Answers to Practice Test Questions 7
Free Energy and Equilibrium

1.

(a) $\Delta G°$ refers to the free energy change for a reaction under standard conditions (i.e. when all reactants and products have an activity of 1). ΔG refers to the free energy change for a reaction under the actual reaction conditions under consideration. If a reaction happens to proceed under standard conditions, the values for ΔG and $\Delta G°$ will be the same.

(b) Reaction iv. (diamond to graphite) is the only reaction for which all reactants and products will always have an activity of 1 (since they are solids).

For reaction i., $\Delta G = \Delta G°$ if the pressure of Cl_2 is 1 bar.

For reaction ii., $\Delta G = \Delta G°$ if the activities of $KOH_{(aq)}$ and $H_2O_{(l)}$ are 1. *(Usually, this would correspond to a 1 mol/L solution of KOH with water acting as an ideal solvent; however, the solution produced is nonideal, making the math more complex.)*

For reaction iii., $\Delta G = \Delta G°$ if Q = 1. That is true as long as $\left(\frac{P_{O_3}}{1\ bar}\right)^2 = \left(\frac{P_{O_2}}{1\ bar}\right)^3$.

2. *Free energy change for a reaction under nonstandard conditions can be calculated from the standard free energy change for the reaction and the reaction quotient.*

Step 1: Write a balanced chemical equation for the reaction

This was provided in the question.

$$H_{2(g)} + Cl_{2(g)} \rightarrow 2\ HCl_{(g)}$$
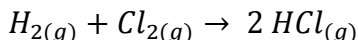
Step 2: Convert temperature to Kelvin (if necessary)

$T = 25\ °C = 298.15\ K$

Step 3: Calculate the standard free energy change for the reaction

$\Delta_r G° = \sum \Delta_f G°(products) - \sum \Delta_f G°(reactants)$

$\Delta_r G° = 2\ \Delta_f G°\left(HCl_{(g)}\right) - \left[\Delta_f G°\left(H_{2(g)}\right) + \Delta_f G°\left(Cl_{2(g)}\right)\right]$

$\Delta_r G° = 2\left(-95.3\frac{kJ}{mol}\right) - \left[\left(0\frac{kJ}{mol}\right) + \left(0\frac{kJ}{mol}\right)\right]$

$\Delta_r G° = -191\frac{kJ}{mol}$

Step 4: Determine activities for all reactants and products

$a_{H_{2(g)}} = \frac{3.5\ bar}{1\ bar} = 3.5$ $a_{HCl_{(g)}} = \frac{0.5\ bar}{1\ bar} = 0.5$

$a_{Cl_{2(g)}} = \frac{3.5\ bar}{1\ bar} = 3.5$

Step 5: Calculate reaction quotient

$Q = \frac{\left(a_{HCl_{(g)}}\right)^2}{\left(a_{H_{2(g)}}\right)\left(a_{Cl_{2(g)}}\right)} = \frac{(0.5)^2}{(3.5)(3.5)} = 0.02$

Step 6: Calculate free energy change for reaction under nonstandard conditions

$$\Delta_r G = \Delta_r G° + RTlnQ$$

$$\Delta_r G = \left(-191\,\frac{kJ}{mol}\right) + \left(8.314\,462\,\frac{J}{mol \cdot K}\right)\left(\frac{1\,kJ}{1000\,J}\right)(298.15\,K)ln(0.02)$$

$$\Delta_r G = \left(-191\,\frac{kJ}{mol}\right) + \left(-9.6\,\frac{kJ}{mol}\right)$$

$$\Delta_r G = -2.00 \times 10^2\,\frac{kJ}{mol}$$

Step 7: Check your work

*Does your answer seem reasonable? Are sig. fig. correct?*

Answer is written in scientific notation to ensure that the number of significant figures is clear (since writing -200 is ambiguous).

All digits of answers to intermediate steps were carried through to the final calculation to prevent rounding error. The answer key only shows significant figures to help you follow them.
$ln(0.02) = -3.9$ (one sig. fig. in 0.02 therefore one decimal place in -3.9).

3.   *The equilibrium constant for a reaction can be calculated from the activities of all reactants and products when equilibrium has been reached.*

Step 1: Write a balanced chemical equation for the reaction

This was provided in the question.

$$4\,HCl_{(g)} + O_{2(g)} \rightarrow\ 2\,Cl_{2(g)} + 2\,H_2O_{(g)}$$
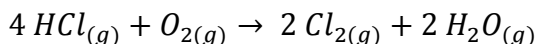
Step 2: Determine activities for all reactants and products

Since all reactants and products are gases, their activity can be determined from the partial pressure (in bar). To calculate pressure from the data provided (mass, temperature and volume), use the ideal gas law. You will first need to calculate the moles of each gas from the mass of that gas and its molar mass. A sample calculation is shown below. Temperature must be in Kelvin.

$$n_{Cl_2} = 60\,g \times \frac{1\,mol}{2(35.5427\,g)} = 0.85\,mol$$

$$PV = nRT$$

$$P_{Cl_2} = \frac{nRT}{V} = \frac{(0.85\,mol)\left(8.314\,462\,\frac{Pa \cdot m^3}{mol \cdot K}\right)(673.15\,K)}{(2\,L)} \times \frac{1000\,L}{1\,m^3} \times \frac{1\,bar}{10^5\,Pa} = 23.68\,bar = 2 \times 10^1\,bar$$

$$a_{Cl_{2(g)}} = \frac{23.68\,bar}{1\,bar} = 23.68 = 2 \times 10^1$$

While each activity only has 1 sig. fig. (due to the volume only having 1 sig. fig.), make sure you carry through all the digits in your calculator when calculating K. Of course, K will only be accurate to 1 sig. fig. as well, so the final answer should be rounded.

The other activities are calculated using the same approach to give:

$$a_{H_2O_{(g)}} = 18.64 = 2 \times 10^1$$

$$a_{HCl_{(g)}} = 15.35 = 2 \times 10^1$$

$$a_{O_{2(g)}} = 6.996 = 7 \times 10^0$$

Step 3: Calculate equilibrium constant

$$K = \frac{\left(a_{Cl_{2(g)}}\right)^2 \left(a_{H_2O_{(g)}}\right)^2}{\left(a_{HCl_{(g)}}\right)^4 \left(a_{O_{2(g)}}\right)} = \frac{(23.68)^2 (18.64)^2}{(15.35)^4 (6.996)} = 0.5$$

Step 4: Check your work

Does your answer seem reasonable? Are sig. fig. correct?

