

## 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)  $w$ ,  $q$ ,  $\Delta E$  and  $\Delta H$  in joules

b) If the gas is slowly heated at a constant volume of 10 L, from 200 K to 300 K, calculate  $w$ ,  $q$ ,  $\Delta E$  and  $\Delta H$ .

**Solution:** a)  $w = -1.663 \text{ KJ}$ ;  $q = q_p = \Delta H = 4.1571 \text{ KJ}$ ;  $\Delta E = 2.49 \text{ KJ}$ ; b)  $w = 0$ ;  $q = q_v = \Delta E = 2.493 \text{ KJ}$ ;  $\Delta H = 4155.8 \text{ J}$

2. Thermal decomposition of potassium chlorate ( $\text{KClO}_3$ ) yields potassium chloride and oxygen where  $\Delta H = -22.3 \text{ kJ/mol}$ . 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  $-436 \text{ kJ/mol}$ .

**Solution:**  $\Delta H_f^0(\text{KClO}_3) = -413.7 \text{ kJ/mol}$

3. The molar enthalpy of vaporization of water is  $40.6 \text{ kJ/mol}$  and its specific heat capacity is  $4.18 \text{ J/g}\cdot^\circ\text{C}$ . Calculate  $\Delta H$  for the process in which  $25 \text{ g}$  of water is converted from liquid at  $10.0^\circ\text{C}$  to vapor at  $25.0^\circ\text{C}$ .

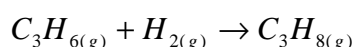
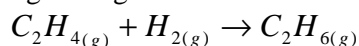
**Solution:**  $\Delta H = 57.96 \text{ KJ}$

4. How many kilograms of water initially at  $30^\circ\text{C}$  are possible to heat up to its transformation in water vapor at  $100^\circ\text{C}$  by burning  $500 \text{ L}$  of  $\text{C}_2\text{H}_4$  under STP conditions?

**Data:** Standard enthalpy of vaporization of water =  $40.6 \text{ kJ/mol}$ ; Standard enthalpy of formation of  $\text{C}_2\text{H}_4 = 52.3 \text{ kJ/mol}$ ; standard enthalpy of formation of  $\text{CO}_2 = -393.13 \text{ kJ/mol}$ ; standard enthalpy of formation of  $\text{H}_2\text{O} (l) = -285.85 \text{ kJ/mol}$ ; specific heat of water =  $4.18 \text{ kJ/kg K}$ ; molar mass of water =  $18 \text{ g/mol}$

**Solution:** Mass of water =  $11.3 \text{ kg}$

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



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

a) Calculate  $\Delta H^\circ$  for these reactions.

b) Using an inductive method demonstrate if the standard enthalpy of formation for any reaction of the

kind  $\text{C}_n\text{H}_{2n(g)} + \text{H}_{2(g)} \rightarrow \text{C}_n\text{H}_{2n+2(g)}$  will have the same enthalpy.

**Solution:**  $\Delta H$  for hydrogenation of  $\text{C}_2\text{H}_4$  is  $-136.36 \text{ kJ/mol}$ ;  $\Delta H$  for hydrogenation of  $\text{C}_3\text{H}_6$  is  $-124.39 \text{ kJ/mol}$ . Additional data are needed to check the rule. From Table 1 (Mahan) we obtain the enthalpies of formation of 1-butene and butane:  $\Delta H_f^0$  (1-butene) =  $-0.54 \text{ kJ/mol}$  and  $\Delta H_f^0$  (1-butane) =  $-125.65 \text{ kJ/mol}$ . From Steele, W.V, Chirico, R.D., J. Phys. Chem. Ref. Data, 22(2), 377 (1983) we find  $\Delta H_f^0$  (1-pentene) =  $-21.5 \text{ kJ/mol}$  and  $\Delta H_f^0$  (1-hexene) =  $-39.71 \text{ kJ/mol}$ . From the corresponding page we find in wikipedia  $\Delta H_f^0$  (pentane) =  $-173.5 \text{ kJ/mol}$  and  $\Delta H_f^0$  (hexane) =  $-167.2 \text{ kJ/mol}$ . The corresponding hydrogenation enthalpies are  $\Delta H_H(\text{C}_4\text{H}_8) = -125.1 \text{ kJ/mol}$ ;  $\Delta H_H(\text{C}_5\text{H}_{10}) = -153 \text{ kJ/mol}$ ;  $\Delta H_H(\text{C}_6\text{H}_{12}) = -127.49 \text{ kJ/mol}$ . So except for small deviations, the rule seems to be followed.

