Explain the following terms or concepts.	**Marks** **1**

Le Châtelier's principle

Used to predict the effect of a change in the conditions on a reaction at equilibrium, this principle predicts that a reaction shifts to counteract the change.

| | | | **Marks** |
| | | | 4 |

- At 700 °C, hydrogen and iodine react according to the following equation.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad K_c = 49.0$$

If 0.250 mol of HI(g) is introduced into a 2.00 L flask at 700 °C, what will be the concentration of $I_2(g)$ at equilibrium?

The initial concentration of HI(g) is 0.250 / 2.00 mol L^{-1} = 0.125 mol L^{-1}.

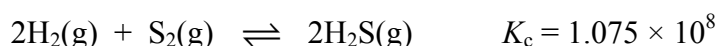|	**H$_2$(g)**	**I$_2$(g)**	$\rightleftharpoons$	**2HI(g)**
Initial	**0**	**0**		**0.125**
Change	**+x**	**+x**		**-2x**
Equilibrium	**x**	**x**		**0.125 - 2x**

Thus,

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.125-2x)^2}{(x)(x)} = \frac{(0.125-2x)^2}{x^2} = 49.0$$

$$(49.0)^{1/2} = \frac{(0.125-2x)}{x}$$

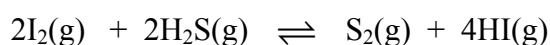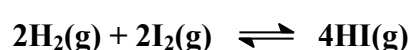**Rearranging gives x = [I$_2$(g)] = 0.0139 M.**

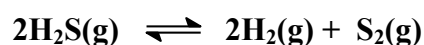| Answer: **0.0139 M** |

Hydrogen also reacts with sulfur at 700 °C:

$$2H_2(g) + S_2(g) \rightleftharpoons 2H_2S(g) \qquad K_c = 1.075 \times 10^8$$

Determine K_c for the following overall equilibrium reaction at 700 °C.
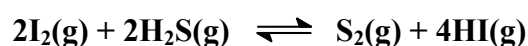
$$2I_2(g) + 2H_2S(g) \rightleftharpoons S_2(g) + 4HI(g)$$

The overall reaction corresponds to the twice the first reaction combined with the reverse of the second reaction:

2H$_2$(g) + 2I$_2$(g) $\rightleftharpoons$ 4HI(g) $K_c(1) = (49.0)^2$

2H$_2$S(g) $\rightleftharpoons$ 2H$_2$(g) + S$_2$(g) $K_c(2) = 1/(1.075 \times 10^8)$

_____

2I$_2$(g) + 2H$_2$S(g) $\rightleftharpoons$ S$_2$(g) + 4HI(g) $K_c(3) = K_c(1) \times K_c(2)$

The 1st reaction is doubled so the original equilibrium constant is squared.

The 2nd reaction is reversed so the reciprocal of the equilibrium constant is used.
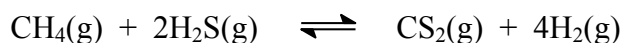
ANSWER CONTINUES ON THE NEXT PAGE

The two reactions are then combined and the overall equilibrium constant is then the product:

$K_c(3) = K_c(1) \times K_c(2) = (49.0)^2 \times (1/(1.075 \times 10^8)) = 2.23 \times 10^{-5}$

Answer: **2.23×10^{-5}**

- Methane, CH_4, reacts with hydrogen sulfide, H_2S, according the following equilibrium:

$$CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g)$$

In an experiment 1.00 mol of CH_4, 2.00 mol of H_2S, 1.00 mol of CS_2 and 2.00 mol of H_2 are mixed in a 250 mL vessel at 960 °C. At this temperature, $K_c = 0.034$ (based on a standard state of 1 mol L^{-1}).

Calculate the reaction quotient, Q, and hence predict in which direction the reaction will proceed to reach equilibrium? Explain your answer.

Using concentration = number of moles / volume, the concentrations when the gases are mixed are:

$[CH_4(g)]$ = 1.00 mol / 0.250 L = 4.00 mol L^{-1}
$[H_2S(g)]$ = 2.00 mol / 0.250 L = 8.00 mol L^{-1}
$[CS_2(g)]$ = 1.00 mol / 0.250 L = 4.00 mol L^{-1}
$[H_2(g)]$ = 2.00 mol / 0.250 L = 8.00 mol L^{-1}

From the chemical equation, the reaction quotient is:

$$Q = \frac{[CS_2(g)][H_2(g)]^4}{[CH_4(g)][H_2S(g)]^2} = \frac{(4.00)(8.00)^4}{(4.00)(8.00)^2} = 64.0$$

As $Q > K_c$, therefore the reaction will shift to the left until $Q = K_c$

Show that the system is at equilibrium when $[CH_4(g)] = 5.56$ M.

A reaction table can be constructed to calculate the equilibrium concentrations:

	$CH_4(g)$ +	$2H_2S(g)$	$\rightleftharpoons$	$CS_2(g)$ +	$4H_2(g)$
Initial	4.00	8.00		4.00	8.00
Change	+x	+2x		-x	-4x
Equilibrium	4.00 + x	8.00 + 2x		4.00 – x	8.00 – 4x

If $[CH_4(g)]_{equilibrium} = 5.56$ M then 4.00 + x = 5.56 M and x = 1.56 M. Hence:

$[CH_4(g)]_{equilibrium}$ = (4.00 + x) M = 5.56 M
$[H_2S(g)]_{equilibrium}$ = (8.00 + 2x) M = 11.12 M
$[CS_2(g)]_{equilibrium}$ = (4.00 – x) M = 2.44 M
$[H_2(g)]_{equilibrium}$ = (8.00 – 4x) M = 1.76 M.

With these concentrations:

$$K_c = \frac{[CS_2(g)][H_2(g)]^4}{[CH_4(g)][H_2S(g)]^2} = \frac{(2.44)(1.76)^4}{(5.56)(11.12)^2} = 0.034$$

	Marks
	3

- Ammonia is synthesised according to the following reaction.

$$N_2(g) \ + \ 3H_2(g) \ \rightleftharpoons \ 2NH_3(g)$$
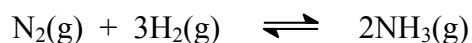
At 500 °C this reaction has a K_c of 6.0×10^{-2}. $\Delta H°$ for this reaction is -92 kJ mol^{-1}. Calculate the value of K_c at 200 °C.

