## How Far

1. A student investigates the reaction between ethanoic acid, $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{I})$ and methanol, $\mathrm{CH}_{3} \mathrm{OH}(\mathrm{I})$, in the presence of an acid catalyst. The equation is shown below.

$$
\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{I})+\mathrm{CH}_{3} \mathrm{OH}(\mathrm{I}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{COOCH}_{3}(\mathrm{I})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I})
$$

The student carries out an experiment to determine the value of $K_{\mathrm{c}}$ for this reaction.
The student mixes 9.6 g of $\mathrm{CH}_{3} \mathrm{OH}$ with 12.0 g of $\mathrm{CH}_{3} \mathrm{COOH}$ and adds the acid catalyst.
When the mixture reaches equilibrium, 0.030 mol of $\mathrm{CH}_{3} \mathrm{COOH}$ remains.
Calculate $K_{c}$ for this equilibrium.

$$
K_{c}=
$$

2. Methanol, CH 3 OH , can be made industrially by the reaction of carbon monoxide with hydrogen, as shown in equilibrium 1.
$\mathrm{CO}(\mathrm{g})+2 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{OH}(\mathrm{g}) \quad \Delta H=-91 \mathrm{~kJ} \mathrm{~mol}^{-1}$
Equilibrium 1
At 298 K , the free energy change, $\Delta G$, for the production of methanol in equilibrium 1 is $-2.48 \times$ $10^{4} \mathrm{~J} \mathrm{~mol}^{-1}$.
$\Delta G$ is linked to $K_{p}$ by the relationship: $\Delta G=-R T \ln K_{p}$.
$R=$ gas constant
$T=$ temperature in $K$.
Calculate $K_{p}$ for equilibrium 1 at 298 K .
Give your answer to 3 significant figures.
$\qquad$ units

3(a). The equilibrium constant $K_{\mathrm{p}}$ and temperature $T$ (in $K$ ) are linked by the mathematical relationship shown in equation 5.1 ( $R=$ Gas constant in $\mathrm{J} \mathrm{mol}^{-1} \mathrm{~K}^{-1}$ and $\Delta H$ is enthalpy change in $\mathrm{J} \mathrm{mol}^{-1}$ ).

$$
\ln K_{\mathrm{p}}=-\frac{\Delta H}{R} \times \frac{1}{T}+\frac{\Delta S}{R}
$$

Equation 5.1

The table shows the values of $K_{p}$ at different temperatures for an equilibrium. Complete the table by adding the missing values of $\frac{1}{T}$ and $\ln K_{p}$.

| Temperature, $\boldsymbol{T} / \mathbf{K}$ | 400 | 500 | 600 | 700 | 800 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{K p}$ | $3.00 \times 10^{58}$ | $5.86 \times 10^{45}$ | $1.83 \times 10^{37}$ | $1.46 \times 10^{31}$ | $1.14 \times 10^{26}$ |
| $\frac{1}{\boldsymbol{T}} / \mathbf{K}^{-1}$ | $2.50 \times 10^{-3}$ |  |  |  |  |
| $\ln K_{p}$ | 135 |  |  |  |  |

(b). State and explain how increasing the temperature affects the position of this equilibrium and whether the forward reaction is exothermic or endothermic.
$\qquad$
$\qquad$
$\qquad$
(c). Plot a graph of $\ln K_{p}$ against $\frac{1}{T}$ using the axes provided on the opposite page.

Use your graph and equation 5.1 to determine $\Delta H$, in $\mathrm{kJ} \mathrm{mol}^{-1}$, for this equilibrium.
Give your answer to 3 significant figures.
$\qquad$

Explain how $\Delta S$ could be calculated from a graph of $\ln K_{p}$ against $\frac{1}{T}$.
$\qquad$
$\qquad$
$\qquad$

4. What is the partial pressure of $\mathrm{O}_{2}$ (in Pa ) in a gas mixture containing $21 \% \mathrm{O}_{2}$ by volume and with a total pressure of $1.0 \times 10^{5} \mathrm{~Pa}$ ?
5. Succinic acid $\left(\mathrm{CH}_{2} \mathrm{COOH}\right)_{2}$ is esterified by ethanol, $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}$, in the presence of an acid catalyst to form an equilibrium mixture.
Succinic acid is esterified by ethanol, $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}$, in the presence of an acid catalyst to form an equilibrium mixture.

