



## Thermochemistry – Solutions

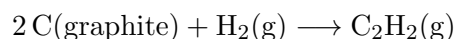
### Exercise 1:

1) A standard enthalpy of formation  $\Delta H_f^\circ$  corresponds to the formation of **1 mol** of a compound from its elements in their standard reference states.

- Reaction (1):  $\text{CaO(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Ca(OH)}_2\text{(s)}$     **Yes**  $\Rightarrow \Delta H_f^\circ(\text{Ca(OH)}_2)$
- Reaction (2): two products formed    **No**
- Reaction (3): not formed from elements    **No**
- Reaction (4): forms 2 mol of CO, not 1    **No**
- Reaction (5): reverse of the formation of  $\text{H}_2\text{O}$ , so  $\Delta H_r^\circ(5) = -\Delta H_f^\circ(\text{H}_2\text{O})$     **No** (but related)

Only reaction **(1)** directly corresponds to  $\Delta H_f^\circ$ .

2) The reference states are: carbon as **graphite**, hydrogen as **dihydrogen gas**.



3) We combine reactions (1)–(5) using Hess's law. The correct linear combination is: (3) + rev(1) + (2) + rev( $\frac{1}{2} \times$  (4)) + rev(5), giving:

Combination	$\Delta H^\circ$ (kJ)
(3): $\text{CaC}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{C}_2\text{H}_2$	−126.4
rev(1): $\text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$	+64.5
(2): $\text{CaO} + 3\text{C} \rightarrow \text{CaC}_2 + \text{CO}$	+464.6
rev( $\frac{1}{2} \times$ 4): $\text{CO} \rightarrow \text{C} + \frac{1}{2}\text{O}_2$	+110.5
rev(5): $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$	−285.8
<b>Net:</b> $2\text{C(graphite)} + \text{H}_2\text{(g)} \rightarrow \text{C}_2\text{H}_2\text{(g)}$	

$$\Delta H_f^\circ(\text{C}_2\text{H}_2) = -126.4 + 64.5 + 464.6 + 110.5 - 285.8 = +227.4 \text{ kJ/mol}$$

4) Using  $\Delta H_r^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$ :

$$\begin{aligned} \Delta H_r^\circ(a) &= [\Delta H_f^\circ(\text{CaO}) + \Delta H_f^\circ(\text{C}_2\text{H}_2)] - [\Delta H_f^\circ(\text{CaC}_2) + \Delta H_f^\circ(\text{H}_2\text{O})] \\ &= [(-634.9) + (227.4)] - [(-59.8) + (-285.8)] \\ &= (-407.5) - (-345.6) \end{aligned}$$

$$\Delta H_r^\circ(a) = -61.9 \text{ kJ/mol}$$

5) The combination (3) – (1) cancels  $\text{Ca(OH)}_2$  and one  $\text{H}_2\text{O}$ , yielding reaction (a) directly:

$$\Delta H_r^\circ(a) = \Delta H_r^\circ(3) - \Delta H_r^\circ(1) = -126.4 + 64.5 = -61.9 \text{ kJ/mol}$$

Conclusion: both methods give the same result, confirming Hess's law.

6) For reaction (a),  $\Delta n_g = 1 - 0 = +1$  (only  $\text{C}_2\text{H}_2$  is gaseous among the relevant species):

$$\begin{aligned}\Delta U &= \Delta H_r^\circ - \Delta n_g RT = -61\,900 - (1)(8.314)(298.15) \\ &= -61\,900 - 2\,479\end{aligned}$$

$$\boxed{\Delta U \approx -64\,379 \text{ J/mol} \approx -64.4 \text{ kJ/mol}}$$

7)  $\Delta H_r^\circ(a) = -61.9 \text{ kJ/mol} < 0 \Rightarrow$  Reaction (a) is **exothermic**.