The equilibrium constant varies with temperature according to the van't Hoff equation:

$$\ln \frac{K_2}{K_1} = \frac{-\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Hence:

$$\ln \frac{K_2}{6.0 \times 10^{-2}} = \frac{+92 \times 10^3}{8.314}\left(\frac{1}{(200+273)} - \frac{1}{(500+273)}\right)$$

$K_2 = 530$

Answer: **530**

- One of the most important reactions in living cells is the splitting of adenosine triphosphate (ATP) to adenosine diphosphate (ADP) and free phosphate (P_i):

$$ATP \rightleftharpoons ADP + P_i$$

Based on a standard state of 1 M, the value of $\Delta G°$ for this reaction at 37 °C is –33 kJ mol^{-1}. Calculate the value of the equilibrium constant for the reaction at this temperature.

The equilibrium constant is related to the free energy change by $\Delta G° = -RT\ln K_p$:

$\Delta G° = -(8.314$ J K^{-1} mol^{-1})$((37 + 273)$ K$) \ln K_p = -33 \times 10^3$ J mol^{-1}

$K_p = 3.6 \times 10^5$

Answer: **3.6×10^5**

The following concentrations are typical in a living cell.

ATP: 5 mM	ADP: 0.1 mM	P_i: 5 mM

Under these conditions, calculate the energy per mole that is available from the splitting of ATP.

With these concentrations, the reaction quotient, Q, is:

$$Q = \frac{[ADP][P_i]}{[ATP]} = \frac{(0.1 \times 10^{-3})(5 \times 10^{-3})}{(5 \times 10^{-3})} = 1 \times 10^{-4}$$

The energy available has the reaction proceeds to equilibrium is then:

$$\Delta G = \Delta G° + RT \ln Q$$
$$= (-33 \times 10^3) + (8.314 \text{ J K}^{-1} \text{ mol}^{-1})((37 + 273) \text{ K}) \ln(1 \times 10^{-4}) = -57 \text{ kJ mol}^{-1}$$

57 kJ is available for every mole of ATP that is split.

Answer: **57 kJ**

- The electron transfer reaction between NADH and oxygen is a spontaneous reaction at 37 °C

$$\text{NADH} + \tfrac{1}{2}O_2 + H^+ \rightarrow \text{NAD}^+ + H_2O \qquad \Delta G = -220 \text{ kJ mol}^{-1}$$

When this reaction is carried out in solution in a test tube via direct mixing of NADH with dissolved oxygen, the reaction releases a significant amount of heat. However, when the reaction occurs in mitochondria during respiration, it produces very little heat. Explain why the heat evolved is much less in mitochondria.

According to the First Law of Thermodynamics, energy can be transferred in the form of heat or work. The amount of energy the reaction releases is constant, so if the heat released in mitochondria is reduced it means more work must be done.

ΔG is the maximum amount of non-*PV* work obtainable from a system. The energy released by the oxidation of NADH in mitochondria is used to do non-*PV* work, *viz.* the pumping of H$^+$ ions across the inner mitochondrial membrane. By storing this energy in the form of an H$^+$ gradient, the amount of energy wasted as heat is reduced.

3

- Consider the following reaction.

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$
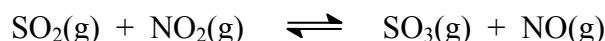
An equilibrium mixture in a 1.00 L vessel was found to contain $[SO_2(g)] = 0.800$ M, $[NO_2(g)] = 0.100$ M, $[SO_3(g)] = 0.600$ M and $[NO(g)] = 0.400$ M. If the volume and temperature are kept constant, what amount (in mol) of $NO(g)$ needs to be added to the reaction vessel to give an equilibrium concentration of $NO_2(g)$ of 0.300 M?

From the chemical equation,

$$K_{eq} = \frac{[SO_3(g)][NO(g)]}{[SO_2(g)][NO_2(g)]}$$

As the original mixture is at equilibrium:

$$K_{eq} = \frac{[SO_3(g)][NO(g)]}{[SO_2(g)][NO_2(g)]} = \frac{(0.600)(0.400)}{(0.800)(0.100)} = 3.00$$

This equilibrium is now disturbed by the addition of x M of $NO(g)$. To re-establish equilibrium, the reaction will shift to the left by an unknown amount y. The reaction table for this is:

	SO₂(g)	NO₂(g)		SO₃(g)	NO(g)
initial	0.800	0.100	⇌	0.600	0.400 + x
change	+y	+y		-y	-y
equilibrium	0.800 + y	0.100 + y		0.600 – y	0.400 + x - y

As $[NO_2(g)] = 0.300$ M at the new equilibrium, $y = (0.300 – 0.100)$ M = 0.200 M. Hence, the new equilibrium concentrations are:

$[SO_2(g)] = (0.800 + 0.200)$ M = 1.000 M
$[NO_2(g)] = 0.300$ M
$[SO_3(g)] = (0.600 – 0.200)$ M = 0.400 M
$[NO(g)] = (0.400 + x – 0.200)$ M = $(0.200 + x)$ M

As the system is at equilibrium,

$$K_{eq} = \frac{[SO_3(g)][NO(g)]}{[SO_2(g)][NO_2(g)]} = \frac{(0.400)(0.200+x)}{(1.000)(0.300)} = 3.00$$

Solving this gives $x = 2.05$ M. As the reaction is carried out in a 1.00 L container, this is also the number of moles required.

Answer: **2.05 mol**

**Marks
2**

- Calculate $\Delta G°$ for the reaction: $2N_2O(g) + 3O_2(g) \rightarrow 4NO_2(g)$

  Data: $4NO(g) \rightarrow 2N_2O(g) + O_2(g)$ $\Delta G° = -139.56 \text{ kJ mol}^{-1}$

              $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $\Delta G° = -69.70 \text{ kJ mol}^{-1}$

Using $\Delta_r G° = \sum\Delta_f G°$(products) – $\sum\Delta_f G°$(reactants), the free energy changes in the 3 reactions are, respectively:

   (1) $\Delta_r G° = 4\Delta_f G°(NO_2(g)) - 2\Delta_f G°(N_2O(g))$

   (2) $\Delta_r G° = 2\Delta_f G°(N_2O(g)) - 4\Delta_f G°(NO(g)) = -139.56 \text{ kJ mol}^{-1}$

   (3) $\Delta_r G° = 2\Delta_f G°(NO_2(g)) - 2\Delta_f G°(NO(g)) = -69.70 \text{ kJ mol}^{-1}$

Taking $2 \times$ (3) – (2) gives:

   $2 \times [2\Delta_f G°(NO_2(g)) - 2\Delta_f G°(NO(g))] - [2\Delta_f G°(N_2O(g)) - 4\Delta_f G°(NO(g))]$
   $= (2 \times [-69.70] - [-139.56]) \text{ kJ mol}^{-1}$

   $4\Delta_f G°(NO_2(g)) - 2\Delta_f G°(N_2O(g)) = +0.16 \text{ kJ mol}^{-1}$

From above, this is equal to the $\Delta_r G°$ for reaction (1) as required.