4.   *Since quantities of all reactants and products in an equilibrium mixture are not provided, a different approach must be used to calculate K. Equilibrium constants can also be calculated from the standard free energy change for a reaction.*

Step 1: Write a balanced chemical equation for the reaction

This was provided in the question.
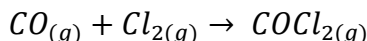
$$CO_{(g)} + Cl_{2(g)} \rightarrow COCl_{2(g)}$$

Step 2: Convert temperature to Kelvin (if necessary)

$$T = 25\ °C = 298.15\ K$$

Step 3: Calculate the standard free energy change for the reaction

$$\Delta_r G° = \sum \Delta_f G°(products) - \sum \Delta_f G°(reactants)$$
$$\Delta_r G° = \Delta_f G°\left(COCl_{2(g)}\right) - \left[\Delta_f G°\left(CO_{(g)}\right) + \Delta_f G°\left(Cl_{2(g)}\right)\right]$$
$$\Delta_r G° = \left(-206\frac{kJ}{mol}\right) - \left[\left(-137.2\frac{kJ}{mol}\right) + \left(0\frac{kJ}{mol}\right)\right]$$
$$\Delta_r G° = -68.8\frac{kJ}{mol} = -69\frac{kJ}{mol}$$

Step 4: Calculate the equilibrium constant from the standard free energy change

$$\Delta_r G° = -RT\ln K$$
$$\ln K = -\frac{\Delta_r G°}{RT}$$
$$\ln K = -\frac{\left(-69\frac{kJ}{mol}\right)}{\left(8.314\ 462\frac{J}{mol·K}\right)(298.15\ K)} \times \frac{1000\ J}{1\ kJ}$$
$$\ln K = 28$$
$$K = e^{28}$$
$$K = 1 \times 10^{12}$$

Step 5: Check your work

Does your answer seem reasonable?

A negative standard free energy indicates a reaction that is thermodynamically allowed in the forward direction. This is consistent with a large equilibrium constant under standard conditions.

5.   *The easiest approach to this question is to calculate Q and compare it to K.*

- *If Q is smaller than K, the forward reaction will proceed.*
- *If Q is larger than K, the reverse reaction will proceed.*
- *If Q is equal to K, the system is already at equilibrium so there is no net reaction.*

Step 1: Write a balanced chemical equation for the reaction

This was provided in the question.

$$H_{2(g)} + I_{2(s)} \rightarrow 2\ HI_{(g)}$$
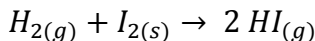
Step 2: Determine activities for all reactants and products

$$a_{H_{2(g)}} = \frac{0.400\ bar}{1\ bar} = 0.400 \qquad\qquad a_{HI_{(g)}} = \frac{0.300\ bar}{1\ bar} = 0.300$$

$$a_{I_{2(s)}} = 1$$

Step 3: Calculate reaction quotient

$$Q = \frac{\left(a_{HI_{(g)}}\right)^2}{\left(a_{H_{2(g)}}\right)\left(a_{I_{2(s)}}\right)} = \frac{(0.300)^2}{(0.400)(1)} = 0.225$$

Step 4: Compare Q to K ($K = 0.352$)

Q < K therefore the reaction will proceed forward (as written).

Step 5: Check your work

Does your answer seem reasonable? Are sig. fig. correct?

6.   *There are two equally valid approaches to this question. Both require calculation of the standard free energy change for the reaction and the reaction quotient for the actual reaction conditions.*

Approach A is to calculate the free energy change for the reaction under these conditions using $\Delta_r G = \Delta_r G° + RT\ln Q$. If $\Delta_r G < 0$, the reaction is spontaneous (thermodynamically allowed in the forward direction).

Approach B is to calculate the equilibrium constant for the reaction from the standard free energy change. If $Q < K$, the reaction is spontaneous (thermodynamically allowed in the forward direction).

Step 1: Write a balanced chemical equation for the reaction
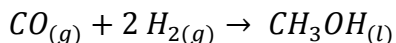
$$CO_{(g)} + 2\ H_{2(g)} \rightarrow CH_3OH_{(l)}$$

Step 2: Convert temperature to Kelvin (if necessary)

$$T = 25\ °C = 298.15\ K$$

Step 3: Calculate the standard free energy change for the reaction

$$\Delta_r G° = \sum \Delta_f G°(products) - \sum \Delta_f G°(reactants)$$

$$\Delta_r G° = \Delta_f G°\left(CH_3OH_{(l)}\right) - \left[\Delta_f G°\left(CO_{(g)}\right) + 2\ \Delta_f G°\left(H_{2(g)}\right)\right]$$

$$\Delta_r G° = \left(-166.3\ \tfrac{kJ}{mol}\right) - \left[\left(-137.2\ \tfrac{kJ}{mol}\right) + 2\left(0\ \tfrac{kJ}{mol}\right)\right]$$

$$\Delta_r G° = -29.1\ \tfrac{kJ}{mol}$$

Step 4: Determine activities for all reactants and products

$$a_{CO_{(g)}} = \frac{0.4\ bar}{1\ bar} = 0.4 \qquad\qquad\qquad a_{CH_3OH_{(l)}} = 1$$

$$a_{H_{2(g)}} = \frac{1.5\ bar}{1\ bar} = 1.5$$

Step 5: Calculate reaction quotient

$$Q = \frac{\left(a_{CH_3OH_{(l)}}\right)}{\left(a_{CO_{(g)}}\right)\left(a_{H_{2(g)}}\right)^2} = \frac{(1)}{(0.4)(1.5)^2} = 1.11 = 1$$

Step 6A: Calculate free energy change for reaction under nonstandard conditions

$$\Delta_r G = \Delta_r G° + RT \ln Q$$

$$\Delta_r G = \left(-29.1 \frac{kJ}{mol}\right) + \left(8.314\ 462 \frac{J}{mol \cdot K}\right)\left(\frac{1\ kJ}{1000\ J}\right)(298.15\ K)\ln(1.11)$$

$$\Delta_r G = \left(-29.1 \frac{kJ}{mol}\right) + \left(0.26 \frac{kJ}{mol}\right)$$

$$\Delta_r G = -28.8 \frac{kJ}{mol}$$

The free energy change for the reaction under these conditions is negative therefore the reaction is thermodynamically allowed and would be worth trying. It is, of course, possible that other factors (particularly kinetics) might make the reaction impractical.

