g)}$ = +241.6 $kJmol^{-1}$

Electron-gain enthalpy of $Cl_{\,(g)}$ = -3.78 eV

Enthalpy of solution of $MgCl_{2\,(s)}$ = -150.5 $kJmol^{-1}$

Enthalpy of hydration of $Cl^-_{\,(g)}$ = -383.7 $kJmol^{-1}$.

(l) Since their discovery in 1985, fullerenes have received the attention of many chemical researchers. Kolesov *et al.* have recently reported the standard enthalpy of combustion and of formation of crystalline C_{60} based on calorimetric measurements (V.P. Kolesov, S.M. Pimenova, V.K. Paviovich, N.B. Tamm, and A.A. Kurskaya, *J. Chem. Thermodynamics*, **28** (1996) p. 1121). In one of their runs, they found the standard specific internal energy of combustion to be -36.0334 kJg^{-1} at 298.15 K. Compute the standard enthalpy of formation and combustion of C_{60}.

(m) Alkyl radicals are important intermediates in the combustion and atmospheric chemistry of hydrocarbons. N. Cohen has reported group additivity tables for the thermochemistry of alkyl radicals in the gas phase (N. Cohen, *J. Phys. Chem.*, **96** (1992) p. 9052). He suggests computing enthalpies of formation based on the following bond-dissociation energies *(ΔU^o)* for C-H bonds:
primary (-(H)C(H)-H), 420.5 $kJmol^{-1}$; secondary (-(C)C(H)-H), 410.5 $kJmol^{-1}$; tertiary (-(C)C(C)-H), 398.3 $kJmol^{-1}$. Estimate the standard enthalpy of formation of (i) $C_2H_5^{\cdot}$, (ii) sec-$C_4H_9^{\cdot}$, and (iii) tert-$C_4H_9^{\cdot}$ (standard enthalpy of formation of 2-methylpropane (g) is -134.2 kJ mol^{-1}.)
-134.2 kJmol-1.)

(n) Silanone (SiH_20) and silanol (SiH_30H) are species believed to be important in the oxidation of silane (SiH_4). These species are much more elusive than their carbon counterparts. Darling and Schlegel (C.L. Darling and H.B. Schlege, *J. Phys. Chem.*, **97** (1993) p. 8207) report the following values for the enthalpies of formation (converted from calories): -98.3 $kJmol^{-1}$ (SiH_20) and -282 $kJmol^{-1}$ (SiH_30H). Compute the standard enthalpies of the following reactions:

(i) $SiH_4(g) + ½\ O_2\ (g) \longrightarrow SiH_30H\ (g)$ (ii) $SiH_4(g) + O_2\ (g) \longrightarrow SiH_20\ (g) + H_2O\ (1)$

(iii) $SiH_30H\ (g) \longrightarrow SiH_2O(g) + H_2\ (g)$

Note that the standard enthalpy of formation of SiH_4 (g) = +34.3 $kJmol^{-1}$ (CRC *Handbook* (1995)).