Answer: **+0.16 kJ mol^{-1}**

- Good wine will turn to vinegar if it is left exposed to air because the alcohol is oxidised to acetic acid. The equation for the reaction is:

  $$CH_3CH_2OH(l) + O_2(g) \rightarrow CH_3COOH(l) + H_2O(l)$$
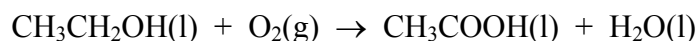
Calculate $\Delta S°$ for this reaction in J K^{-1} mol^{-1}.

2

Data:		$S°$ (J K^{-1} mol^{-1})		$S°$ (J K^{-1} mol^{-1})
	$C_2H_5OH(l)$	161	$CH_3COOH(l)$	160.
	$O_2(g)$	205.0	$H_2O(l)$	69.96

Using $\Delta_r S° = \sum S°$(products) – $\sum\Delta S°$(reactants),

   $\Delta_r S° = [S°(CH_3COOH(l) + S°(H_2O(l)] – [S°(CH_3CH_2OH(l) + S°(O_2)]$
   $= ([160. + 69.96] – [161 + 205.0]) \text{ J K}^{-1}\text{mol}^{-1}$
   $= -136 \text{ J K}^{-1}\text{mol}^{-1}$

Answer: **-136 J K^{-1}mol^{-1}**

- Consider the following reaction.

$$SO_2(g) + NO_2(g) \rightleftharpoons NO(g) + SO_3(g)$$

At 460 °C this reaction has a value of $K_c = 85.0$. Suppose 0.100 mol of SO_2, 0.0600 mol of NO_2, 0.0800 mol of NO and 0.120 mol of SO_3 are placed in a 10.0 L container at this temperature. What are the concentrations of all of the gases when the system reaches equilibrium?

The initial concentrations are:

$[SO_2(g)]$ = number of moles / volume = (0.100 mol) / (10.0 L) = **0.0100 M**

$[NO_2(g)]$ = (0.0600 mol) / (10.0 L) = **0.00600 M**

$[NO(g)]$ = (0.0800 mol) / (10.0 L) = **0.00800 M**

$[SO_3(g)]$ = (0.120 mol) / (10.0 L) = **0.0120 M**

The reaction quotient can be used to predict the direction that the reaction will shift:

$$Q = \frac{[NO(g)][SO_3(g)]}{[SO_2(g)][NO_2(g)]} = \frac{(0.0120)(0.00800)}{(0.0100)(0.00600)} = 1.6$$

As $Q < K$, the reaction will shift to the right – to increase the amount of products and decrease the amount of reactants. The reaction table is then:

	$SO_2(g)$	$NO_2(g)$	$\rightleftharpoons$	$NO(g)$	$SO_3(g)$
initial	0.0100	0.00600		0.00800	0.0120
change	-x	-x		+x	+x
equilibrium	0.0100 – x	0.00600 – x		0.00800 + x	0.0120 + x

Hence,

$$K = \frac{(0.00800+x)(0.0120+x)}{(0.0100-x)(0.00600-x)} = 85.0$$

$$85.0(x^2 - 0.01600x + 0.0000600) = x^2 + 0.02000x + 0.000096$$

$$84.0x^2 - 1.38x + 0.005004 = 0$$

Solving this quadratic equation gives $x = 0.0054$ and 0.011. The second root is not possible, as it leads to negative concentrations for the reactants.

Using $x = 0.0054$ M gives,

$[SO_2(g)]$ = (0.0100 – 0.0054) M = **0.00460 M**

$[NO_2(g)]$ = (0.00600 – 0.0054) M = **0.000597 M**

$[NO(g)]$ = (0.00800 + 0.0054) M = **0.0134 M**

$[SO_3(g)]$ = (0.0120 + 0.0054) M = **0.0174 M**

$[SO_2(g)]$ = **0.00460 M**	$[NO_2(g)]$ = **0.000597 M**
$[SO_3(g)]$ = **0.0174 M**	$[NO(g)]$ = **0.0134 M**

**Marks
2**

- Consider the ammonia synthesis reaction shown below.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_c = 6.0 \times 10^{-2} \text{ at } 500 \text{ °C}$$
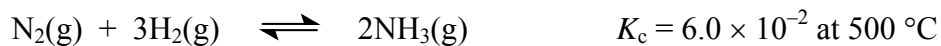
$\Delta H°$ for this reaction is –92 kJ mol^{-1}. Calculate the value of K_c at 200 °C.

Using the Van't Hoff equation,

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

with $K_1 = 6.0 \times 10^{-2}$ at $T_1 = (500 + 273)$ K = 773 K, the value of K_2 at $T_2 = (200 + 273)$ K = 473 K can be calculated:

$$\ln\left(\frac{K_2}{6.0 \times 10^{-2}}\right) = \frac{(-92 \times 10^3 \text{ J mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})}\left(\frac{1}{(473 \text{ K})} - \frac{1}{(773 \text{ K})}\right)$$

$K_2 = 530$

Answer: **530**

**Marks
3**

- Consider the following reaction.

$$H_2O(g) + Cl_2O(g) \rightleftharpoons 2HOCl(g) \qquad K_p = 0.090 \text{ at } 298 \text{ K}$$

Calculate $\Delta G°$ (in J mol^{-1}) for this reaction.

Using $\Delta G° = -RT\ln K_p$:

$\Delta G° = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln(0.090) = 5.97 \times 10^3 \text{ J mol}^{-1}$

	$\Delta G° = $ **5.97 kJ mol^{-1}**

Calculate ΔG (in J mol^{-1}) at 25 °C when $p(H_2O) = 18$ mmHg, $p(Cl_2O) = 2.0$ mmHg and $p(HOCl) = 0.10$ mmHg.