Step 6B: Calculate equilibrium constant from standard free energy change

$$\Delta_r G° = -RT \ln K$$

$$\ln K = -\frac{\Delta_r G°}{RT}$$

$$\ln K = -\frac{\left(-29.1 \frac{kJ}{mol}\right)}{\left(8.314\ 462 \frac{J}{mol \cdot K}\right)(298.15\ K)} \times \frac{1000\ J}{1\ kJ}$$

$$\ln K = 11.7$$

$$K = e^{11.7}$$

$$K = 1 \times 10^5 \qquad\qquad\qquad \textbf{\textit{compare to } Q = 1}$$

Since $Q < K$, the reaction is thermodynamically allowed under these conditions and would be worth trying. It is, of course, possible that other factors (particularly kinetics) might make the reaction impractical.

Step 7: Check your work

Does your answer seem reasonable?

7.   *As in question 6, there are two approaches to this question. Both require the calculation of the*
standard free energy change for the reaction and the reaction quotient.

Step 1: Write a balanced chemical equation for the reaction

$$2\,SO_{2(g)} + O_{2(g)} \rightarrow 2\,SO_{3(g)}$$
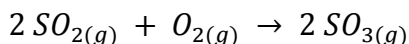
Step 2: Convert temperature to Kelvin (if necessary)

$$T = 25.00\,°C = 298.15\,K$$

Step 3: Calculate the standard free energy change for the reaction

$$\Delta_r G° = \sum \Delta_f G°(products) - \sum \Delta_f G°(reactants)$$

$$\Delta_r G° = 2\,\Delta_f G°\big(SO_{3(g)}\big) - \big[2\,\Delta_f G°\big(SO_{2(g)}\big) + \Delta_f G°\big(O_{2(g)}\big)\big]$$

$$\Delta_r G° = 2\left(-371.1\,\tfrac{kJ}{mol}\right) - \left[2\left(-300.2\,\tfrac{kJ}{mol}\right) + \left(0\,\tfrac{kJ}{mol}\right)\right]$$

$$\Delta_r G° = -141.8\,\tfrac{kJ}{mol}$$

Step 4: Determine activities for all reactants and products

$$a_{SO_{2(g)}} = \frac{0.45\,bar}{1\,bar} = 0.45 \qquad\qquad a_{SO_{3(g)}} = \frac{5.00\,bar}{1\,bar} = 5.00$$

$$a_{O_{2(g)}} = \frac{0.21\,bar}{1\,bar} = 0.21$$

Step 5: Calculate reaction quotient

$$Q = \frac{\big(a_{SO_{3(g)}}\big)^2}{\big(a_{SO_{2(g)}}\big)^2 \big(a_{O_{2(g)}}\big)} = \frac{(5.00)^2}{(0.45)^2(0.21)} = 588 = 5.9 \times 10^2$$

Step 6A: Calculate free energy change for reaction under nonstandard conditions

$$\Delta_r G = \Delta_r G° + RTlnQ$$

$$\Delta_r G = \left(-141.8\,\tfrac{kJ}{mol}\right) + \left(8.314\,462\,\tfrac{J}{mol\cdot K}\right)\left(\tfrac{1\,kJ}{1000\,J}\right)(298.15\,K)ln(588)$$

$$\Delta_r G = \left(-141.8\,\tfrac{kJ}{mol}\right) + \left(15.8\,\tfrac{kJ}{mol}\right)$$

$$\Delta_r G = -126.0\,\tfrac{kJ}{mol}$$

The free energy change for the reaction under these conditions is negative therefore the reaction
is thermodynamically allowed.

Step 6B: Calculate equilibrium constant from standard free energy change

$$\Delta_r G° = -RTlnK$$

$$lnK = -\frac{\Delta_r G°}{RT}$$

$$lnK = -\frac{\left(-141.8\,\tfrac{kJ}{mol}\right)}{\left(8.314\,462\,\tfrac{J}{mol\cdot K}\right)(298.15\,K)} \times \frac{1000\,J}{1\,kJ}$$

$$lnK = 57.20$$

$$K = e^{57.20}$$

$$K = 7.0 \times 10^{24} \qquad\qquad\qquad\qquad\quad \boldsymbol{compare\ to\ Q = 5.9 \times 10^2}$$

Since $Q < K$, the reaction is thermodynamically allowed under these conditions.

Step 7: Check your work

Does your answer seem reasonable?

8.

(a) $\quad Q = \dfrac{\left(a_{KCl_{(s)}}\right)^2 \left(a_{O_{2(g)}}\right)^3}{\left(a_{KClO_{3(s)}}\right)^2}$

(b) $\quad Q = \dfrac{(1)^2 \left(\frac{P_{O_{2(g)}}}{1\ bar}\right)^3}{(1)^2} = \left(\dfrac{P_{O_{2(g)}}}{1\ bar}\right)^3$

(c) *Equilibrium constants can be calculated from the standard free energy change for a reaction. The equilibrium constant can then be used to calculate the activity of oxygen gas (and therefore the partial pressure of oxygen gas) at equilibrium.*

Step 1: Write a balanced chemical equation for the reaction

This was provided in the question.

