Thermochemistry

Exercise 1:

Acetylene C_2H_2 is produced by the action of water on calcium carbide CaC_2 according to the following reaction (a):

$$\text{(a)} \quad CaC_2(s) + H_2O(l) \longrightarrow CaO(s) + C_2H_2(g)$$

The standard enthalpies of the following reactions at 298.15 K are given:

	Reaction	ΔH_r° **(kJ)**
(1)	$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$	−64.5
(2)	$CaO(s) + 3\ C(\text{graphite}) \rightarrow CaC_2(s) + CO(g)$	+464.6
(3)	$CaC_2(s) + 2\ H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2(g)$	−126.4
(4)	$2\ C(\text{graphite}) + O_2(g) \rightarrow 2\ CO(g)$	−221.0
(5)	$H_2O(l) \rightarrow H_2(g) + \frac{1}{2}\ O_2(g)$	+285.8

1/ Among reactions (1)–(5), identify those for which ΔH_r° corresponds to ΔH_f°.

2/ Write the formation reaction of acetylene at 298.15 K under standard conditions, clearly indicating the reference state of the elements constituting acetylene.

3/ Calculate the standard enthalpy of formation of acetylene at 298.15 K.

4/ Given at 298.15 K: $\Delta H^\circ f(CaC_2) = -59.8$ kJ/mol and $\Delta H^\circ f(CaO) = -634.9$ kJ/mol. Calculate $\Delta H^\circ r$ of reaction (a) from the standard enthalpies of formation of reactants and products.

5/ Calculate again the standard enthalpy of reaction (a) using the standard enthalpies of reactions (1)–(5), and conclude.

6/ Calculate the change in internal energy ΔU accompanying reaction (a).

7/ Is reaction (a) endothermic or exothermic?

8/ Same question for reactions (1)–(5).

9/ Calculate the standard enthalpy of reaction (a) at 350 K, assuming that the heat capacities of reactants and products are independent of temperature. Given in $J{\cdot}mol^{-1}{\cdot}K^{-1}$: $C_p(CaC_2(s)) = 62.7$; $C_p(H_2O(l)) = 75.3$; $C_p(CaO(s)) = 42.0$; $C_p(C_2H_2(g)) = 44.0$.

10/ Given in $J{\cdot}K^{-1}{\cdot}mol^{-1}$: $C_p = 27.2 + 4.2 \times 10^{-3}\,T$ for oxygen and carbon monoxide ; $C_p = 4.6 + 2 \times 10^{-2}\,T$ for carbon. Calculate the standard enthalpy of reaction (4) at 850 K.

11/ Given at 298.15 K: $\Delta H^\circ f(CO_2(g)) = -393.5$ kJ/mol. Calculate the standard enthalpy of partial combustion of acetylene and $\Delta H^\circ_{\text{comb}}$ of acetylene.

12/ The complete combustion of 2.0 g of acetylene is carried out in a bomb calorimeter. Determine the temperature rise ΔT, given that the heat capacity of the calorimeter and its accessories is 2.0 kJ/K.

Exercise 2:

I/ Hexadecane, $C_{16}H_{34}$, is a hydrocarbon whose standard enthalpy of combustion is $-10\,700$ kJ·mol^{-1} at 298.15 K.

1/ Calculate $\Delta H°f(C_{16}H_{34}(l))$ in kJ·mol^{-1} at 298.15 K.

2/ Calculate $\Delta U^{\circ}_{\text{comb}}(C_{16}H_{34}(l))$ in kJ·mol^{-1} at 298.15 K.

3/ Hexadecane is an alkane whose structure is close to that of lipids. Compare the calorific value of hexadecane with that of a fatty substance, which is on average 9.0 kcal/g.

II/ We consider the formation reaction of octane, C_8H_{18}, at 298.15 K according to the Hess cycle shown below:

$$\begin{array}{ccc} 8\ \text{C(s, graphite)} + 9\ \text{H}_2\text{(g)} & \longrightarrow \Delta H°f \longrightarrow & \text{C}_8\text{H}_{18}\text{(liq)} \\ \downarrow Q_1 \quad \downarrow Q_2 & & \downarrow Q_4 \\ 8\ \text{C(g)} + 18\ \text{H(g)} & \longrightarrow Q_3 \longrightarrow & \text{C}_8\text{H}_{18}\text{(g)} \end{array}$$

1/ Identify the heats Q_1 ; Q_2 ; Q_3 ; Q_4.

2/ Calculate $\Delta H°f(C_8H_{18}(l))$ from the cycle.

3/ Calculate $\Delta H°f(C_8H_{18}(l))$ from the standard enthalpy of combustion of octane. Conclude.