The reaction quotient, Q, for this reaction is given by:

$$Q = \frac{(p_{HOCl})^2}{(p_{H_2O})(p_{Cl_2O})} = \frac{(0.10)^2}{(18) \times (2.0)} = 0.00028$$

Hence:

$\Delta G = \Delta G° + RT\ln Q$

$= (5.97 \times 10^3 \text{ J mol}^{-1}) + (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln(0.00028)$

$= -14.3 \times 10^3 \text{ J mol}^{-1}$

	Answer: **-14.3 kJ mol^{-1}**

	Marks
Explain the following terms or concepts.	3

a) Lewis acid

A Lewis acid is a species that can accept an electron pair.

This includes both the H$^+$ and species such as BF$_3$ and Fe^{2+}:

$$H^+ + OH^- \rightleftharpoons H_2O$$

$$BF_3 + F^- \rightleftharpoons BF_4^-$$

$$Fe^{2+} + 6H_2O \rightleftharpoons [Fe(OH_2)_6]^{2+}$$

b) 3rd Law of Thermodynamics

The entropy of a perfect crystal is 0 at 0 K.

c) Brownian motion

The random motion of particles in a liquid that increase with increasing temperature.

- $\Delta_{vap}H° = 34.0$ kJ mol^{-1} for benzene, which has a boiling point of 80.1 °C. What is the entropy change for the vaporisation of benzene in J K^{-1} mol^{-1}?   **2**

At the boiling point, $\Delta_{vap}G° = 0$ J mol^{-1}. As $\Delta_{vap}G° = \Delta_{vap}H° - T\Delta_{vap}S°$:

$$0 \text{ J mol}^{-1} = (34.0 \times 10^3 \text{ J mol}^{-1}) - ((80.1 + 273)) \text{ K}) \times \Delta_{vap}S°$$

$$\Delta_{vap}S° = +96.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

Answer: **+96.3 J K^{-1} mol^{-1}**

Marks
3

- A mixture of NaCl (5.0 g) and AgNO$_3$ (5.0 g) was added to 1.0 L of water. What are the concentrations of Ag$^+$(aq), Cl$^-$(aq) and Na$^+$(aq) ions in solution after equilibrium has been established? K_{sp}(AgCl) = 1.8×10^{-10}.

The molar masses of the two salts are:

$$M_{NaCl} = (22.99 \text{ (Na)} + 35.45 \text{ (Cl)}) \text{ g mol}^{-1} = 58.44 \text{ g mol}^{-1}$$

$$M_{AgNO_3} = (107.87 \text{ (Ag)} + 14.01 \text{ (N)} + 3 \times 16.00) \text{ g mol}^{-1} = 169.88 \text{ g mol}^{-1}$$

The number of moles of salt added to the solution are therefore:

$$\text{number of moles of NaCl} = \frac{\text{mass}}{\text{molar mass}} = \frac{5.0}{58.44 \text{ g mol}^{-1}} = 0.0855 \text{ mol}$$

$$\text{number of moles of AgNO}_3 = \frac{5.0}{169.88 \text{ g mol}^{-1}} = 0.0294 \text{ mol}$$

As 1.0 L of water is present, the initial concentrations of the ions are [Na$^+$(aq)] = 0.086 M, [Cl$^-$(aq)] = 0.086 M and [Ag$^+$(aq)] = 0.029 mol. The Na$^+$(aq) will form any precipitate with the ions present: [Na$^+$(aq)] = 0.086 M.

The ionic product for the precipitation of AgCl(s) is given by:

$$Q_{sp} = [\text{Ag}^+\text{(aq)}][\text{Cl}^-\text{(aq)}] = (0.029)(0.086) = 0.0025$$

As $Q_{sp} \gg K_{sp}$, precipitation of AgCl(s) will occur. As [Ag$^+$(aq)] < [Cl$^-$(aq)], the silver ion concentration is limiting and so:

$$[\text{Cl}^-\text{(aq)}] = (0.086 - 0.029) \text{ M} = 0.056 \text{ M}$$

As AgCl(s) is present, [Ag$^+$(aq)] is given by the solubility product:

$$K_{sp} = [\text{Ag}^+\text{(aq)}][\text{Cl}^-\text{(aq)}] = 1.8 \times 10^{-10}$$

$$[\text{Ag}^+\text{(aq)}] = (1.8 \times 10^{-10}) / (0.056) \text{ M} = 3.2 \times 10^{-9} \text{ M}$$

[Ag$^+$(aq)] = **3.2×10^{-9} M**	[Cl$^-$(aq)] = **0.056 M**	[Na$^+$(aq)] = **0.086 M**

Marks
5

- At 700 °C, hydrogen and iodine react according to the following equation.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad K_c = 49.0$$

Hydrogen also reacts with sulfur at 700 °C:

$$2H_2(g) + S_2(g) \rightleftharpoons 2H_2S(g) \qquad K_c = 1.075 \times 10^8$$

Determine K_c for the following overall equilibrium reaction at 700 °C.

$$2I_2(g) + 2H_2S(g) \rightleftharpoons S_2(g) + 4HI(g)$$

The overall reaction corresponds to the twice the first reaction combined with the reverse of the second reaction:

$2H_2(g) + 2I_2(g) \rightleftharpoons 4HI(g)$ $\qquad$ **$K_c(1) = (49.0)^2$**

$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$ $\qquad$ **$K_c(2) = 1/(1.075 \times 10^8)$**

$2I_2(g) + 2H_2S(g) \rightleftharpoons S_2(g) + 4HI(g)$ $\qquad$ **$K_c(3) = K_c(1) \times K_c(2)$**
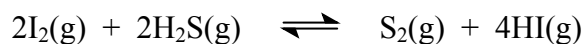
The 1st reaction is doubled so the original equilibrium constant is squared.

The 2nd reaction is reversed so the reciprocal of the equilibrium constant is used.

The two reactions are then combined and the overall equilibrium constant is then the product:

$K_c(3) = K_c(1) \times K_c(2) = (49.0)^2 \times (1/(1.075 \times 10^8) = 2.23 \times 10^{-5}$

$K_c = 2.23 \times 10^{-5}$

What is the standard free energy change at 700 °C for this overall equilibrium reaction?

The equilibrium constant in terms of pressures is first converted into the equilibrium constant in terms of pressures using $K_p = K_c(RT)^{\Delta n}$. The reaction involves the conversion of 4 mol of gas to 5 mol of gas so $\Delta n = +1$ and:

$K_p = K_c(RT)^{\Delta n} = (2.23 \times 10^{-5}) \times (0.08206 \times 973)^1 = 0.00178$

Note that as K_c is in terms of concentration units of mol L^{-1}, $R = 0.08206$ atm L mol^{-1} K^{-1} has been used.

