UNIVERSITY OF MALTA

DEPARTMENT OF CHEMISTRY

CH237 - Chemical Thermodynamics and Kinetics

Tutorial Sheet 3

1. (a) The temperature of a bomb calorimeter rose by 1.617 K when a current of 3.20A was passed for 27.0s from a 12.0V source. Calculate the calorimeter constant.

(b) When 120 mg of naphthalene, $C_{10}H_8(s)$, was burned in a bomb calorimeter the temperature rose by 3.05 K. Calculate the cilorimeter constant. By how much will the temperature rise when 100 mg of phenol, $C_6H_{10}OH_{(s)}$, is burned in the calorimeter under the same conditions?

(c) When 0.3212 g of glucose was burned in a bomb calorimeter of calorimeter constant 641 JK-' the temperature rose 7.793 K. Calculate (i) the standard molar enthalpy of combustion, (ii) the standard internal energy of combustion, and (ii) the standard enthalpy of formation of glucose.

(d) The standard enthalpy of formation of the metallocene bis-(benzene)chromium was measured in a calorimeter. It was found for the reaction $Cr(C_6H_6)_{2\ (s)} \rightarrow Cr_{(s)} + 2C_6H_{6\ (g)}$ that $\Delta_r U^o(583\ K) = +8.0$ kJ mol^{-1}. Find the corresponding reaction enthalpy and estimate the standard enthalpy of formation of the compound at 583 K. The constant-pressure molar heat capacity of benzene is 140 JK^{-1}mol^{-1} in its liquid range and 28 JK mol^{-1} as a gas. The boiling point of benzene is 353K.

2 (a) Calculate the change in entropy when 25 kJ of energy is transferred reversibly and isothermally as heat to a large block of iron at (i) 0°C,(ii) 100°C.

(b) Calculate the molar entropy of a constant-volume sample of neon at 500 K given that it is 146.22 J K^{-1} mol^{-1} at 298 K.

(c) A sample consisting of 1.00 mol of a monatomic perfect gas with $C_{V,m}=3R/2$ is heated from 100°C to 300°C at constant pressure. Calculate ΔS (for the system).

(d) Calculate ΔS (for the system) when the state of 3.00 mol of a monatomic perfect gas, for which $C_{V,m} = 5R/2$, is changed from 25 °C and 1.00 atm to 125°C and 5.00 atm. How do you rationalize the sign of ΔS?

(e) A sample consisting of 3.00 mol of a diatomic perfect gas at 200 K is compressed reversibly and adiabatically until its temperature reaches 250 K. Given that $C_{V,m} = 27.5$ JK^{-1} mol^{-1}. calculate q, w. $\Delta U, \Delta H$ and ΔS.

(f) Calculate the increase in entropy when 1.00 mol of a monatomic perfect gas with $C_{p,m} = 5R/2$ is heated from 300 K to 600 K and simultaneously expanded from 30.0 L to 50.0 L.

(g) A system undergoes a process in which the entropy change is $+2.41$ JK^{-1}. During the process, 1.00 kJ of heat is added to the system at 500 K. Is the process thermodynamically reversible? Explain your reasoning.

(h) A sample of aluminium of mass 1.75 kg is cooled at constant pressure from 300 K to 265 K. Calculate (i) the energy that must be removed as heat and (ii) the change in entropy of the sample.

(i) A sample of perfect gas that initially occupies 15.0 L at 250 K and 1.00 atm is compressed isothermally. To what volume must the gas be compressed to reduce its entropy by 5.0 JK^{-1}?

(j) Calculate the change in entropy when 50g of water at 80°C is poured into 100g of water at 10°C in an isolated container assuming that $C_{p,m} = 75.5$ J K^{-1} mol^{-1}.

(k) Calculate ΔS when 200g of (i) water at 0°C and (ii) ice at 0°C is added to 200g of water at 90°C in an isolated container.

(l) Calculate ΔH and ΔS_{TOT}, when two copper blocks, each of mass 10.0 kg, one at 100°C and the other at 0°C, are placed in contact in an isolated container. The specific heat capacity of copper is 0.385 $JK^{-1}g^{-1}$ and may be assumed constant over the temperature range involved.

(m) Consider a system consisting of 2.0 mol CO_2 (g), initially at 25°C and 10 atm and confined to a cylinder of cross-section 10.0 cm^2. It is allowed to expand adiabatically against an external pressure of 1.0 atm until the piston has moved outwards through 20 cm. Assume that carbon dioxide may be considered as a perfect gas with $C_{V,m} = 28.8$ JK^{-1} mol^{-1} and calculate q, w, ΔU, ΔT and ΔS.

(n) The standard molar entropy of NH_3(g) is 192.45 JK^{-1} mol^{-1} at 298 K, and its heat capacity is given by $C_{p,m} = a + bT + cT^2$ where $a = 29.75$ JK^{-1} mol^{-1}, $b = 25.1$ x 10^{-3} JK^{-2} mol^{-1} and $c = -1.55$ x 10^5 $JK^{-3}mol^{-1}$. Calculate the standard molar entropy at (i) 100°C and (b) 500°C.

(o) Find an expression for the change in entropy when two blocks of the same substance and of equal mass, one at the temperature T_h and the other at T_c, are brought into thermal contact and allowed to reach equilibrium. Evaluate this change in entropy for two blocks of copper, each of mass 500 g, with $C_{p,m} = 24.4$ $JK^{-1}mol^{-1}$ taking $T_h = 500$ K and $T_c = 250$ K. [Hint: the final temperature, $T_f = \frac{1}{2}(T_h+T_c)$]

3 (a) The enthalpy of vaporization of chloroform ($CHCl_3$) is 29.4 kJ mol^{-1} at its normal boiling point of 34.88 K. Calculate (i) the entropy of vaporization of chloroform at this temperature and (ii) the entropy change of the surroundings.

(b) The enthalpy of vaporization of methanol is 35.27 $kJmol^{-1}$ at its normal boiling point of 64.1°C. Calculate (i) the entropy of vaporization of methanol at this temperature and (ii) the entropy change of the surroundings.

(c) Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when a sample of nitrogen gas of mass 14 g at 298 K and 1.00 bar doubles its volume in (i) an isothermal reversible expansion, (ii) an isothermal irreversible expansion against $p_{ex} = 0$, and (iii) an adiabatic reversible expansion.

(d)   Calculate the difference in molar entropy (i) between liquid water and ice at -5°C. (ii) between liquid water and its vapour at 95°C and 1.00 atm. The differences in heat capacities on melting and on vaporization are 37.3 JK^{-1} mol^{-1} and -41.9 JK^{-1} mol^{-1}, respectively. Distinguish between the entropy changes of the sample, the surroundings, and the total system, and discuss the spontaneity of the transitions at the two temperatures.

(e)   1.00 mol of a perfect gas at 27 °C is expanded isothermally from an initial pressure of 3.00 atm to a final pressure of 1.00 atm in two ways: (i) reversibly, and (ii) against a constant external pressure of 1.00 atm. Determine the values of q, w, ΔU, ΔH, ΔS, ΔS_{surr} and ΔS_{tot} for each path.

(f)   A sample of 1.00 mol of a monatomic perfect gas at 27°C and 1.00 arm is expanded adiabatically in two ways: (i) reversibly to 0.50 atm, and (ii) against a constant external pressure of 0.50 atm. Determine the values of q, w, ΔU, ΔH, ΔS, ΔS_{surr} and ΔS_{tot} for each path where the data permit. (Take $C_{V,m} = 3R/2$.)