Data: $\Delta H°f(CO_2(g)) = -393.5$ kJ/mol ; $\Delta H°f(H_2O(l)) = -285.8$ kJ/mol
$Q_1 = 5734$ kJ ; $Q_2 = 3933$ kJ ; $Q_3 = -9863$ kJ ; $Q_4 = -41.4$ kJ

Exercise 3:

A/ 1 g of graphite ($_6$C ; $M = 12$ g/mol) burns in a bomb calorimeter in an excess of oxygen at 298 K and 1 atm according to the following reaction:

$$\mathrm{C(graphite) + O_2(g) \longrightarrow CO_2(g)}$$

During this reaction, the temperature in the calorimeter, whose heat capacity is 32.8 kJ·K^{-1}, increases by 1°C.

1/ Calculate the enthalpy change accompanying this reaction.

2/ Calculate the enthalpy of combustion ΔH_{comb} of graphite.

3/ What is the enthalpy of formation of CO_2?

4/ The internal energy of combustion $\Delta U_{\text{comb}} = \Delta H_{\text{comb}}$ for graphite. Justify this statement.

5/ Is the combustion of graphite exothermic or endothermic?

B/ We consider the following reaction:

$$\mathrm{PbO(s) + CO(g) \longrightarrow Pb(s) + CO_2(g)}$$

1/ Calculate the standard enthalpy ΔH_r° of the reaction at 298 K and 1000 K, considering C_p constant over this temperature interval.

2/ Calculate the standard entropy ΔS_r° of the reaction at 298 K and 1000 K and comment on its sign.

3/ Calculate the standard molar entropy change of the surroundings $\Delta S_{\text{ext}}^\circ$ and the total entropy change ΔS_{tot} at 298 K and 1000 K, and indicate whether these results are in agreement with the 2nd law of thermodynamics.

4/ Calculate the standard Gibbs free energy ΔG_r° at 298 K and 1000 K. Deduce whether, at equilibrium, there are more reactants or products in the reaction medium at these temperatures.

Data: $R = 8.314$ J·K^{-1}·mol^{-1}

Compound	**CO(g)**	**CO_2(g)**	**Pb(s)**	**PbO(s)**
$\Delta H^\circ f$ (kJ·mol^{-1})	−26.42	—	—	−52.40
S° (J·mol^{-1}·K^{-1})	47.32	51.05	15.60	16.43
c_p (J·mol^{-1}·K^{-1})	6.75	8.90	6.34	11.07

Exercise 4:

A/ Consider reaction (1):

$$CH_3OH(L) + H_2(g) \longrightarrow CH_4(g) + H_2O(L) \qquad (1)$$

1. Using Hess's law, calculate the standard enthalpy ΔH_r°, 298 K of this reaction.
2. Calculate the standard enthalpy of reaction (1) at 60°C.
3. Calculate the bond energy of the O–H bond in the gaseous methanol molecule $CH_3OH(g)$.

B/ The molar enthalpy of combustion of methane at 25°C and under one atmosphere is −212.8 kcal. (Water produced is in the liquid state.)

a) Write the combustion reaction of methane (CH_4).

b) Calculate the molar enthalpy of combustion of methane under one atmosphere at 1273 K.

Data: 1 cal = 4.18 J

Compound	$CH_4(g)$	$H_2O(L)$	$H_2(g)$	$CH_3OH(L)$	$CO_2(g)$	$O_2(g)$	$H_2O(g)$	$CH_3OH(g)$
$\Delta H^\circ f$ (kJ/mol) (25°C)	−75.4	−285.2	0	−238.6	/	/	/	/
C_p (J·mol^{-1}·K^{-1})	35.3	75.2	27.8	81.6	36.4	34.7	38.2	53.5

$\Delta H^\circ_{vap}(H_2O) = 44$ kJ·mol^{-1}; $\Delta H^\circ_{vap}(CH_3OH) = 35.4$ kJ·mol^{-1}; ΔH°_{sub}(C,solid) = 718 kJ·mol^{-1}

Bond enthalpies in H_2 and O_2: $\Delta H^\circ_{H–H} = E_{H–H} = -436$ kJ·mol^{-1} (in H_2); $\Delta H^\circ_{O=O} = E_{O=O} = -493$ kJ·mol^{-1} (in O_2)

Bond enthalpies in $CH_3OH(g)$: $\Delta H^\circ_{C–H} = E_{C–H} = -413$ kJ·mol^{-1}; $\Delta H^\circ_{C–O} = E_{C–O} = -315$ kJ·mol^{-1}