Exercises Topic 4: Thermochemistry

1. One mol of an ideal gas is heated very slowly from 200 to 400 K at a constant pressure of 2 atm. Assuming that heat capacity at constant pressure is 5/2 R, calculate:

a) w, q, ΔE and ΔH in joules

b) If the gas is slowly heated at a constant volume of 10 L, from 200 K to 300 K, calculate w, q, ΔE and ΔH.

Solution: a) w = -1.663 KJ; q = q_P = ΔH = 4.1571 KJ; ΔE = 2.49 KJ; b) w = 0; q = q_V = ΔE = 2.493 KJ; ΔH = 4155.8 J

2. Thermal decomposition of potassium chlorate ($KClO_3$) yields potassium chloride and oxygen where ΔH = -22.3 kJ/mol. Determine the value of the standard enthalpy of formation of potassium chlorate from its elements in standard state if the standard enthalpy of formation of potassium chloride is -436 kJ/mol.

Solution: $\Delta H^0_f(KClO_3)$ = -413.7 kJ/mol

3. The molar enthalpy of vaporization of water is 40.6 kJ/mol and its specific heat capacity is 4.18 J/g·ºC. Calculate ΔH for the process in which 25 g of water is converted from liquid at 10.0 ºC to vapor at 25.0 ºC.

Solution: ΔH = 57.96 KJ

4. How many kilograms of water initially at 30 ºC are possible to heat up to its transformation in water vapor at 100ºC by burning 500 L of C_2H_4 under STP conditions?

Data: Standard enthalpy of vaporization of water = 40.6 kJ/mol.; Standard enthalpy of formation of C_2H_4 = 52.3 kJ/mol; standard enthalpy of formation of CO_2 = -393.13 kJ/mol; standard enthalpy of formation of H_2O (l) = -285.85 kJ/mol; specific heat of water = 4.18 kJ/kg K; molar mass of water = 18 g/mol

Solution: Mass of water = 11.3 kg

5. Ethylene and propylene can be transformed into ethane and propane according to the following hydrogenating reactions

$$C_2H_{4(g)} + H_{2(g)} \to C_2H_{6(g)}$$

$$C_3H_{6(g)} + H_{2(g)} \to C_3H_{8(g)}$$

The standard molar enthalpy of formation (in kJ/mol at 298.15 K) of ethylene, propylene, ethane and propane are: +52.51, +19.71, -83.85 and -104.68 respectively.

a) Calculate ΔHº for these reactions.

b) Using an inductive method demonstrate if the standard enthalpy of formation for any reaction of the kind $C_nH_{2n(g)} + H_{2(g)} \to C_nH_{2n+2(g)}$ will have the same enthalpy.

Solution: ΔH for hydrogenation of C_2H_4 is-136.36 kJ/mol; ΔH for hydrogenation of C_3H_6 is -124.39 kJ/mol. Additional data are needed to check the rule. From Table 1 (Mahan) we obtain the enthalpies of formation of 1-butene and butane: ΔH^0_f (1-butene) =-0.54 kJ/mol and ΔH^0_f (1-butane) = -125.65 kJ/mol. From Steele, W.V, Chirico, R.D., J. Phys. Chem. Ref. Data, 22(2), 377 (1983) we find ΔH^0_f (1-pentene) = -21.5 kJ/mol and ΔH^0_f (1-hexene) = -39.71 kJ/mol. From the corresponding page we find in wikipedia ΔH^0_f (pentane) = -173.5 kJ/mol and ΔH^0_f (hexane) = -167.2 kJ/mol. The corresponding hydrogenation enthalpies are $\Delta H_H(C_4H_8)$ = -125.1 kJ/mol; $\Delta H_H(C_5H_{10})$ = -153 kJ/mol; $\Delta H_H(C_6H_{12})$ = -127.49 kJ/mol. So except for small deviations, the rule seems to be followed.

6. Calculate the entropy change of: a) an ideal gas that is heated at a constant pressure of 1 atm from 300 K to 450 K and b) an ideal gas that is heated at a constant volume of 1L from 200 K to 300 K. **Hint**. Use the same heat capacity values as in exercise 5.1

Solution: a) ΔS = 8.42 J/K; b) ΔS = 5.06 J/K

7. The molar enthalpies of fusion and vaporization of benzene are 0.9 kJ/mol and 31.0 kJ/mol, respectively. Benzene normal melting and boiling points are 5.5 ºC and 80.1 ºC respectively. C_P (in J/mol·K) values of benzene in the solid, liquid and gas states are 118.4, 134.8 and 82.44 respectively. Calculate the benzene entropy change when 1 mol of benzene is heated from -20ºC to 100ºC.