The equilibrium constant, $K_{c}$, for this equilibrium can be calculated using the amounts, in moles, of the components in the equilibrium mixture, using expression 5.1.

$$
K_{\mathrm{c}}=\frac{n\left(\left(\mathrm{CH}_{2} \mathrm{COOC}_{2} \mathrm{H}_{5}\right)_{2}\right) \times n\left(\mathrm{H}_{2} \mathrm{O}\right)^{2}}{n\left(\left(\mathrm{CH}_{2} \mathrm{COOH}\right)_{2}\right) \times n\left(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}\right)^{2}} \quad \quad \text { Expression } 5.1
$$

A student carries out an experiment to determine the value of $K_{\mathrm{c}}$ for this equilibrium.
. The student mixes together 0.0500 mol of succinic acid and 0.150 mol of ethanol, with a small amount of an acid catalyst.

- The mixture is allowed to reach equilibrium.
- The student determines that 0.0200 mol of succinic acid are present in the equilibrium mixture.
i. Which technique could be used to determine the equilibrium amount of succinic acid?
ii. Write the equation for the equilibrium reaction that takes place.
iii. Draw the skeletal formula of the ester present in the equilibrium mixture.
iv. $\quad K_{\mathrm{c}}$ is the equilibrium constant in terms of equilibrium concentrations.

Why can expression 5.1 be used to calculate $K_{\mathrm{c}}$ for this equilibrium?
$\qquad$
v. Calculate the value of $K_{\mathrm{c}}$ for this reaction.

Show your working.

$$
K_{\mathrm{c}}=
$$

6(a). Nitrogen monoxide, NO , and oxygen, $\mathrm{O}_{2}$, react to form nitrogen dioxide, $\mathrm{NO}_{2}$, in the reversible reaction shown in equilibrium 18.1.

$$
2 \mathrm{NO}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NO}_{2}(\mathrm{~g}) \quad \text { Equilibrium } 18.1
$$

Write an expression for $K_{c}$ for this equilibrium and state the units.

$$
K_{\mathrm{c}}=
$$

Units =
(b). A chemist mixes together nitrogen and oxygen and pressurises the gases so that their total gas volume is $4.0 \mathrm{dm}^{3}$.

- The mixture is allowed to reach equilibrium at constant temperature and volume.
- The equilibrium mixture contains 0.40 mol NO and $0.80 \mathrm{~mol} \mathrm{O}_{2}$.
- Under these conditions, the numerical value of $K_{\mathrm{c}}$ is 45 .

Calculate the amount, in mol, of $\mathrm{NO}_{2}$ in the equilibrium mixture.
(c). The values of $K_{\mathrm{p}}$ for equilibrium 18.1 at 298 K and 1000 K are shown below.

$$
2 \mathrm{NO}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NO}_{2}(\mathrm{~g}) \quad \text { Equilibrium } 18.1
$$

| Temperature $/ \mathbf{K}$ | $\boldsymbol{K}_{\mathrm{p}} / \mathbf{~ a t m}^{\mathbf{- 1}}$ |
| :---: | :---: |
| 298 | $K_{\mathrm{p}}=2.19 \times 10^{12}$ |
| 1000 | $K p=2.03 \times 10^{-1}$ |

i. Predict, with a reason, whether the forward reaction is exothermic or endothermic.
$\qquad$
$\qquad$
ii. The chemist increases the pressure of the equilibrium mixture at the same temperature.

State, and explain in terms of $K_{\mathrm{p}}$, how you would expect the equilibrium position to change.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
7. A chemist investigates the equilibrium reaction between sulfur dioxide, oxygen, and sulfur trioxide, shown below.

$$
2 \mathrm{SO}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{SO}_{3}(\mathrm{~g})
$$

- The chemist mixes together $\mathrm{SO}_{2}$ and $\mathrm{O}_{2}$ with a catalyst.
- The chemist compresses the gas mixture to a volume of $400 \mathrm{~cm}^{3}$.
- The mixture is heated to a constant temperature and is allowed to reach equilibrium without changing the total gas volume.

The equilibrium mixture contains $0.0540 \mathrm{~mol}_{\mathrm{SO}_{2}}$ and $0.0270 \mathrm{~mol} \mathrm{O}_{2}$.
At the temperature used, the numerical value for $K_{\mathrm{c}}$ is $3.045 \times 10^{4} \mathrm{dm}^{3} \mathrm{~mol}^{-1}$.
i. Write the expression for $K_{\mathrm{c}}$ and the units of $K_{\mathrm{c}}$ for this equilibrium.
ii. Determine the amount, in mol, of $\mathrm{SO}_{3}$ in the equilibrium mixture at this temperature.