$2\ KClO_{3(s)} \rightarrow 2\ KCl_{(s)} + 3\ O_{2(g)}$
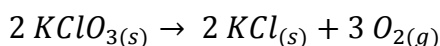
Step 2: Convert temperature to Kelvin (if necessary)

$T = 25\ °C = 298.15\ K$

Step 3: Calculate the standard free energy change for the reaction

$\Delta_r G° = \sum \Delta_f G°(products) - \sum \Delta_f G°(reactants)$

$\Delta_r G° = \left[2\,\Delta_f G°\left(KCl_{(s)}\right) + 3\,\Delta_f G°\left(O_{2(g)}\right)\right] - 2\,\Delta_f G°\left(KClO_{3(s)}\right)$

$\Delta_r G° = \left[2\left(-409.1\frac{kJ}{mol}\right) + 3\left(0\frac{kJ}{mol}\right)\right] - 2\left(-296.3\frac{kJ}{mol}\right)$

$\Delta_r G° = -225.6\frac{kJ}{mol}$

Step 4: Calculate the equilibrium constant from the standard free energy change

$\Delta_r G° = -RTlnK$

$lnK = -\dfrac{\Delta_r G°}{RT}$

$lnK = -\dfrac{\left(-225.6\frac{kJ}{mol}\right)}{\left(8.314\ 462\frac{J}{mol\cdot K}\right)(298.15\ K)} \times \dfrac{1000\ J}{1\ kJ}$

$lnK = 91.01$

$K = e^{91.01}$

$K = 3.3 \times 10^{39}$

Step 5: Calculate the equilibrium pressure of $O_{2(g)}$ from the equilibrium constant

K is simply Q under equilibrium conditions. Therefore, to find the equilibrium pressure of $O_{2(g)}$:

$K = \left(\dfrac{P_{O_{2(g)}}}{1\ bar}\right)^3$

$P_{O_{2(g)}} = \sqrt[3]{K} \cdot 1\ bar$

$P_{O_{2(g)}} = \sqrt[3]{3.3 \times 10^{39}} \cdot 1\ bar$

$P_{O_{2(g)}} = 1.5 \times 10^{13}\ bar$

Step 6: Check your work

Does your answer seem reasonable?

A negative standard free energy indicates a reaction that is thermodynamically allowed in the forward direction. This is consistent with a large equilibrium constant under standard conditions. The very large equilibrium constant is consistent with a very high partial pressure of the oxygen gas produced by the time that equilibrium would be reached.

(d)   In order to reach equilibrium, enough $KClO_3$ must react to produce over ten trillion bars of oxygen – more than ten trillion times atmospheric pressure. That's a *lot* of $KClO_3$ and would require a very strong container. As such, the reaction is likely to stop before reaching equilibrium. Also, it is unlikely that oxygen is still in the gas phase at this high pressure.

In a 1 L flask, more than 600 billion moles of oxygen would be needed to reach this pressure. That would require more than 49 trillion grams of KClO₃ – a lot of salt to fit in a 1 L container!

9.

(a)   In the standard state, all activities are 1 therefore $Q = 1$.

 This makes $\ln Q = 0$ therefore $\Delta G = \Delta G°$

(b)   i.   Increasing the concentration of a reactant increases its activity. This decreases Q.

 As Q decreases, $\ln Q$ decreases. Therefore, ΔG becomes more negative and the reaction becomes more favoured in the forward direction.

 ii.   Decreasing the volume increases the pressures of all reactants and products that are gases. This increases all of their activities.

 If there are more gas molecules on the reactant side then the denominator of Q will increase by more than the numerator therefore Q decreases. As Q decreases, $\ln Q$ decreases. Therefore, ΔG becomes more negative and the reaction becomes more favoured in the forward direction.

 The second part of the argument could equally be made for a reaction with more gaseous products – in which case, Q increases, lnQ increases and ΔG becomes more positive, making the reaction more favoured in the reverse direction.

10.

(a) $P_{4(s)} + 5\,O_{2(g)} \;\rightarrow\; P_4O_{10(s)}$
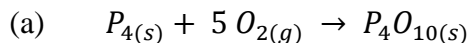
(b) $Q = \dfrac{\left(a_{P_4O_{10(s)}}\right)}{\left(a_{P_{4(s)}}\right)\left(a_{O_{2(g)}}\right)^5}$

(c)   **Step 1: Write a balanced chemical equation for the reaction**

 see part (a)

 Step 2: Convert temperature to Kelvin (if necessary)

 $T = 25\,°C = 298.15\,K$

Step 3: Calculate the standard free energy change for the reaction

$\Delta_r G° = \sum \Delta_f G°(products) - \sum \Delta_f G°(reactants)$

$\Delta_r G° = \Delta_f G°(P_4O_{10(s)}) - [\Delta_f G°(P_{4(s)}) + 5\,\Delta_f G°(O_{2(g)})]$

$\Delta_r G° = \left(-2697.7\,\frac{kJ}{mol}\right) - \left[\left(0\,\frac{kJ}{mol}\right) + 5\left(0\,\frac{kJ}{mol}\right)\right]$

$\Delta_r G° = -2697.7\,\frac{kJ}{mol}$

Step 4: Determine activities for all reactants and products

$a_{P_{4(s)}} = 1$ $\qquad\qquad\qquad\qquad\qquad\qquad a_{P_4O_{10(s)}} = 1$

$a_{O_{2(g)}} = \frac{0.21\,bar}{1\,bar} = 0.21$

Step 5: Calculate reaction quotient

$Q = \dfrac{\left(a_{P_4O_{10(s)}}\right)}{\left(a_{P_{4(s)}}\right)\left(a_{O_{2(g)}}\right)^5} = \dfrac{(1)}{(1)(0.21)^5} = 2.4 \times 10^3$

Step 6: Calculate free energy change for reaction under nonstandard conditions

$\Delta_r G = \Delta_r G° + RTlnQ$

$\Delta_r G = \left(-2697.7\,\frac{kJ}{mol}\right) + \left(8.314\,462\,\frac{J}{mol \cdot K}\right)\left(\frac{1\,kJ}{1000\,J}\right)(298.15\,K)ln(2.4 \times 10^3)$

$\Delta_r G = \left(-2697.7\,\frac{kJ}{mol}\right) + \left(19.3\,\frac{kJ}{mol}\right)$

$\Delta_r G = -2678.4\,\frac{kJ}{mol}$

The free energy change for the reaction under these conditions is negative therefore the reaction is thermodynamically allowed in the forward direction.

Step 7: Check your work

Does your answer seem reasonable?

We know from CHEM 1000 that white phosphorus reacts readily with oxygen, so it makes sense that the forward reaction is thermodynamically allowed for atmospheric levels of oxygen.

11. *Equilibrium constants can be calculated from the standard free energy change for a reaction.*

Step 1: Write a balanced chemical equation for the reaction

This was provided in the question.