8)

Reaction	$\Delta H_r^\circ$ (kJ)	Nature
(1)	-64.5	Exothermic
(2)	+464.6	Endothermic
(3)	-126.4	Exothermic
(4)	-221.0	Exothermic
(5)	+285.8	Endothermic

9) Kirchoff's law with constant  $C_p$ :

$$\Delta C_p = [C_p(\text{CaO}) + C_p(\text{C}_2\text{H}_2)] - [C_p(\text{CaC}_2) + C_p(\text{H}_2\text{O})] = (42.0 + 44.0) - (62.7 + 75.3) = -52.0 \text{ J mol}^{-1}\text{K}^{-1}$$

$$\Delta H_r^\circ(350) = -61\,900 + (-52.0)(350 - 298.15) = -61\,900 - 2\,696$$

$$\boxed{\Delta H_r^\circ(350 \text{ K}) \approx -64.6 \text{ kJ/mol}}$$

10) Reaction (4):  $2\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}(\text{g})$

$$\Delta C_p = 2C_p(\text{CO}) - 2C_p(\text{C}) - C_p(\text{O}_2) = 18.0 - 35.8 \times 10^{-3} T \quad [\text{J mol}^{-1}\text{K}^{-1}]$$

$$\int_{298}^{850} (18.0 - 35.8 \times 10^{-3} T) dT = 18.0 \times 552 - \frac{35.8 \times 10^{-3}}{2} (850^2 - 298^2) = 9\,936 - 11\,343 = -1\,407 \text{ J/mol}$$

$$\boxed{\Delta H_r^\circ(4)(850 \text{ K}) = -221.0 + (-1.41) \approx -222.4 \text{ kJ/mol}}$$

11) Complete combustion:  $\text{C}_2\text{H}_2(\text{g}) + \frac{5}{2}\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$

$$\Delta H_{\text{comb}}^\circ = [2(-393.5) + (-285.8)] - 227.4 = -1\,072.8 - 227.4$$

$$\boxed{\Delta H_{\text{comb}}^\circ(\text{C}_2\text{H}_2) = -1\,300.2 \text{ kJ/mol}}$$

Partial combustion (to CO):  $\text{C}_2\text{H}_2 + \frac{3}{2}\text{O}_2 \rightarrow 2\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{l})$ , with  $\Delta H_f^\circ(\text{CO}) = \frac{1}{2} \times (-221.0) = -110.5 \text{ kJ/mol}$ :

$$\Delta H_{\text{partial}}^\circ = [2(-110.5) + (-285.8)] - 227.4 = -506.8 - 227.4$$

$$\boxed{\Delta H_{\text{partial}}^\circ = -734.2 \text{ kJ/mol}}$$

12) A bomb calorimeter measures  $\Delta U$ . We first compute  $\Delta U_{\text{comb}}^\circ$ :

$$\Delta n_g = 2 - \frac{5}{2} = -\frac{1}{2}$$

$$\Delta U_{\text{comb}}^{\circ} = \Delta H_{\text{comb}}^{\circ} - \Delta n_g RT = -1\,300\,200 - \left(-\frac{1}{2}\right)(8.314)(298.15) \approx -1\,298\,961 \text{ J/mol}$$

Moles of  $\text{C}_2\text{H}_2$  burned ( $M = 26 \text{ g/mol}$ ):  $n = 2.0/26 = 0.07692 \text{ mol}$

$$q = n |\Delta U_{\text{comb}}^{\circ}| = 0.07692 \times 1\,299.0 = 99.9 \text{ kJ}$$

$$\Delta T = \frac{q}{C_{\text{cal}}} = \frac{99.9}{2.0} \quad \boxed{\Delta T \approx 50 \text{ K}}$$

## Exercise 2:

### Part I – Hexadecane $\text{C}_{16}\text{H}_{34}$

Complete combustion:  $\text{C}_{16}\text{H}_{34}(\text{l}) + \frac{49}{2} \text{O}_2(\text{g}) \rightarrow 16 \text{CO}_2(\text{g}) + 17 \text{H}_2\text{O}(\text{l})$

I-1) From  $\Delta H_{\text{comb}}^{\circ} = \sum \Delta H_f^{\circ}(\text{prod}) - \sum \Delta H_f^{\circ}(\text{react})$ :

$$-10\,700 = [16(-393.5) + 17(-285.8)] - \Delta H_f^{\circ}(\text{C}_{16}\text{H}_{34}) = -11\,154.6 - \Delta H_f^{\circ}(\text{C}_{16}\text{H}_{34})$$

$$\boxed{\Delta H_f^{\circ}(\text{C}_{16}\text{H}_{34}(\text{l})) = -454.6 \text{ kJ/mol}}$$