Give your final answer to an appropriate number of significant figures.
Show all your working.
equilibrium amount of $\mathrm{SO}_{3}$
8. Iron can be extracted from its ore $\mathrm{Fe}_{3} \mathrm{O}_{4}$ using carbon.

Several equilibria are involved including equilibrium 18.1, shown below.
equilibrium 18.1

$$
\mathrm{Fe}_{3} \mathrm{O}_{4}(\mathrm{~s})+4 \mathrm{C}(\mathrm{~s}) \rightleftharpoons 3 \mathrm{Fe}(\mathrm{~s})+4 \mathrm{CO}(\mathrm{~g}) \begin{aligned}
& \Delta H=+676.4 \mathrm{~kJ} \mathrm{~mol}^{-1} \\
& \Delta S=+703.1 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}
\end{aligned}
$$

i. Why is equilibrium 18.1 a heterogeneous equilibrium?
$\qquad$
ii. Write the expression for $K_{\mathrm{p}}$ for equilibrium 18.1.
iii. The forward reaction in equilibrium 18.1 is only feasible at high temperatures.

- Show that the forward reaction is not feasible at $25^{\circ} \mathrm{C}$.
o Calculate the minimum temperature, in K , for the forward reaction to be feasible.
minimum temperature $=$
iv. Another equilibrium involved in the extraction of iron from $\mathrm{Fe}_{3} \mathrm{O}_{4}$ is shown below.

$$
\mathrm{Fe}_{3} \mathrm{O}_{4}(\mathrm{~s})+4 \mathrm{CO}(\mathrm{~g}) \rightleftharpoons 3 \mathrm{Fe}(\mathrm{~s})+4 \mathrm{CO}_{2}(\mathrm{~g})
$$

$$
\Delta H=-13.5 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

Enthalpy changes of formation, $\Delta \mathrm{f} H$, for $\mathrm{Fe}_{3} \mathrm{O}_{4}(\mathrm{~s})$ and $\mathrm{CO}_{2}(\mathrm{~g})$ are shown in the table.

| Compound | $\Delta_{\mathrm{f}} \boldsymbol{H} / \mathbf{k J ~ m o l}^{-1}$ |
| :--- | :--- |
| $\mathrm{Fe}_{3} \mathrm{O}_{4}(\mathrm{~s})$ | -1118.5 |
| $\mathrm{CO}_{2}(\mathrm{~g})$ | -393.5 |

Calculate the enthalpy change of formation, $\Delta_{\mathrm{f}} H$, for $\mathrm{CO}(\mathrm{g})$.

### 5.1.2 How Far

9. Peroxycarboxylic acids are organic compounds with the COOOH functional group.

Peroxyethanoic acid, $\mathrm{CH}_{3} \mathrm{COOOH}$, is used as a disinfectant.
i. Suggest the structure for $\mathrm{CH}_{3} \mathrm{COOOH}$.

The COOOH functional group must be clearly displayed.
ii. Peroxyethanoic acid can be prepared by reacting hydrogen peroxide with ethanoic acid. This is a heterogeneous equilibrium.
$\mathrm{H}_{2} \mathrm{O}_{2}(\mathrm{aq})+\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{COOOH}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \quad K_{\mathrm{c}}=0.37 \mathrm{dm}^{3} \mathrm{~mol}^{-1}$

A $250 \mathrm{~cm}^{3}$ equilibrium mixture contains concentrations of $0.500 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{H}_{2} \mathrm{O}_{2}(\mathrm{aq})$ and 0.500 mol $\mathrm{dm}^{-3} \mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$.

Calculate the amount, in mol, of peroxyethanoic acid in the equilibrium mixture.