As $\Delta G° = -RT\ln K_p$:

$\Delta G° = -(8.314$ J K^{-1} $mol^{-1}) ° (973$ K$) \times \ln(0.00178) = +51.2$ kJ mol^{-1}

Answer: **+51.2 kJ mol^{-1}**

THIS QUESTION CONTINUES ON THE NEXT PAGE.

If 0.250 mol of HI(g) is introduced into a 2.00 L flask at 700 °C, what will be the concentration of I_2(g) at equilibrium?

The initial concentration of HI(g) is 0.250 / 2.00 mol L^{-1} = 0.125 mol L^{-1}.

	H$_2$(g)	I$_2$(g)	$\rightleftharpoons$	2HI(g)
Initial	0	0		0.125
Change	+x	+x		-2x
Equilibrium	x	x		0.125 - 2x

Thus,

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.125-2x)^2}{(x)(x)} = \frac{(0.125-2x)^2}{x^2} = 49.0 \text{ (from 2008-N-5)}$$

$$(49.0)^{1/2} = \frac{(0.125-2x)}{x}$$

Rearranging gives x = [I_2(g)] = 0.0139 M.

Answer: **0.0139 M**

If 0.274 g of H$_2$S were now introduced into the same flask, what would be the concentration of S$_2$(g) at equilibrium?

The molar mass of H$_2$S is (2 × 1.008 (H) + 32.06 (S)) = 34.08 g mol^{-1}. Hence, 0.274 g of H$_2$S corresponds to:

number of moles = mass / molar mass
= (0.274 g) / (34.08 g mol^{-1}) = 8.04 × 10^{-3} mol

The initial concentration of H$_2$S is thus 8.04 × 10^{-3} mol / 2.00 M = 4.02 × 10^{-3} M.

From above, [I_2(g)] = 0.0139 M and [HI(g)] = (0.125 – 2 × 0.0139) M = 0.0972 M.

Using the overall equilibrium reaction derived in 2008-N-5:

	2I$_2$(g)	2H$_2$S(g)	$\rightleftharpoons$	S$_2$(g)	4HI(g)
Initial	0.0139	0.00402		0	0.0972
Change	-2x	-2x		+x	+4x
Equilibrium	0.0139 - 2x	0.00402 – 2x		x	0.0972 + 4x

ANSWER CONTINUES ON THE NEXT PAGE

Thus,

$$K_c = \frac{[S_2][HI]^4}{[I_2]^2[H_2S]^2} = \frac{(x)(0.0972+4x)^4}{(0.0139-2x)^2(0.00402-2x)^2}$$

$$\sim \frac{(x)(0.0972)^4}{(0.0139)^2(0.00402)^2} = 2.23 \times 10^{-5} \text{ (from 2008-N-5)}$$

where the small x approximation has been used as K_c is so small. This gives:

$x = [S_2(g)] = 7.82 \times 10^{-10}$ M

Answer: **7.82×10^{-10} M**

**Marks
5**

- Consider the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$\Delta H° = -198.4$ kJ mol^{-1} and $\Delta S° = -187.9$ J K^{-1} mol^{-1} at 25 °C.

Show that this reaction is spontaneous at 25 °C.

Using $\Delta G° = \Delta H° - T\Delta S°$,

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

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

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

An increase in volume corresponds to a decrease in pressure. According to Le Chatelier's principle, the reaction will shift to increase the pressure. It does this by favouring the side with a *greater* number of gaseous molecules:

The reaction will shift to the left (3 moles of gas on the left, 2 moles of gas on the right).

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

Using $\Delta G° = -RT\ln K$,

> -142.2×10^3 J mol$^{-1} = -(8.314$ J K^{-1} mol$^{-1}) \times ((25 + 273)$ K$) \times \ln K$

> $K = 9.170 \times 10^{24}$ **(essentially complete conversion to products)**

$K = 9.170 \times 10^{24}$ **(no units)**

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

The reaction is non-spontaneous when $\Delta G° > 0$, or when $\Delta H° - T\Delta S° > 0$:

> $(-198.4 \times 10^3$ J mol$^{-1}) - T \times (-187.9$ J mol$^1) > 0$

> $T > \dfrac{-198.4 \times 10^3 \,\text{J mol}^{-1}}{-187.9 \,\text{J mol}^{-1}}$ **so $T > 1055$ K**

Note that, as demonstrated above, the reaction is spontaneous at 298 K and, as the reaction is exothermic, it becomes less favourable as the temperature increases (Le Chatelier's principle).
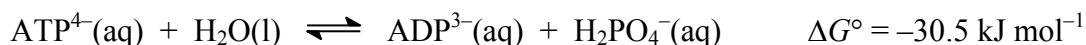
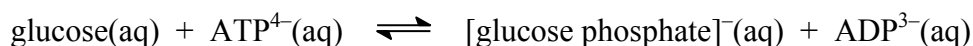| Answer: $T > 1055$ K |
|---|

	Marks
	6

- The first step in the metabolism of glucose in biological systems is the addition of a phosphate group in a dehydration-condensation reaction:

$$\text{glucose(aq)} + \text{H}_2\text{PO}_4^-\text{(aq)} \;\rightleftharpoons\; [\text{glucose phosphate}]^-\text{(aq)} + \text{H}_2\text{O(l)}$$
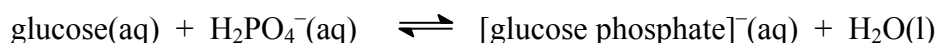
The free energy change associated with this reaction is $\Delta G° = 13.8$ kJ mol^{-1}. The reaction is driven forwards by harnessing the free energy associated with the hydrolysis of adenosine triphosphate, ATP^{4-}, to adenosine diphosphate, ADP^{3-}:

$$\text{ATP}^{4-}\text{(aq)} + \text{H}_2\text{O(l)} \;\rightleftharpoons\; \text{ADP}^{3-}\text{(aq)} + \text{H}_2\text{PO}_4^-\text{(aq)} \qquad \Delta G° = -30.5 \text{ kJ mol}^{-1}$$

The overall reaction is thus:

$$\text{glucose(aq)} + \text{ATP}^{4-}\text{(aq)} \;\rightleftharpoons\; [\text{glucose phosphate}]^-\text{(aq)} + \text{ADP}^{3-}\text{(aq)}$$

Calculate the equilibrium constant associated with this overall reaction at body temperature (37 °C).

