Marks 5

- For the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ at 25 °C

  $\Delta H° = -198.4$ kJ mol^{-1} and $\Delta S° = -187.9$ J K^{-1} mol^{-1}

  Show that this reaction is spontaneous in the forward direction at 25 °C.

As $\Delta G^o = \Delta H^o - T\Delta S^o$,

$$\Delta G^o = ((-198.4 \times 10^3)\ \text{J mol}^{-1}) - ((25 + 273)\ \text{K}) \times (-187.9\ \text{J K}^{-1}\ \text{mol}^{-1})$$
$$= -142400\ \text{J mol}^{-1} = -142.4\ \text{kJ mol}^{-1}$$

As $\Delta G^o < 0$, the reaction is spontaneous.

If the volume of the reaction system is increased at 25 °C, in which direction will the equilibrium move?

In the reaction, 3 mol of gas → 2 mol of gas. In the volume of the reaction system is increased, the pressure will decrease. The reaction will shift to produce more gas: it will shift to the left (reactants).

Calculate the value of the equilibrium constant, K_p, at 25 °C.

Using $\Delta G^o = -RT\ln K_p$:

$$(-142.4 \times 10^3)\ \text{J mol}^{-1} = -(8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) \times ((25 + 273)\ \text{K}) \times \ln K_p$$

$$K_p = 9.3 \times 10^{24}$$

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Assuming $\Delta H°$ and $\Delta S°$ are independent of temperature, in which temperature range is the reaction non-spontaneous?

The reaction is spontaneous as long as $\Delta H^o - T\Delta S^o < 0$. $\Delta G^o = 0$ when

$$T = \frac{\Delta H°}{\Delta S°} = \frac{(-198.4 \times 10^3\ \text{J mol}^{-1})}{(-187.9\ \text{J K}^{-1}\ \text{mol}^{-1})} = 1056\ \text{K}$$

The reaction is spontaneous below this temperature and non-spontaneous above it.

Answer: $T > 1056$ K

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- Glucose is a common food source. The net reaction for its metabolism in humans is:

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

Calculate $\Delta H°$ for this reaction given the following heats of formation.

$\Delta H°_f$ ($C_6H_{12}O_6(s)$) = –1274 kJ mol^{-1}, $\Delta H°_f$ ($CO_2(g)$) = –393 kJ mol^{-1} and $\Delta H°_f$ ($H_2O(l)$) = –285 kJ mol^{-1}

Using $\Delta_{rxn}H^0 = \sum m\Delta_f H^0(\text{products}) - \sum n\Delta_f H^0(\text{reactants})$:

$$\Delta_{rxn}H° = [6\times\Delta_f H°(CO_2(g)) + 6\times\Delta_f H°(H_2O(l))] - [\Delta_f H°(C_6H_{12}O_6(g))]$$
$$= [(6\times -393) + (6\times -285)] - [(-1274)] = -2794\,\text{kJ mol}^{-1}$$

(Note that $\Delta_f H°(O_2(g)) = 0$ as it is an element in its standard state).

Answer: **-2794 kJ mol^{-1}**

If the combustion of glucose is carried out in air, water is produced as a vapour. Calculate the $\Delta H°$ for the combustion of glucose in air given that

$$H_2O(l) \rightarrow H_2O(g) \qquad \Delta H° = +44 \text{ kJ mol}^{-1}$$

As vaporising liquid water requires energy (+44 kJ mol^{-1}), the combustion enthalpy is reduced. Six moles of H_2O are produced in the combustion so the enthalpy of combustion is reduced to:

-2794 + (6 × +44) = -2530 kJ mol^{-1}

Answer: **-2530 kJ mol^{-1}**

Will ΔS be different for the two oxidation reactions? If so, how will it differ and why?

As gaseous molecules have higher entropy than liquid phase molecules, oxidation to produce $H_2O(g)$ will lead to a higher value for ΔS than oxidation to produce $H_2O(l)$.

Marks 5

- Stearic acid, $C_{18}H_{36}O_2$, is a fatty acid common in animal fats and vegetable oils and is a valuable energy source for mammals. The net reaction for its metabolism in humans is:

$$C_{18}H_{36}O_2(s) + 26O_2(g) \rightarrow 18CO_2(g) + 18H_2O(l)$$

Calculate $\Delta H°$ for this reaction given the following heats of formation.