## Chemistry for Biomedical Engineering. Exercises Topic 4

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Authors: Juan Baselga & María González

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)  $\Delta S = 8.42 \text{ J/K}$ ; b)  $\Delta S = 5.06 \text{ J/K}$

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 °C and 80.1 °C 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 -20°C to 100°C.

**Solution:**  $\Delta S = 138.87 \text{ J/K}$

8. Determine the standard enthalpy of combustion for  $\text{H}_2$  at 210 °C using the following data:  $\Delta H^\circ_{\text{comb}}(\text{H}_2)_{25^\circ\text{C}} = -68320 \text{ cal mol}^{-1}$ ,  $\Delta H^\circ_{\text{vap}}(\text{H}_2\text{O})_{100^\circ\text{C}} = 9720 \text{ cal mol}^{-1}$ ,  $C_p(\text{H}_2) = 6.62 \text{ cal}$ ,  $C_p(\text{O}_2) = 6.76 \text{ cal mol}^{-1} \text{ K}^{-1}$ ,  $C_p(\text{H}_2\text{O}, \text{l}) = 18 \text{ cal mol}^{-1} \text{ K}^{-1}$ ,  $C_p(\text{H}_2\text{O}, \text{g}) = 8.22 \text{ cal mol}^{-1} \text{ K}^{-1}$ .

**Solution:**  $\Delta H^\circ_{\text{C}} = -58195.8 \text{ cal/mol}$

9. Use the data presented in the following table to determine the values of  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  for the chemical synthesis of one mol of ammonia from nitrogen and hydrogen at 298 K and 600 K.

	$\Delta H^\circ_{298}(\text{kcal/mol})$	$\Delta S^\circ_{298\text{K}}(\text{cal/mol}\cdot\text{K})$	$C_p(\text{cal/mol}\cdot\text{K})$
$\text{N}_2$	0.0	45.767	6.52
$\text{H}_2$	0.0	31.211	6.94
$\text{NH}_3$	-11.04	46.010	6.19

**Solution:** a) At 298 K:  $\Delta H^\circ_{\text{f}}(\text{NH}_3) = -11.04 \text{ kcal}$ ;  $\Delta S^\circ_{\text{f}}(\text{NH}_3) = -23.69 \text{ cal/K}$ ;  $\Delta G^\circ_{\text{f}}(\text{NH}_3) = -3976.8 \text{ cal}$ ; b) At 500 K:  $\Delta H^\circ_{\text{f}}(\text{NH}_3) = -13.3 \text{ Kcal}$ ;  $\Delta S^\circ_{\text{f}}(\text{NH}_3) = -5.23 \text{ cal/K}$ ;  $\Delta G^\circ_{\text{f}}(\text{NH}_3) = -10.16 \text{ Kcal}$ .

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

- $2\text{C}(\text{diamond}) + 3\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{l})$
- $\text{C}(\text{graphite}) + 3\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \frac{1}{2}\text{C}_2\text{H}_5\text{OH}(\text{l})$
- $2\text{C}(\text{graphite}) + 3\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{l})$
- $2\text{C}(\text{graphite}) + 6\text{H}(\text{g}) + \text{O}(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{l})$

**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:  $\text{N}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightleftharpoons 2\text{NO}_{(\text{g})}$ . 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 25°C is 86.55 kJ/mol. Calculate  $\Delta G^\circ$  at 2000 K and the reaction enthalpy.

**Solution:**  $\Delta G^\circ$  at 2000 K = +64.88 kJ/mol;  $\Delta H^\circ$  at 2000 K = 89.60 kJ/mol

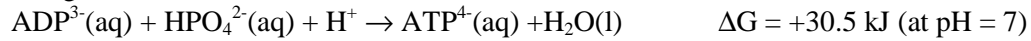
15. Elemental sulfur exists in several allotropic forms, being rhombic sulfur the most stable under normal conditions and monoclinic sulfur slightly less stable. The standard enthalpies of combustion of the two allotropes to yield sulfur dioxide are  $-296.8 \text{ kJ}\cdot\text{mol}^{-1}$  and  $-297.2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

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

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 °C. (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 °C?

**Solution:** d $\Delta S$ /dt = 0.341 J/K·s; (b) 1.23 kJ/K; (c) d $\Delta S$ /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:



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