The overall reaction is the sum of the two reactions:

$$\Delta G° \text{ (kJ mol}^{-1}\text{)}$$

glucose(aq) + H$_2$PO$_4^-$(aq) $\rightleftharpoons$ [glucose phosphate]$^-$(aq) + H$_2$O(l)　　13.8

ATP^{4-}(aq) + H$_2$O(l) $\rightleftharpoons$ ADP^{3-}(aq) + H$_2$PO$_4^-$(aq)　　　　　　-30.5

glucose(aq)+ATP^{4-}(aq) $\rightleftharpoons$ [glucose phosphate]$^-$(aq)+ADP^{3-}(aq)　　-16.7

For the overall reaction, $\Delta G° = ((13.8) + (-30.5))$ kJ mol^{-1} = -16.7 kJ mol^{-1}. Using $\Delta G° = -RT\ln K$,

$-16.7 \times 10^3 = -8.314 \times (37 + 273)\ln K$　or　$K = e^{6.48} = 652$

Answer: **$K = 652$　(no units)**

This overall equilibrium reaction is investigated by adding 0.0100 mol of ATP^{4-} to a flask containing 175 mL of a 0.0500 M aqueous solution of glucose at 37 °C. What percentage of the ATP^{4-} will have been consumed when the system reaches equilibrium?

The initial concentration of ATP^{4-} is $\dfrac{n}{V} = \dfrac{0.0100 \,\text{mol}}{0.175 \,\text{L}} = 0.0571$ M. The reaction table is then:

	glucose(aq)	**ATP^{4-}(aq)**	$\rightleftharpoons$	**[glucose phosphate]$^-$(aq)**	**ADP^{3-}(aq)**
initial	**0.0500**	**0.0571**		**0**	**0**
change	**-x**	**-x**		**+x**	**+x**
equilibrium	**0.0500-x**	**0.0571-x**		**x**	**x**

At equilibrium,

$$K = \frac{[\text{glucose-phosphate}^-\text{(aq)}][\text{ADP}^{3-}\text{(aq)}]}{[\text{glucose(aq)}][\text{ATP}^{4-}\text{(aq)}]} = \frac{x^2}{(0.0500 - x)(0.0571 - x)} = 652$$

ANSWER CONTINUES ON THE NEXT PAGE

As the equilibrium constant is large so is x and this expression cannot be approximated. Instead, the full quadratic equation must be solved.

$x^2 = 652(0.0500-x)(0.0571-x)$ **or**

$651x^2 -652(0.0500+0.0571)+ (652\times0.0500\times0.0571) = 0$

The two roots are $x_1 = 0.0578$ M and $x_2 = 0.0495$ M. As x_1 gives a negative [glucose(aq)], it is not physically significant. As x is the concentration consumed, using x_2 gives:

$$\text{percentage of ATP}^{4-}\text{(aq) consumed} = \frac{0.0495\,M}{0.0571\,M}\times100\% = 87\%$$

Answer: **87%**

Suggest two simple ways of further reducing the remaining percentage of ATP^{4-}.

The remaining ATP^{4-} can be reduced by (i) adding more glucose and (ii) reducing the temperature. Removal of either product would also drive the reaction to the right but would be very difficult to achieve in practice.

**Marks
3**

- Acetylene, C_2H_2, is an important fuel in welding. It is produced in the laboratory when calcium carbide, CaC_2, reacts with water:

$$CaC_2(s) + 2H_2O(l) \rightarrow C_2H_2(g) + Ca(OH)_2(s)$$
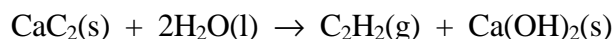
For a sample of C_2H_2 collected over water, the total gas pressure was 748 mmHg and the volume was 543 mL. At the gas temperature (23 °C), the vapour pressure of water is 21 mmHg. What mass of acetylene was collected?

The total pressure is the sum of the partial pressures due to $C_2H_2(g)$ and $H_2O(g)$:

$$p_{total} = 748 \text{ mmHg} = p_{H_2O} + p_{C_2H_2} = (21 \text{ mmHg}) + p_{C_2H_2}$$
$$p_{C_2H_2} = (748 - 21) = 727 \text{ mmHg}$$

As 760 mmHg corresponds to 1 atm, $p_{C_2H_2} = \dfrac{727}{760}$ atm = 0.957 atm. Using the ideal gas law, $pV = nRT$, the number of moles of C_2H_2 formed is:

$$n = \frac{pV}{RT} = \frac{(0.957 \text{ atm}) \times (0.543 \text{ L})}{(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times ((23 + 273) \text{ K})} = 0.0214 \text{ mol}$$

The molar mass of C_2H_2 is $(2 \times 12.01$ (C)$) + (2 \times 1.008$ (H)$) = 26.036$ g mol^{-1}. This amount therefore corresponds to a mass of,

**mass = number of moles × molar mass = 0.0214 mol × 26.036 g mol^{-1}
= 0.557 g**

Answer: **0.557 g**

The solubility of acetylene in water at 22.0 °C is small. If the temperature were raised, would you expect this solubility to increase or decrease?

The solubility of gases in water decreases with temperature. The dissolution of a gas is entropically disfavoured and only occurs because it is exothermic. Like all exothermic process, the process becomes less favourable at higher temperatures (Le Chatelier's principle).

- The isomerisation of glucose-6-phosphate (G6P) to fructose-6-phosphate (F6P) is a key step in the metabolism of glucose for energy.

$$G6P \rightleftharpoons F6P$$

At 298 K, the equilibrium constant for the isomerisation is 0.510. Calculate the value of $\Delta G°$ at 298 K.

$\Delta G° = -RT\ln K = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln(0.510)$
$\quad = +1670 \text{ J mol}^{-1} = +1.67 \text{ kJ mol}^{-1}$

Answer: **+1.67 kJ mol⁻¹**

Calculate ΔG at 298 K when the [F6P] / [G6P] ratio = 10.