10(a). lodine, $\mathrm{I}_{2}$, is a grey-black solid that is not very soluble in water.
Equilibrium 1 is set up with the equilibrium position well to the left.

$$
\mathrm{I}_{2}(\mathrm{~s}) \rightleftharpoons \mathrm{I}_{2}(\mathrm{aq}) \quad \text { Equilibrium } 1
$$

Solid iodine is much more soluble in an aqueous solution of potassium iodide, $\mathrm{KI}(\mathrm{aq})$, than in water.
Equilibrium 2 is set up.

$$
I_{2}(\mathrm{aq})+\mathrm{I}^{-}(\mathrm{aq}) \rightleftharpoons \mathrm{I}_{3}^{-}(\mathrm{aq})
$$

## Equilibrium 2

A student dissolves $\mathrm{I}_{2}$ in $\mathrm{KI}(\mathrm{aq})$.
The resulting $200 \mathrm{~cm}^{3}$ equilibrium mixture contains:

$$
\begin{aligned}
& 4.00 \times 10^{-5} \mathrm{~mol} \mathrm{I}_{2}(\mathrm{aq}) \\
& 9.404 \times 10^{-2} \mathrm{~mol} \mathrm{I}^{-}(\mathrm{aq}) \\
& 1.96 \times 10^{-3} \mathrm{~mol} \mathrm{I}_{3}^{-}(\mathrm{aq}) .
\end{aligned}
$$

Calculate $K_{\mathrm{c}}$ for equilibrium 2.
Give your answer to an appropriate number of significant figures.
$\qquad$ units
(b). The student adds an excess of aqueous silver nitrate, $\mathrm{AgNO}_{3}(\mathrm{aq})$, to the equilibrium mixture.

Predict what would be observed.
Explain the observations in terms of both equilibrium 1 and equilibrium 2 and any species formed.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$


1 A chemist investigated methods to improve the synthesis of sulfur trioxide from sulfur dioxide and oxygen.
1.

$$
2 \mathrm{SO}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{SO}_{3}(\mathrm{~g})
$$

The chemist:

- mixed together $1.00 \mathrm{~mol} \mathrm{SO}_{2}$ and $0.500 \mathrm{~mol} \mathrm{O}_{2}$ with a catalyst at room temperature
- compressed the gas mixture to a volume of $250 \mathrm{~cm}^{3}$
- allowed the mixture to reach equilibrium at constant temperature and without changing the total gas volume.

At equilibrium, $82.0 \%$ of the $\mathrm{SO}_{2}$ had been converted into $\mathrm{SO}_{3}$.
i. Determine the concentrations of $\mathrm{SO}_{2}, \mathrm{O}_{2}$ and $\mathrm{SO}_{3}$ present at equilibrium and calculate $K_{c}$ for this reaction.

$$
K_{\mathrm{c}}=
$$

$\qquad$ units
ii. Explain what would happen to the pressure as the system was allowed to reach equilibrium.
$\qquad$
$\qquad$
iii. The value of $K_{c}$ for this equilibrium decreases with increasing temperature.

Predict the sign of the enthalpy change for the forward reaction. State the effect on the equilibrium yield of $\mathrm{SO}_{3}$ of increasing the temperature at constant pressure.
$\Delta H:$
$\qquad$

Effect on $\mathrm{SO}_{3}$ yield:
$\qquad$
..... [1]
iv. The chemist repeated the experiment at the same temperature with $1.00 \mathrm{~mol} \mathrm{SO}_{2}$ and an excess of $\mathrm{O}_{2}$.
The gas mixture was still compressed to a volume of $250 \mathrm{~cm}^{3}$.
State and explain, in terms of $K_{c}$, how the equilibrium yield of $\mathrm{SO}_{3}$ would be different from the yield in the first experiment.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
[3].

12(a). Ethyne gas, $\mathrm{C}_{2} \mathrm{H}_{2}$, is manufactured in large quantities for a variety of uses.
Much of this ethyne is manufactured from methane as shown in the equation below.

$$
2 \mathrm{CH}_{4}(\mathrm{~g}) \rightleftharpoons \mathrm{C}_{2} \mathrm{H}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \quad \Delta \mathrm{H}=+377 \mathrm{kJmol}^{-1}
$$

Write an expression for $K_{\mathrm{c}}$ for this equilibrium.
(b). A research chemist investigates how to improve the synthesis of ethyne from methane at a high temperature.

- The chemist adds $\mathrm{CH}_{4}$ to a $4.00 \mathrm{dm}^{3}$ container.
- The chemist heats the container and allows equilibrium to be reached at constant temperature. The total gas volume does not change.
- The equilibrium mixture contains $9.36 \times 10^{-2} \mathrm{~mol} \mathrm{CH}_{4}$ and $0.168 \mathrm{~mol} \mathrm{C}_{2} \mathrm{H}_{2}$.
i. Calculate the amount, in mol , of $\mathrm{H}_{2}$ in the equilibrium mixture.

$$
\text { amount of } \mathrm{H}_{2}=
$$

ii. Calculate the equilibrium constant, $K_{\mathrm{c}}$, at this temperature, including units.