I-2)  $\Delta n_g = 16 - \frac{49}{2} = -8.5$

$$\Delta U_{\text{comb}}^{\circ} = \Delta H_{\text{comb}}^{\circ} - \Delta n_g RT = -10\,700 - (-8.5)(8.314 \times 10^{-3})(298.15) = -10\,700 + 21.06$$

$$\boxed{\Delta U_{\text{comb}}^{\circ} \approx -10\,678.9 \text{ kJ/mol}}$$

I-3)  $M(\text{C}_{16}\text{H}_{34}) = 16 \times 12 + 34 = 226 \text{ g/mol}$

$$\text{Calorific value} = \frac{10\,700}{226} = 47.3 \text{ kJ/g} = \frac{47.3}{4.18} \approx 11.3 \text{ kcal/g}$$

This is **higher** than the average fatty substance (9.0 kcal/g), consistent with hexadecane being a pure hydrocarbon with a higher H/C ratio than a typical lipid (which contains oxygen).

### Part II – Octane $\text{C}_8\text{H}_{18}$ Hess Cycle

II-1) Identification of the heats:

- $Q_1$ : Atomization enthalpy of  $8 \text{C}(\text{graphite}) \rightarrow 8 \text{C}(\text{g})$  ( $8 \times$  sublimation enthalpy of C)
- $Q_2$ : Atomization enthalpy of  $9 \text{H}_2(\text{g}) \rightarrow 18 \text{H}(\text{g})$  ( $9 \times$  dissociation enthalpy of  $\text{H}_2$ )
- $Q_3$ : Enthalpy of formation of  $\text{C}_8\text{H}_{18}(\text{g})$  from gaseous atoms (sum of all bond formation enthalpies in octane)
- $Q_4$ : Condensation enthalpy  $\text{C}_8\text{H}_{18}(\text{g}) \rightarrow \text{C}_8\text{H}_{18}(\text{l})$ , i.e.  $-\Delta H_{\text{vap}}^{\circ}(\text{C}_8\text{H}_{18})$

II-2) From the Hess cycle:  $\Delta H_f^{\circ} = Q_1 + Q_2 + Q_3 + Q_4$

$$\Delta H_f^{\circ} = 5\,734 + 3\,933 + (-9\,863) + (-41.4)$$

$$\boxed{\Delta H_f^{\circ}(\text{C}_8\text{H}_{18}(\text{l})) = -237.4 \text{ kJ/mol}}$$

II-3) Combustion reaction:  $\text{C}_8\text{H}_{18}(\text{l}) + \frac{25}{2} \text{O}_2(\text{g}) \rightarrow 8 \text{CO}_2(\text{g}) + 9 \text{H}_2\text{O}(\text{l})$

Using  $\Delta H_f^\circ(\text{C}_8\text{H}_{18}(\text{l})) = -237.4 \text{ kJ/mol}$  from II-2, and applying  $\Delta H_{\text{comb}}^\circ = \sum \Delta H_f^\circ(\text{prod}) - \sum \Delta H_f^\circ(\text{react})$ :

$$\Delta H_{\text{comb}}^\circ = [8(-393.5) + 9(-285.8)] - (-237.4) = [-3148.0 + (-2572.2)] + 237.4 = -5720.2 + 237.4$$

$$\boxed{\Delta H_{\text{comb}}^\circ(\text{C}_8\text{H}_{18}(\text{l})) = -5482.8 \text{ kJ/mol}}$$

*Conclusion:* This result is obtained purely from the Hess-cycle formation enthalpy found in II-2. The small discrepancy with tabulated values ( $\approx -5471 \text{ kJ/mol}$ ) reflects the approximate nature of average bond enthalpies used in computing  $Q_3$ .

### Exercise 3:

#### Part A – Combustion of Graphite

A-1) Heat released for 1 g of graphite:

$$q = C_{\text{cal}} \times \Delta T = 32.8 \times 1 = 32.8 \text{ kJ}$$

A-2)  $M(\text{C}) = 12 \text{ g/mol}$ , so  $n = 1/12 \text{ mol}$ :

$$\boxed{\Delta H_{\text{comb}} = -32.8 \times 12 = -393.6 \text{ kJ/mol}}$$

A-3) The reaction  $\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$  is precisely the formation reaction of  $\text{CO}_2$ , therefore:

$$\boxed{\Delta H_f^\circ(\text{CO}_2) = -393.6 \text{ kJ/mol}}$$

(Standard value:  $-393.5 \text{ kJ/mol}$  – excellent agreement.)