The reaction quotient, for the reaction, is $Q = \dfrac{[\text{F6P}]}{[\text{G6P}]} = 10$

Using $\Delta G = \Delta G° + RT\ln Q$,

$\Delta G = (+1.67 \times 10^3 \text{ J mol}^{-1}) + (8.314 \times 298 \text{ J mol}^{-1}) \times \ln(10)$
$\quad = +7400 \text{ J mol}^{-1} = +7.4 \text{ kJ mol}^{-1}$

Answer: **+7.4 kJ mol⁻¹**

In which direction will the reaction shift in order to establish equilibrium? Why?

As ΔG is positive, the forward reaction is non-spontaneous and the backward reaction is spontaneous. The reaction thus shift backwards, increasing [G6P] and reducing [F6P] until $Q = K$.

Sketch a graph of G_{sys} *versus* "extent of reaction", with a curve showing how G_{sys} varies as G6P is converted to F6P. Indicate the position on this curve corresponding to the point where [F6P] / [G6P] ratio = 10. Indicate on the graph that section of the curve where $Q > K$.
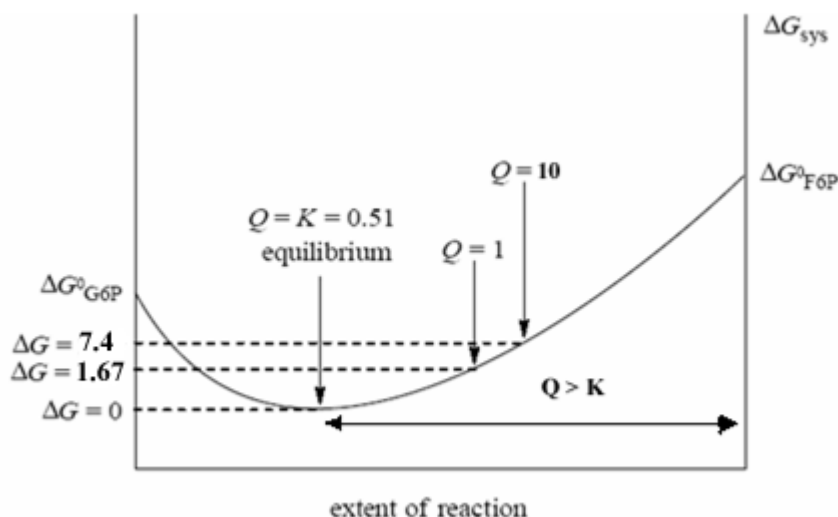
The $CO(g)$ in water gas can be reacted further with $H_2O(g)$ in the so-called "water-gas shift" reaction:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$
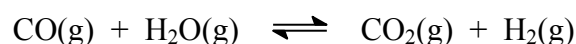
At 900 K, $K_c = 1.56$ for this reaction. A sample of water gas flowing over coal at 900 K contains a 1:1 mole ratio of $CO(g)$ and $H_2(g)$, as well as 0.250 mol L^{-1} $H_2O(g)$. This sample is placed in a sealed container at 900 K and allowed to come to equilibrium, at which point it contains 0.070 mol L^{-1} $CO_2(g)$. What was the initial concentration of $CO(g)$ and $H_2(g)$ in the sample?

The reaction table is

	$CO(g)$	**$H_2O(g)$**	$\rightleftharpoons$	**$CO_2(g)$**	**$H_2(g)$**
initial	x	0.250		0	x
change	-0.070	-0.070		+0.070	+0.070
equilibrium	x – 0.070	0.250 – 0.070		0.070	x + 0.070

The equilibrium constant in terms of concentrations, K_c, is:

$$K_c = \frac{[CO_2(g)][H_2(g)]}{[H_2O(g)][CO(g)]} = \frac{(0.070)(x + 0.070)}{(0.180)(x - 0.070)} = 1.56$$

$x = [CO(g)]_{initial} = [H_2(g)]_{initial} = \textbf{0.12 mol L}^{\textbf{-1}}$

$[CO] = [H_2] = \textbf{0.12 mol L}^{\textbf{-1}}$

If the walls of the container are chilled to below 100 ºC, what will be the effect on the concentration of $CO_2(g)$?

At temperatures below 100 °C, the water vapour will condense to form $H_2O(l)$. Following Le Chatelier's principle, the equilibrium will shift to the left as $[H_2O(g)]$ is reduced by this process and so $[CO_2(g)]$ will decrease.

**Marks
6**

- The isomerisation of glucose-6-phosphate (G6P) to fructose-6-phosphate (F6P) is a key step in the metabolism of glucose for energy. At 298 K,

$$G6P \rightleftharpoons F6P \qquad \Delta G° = 1.67 \text{ kJ mol}^{-1}$$

Calculate the equilibrium constant for this process at 298 K.

Using $\Delta G° = -RT\ln K$,

$1.67 \times 10^3 = -(8.314) \times (298) \times \ln K$

$K = 0.510$

Answer: **K = 0.510**

What is the free energy change (in kJ mol^{-1}) involved in a mixture of 3.00 mol of F6P and 2.00 mol of G6P reaching equilibrium at 298 K?
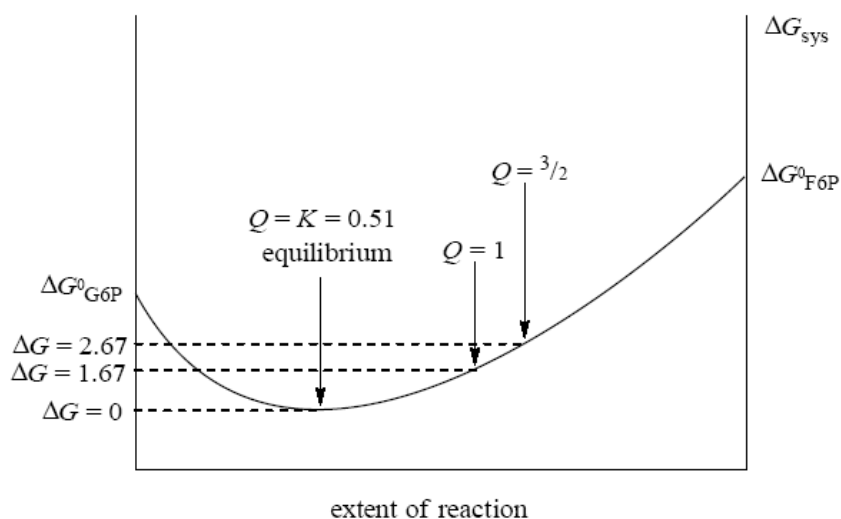
The reaction quotient, for the reaction, is $Q = \dfrac{[F6P]}{[G6P]} = \dfrac{3.00}{2.00} = 1.50$.