Solution: ΔS = 138.87 J/K

8. Determine the standard enthalpy of combustion for H_2 at 210 ºC using the following data: $\Delta H^o comb(H_2) 25ºC = -68320$ cal mol^{-1}, $\Delta H^o vap(H_2O) 100ºC = 9720$ cal mol^{-1}, $C_P(H_2) = 6.62$ cal, $C_P(O_2) = 6.76$ cal mol^{-1} K^{-1}, $C_P(H_2O,l) = 18$ cal mol^{-1} K^{-1}, $C_P(H_2O,g) = 8.22$ cal mol^{-1} K^{-1}.

Solution: $\Delta H^o_C = -58195.8$ cal/mol

9. Use the data presented in the following table to determine the values of ΔH^o, ΔS^o and ΔG^o for the chemical synthesis of one mol of ammonia from nitrogen and hydrogen at 298 K and 600 K.

	ΔH^o_{298}(kcal/mol)	ΔS^o_{298K}(cal/mol·K)	C_p(cal/mol·K)
N_2	0.0	45.767	6.52
H_2	0.0	31.211	6.94
NH_3	-11.04	46.010	6.19

Solution: a) At 298 K: $\Delta H^o_f (NH_3) = -11.04$ kcal; $\Delta S^o_f (NH_3) = -23.69$ cal/K; $\Delta G^o_f (NH_3) = -3976.8$ cal.; b) At 500 K: $\Delta H^o_f (NH_3) = -13.3$ Kcal; $\Delta S^o_f (NH_3) = -5.23$ cal/K; $\Delta G^o_f (NH_3) = -10.16$ Kcal.

11. Explain briefly in which of the following reactions the absorbed heat would be the same than that corresponding to the standard enthalpy of formation of ethanol

a. $2C(diamond) + 3H_2 (g) + ½ O_2 (g) \rightarrow C_2H_5OH (l)$
b. $C(graphite) + 3H_2 (g) + 1/2O_2 (g) \rightarrow 1/2C_2H_5OH (l)$
c. $2C(graphite) + 3H_2 (g) + ½ O_2 (g) \rightarrow C_2H_5OH (l)$
d. $2C(graphite) + 6H (g) + O (g) \rightarrow C_2H_5OH (l)$

Solution: c) Because all reactants and products are in their standard state and one mol of product is formed.

12. Consider formation reaction of nitric oxide: $N_{2(g)} + O_{2(g)} \Leftrightarrow 2NO_{(g)}$. The equilibrium constant at 1800 K is $1.11 \cdot 10^{-2}$ and at 2000 K it is $2.02 \cdot 10^{-2}$. The standard free energy at 25ºC is 86.55 kJ/mol. Calculate ΔG^o at 2000 K and the reaction enthalpy.

Solution: ΔG^o at 2000 K = +64.88 kJ/mol; ΔH^o at 2000 K = 89.60 kJ/mol

15. Elemental sulfur exists in several allotropic forms, being rhombic sulfur the most stable under normal conditions and monoclinic sulfur slightly less stable. The standard enthalpies of combustion of the two allotropes to yield sulfur dioxide are -296.8 kJ·mol^{-1} and -297.2 kJ·mol^{-1} respectively. Calculate the enthalpy of the rhombic → monoclinic transition.

Solution: $\Delta H_{rh \rightarrow mono} = +0.4$ kJ/mol

16. A human body generates heat at a rate of about 100 watts. (a) At what rate does your body heat generate entropy in your surroundings, taken to be at 20 ºC. (b) How much entropy do you generate each hour?. (c) Would the entropy generated be greater or less if you were in a room kept at 30 ºC?

Solution: dΔS/dt = 0.341 J/K·s; (b) 1.23 kJ/K; (c) dΔS/dt = 0.319 J/K·s

17. Coupled reactions are used in organisms to drive important biochemical processes. Individual chemical reactions may be added together to form a net reaction, and the overall reaction Gibbs free energy is the sum of the individual Gibbs free energies of reaction. For example, the generation of ATP from ADP is nonspontaneous and must itself be coupled to a spontaneous reaction as in the following set:

$ADP^{3-}(aq) + HPO_4^{2-}(aq) + H^+ \rightarrow ATP^{4-}(aq) + H_2O(l)$ $\Delta G = +30.5$ kJ (at pH = 7)
$NADH(aq) \rightarrow NAD^+(aq) + H^+(aq) + 2e^-$ $\Delta G = -158.3$ kJ (at pH = 7)
$1/2O_2(g) + 2H_+(aq) + 2e^- \rightarrow H_2O(l)$ $\Delta G = -61.9$ kJ (at pH = 7)

What amount in moles of ATP could be formed if all the Gibbs free energy released in the oxidation of 6 mol NADH were used to generate ATP?

Solution: 43.4 mol of ATP