Give your answer to three significant figures.

$$
K_{\mathrm{c}}=
$$

units
iii. Calculate the amount, in mol , of $\mathrm{CH}_{4}$ that the chemist originally added to the container.
amount of $\mathrm{CH}_{4}=$
(c). The chemist repeats the experiment three times. In each experiment the chemist makes one change but uses the same initial amount of $\mathrm{CH}_{4}$.

Complete the table to show the predicted effect of each change compared with the original experiment.

Only use the words greater, smaller or same.

| Change | $\boldsymbol{K}_{\mathbf{c}}$ | Equilibrium amount <br> of $\mathbf{C}_{2} \mathbf{H}_{2}(\mathbf{g}) / \mathrm{mol}$ | Initial rate |
| :--- | :--- | :--- | :--- |
| The container is <br> heated at constant <br> pressure |  |  |  |
| A smaller container is <br> used |  |  |  |
| A catalyst is added to <br> $\mathrm{CH}_{4}$ at the start |  |  |  |

13(a). A research chemist investigates how the value of $K_{c}$ changes with temperature.
$\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g}) \quad \Delta H=-92 \mathrm{~kJ} \mathrm{~mol}^{-1}$

- The chemist mixes 0.800 mol of $\mathrm{N}_{2}(\mathrm{~g})$ and $2.400 \mathrm{~mol}^{2} \mathrm{H}_{2}(\mathrm{~g})$ and leaves the mixture to reach equilibrium at $300^{\circ} \mathrm{C}$.
- The total volume of the equilibrium mixture is $5.00 \mathrm{dm}^{3}$.
- At equilibrium, 0.360 mol of $\mathrm{NH}_{3}(\mathrm{~g})$ has formed.

Calculate the value of $K_{\mathrm{c}}$ under these conditions.
Show all your working.

$$
K_{c}=
$$

$\qquad$ units
(b). Ammonia, $\mathrm{NH}_{3}$, is manufactured by the chemical industry from nitrogen and hydrogen gases.

$$
\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g}) \quad \Delta H=-92 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

- An iron catalyst is used which provides several benefits for sustainability.
- The chemical industry uses operational conditions that are different from the conditions predicted to give a maximum equilibrium yield.

The chemist adds more nitrogen to the equilibrium mixture in (b).

$$
\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g}) \quad \Delta H=-92 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

The temperature is kept at 300 K and the volume at $5.00 \mathrm{dm}^{3}$.
The chemist predicts that the addition of nitrogen will increase the proportion of $\mathrm{H}_{2}(\mathrm{~g})$ that reacts.
i. Explain whether the chemist's prediction is correct.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
ii. Suggest why the chemist is more concerned with increasing the proportion of $\mathrm{H}_{2}$ that reacts rather than the proportion of $\mathrm{N}_{2}$ that reacts
$\qquad$
$\qquad$
$\qquad$

14(a). Ammonia is a gas with covalently-bonded molecules consisting of nitrogen and hydrogen atoms.
Ammonia can be made from the reaction of nitrogen and hydrogen in the Haber process.

> Fe catalyst
$\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \quad 450^{\circ} \mathrm{C}$ and $200 \mathrm{kPa} 2 \mathrm{NH}_{3}(\mathrm{~g}) \quad \Delta H=-92 \mathrm{~kJ} \mathrm{~mol}^{-1} \quad$ Equation 1
What effect will increasing the temperature have on the composition of the equilibrium mixture and on the value of the equilibrium constant?

Explain your answer.
$\qquad$
$\qquad$
$\qquad$
$\qquad$

### 5.1.2 How Far

(b). A chemist mixes together $0.450 \mathrm{~mol}_{2}$ with $0.450 \mathrm{~mol} \mathrm{H}_{2}$ in a sealed container.

The mixture is heated and allowed to reach equilibrium.
At equilibrium, the mixture contains $0.400 \mathrm{~mol} \mathrm{~N}_{2}$ and the total pressure is 500 kPa .
Calculate $K_{p}$.
Show all your working.
Include units in your answer.
$K_{p}=$
units
[5]