$Cl_{2(g)} + 2\,OH^-_{(aq)} \rightarrow Cl^-_{(aq)} + OCl^-_{(aq)} + H_2O_{(l)}$
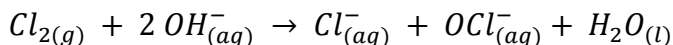
Step 2: Convert temperature to Kelvin (if necessary)

$T = 25\,°C = 298.15\,K$

Step 3: Calculate the standard free energy change for the reaction

$\Delta_r G° = \sum \Delta_f G°(products) - \sum \Delta_f G°(reactants)$

$\Delta_r G° = [\Delta_f G°(Cl^-_{(aq)}) + \Delta_f G°(OCl^-_{(aq)}) + \Delta_f G°(H_2O_{(l)})] - [\Delta_f G°(Cl_2) + 2\,\Delta_f G°(OH^-_{(aq)})]$

$\Delta_r G° = \left[\left(-131.0\,\frac{kJ}{mol}\right) + \left(-36.8\,\frac{kJ}{mol}\right) + \left(-237.1\,\frac{kJ}{mol}\right)\right] - \left[\left(0\,\frac{kJ}{mol}\right) + 2\left(-157.2\,\frac{kJ}{mol}\right)\right]$

$\Delta_r G° = -90.5\,\frac{kJ}{mol}$

Step 4: Calculate the equilibrium constant from the standard free energy change

$\Delta_r G° = -RT \ln K$

$\ln K = -\dfrac{\Delta_r G°}{RT}$

$\ln K = -\dfrac{\left(-90.5\frac{kJ}{mol}\right)}{\left(8.314\,462\frac{J}{mol \cdot K}\right)(298.15\ K)} \times \dfrac{1000\ J}{1\ kJ}$

$\ln K = 36.5$

$K = e^{36.5}$

$K = 7 \times 10^{15}$

Step 5: Check your work

*Does your answer seem reasonable?*

A negative standard free energy indicates a reaction that is thermodynamically allowed in the forward direction. This is consistent with a large equilibrium constant under standard conditions.

12.

(a) $\quad Q = \dfrac{\left(a_{BF_{3(g)}}\right)^2 \left(a_{H_2O_{(l)}}\right)^3}{\left(a_{B_2O_{3(s)}}\right)\left(a_{HF_{(g)}}\right)^6}$

(b) **Step 1: Write a balanced chemical equation for the reaction**

This was provided in the question.

$B_2O_{3(s)} + 6\ HF_{(g)} \rightarrow 2\ BF_{3(g)} + 3\ H_2O_{(l)}$
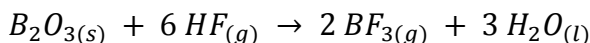
Step 2: Convert temperature to Kelvin (if necessary)

$T = 25.00\ °C = 298.15\ K$

Step 3: Calculate the standard free energy change for the reaction

$\Delta_r G° = \sum \Delta_f G°(products) - \sum \Delta_f G°(reactants)$

$\Delta_r G° = \left[2\ \Delta_f G°\left(BF_{3(g)}\right) + 3\ \Delta_f G°\left(H_2O_{(l)}\right)\right] - \left[\Delta_f G°\left(B_2O_{3(s)}\right) + 6\ \Delta_f G°\left(HF_{(g)}\right)\right]$

$\Delta_r G° = \left[2\left(-1120.3\frac{kJ}{mol}\right) + 3\left(-237.1\frac{kJ}{mol}\right)\right] - \left[\left(-1193.7\frac{kJ}{mol}\right) + 6\left(-273.2\frac{kJ}{mol}\right)\right]$

$\Delta_r G° = -119.0\frac{kJ}{mol}$

Step 4: Determine activities for all reactants and products

$a_{B_2O_{3(s)}} = 1$ $\qquad\qquad\qquad\qquad\qquad a_{BF_{3(g)}} = \dfrac{0.36\ bar}{1\ bar} = 0.36$

$a_{HF_{(g)}} = \dfrac{0.25\ bar}{1\ bar} = 0.25$ $\qquad\qquad a_{H_2O_{(l)}} = 1$

Step 5: Calculate reaction quotient

$Q = \dfrac{\left(a_{BF_{3(g)}}\right)^2 \left(a_{H_2O_{(l)}}\right)^3}{\left(a_{B_2O_{3(s)}}\right)\left(a_{HF_{(g)}}\right)^6} = \dfrac{(0.36)^2(1)^3}{(1)(0.25)^6} = 531 = 5.3 \times 10^2$

Step 6: Calculate free energy change for reaction under nonstandard conditions

$\Delta_r G = \Delta_r G° + RTlnQ$

$\Delta_r G = \left(-119.0\frac{kJ}{mol}\right) + \left(8.314\ 462\frac{J}{mol \cdot K}\right)\left(\frac{1\ kJ}{1000\ J}\right)(298.15\ K)ln(5.3 \times 10^2)$

$\Delta_r G = \left(-119.0\frac{kJ}{mol}\right) + \left(15.5\frac{kJ}{mol}\right)$

$\Delta_r G = -103.4\frac{kJ}{mol}$

The free energy change for the reaction under these conditions is negative therefore the reaction is thermodynamically allowed in the forward direction.
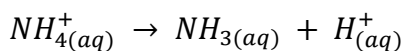
Step 7: Check your work

Does your answer seem reasonable?

13. *Equilibrium constants can be calculated from the standard free energy change for a reaction.*

Step 1: Write a balanced chemical equation for the reaction

This was provided in the question.