A-4) From  $\Delta H = \Delta U + \Delta n_g RT$ : the reaction has  $\Delta n_g = 1 - 1 = 0$ , therefore  $\Delta H = \Delta U$ .  
□

A-5)  $\Delta H_{\text{comb}} = -393.6 \text{ kJ/mol} < 0 \Rightarrow$  **Exothermic** (confirmed by the temperature rise in the calorimeter).

#### Part B – Reduction of PbO by CO

B-1)

$$\begin{aligned} \Delta H_r^\circ(298) &= [\Delta H_f^\circ(\text{Pb}) + \Delta H_f^\circ(\text{CO}_2)] - [\Delta H_f^\circ(\text{PbO}) + \Delta H_f^\circ(\text{CO})] \\ &= [0 + (-393.5)] - [(-52.40) + (-26.42)] = -393.5 + 78.82 \end{aligned}$$

$$\boxed{\Delta H_r^\circ(298 \text{ K}) = -314.68 \text{ kJ/mol}}$$

$$\Delta C_p = [C_p(\text{Pb}) + C_p(\text{CO}_2)] - [C_p(\text{PbO}) + C_p(\text{CO})] = (6.34 + 8.90) - (11.07 + 6.75) = -2.58 \text{ J mol}^{-1} \text{K}^{-1}$$

$$\Delta H_r^\circ(1000) = -314680 + (-2.58)(1000 - 298) = -314680 - 1811$$

$$\boxed{\Delta H_r^\circ(1000 \text{ K}) = -316.49 \text{ kJ/mol}}$$

B-2)

$$\Delta S_r^\circ(298) = [S^\circ(\text{Pb}) + S^\circ(\text{CO}_2)] - [S^\circ(\text{PbO}) + S^\circ(\text{CO})] = (15.60 + 51.05) - (16.43 + 47.32) = +2.90 \text{ J mol}^{-1} \text{K}^{-1}$$

$$\Delta S_r^\circ(1000) = 2.90 + (-2.58) \ln \frac{1000}{298} = 2.90 - 3.12$$

$$\boxed{\Delta S_r^\circ(298) = +2.90 \text{ J mol}^{-1}\text{K}^{-1} \quad ; \quad \Delta S_r^\circ(1000) \approx -0.22 \text{ J mol}^{-1}\text{K}^{-1}}$$

*Comment:*  $\Delta S_r^\circ$  is very small because equal moles of gas appear on each side (1 CO  $\rightarrow$  1 CO<sub>2</sub>); the sign change with temperature is due to the  $\Delta C_p$  correction.

**B-3)**

At 298 K:

$$\Delta S_{\text{ext}}^\circ = -\frac{\Delta H_r^\circ}{T} = -\frac{-314\,680}{298} = +1\,056 \text{ J mol}^{-1}\text{K}^{-1} \quad ; \quad \Delta S_{\text{tot}} = 2.90 + 1\,056 = +1\,058.9 \text{ J mol}^{-1}\text{K}^{-1} > 0$$

At 1000 K:

$$\Delta S_{\text{ext}}^\circ = -\frac{-316\,490}{1000} = +316.49 \text{ J mol}^{-1}\text{K}^{-1} \quad ; \quad \Delta S_{\text{tot}} = -0.22 + 316.49 = +316.27 \text{ J mol}^{-1}\text{K}^{-1} > 0 \checkmark$$

Both results satisfy  $\Delta S_{\text{tot}} > 0$ , in agreement with the **2nd law of thermodynamics**.

**B-4)**

At 298 K:

$$\Delta G^\circ(298) = \Delta H^\circ - T \Delta S^\circ = -314\,680 - (298)(2.90) = -314\,680 - 864$$

$$\boxed{\Delta G^\circ(298) \approx -315.5 \text{ kJ/mol}}$$

At 1000 K:

$$\Delta G^\circ(1000) = -316\,490 - (1000)(-0.22) = -316\,490 + 220$$

$$\boxed{\Delta G^\circ(1000) \approx -316.3 \text{ kJ/mol}}$$

Since  $\Delta G^\circ \ll 0$  at both temperatures, equilibrium strongly favors the **products** (Pb and CO<sub>2</sub>) at both 298 K and 1000 K.