ΔH_f^o $(C_{18}H_{36}O_2(s)) = -948$ kJ mol^{-1}, ΔH_f^o $(CO_2(g)) = -393$ kJ mol^{-1} and ΔH_f^o $(H_2O(l)) = -285$ kJ mol^{-1}

Using $\Delta_{rxn}H^o = \sum m\Delta_f H^o(\text{products}) - \sum n\Delta_f H^o(\text{reactants})$, the heat of the reaction as written is:

$$\Delta_{rxn}H^o = [18\Delta_f H^o(CO_2(g)) + 18\Delta_f H^o(H_2O(g))] - [\Delta_f H^o(C_{18}H_{36}O_2(s)) + 26\Delta_f H^o(O_2(g))]$$
$$= [(18\times -393) + (18\times -285)] - [(-948) + (26\times 0)] = -11256\,\text{kJ mol}^{-1}$$

$\Delta_f H^o(O_2(g)) = 0$ for an element already in their standard states.

Answer: **-11256 kJ mol^{-1}**

If the combustion of stearic acid is carried out in air, water is produced as a vapour. Calculate the $\Delta H°$ for the combustion of stearic acid in air given that

$$H_2O(l) \rightarrow H_2O(g) \qquad \Delta H° = +44 \text{ kJ mol}^{-1}$$

Energy must be provided to vaporize the water so the enthalpy of combustion is reduced:

$\Delta_{comb}H^o$ = -11256 + (18 × 44) = -10464 kJ mol^{-1}

Answer: **-10464 kJ mol^{-1}**

Will ΔS be different for the two oxidation reactions? If so, how will it differ and why?

The entropy of $H_2O(g)$ is greater than that of $H_2O(l)$ so ΔS will be greater. In the oxidation reaction which produces $H_2O(l)$, 26 mol of gas are converted into 18 mol of gas so that ΔS will be negative. In the oxidation reaction which produces $H_2O(g)$, 26 mol of gas are converted into (18 + 18) = 36 mol of gas and ΔS will be positive.

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Calculate the mass of carbon dioxide produced by the complete oxidation of 1.00 g of stearic acid.

The molar mass of stearic acid, $C_{18}H_{36}O_2$, is:

18×12.01 (C) + 36×1.008 (H) + 2×16.00 (O) = 284.468

1.0 g therefore contains:

$$\textbf{number of moles of stearic acid} = \frac{\textbf{mass}}{\textbf{molar mass}} = \frac{1.00}{284.468} = 0.00352\,\text{mol}$$

As 18 mol of CO_2 are produced for every mole of stearic acid:

number of moles of $CO_2 = 18 \times 0.00352 = 0.0633$ mol

The molar mass of CO_2 is (12.01 (C) + 2×16.00 (O)) = 44.01. The mass of CO_2 is thus:

mass of CO_2 = number of moles × molar mass = $0.0633 \times 44.01 = 2.78$ g

Answer: **2.78 g**

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- Nitrous oxide decomposes at 25 °C according to the following equation.

$$2N_2O(g) \rightleftharpoons 2N_2(g) + O_2(g) \qquad K_p = 1.8 \times 10^{36}$$

What is the value for K_p at 40 °C?

Using $\Delta_r G° = -RT\ln K_p$, at 25 °C (= 298 K):

$\Delta_r G° = -(8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K}) \times \ln(1.8 \times 10^{36}) = -207\ \text{kJ mol}^{-1}$

Assuming that $\Delta_r G°$ does not change over the temperature range, at 40 °C = 313 K:

$$\ln K_p = \frac{\Delta_r G°}{RT} = \frac{(210 \times 10^3\ \text{J mol}^{-1})}{(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(298\ \text{K})} = 79$$

$K_p = 3.3 \times 10^{34}$

Answer: **3.3×10^{34}**

Is the reaction endothermic or exothermic? Give a reason for your answer.

The equilibrium constant decreases when the temperature increases. This is consistent with an exothermic reaction since these become less favourable as the temperature increases (Le Chatelier's principle).

Marks 5

- Stearic acid, $C_{18}H_{36}O_2$, is a fatty acid common in animal fats and vegetable oils and is a valuable energy source for mammals. The net reaction for its metabolism in humans is:

$$C_{18}H_{36}O_2(s) + 26O_2(g) \rightarrow 18CO_2(g) + 18H_2O(l)$$

Calculate $\Delta H°$ for this reaction given the following heats of formation.