$NH_{4(aq)}^{+} \rightarrow NH_{3(aq)} + H_{(aq)}^{+}$

Step 2: Convert temperature to Kelvin (if necessary)

$T = 25\ °C = 298.15\ K$

Step 3: Calculate the standard free energy change for the reaction

$\Delta_r G° = \sum \Delta_f G°(products) - \sum \Delta_f G°(reactants)$

$\Delta_r G° = \left[\Delta_f G°\left(NH_{3(aq)}\right) + \Delta_f G°\left(H_{(aq)}^{+}\right)\right] - \Delta_f G°\left(NH_{4(aq)}^{+}\right)$

$\Delta_r G° = \left[\left(-26.50\frac{kJ}{mol}\right) + \left(0\frac{kJ}{mol}\right)\right] - \left(-79.31\frac{kJ}{mol}\right)$

$\Delta_r G° = +52.81\frac{kJ}{mol}$

Step 4: Calculate the equilibrium constant from the standard free energy change

$\Delta_r G° = -RTlnK$

$lnK = -\frac{\Delta_r G°}{RT}$

$lnK = -\frac{\left(+52.81\frac{kJ}{mol}\right)}{\left(8.314\ 462\frac{J}{mol \cdot K}\right)(298.15\ K)} \times \frac{1000\ J}{1\ kJ}$

$lnK = -21.30$

$K = e^{-21.30}$

$K = 5.6 \times 10^{-10}$

Step 5: Check your work

Does your answer seem reasonable?

A positive standard free energy indicates a reaction that is thermodynamically allowed in the reverse direction. This is consistent with an equilibrium constant significantly smaller than 1 under standard conditions.

14. *As in questions 6 and 7, there are two approaches to this question. Both require the calculation of the standard free energy change for the reaction and the reaction quotient.*

Step 1: Write a balanced chemical equation for the reaction

This was provided in the question.

$$Mg_{(s)} + 2\,H^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_{2(g)}$$
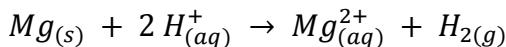
Step 2: Convert temperature to Kelvin (if necessary)

$$T = 25.00\,°C = 298.15\,K$$

Step 3: Calculate the standard free energy change for the reaction

$$\Delta_r G° = \sum \Delta_f G°(products) - \sum \Delta_f G°(reactants)$$

$$\Delta_r G° = \left[\Delta_f G°\left(Mg^{2+}_{(aq)}\right) + \Delta_f G°\left(H_{2(g)}\right)\right] - \left[\Delta_f G°\left(Mg_{(s)}\right) + 2\,\Delta_f G°\left(H^+_{(aq)}\right)\right]$$

$$\Delta_r G° = \left[\left(-454.8\,\tfrac{kJ}{mol}\right) + \left(0\,\tfrac{kJ}{mol}\right)\right] - \left[\left(0\,\tfrac{kJ}{mol}\right) + 2\left(0\,\tfrac{kJ}{mol}\right)\right]$$

$$\Delta_r G° = -454.8\,\tfrac{kJ}{mol}$$

Step 4: Determine activities for all reactants and products

$$a_{Mg_{(s)}} = 1 \qquad\qquad a_{Mg^{2+}_{(aq)}} = \frac{0.100\,M}{1\,M} = 0.100$$

$$a_{H^+_{(aq)}} = 10^{-pH} = 10^{-6.00} = 1.00 \times 10^{-6} \qquad\qquad a_{H_{2(g)}} = \frac{2.00\,bar}{1\,bar} = 2.00$$

Step 5: Calculate reaction quotient

$$Q = \frac{\left(a_{Mg^{2+}_{(aq)}}\right)\left(a_{H_{2(g)}}\right)}{\left(a_{Mg_{(s)}}\right)\left(a_{H^+_{(aq)}}\right)^2} = \frac{(0.100)(2.00)}{(1)(1.00 \times 10^{-6})^2} = 2.00 \times 10^{11}$$

Step 6A: Calculate free energy change for reaction under nonstandard conditions

$$\Delta_r G = \Delta_r G° + RT\ln Q$$

$$\Delta_r G = \left(-454.8\,\tfrac{kJ}{mol}\right) + \left(8.314\,462\,\tfrac{J}{mol\cdot K}\right)\left(\tfrac{1\,kJ}{1000\,J}\right)(298.15\,K)\ln(2.00 \times 10^{11})$$

$$\Delta_r G = \left(-454.8\,\tfrac{kJ}{mol}\right) + \left(64.506\,\tfrac{kJ}{mol}\right)$$

$$\Delta_r G = -390.3\,\tfrac{kJ}{mol}$$

The free energy change for the reaction under these conditions is negative therefore the reaction is thermodynamically allowed.

Step 6B: Calculate equilibrium constant from standard free energy change

$$\Delta_r G° = -RT\ln K$$

$$\ln K = -\frac{\Delta_r G°}{RT}$$

$$\ln K = -\frac{\left(-454.8\,\tfrac{kJ}{mol}\right)}{\left(8.314\,462\,\tfrac{J}{mol\cdot K}\right)(298.15\,K)} \times \frac{1000\,J}{1\,kJ}$$

$$\ln K = 183.5$$

$$K = e^{183.5}$$

$$K = 4.759 \times 10^{79} \qquad\qquad\qquad \textit{\textbf{compare to }} Q = \textbf{6.00} \times \textbf{10}^{\textbf{11}}$$

Since $Q < K$, the reaction is thermodynamically allowed under these conditions.

Step 7: Check your work

Does your answer seem reasonable?

In CHEM 1000, you learned that acids react with metals to produce hydrogen gas. It therefore makes sense that this reaction is thermodynamically favoured in the forward direction (given that neither product has a particularly high activity).

15. *The standard free energy change for this reaction can be calculated from the equilibrium constant. It can then be used (along with standard free energies of formation for all other products and reactants) to calculate the standard free energy of formation of $Ba^{2+}_{(aq)}$.*

Step 1: Write a balanced chemical equation for the reaction

This was provided in the question.

