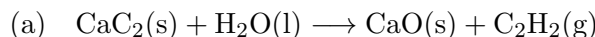




Thermochemistry

Exercise 1:

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



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

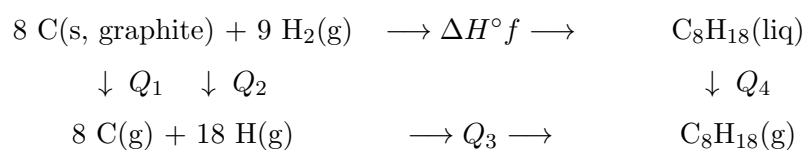
- 1/ Among reactions (1)–(5), identify those for which ΔH_r° corresponds to ΔH_f° .
- 2/ Write the formation reaction of acetylene at 298.15 K under standard conditions, clearly indicating the reference state of the elements constituting acetylene.
- 3/ Calculate the standard enthalpy of formation of 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 ΔH_{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 $-10\,700\text{ kJ}\cdot\text{mol}^{-1}$ at 298.15 K .

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

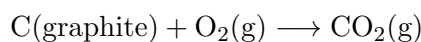


- 1/ Identify the heats Q_1 ; Q_2 ; Q_3 ; Q_4 .
- 2/ Calculate $\Delta H^\circ f(C_8H_{18}(l))$ from the cycle.
- 3/ Calculate $\Delta H^\circ f(C_8H_{18}(l))$ from the standard enthalpy of combustion of octane. Conclude.

Data: $\Delta H^\circ f(\text{CO}_2(\text{g})) = -393.5\text{ kJ/mol}$; $\Delta H^\circ f(\text{H}_2\text{O}(l)) = -285.8\text{ kJ/mol}$
 $Q_1 = 5734\text{ kJ}$; $Q_2 = 3933\text{ kJ}$; $Q_3 = -9863\text{ kJ}$; $Q_4 = -41.4\text{ kJ}$

Exercise 3:

A/ 1 g of graphite (${}^6\text{C}$; $M = 12 \text{ g/mol}$) burns in a bomb calorimeter in an excess of oxygen at 298 K and 1 atm according to the following reaction:



During this reaction, the temperature in the calorimeter, whose heat capacity is $32.8 \text{ kJ}\cdot\text{K}^{-1}$, 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:



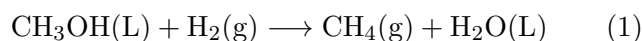
- 1/ Calculate the standard enthalpy ΔH_r° of the reaction at 298 K and 1000 K, considering C_p constant over this temperature interval.
- 2/ Calculate the standard entropy ΔS_r° of the reaction at 298 K and 1000 K and comment on its sign.
- 3/ Calculate the standard molar entropy change of the surroundings $\Delta S_{\text{ext}}^\circ$ 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: $R = 8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

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):



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 $\text{CH}_3\text{OH}(\text{g})$.

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	$\text{CH}_4(\text{g})$	$\text{H}_2\text{O}(\text{L})$	$\text{H}_2(\text{g})$	$\text{CH}_3\text{OH}(\text{L})$	$\text{CO}_2(\text{g})$	$\text{O}_2(\text{g})$	$\text{H}_2\text{O}(\text{g})$	$\text{CH}_3\text{OH}(\text{g})$
ΔH_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

$\Delta H_{\text{vap}}^\circ(\text{H}_2\text{O}) = 44 \text{ kJ}\cdot\text{mol}^{-1}$; $\Delta H_{\text{vap}}^\circ(\text{CH}_3\text{OH}) = 35.4 \text{ kJ}\cdot\text{mol}^{-1}$; $\Delta H_{\text{sub}}^\circ(\text{C},\text{solid}) = 718 \text{ kJ}\cdot\text{mol}^{-1}$

Bond enthalpies in H_2 and O_2 : $\Delta H_{\text{H-H}}^\circ = E_{\text{H-H}} = -436 \text{ kJ}\cdot\text{mol}^{-1}$ (in H_2); $\Delta H_{\text{O=O}}^\circ = E_{\text{O=O}} = -493 \text{ kJ}\cdot\text{mol}^{-1}$ (in O_2)

Bond enthalpies in $\text{CH}_3\text{OH}(\text{g})$: $\Delta H_{\text{C-H}}^\circ = E_{\text{C-H}} = -413 \text{ kJ}\cdot\text{mol}^{-1}$; $\Delta H_{\text{C-O}}^\circ = E_{\text{C-O}} = -315 \text{ kJ}\cdot\text{mol}^{-1}$