Using $\Delta G = \Delta G° + RT\ln Q$,

$\Delta G = (1.67 \times 10^3) + (8.314 \times 298) \times \ln(1.50) = +2670 \text{ J mol}^{-1} = +2.67 \text{ kJ mol}^{-1}$

Answer: **+2.67 kJ mol^{-1}**

Sketch a graph of G_{sys} *versus* "extent of reaction", with a curve showing how G_{sys} varies as G6P is converted to F6P. Indicate the position on this curve corresponding to 3.00 mol of F6P and 2.00 mol of G6P.

- A mixture of 0.500 mol of $NO_2(g)$ and 0.500 mol of $N_2O_4(g)$ is allowed to reach equilibrium in a 10.0 L vessel maintained at 298 K. The equilibrium is described by the equation below. $\Delta H° = -15$ kJ mol^{-1} for the forward reaction.

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad\qquad K_c = 1.2 \times 10^2 \text{ M}^{-1}$$

Show that the system is at equilibrium when the concentration of $NO_2(g)$ is 0.023 M.

The concentrations of $NO_2(g)$ and $N_2O_4(g)$ at the start are:

$$\mathbf{[NO_2(g)] = [N_2O_4(g)] = \frac{number\,of\,moles}{volume} = \frac{0.500\,mol}{10.0\,L} = 0.0500\,M}$$

$[NO_2(g)]$ decreases during the reaction and so $[N_2O_4(g)]$ increases. From the chemical equation, *one* mole of $N_2O_4(g)$ is produced for every *two* moles of NO(g) that are lost.

The change in $[NO_2(g)] = (0.0500 - 0.023)$ M = 0.027 M. Hence,

$$\mathbf{[N_2O_4(g)]_{equilibrium} = (0.0500 + ½ \times 0.027)\,M = 0.064\,M}$$

With these concentrations, the reaction quotient, *Q*, is given by:

$$\mathbf{Q = \frac{[N_2O_4(g)]}{[NO_2(g)]^2} = \frac{(0.064)}{(0.023)^2} = 120 = 1.2 \times 10^2}$$

As $Q = K$, the reaction is at equilibrium.

Discuss the effect an increase in temperature, at constant volume, would have on the concentration of $NO_2(g)$.

As $\Delta H° = -15$ kJ mol^{-1} for the forward reaction, the reaction is exothermic. If the temperature is increased, the system will respond by removing heat. It will do this by shifting towards the reactant ($NO_2(g)$) as the backward reaction is endothermic. Hence, $[NO_2(g)]$ will increase.

State with a brief reason whether the concentration of $NO_2(g)$ is increased, decreased, or unchanged when argon gas (0.2 mol) is injected while the temperature and volume remain constant.

Adding argon will increase the pressure inside the vessel will increase. However, the inert gas does not change the volume so all reactant and product concentrations remain the same.

- A key step in the metabolism of glucose for energy is the isomerism of glucose-6-phosphate (G6P) to fructose-6-phosphate (F6P);

$$G6P \rightleftharpoons F6P$$

At 298 K, the equilibrium constant for the isomerisation is 0.510. Calculate $\Delta G°$ at 298 K.

Using $\Delta G° = -RT\ln K$:

$$\Delta G° = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln(0.510)$$
$$= +1670 \text{ J mol}^{-1} = +1.6 \text{ kJ mol}^{-1}$$

Answer: **+1.6 kJ mol^{-1}**

Calculate ΔG at 298 K when the [F6P] / [G6P] ratio = 10.

Using $\Delta G = \Delta G° + RT\ln Q$, when the reaction quotient $Q = \dfrac{[F6P]}{[G6P]} = 10$:

$$\Delta G = (+1670 \text{ J mol}^{-1}) + (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln(10)$$
$$= +7400 \text{ J mol}^{-1} = +7.4 \text{ kJ mol}^{-1}$$

Answer: **+7.4 kJ mol^{-1}**

In which direction will the reaction shift in order to establish equilibrium? Why?

As $Q > K$, the reaction will shift to decrease Q. It will do this by reducing the amount of product and increasing the amount of reactant: it will shift to the left.

Equivalently, as $\Delta G = +7.4 \text{ kJ mol}^{-1}$, the forward process is non-spontaneous and the backward reaction is spontaneous.

THE ANSWER CONTINUES ON THE NEXT PAGE

- The specific heat capacity of water is 4.18 J g^{-1} K^{-1} and the specific heat capacity of copper is 0.39 J g^{-1} K^{-1}. If the same amount of energy were applied to a 1.0 mol sample of each substance, both initially at 25 °C, which substance would get hotter? Show all working.

As $q = C \times m \times \Delta T$, the temperature increase is given by $\Delta T = \dfrac{q}{C \times m}$.

As H_2O has a molar mass of (2 × 1.008 (H) + 16.00 (O)) g mol^1 = 18.016 g mol^1, 1.0 mol has a mass of 18 g. The temperature increase is therefore:

$$\Delta T = \frac{q}{C_{H_2O} \times m_{H_2O}} = \frac{q}{(4.18\,J\,g^{-1}\,K^{-1}) \times (18g)} = \frac{q}{(75\,J\,K^{-1})}$$

As Cu has an atomic mass of 63.55 g mol^1, 1.0 mol has a mass of 64 g. The temperature increase is therefore:

$$\Delta T = \frac{q}{C_{Cu} \times m_{Cu}} = \frac{q}{(0.39\,J\,g^{-1}\,mol^{-1}) \times (64g)} = \frac{q}{(25\,J\,K^{-1})}$$

As the same amount of energy is supplied to both, q is the same for both. The temperature increase of the copper is therefore higher.

Answer: **copper**

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 at 25 °C.

A reaction is spontaneous if $\Delta G° < 0$. Using $\Delta G° = \Delta H° - T\Delta S°$:

$$\Delta G° = (-198.4 \times 10^3 \text{ J mol}^1) - ((25 + 273) \text{ K}) \times (-187.9 \text{ J K}^{-1} \text{ mol}^{-1})$$
$$= -142000 \text{ J mol}^{-1} = -142 \text{ kJ mol}^{-1}$$

Hence, $\Delta G° < 0$ and the reaction is spontaneous.

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

In the reaction, three moles of gas are converted into two moles of gas. Increasing the volume lowers the pressure. The system responds by acting to increase the pressure – it shifts to the left (more reactants).