$$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$
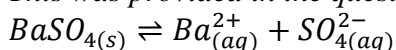
Step 2: Convert temperature to Kelvin (if necessary)

$$T = 25 \,°C = 298.15 \, K$$

Step 3: Calculate the standard free energy change from the equilibrium constant

$$\Delta_r G° = -RTlnK$$

$$\Delta_r G° = -\left(8.314\,462\,\frac{J}{mol \cdot K}\right)(298.15 \, K)ln(1.1 \times 10^{-10})$$

$$\Delta_r G° = \left(5.684 \times 10^4 \,\frac{J}{mol}\right)\left(\frac{1 \, kJ}{1000 \, J}\right)$$

$$\Delta_r G° = +56.84\,\frac{kJ}{mol}$$

Step 4: Calculate the standard free energy of formation for $Ba^{2+}_{(aq)}$

$$\Delta_r G° = \sum \Delta_f G°(products) - \sum \Delta_f G°(reactants)$$

$$\Delta_r G° = \left[\Delta_f G°\left(Ba^{2+}_{(aq)}\right) + \Delta_f G°\left(SO^{2-}_{4(aq)}\right)\right] - \Delta_f G°\left(BaSO_{4(s)}\right)$$

$$\Delta_f G°\left(Ba^{2+}_{(aq)}\right) = \Delta_r G° - \Delta_f G°\left(SO^{2-}_{4(aq)}\right) + \Delta_f G°\left(BaSO_{4(s)}\right)$$

$$\Delta_f G°\left(Ba^{2+}_{(aq)}\right) = \left(+56.84\,\frac{kJ}{mol}\right) - \left(-744.5\,\frac{kJ}{mol}\right) + \left(-1362\,\frac{kJ}{mol}\right)$$

$$\Delta_f G°\left(Ba^{2+}_{(aq)}\right) = -561\,\frac{kJ}{mol}$$

This is very close to the value provided on the data sheet $\left(-560.8\,\frac{kJ}{mol}\right)$.

Step 5: Check your work

Does your answer seem reasonable?

16. *As in questions 6, 7, and 14, there are two approaches to this question. Both require the calculation of the standard free energy change for the reaction and the reaction quotient.*

Step 1: Write a balanced chemical equation for the reaction

$$Ca^{2+}_{(aq)} + 2\,F^-_{(aq)} \rightleftharpoons CaF_{2(s)}$$
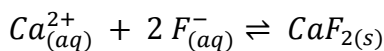
Step 2: Convert temperature to Kelvin (if necessary)

$$T = 25\,°C = 298.15\,K$$

Step 3: Calculate the standard free energy change for the reaction

$$\Delta_r G° = \sum \Delta_f G°(products) - \sum \Delta_f G°(reactants)$$

$$\Delta_r G° = \Delta_f G°\left(CaF_{2(s)}\right) - \left[\Delta_f G°\left(Ca^{2+}_{(aq)}\right) + 2\,\Delta_f G°\left(F^-_{(aq)}\right)\right]$$

$$\Delta_r G° = \left(-1167\,\frac{kJ}{mol}\right) - \left[\left(-553.6\,\frac{kJ}{mol}\right) + 2\left(-278.8\,\frac{kJ}{mol}\right)\right]$$

$$\Delta_r G° = -55.8\,\frac{kJ}{mol} = -56\,\frac{kJ}{mol}$$

Step 4: Determine activities for all reactants and products

Because two solutions were combined, the total volume increased; however, the number of moles of each ion did not. As such, the concentrations must be re-calculated for the new total volume before they can be used to calculate activities.

$$V_{total} = 15\,mL + 25\,mL = 40\,mL$$

$$M_1 V_1 = M_2 V_2 \text{ therefore } M_2 = \frac{M_1 V_1}{V_2}$$

$$M_{Ca^{2+}} = \frac{\left(2.8\times10^{-4}\,\frac{mol}{L}\right)(15\,mL)}{(40\,mL)} = 1.05 \times 10^{-4}\,\frac{mol}{L} = 1.1 \times 10^{-4}\,\frac{mol}{L}$$

$$M_{F^-} = \frac{\left(8.6\times10^{-3}\,\frac{mol}{L}\right)(25\,mL)}{(40\,mL)} = 5.375 \times 10^{-3}\,\frac{mol}{L} = 5.4 \times 10^{-3}\,\frac{mol}{L}$$

Having done this, now calculate the activities.

$$a_{Ca^{2+}_{(aq)}} = \frac{1.1\times10^{-4}\,\frac{mol}{L}}{1\,\frac{mol}{L}} = 1.1 \times 10^{-4} \qquad\qquad a_{CaF_{2(s)}} = 1$$

$$a_{F^-_{(aq)}} = \frac{5.4\times10^{-3}\,\frac{mol}{L}}{1\,\frac{mol}{L}} = 5.4 \times 10^{-3}$$

Step 5: Calculate reaction quotient

$$Q = \frac{\left(a_{CaF_{2(s)}}\right)}{\left(a_{Ca^{2+}_{(aq)}}\right)\left(a_{F^-_{(aq)}}\right)^2} = \frac{(1)}{(1.1\times10^{-4})(5.4\times10^{-3})^2} = 3.3 \times 10^8$$

Step 6A: Calculate free energy change for reaction under nonstandard conditions

$$\Delta_r G = \Delta_r G° + RT\ln Q$$

$$\Delta_r G = \left(-56\,\frac{kJ}{mol}\right) + \left(8.314\,462\,\frac{J}{mol\cdot K}\right)\left(\frac{1\,kJ}{1000\,J}\right)(298.15\,K)\ln(3.3 \times 10^8)$$

$$\Delta_r G = \left(-56\,\frac{kJ}{mol}\right) + \left(48.6\,\frac{kJ}{mol}\right)$$

$$\Delta_r G = -7\,\frac{kJ}{mol}$$

The free energy change for the reaction under these conditions is negative therefore the reaction is thermodynamically allowed. We therefore expect $CaF_{2(s)}$ to precipitate.

Step 6B: Calculate equilibrium constant from standard free energy change

$$\Delta_r G° = -RT \ln K$$

$$\ln K = -\frac{\Delta_r G°}{RT}$$

$$\ln K = -\frac{\left(-56\frac{kJ}{mol}\right)}{\left(8.314\,462\frac{J}{mol \cdot K}\right)(298.15\ K)} \times \frac{1000\ J}{1\ kJ}$$

$$\ln K = 23$$

$$K = e^{23}$$

$$K = 6 \times 10^9 \hspace{4cm} \textit{compare to } \boldsymbol{Q = 3.3 \times 10^8}$$

Since $Q < K$, the reaction is thermodynamically allowed under these conditions, so we expect $CaF_{2(s)}$ to precipitate.

Step 7: Check your work

Does your answer seem reasonable?

17.

(a)   temperature is 25 °C (298.15 K)

pressures of all gases are 1 bar

(b) $\Delta_r G°$ must be negative

For a reaction to proceed in the forward direction, Δ_rG must be negative for those conditions. Since this reaction proceeds in the forward direction under standard conditions, Δ_rG° must be negative.