**Exercise 4:****Part A – Reaction (1):** CH<sub>3</sub>OH(L) + H<sub>2</sub>(g)  $\rightarrow$  CH<sub>4</sub>(g) + H<sub>2</sub>O(L)**A-1)**

$$\begin{aligned} \Delta H_r^\circ(298) &= [\Delta H_f^\circ(\text{CH}_4) + \Delta H_f^\circ(\text{H}_2\text{O(L)})] - [\Delta H_f^\circ(\text{CH}_3\text{OH(L)}) + \Delta H_f^\circ(\text{H}_2)] \\ &= [(-75.4) + (-285.2)] - [(-238.6) + 0] = -360.6 + 238.6 \end{aligned}$$

$$\boxed{\Delta H_r^\circ(298 \text{ K}) = -122.0 \text{ kJ/mol}}$$

**A-2)**  $T_2 = 60 + 273.15 = 333.15 \text{ K}$ 

$$\Delta C_p = [C_p(\text{CH}_4) + C_p(\text{H}_2\text{O(L)})] - [C_p(\text{CH}_3\text{OH(L)}) + C_p(\text{H}_2)] = (35.3 + 75.2) - (81.6 + 27.8) = +1.1 \text{ J mol}^{-1}\text{K}^{-1}$$

$$\Delta H_r^\circ(333) = -122\,000 + (1.1)(333.15 - 298.15) = -122\,000 + 38.5$$

$$\boxed{\Delta H_r^\circ(333 \text{ K}) \approx -121.96 \text{ kJ/mol}}$$

The variation is negligible owing to the very small  $\Delta C_p$ .

**A-3)** We determine  $E_{\text{O-H}}$  in CH<sub>3</sub>OH(g) via a Hess cycle.*Step 1 – Formation enthalpy of gaseous methanol:*

$$\Delta H_f^\circ(\text{CH}_3\text{OH(g)}) = \Delta H_f^\circ(\text{CH}_3\text{OH(L)}) + \Delta H_{\text{vap}}^\circ = -238.6 + 35.4 = -203.2 \text{ kJ/mol}$$

Step 2 – Enthalpy to go from standard elements to gaseous atoms (for  $\text{C}(\text{s}) + 2\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ ):

$$\Delta H_{\text{atoms}} = \Delta H_{\text{sub}}^{\circ}(\text{C}) + 2(+436) + \frac{1}{2}(+493) = 718 + 872 + 246.5 = 1836.5 \text{ kJ}$$

Step 3 – Bond content of  $\text{CH}_3\text{OH}(\text{g})$  (3 C–H, 1 C–O, 1 O–H):

$$\Delta H_{\text{atomization}} = 3 E_{\text{C–H}} + E_{\text{C–O}} + E_{\text{O–H}} = 3(413) + 315 + E_{\text{O–H}} = 1554 + E_{\text{O–H}}$$

Step 4 – Hess cycle closure:

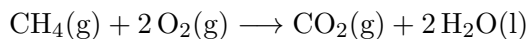
$$\Delta H_f^{\circ}(\text{CH}_3\text{OH}(\text{g})) = \Delta H_{\text{atoms}} - \Delta H_{\text{atomization}}$$

$$-203.2 = 1836.5 - (1554 + E_{\text{O–H}}) = 282.5 - E_{\text{O–H}}$$

$$\boxed{E_{\text{O–H}} = 282.5 + 203.2 = +485.7 \text{ kJ/mol}}$$

### Part B – Combustion of Methane $\text{CH}_4$

**B-a)** Combustion reaction:



**B-b)**  $\Delta H_{\text{comb}}^{\circ}(298) = -212.8 \text{ kcal} \times 4.18 = -889.5 \text{ kJ/mol}$  (water in liquid state).

At 1273 K water is gaseous; we first correct the reference state:

$$\Delta H_{\text{comb, g}}^{\circ}(298) = -889.5 + 2(44) = -801.5 \text{ kJ/mol}$$

Combustion with  $\text{H}_2\text{O}(\text{g})$ :  $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$

$$\Delta C_p = [C_p(\text{CO}_2) + 2 C_p(\text{H}_2\text{O}(\text{g}))] - [C_p(\text{CH}_4) + 2 C_p(\text{O}_2)] = (36.4 + 76.4) - (35.3 + 69.4) = +8.1 \text{ J mol}^{-1} \text{K}^{-1}$$

$$\Delta H_{\text{comb}}^{\circ}(1273) = -801500 + (8.1)(1273 - 298) = -801500 + 7898$$

$$\boxed{\Delta H_{\text{comb}}^{\circ}(\text{CH}_4, 1273 \text{ K}) \approx -793.6 \text{ kJ/mol}}$$