Compound	$C_{18}H_{36}O_2(s)$	$CO_2(g)$	$H_2O(l)$
$\Delta_f H°$ / kJ mol^{-1}	–948	–393	–285

Using $\Delta_{rxn}H° = \Sigma m\Delta_f H°$(products) - $\Sigma n\Delta_f H°$(reactants), the enthalpy of the combustion of the reaction with excess O_2 is:

$\Delta H° = (18\Delta_f H°(CO_2(g)) + 18\Delta_f H°(H_2O(l)) - (\Delta_f H°(C_{18}H_{36}O_2(s))$

$= [(18 \times -393 + 18 \times -285) – (-948)]$ kJ mol^{-1} = –11300 kJ mol^{-1}

As $O_2(g)$ is an element in its standard state, its $\Delta_f H°$ is zero.

$\Delta H° =$ **–11300 kJ mol^{-1}**

If the combustion of stearic acid is carried out in air, water is produced as a vapour. Calculate the $\Delta H°$ for the combustion of stearic acid in air given that:

$$H_2O(l) \rightarrow H_2O(g) \qquad \Delta H° = +44 \text{ kJ mol}^{-1}$$

The reaction now needs vapourisation of $18H_2O(l)$ which requires *input* of (18 × 44) kJ mol^{-1}. The combustion enthalpy is reduced to:

$\Delta H° = (-11300 \text{ kJ mol}^{-1}) + (18 \times 44 \text{ kJ mol}^{-1}) = –10500 \text{ kJ mol}^{-1}$

$\Delta H° =$ **–10500 kJ mol^{-1}**

Will ΔS be different for the two oxidation reactions? If so, how will it differ and why?

ΔS will be greater for the air-oxidation as the product $H_2O(g)$ has a much greater entropy than the product $H_2O(l)$ - gases are much more disordered than liquids.

Calculate the mass of carbon dioxide produced by the complete oxidation of 1.00 g of stearic acid.

The molar mass of stearic acid, $C_{18}H_{36}O_2$, is:

molar mass = (18 × 12.01 (C) + 36 × 1.008 (H) + 2 × 16.00 (H)) g mol^{-1}
= 284.47 g mol^{-1}

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The number of moles in 1.00 g is therefore:

number of moles = mass / molar mass
= (1.00 g) / (284.47 g mol^{-1}) = 0.00353 mol

The chemical equation shows that 18 mol of CO_2(g) are produced from every 1 mol of $C_{18}H_{36}O_2$(s). The number of moles of CO_2(g) produced is therefore (18 × 0.00353 mol) = 0.06328 mol.

The molar mass of CO_2 is (12.01 (C) + 2 × 16.00 (O)) g mol^{-1} = 44.01 g mol^{-1}. The mass of CO_2 produced is therefore:

mass of CO_2 = number of moles × molar mass
= (0.06328 mol) × (44.01 g mol^{-1}) = 2.78 g

Answer: **2.78 g**

Marks 5

- The autoionisation of water conforms to the following balanced equation:

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad \Delta H = 56.3 \text{ kJ mol}^{-1}$$

Is this an exothermic or endothermic reaction?

Endothermic (as ΔH is positive).

What will happen to the equilibrium if the temperature is raised?

The reaction will shift to the right. From le Chatelier's principle, the equilibrium will shift to reduce the effect of the change. As the forward reaction is endothermic, it is able to mitigate the increase in temperature by shifting forwards.

The equilibrium constant, K, for this reaction is 1.8×10^{-16} at 25 °C. Calculate ΔG.

Using $\Delta G = -RT\ln K$,

$$\Delta G = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times ((25 + 273) \text{ K}) \times 1.8 \times 10^{-16} = +89 \text{ kJ mol}^{-1}$$

Answer: **+89 kJ mol^{-1}**

Why is ΔG not equal to ΔH for this reaction?

By definition, $\Delta G = \Delta H - T\Delta S$. As the entropy change for the reaction and the temperature are not zero, so $\Delta G \neq \Delta H$.

The pH of pure water is 6.81 at 37 °C. Is water acidic, basic or neutral at this temperature? Explain.

Neutral. Pure water is neutral at all temperatures as the chemical equation always gives $[H_3O^+(aq)] = [OH^-(aq)]$. A pH value of 7.0 only corresponds to a neutral solution at 25 ^{o}C.