(c) $\Delta_r S°$ is expected to be negative

Gases have larger entropy values than other states of matter. Since this reaction consumes two moles of gas but only generates one mole of gas, the entropy of the system is expected to decrease.

(d) $\Delta_r H°$ is expected to be negative

either: In this reaction, no bonds are broken while one bond is formed. Heat is released when bonds are formed. Therefore, this reaction is exothermic (negative Δ_rH).

or: In order for a reaction to proceed, it must be favoured by enthalpy and/or entropy. This reaction proceeds but is not favoured by entropy. Therefore, it must be favoured by enthalpy (exothermic therefore negative Δ_rH).

(e)   This reaction will not be favoured at sufficiently high temperatures.

$$\Delta_r G = \Delta_r H - T\Delta_r S$$

$\Delta_r H$ and $T\Delta_r S$ are both negative.

At high temperatures, the $T\Delta_r S$ term will dominate: a larger negative number will be subtracted from a smaller negative number. This will give a positive number for $\Delta_r G$, and reactions with positive $\Delta_r G$ are not favoured in the forward direction.

18.

(a) The derivation is flawed. Equilibrium constants are based on <u>activities</u> of substances. When considering solutes in an ideal solution, the activity is equal to its molarity (divided by 1 M). In this system, however, water is not a solute. It is a pure liquid. So, its activity is equal to 1. Therefore, the pK$_a$ of water should be equal to the pK$_w$ of water – which is 14 not 15.7.

Even if we were discussing a solution, water is still the solvent <u>not</u> the solute. As such, we should use the mole fraction of water molecules <u>not</u> the molarity. The mole fraction of water molecules is extremely close to 1 – and cannot possibly be greater than 1!

(b) *Equilibrium constants can be calculated from the standard free energy change for a reaction.*

Step 1: Write a balanced chemical equation for the reaction

$$H_2O_{(l)} \rightarrow H^+_{(aq)} + OH^-_{(aq)}$$
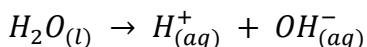
Step 2: Convert temperature to Kelvin (if necessary)

$$T = 25\ °C = 298.15\ K$$

Step 3: Calculate the standard free energy change for the reaction

$$\Delta_r G° = \sum \Delta_f G°(products) - \sum \Delta_f G°(reactants)$$

$$\Delta_r G° = \left[\Delta_f G°\left(H^+_{(aq)}\right) + \Delta_f G°\left(OH^-_{(aq)}\right)\right] - \Delta_f G°\left(H_2O_{(l)}\right)$$

$$\Delta_r G° = \left[\left(0\frac{kJ}{mol}\right) + \left(-157.2\frac{kJ}{mol}\right)\right] - \left(-237.1\frac{kJ}{mol}\right)$$

$$\Delta_r G° = +79.9\frac{kJ}{mol}$$

Step 4: Calculate the equilibrium constant from the standard free energy change

$$\Delta_r G° = -RTlnK$$

$$lnK = -\frac{\Delta_r G°}{RT}$$

$$lnK = -\frac{\left(+79.9\frac{kJ}{mol}\right)}{\left(8.314\ 462\frac{J}{mol·K}\right)(298.15\ K)} \times \frac{1000\ J}{1\ kJ}$$

$$lnK = -32.2$$

$$K = e^{-32.2}$$

$$K = 1 \times 10^{-14}$$
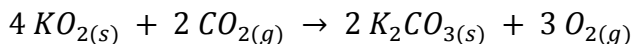
Step 5: Check your work

Does your answer seem reasonable?

This answer matches the officially defined value of K$_w$ = 1×10^{-14}.

19.

(a) **Step 1: Write a balanced chemical equation for the reaction**
This was provided in the question.

$$4\,KO_{2(s)} + 2\,CO_{2(g)} \rightarrow 2\,K_2CO_{3(s)} + 3\,O_{2(g)}$$

Step 2: Write equilibrium constant expression

$$K = \frac{\left(a_{K_2CO_{3(s)}}\right)^2 \left(a_{O_{2(g)}}\right)^3}{\left(a_{KO_{2(s)}}\right)^4 \left(a_{CO_{2(g)}}\right)^2}$$

Step 3: Determine activities for as many reactants and products as possible

$a_{KO_{2(s)}} = 1$

$a_{K_2CO_{3(s)}} = 1$

$a_{CO_{2(g)}} = \frac{0.073\ bar}{1\ bar} = 0.073$

$a_{O_{2(g)}} =???$

Step 4: Solve for missing activity by substituting equilibrium constant and known activities into equilibrium constant expression

$$28.5 = \frac{(1)^2 \left(a_{O_{2(g)}}\right)^3}{(1)^4 (0.073)^2}$$

$$(28.5)(0.073)^2 = \left(a_{O_{2(g)}}\right)^3$$

$$a_{O_{2(g)}} = \sqrt[3]{(28.5)(0.073)^2}$$

$$a_{O_{2(g)}} = 0.53$$

Step 5: Calculate partial pressure of $O_{2(g)}$ from activity

$$a_{O_{2(g)}} = \frac{p_{O_{2(g)}}}{1\ bar}$$

$$p_{O_{2(g)}} = a_{O_{2(g)}} \cdot 1\ bar$$

$$p_{O_{2(g)}} = (0.53) \cdot 1\ bar$$

$$p_{O_{2(g)}} = 0.53\ bar$$

Step 6: Check your work
Does your answer seem reasonable?
0.53 bar is about half of the total normal atmospheric pressure (for all gases; not just oxygen). The answer therefore is of the expected order of magnitude.

(b) Answers could include:
- The reaction will produce a constant partial pressure of oxygen (until the KO_2 runs out) as long as the partial pressure of carbon dioxide is constant. There is no 'decay' in the production of oxygen as the KO_2 is consumed. This is because the activities of KO_2 and K_2CO_3 are both constant since they are both solids.)
- The KO_2 reacts with CO_2 to produce O_2. We breathe in O_2 and breathe out CO_2. So, the breathing device is therefore using the 'waste product' of our respiration as a reactant.
- The byproduct of this reaction is K_2CO_3 which is relatively nontoxic.