## CHEM1612 Answers to Problem Sheet 5

1. Isotonic solutions have the same osmotic pressure. The osmotic pressure, $\Pi$, is given by:

$$
\Pi=c R T
$$

where $\mathbf{c}$ is the concentration of particles in the solution (in $\mathbf{m o l} \mathbf{m}^{-3}$ ). Hence,

$$
\begin{aligned}
\mathrm{c} & =\frac{\Pi}{\mathrm{RT}}=\frac{\left(8.3 \times 10^{-5} \times 1.013 \times 10^{5} \mathrm{~Pa}\right)}{\left(8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right) \times((25+273) \mathrm{K})} \\
& =3.4 \times 10^{-3} \mathrm{~mol} \mathrm{~m}^{-3}=3.4 \times 10^{-6} \mathrm{M}
\end{aligned}
$$

Note: $1 \mathrm{~L}=1 \mathrm{dm}^{3}$. Hence, $1 \mathrm{~m}^{\mathbf{3}}=1000 \mathrm{dm}^{\mathbf{3}}=1000 \mathrm{~L}$. Therefore, $1 \mathbf{~ m o l ~ m}{ }^{-\mathbf{3}}=10^{-3}$ $\mathrm{mol} \mathrm{dm} ~=10^{-3} \mathrm{M}$.
2. The osmotic pressure for strong electrolyte solutions is given by:

$$
\Pi=i \times(c R T)
$$

where $i$ is the number ( mol ) of particles in solution produced by the amount (mol) of dissolved solute.

For $1 \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}, c=1 \times 10^{3} \mathrm{~mol} \mathrm{~m}{ }^{-3}$ and $i=2-3\left(\mathrm{as}_{2} \mathrm{SO}_{4} \rightarrow \mathrm{H}^{+}+\mathrm{HSO}_{4}^{-}\right.$, and $\mathrm{HSO}_{4}{ }^{-} \leftrightarrow \mathrm{H}^{+}+\mathrm{SO}_{4}{ }^{2-}$ ). The second reaction doesn't go to completion because $\mathrm{HSO}_{4}{ }^{-}$is a weak acid. Therefore, each mole of $\mathrm{H}_{2} \mathrm{SO}_{4}$ produces somewhere between two and three moles of particles). Hence, $\Pi=2-3 \times 1 \times 10^{3} \times$ RT $=2$ 3000RT.

For $1 \mathrm{M} \mathrm{HCl}, c=1000 \mathrm{~mol} \mathrm{~m} ~$ and $i=2\left(\right.$ as $\mathrm{HCl} \rightarrow \mathrm{H}^{+}+\mathrm{Cl}^{-3}$, each mole of HCl produces two moles of particles). Hence, $\Pi=2 \times 1000 \times R T=2000 R T$

For 0.5 M glucose, $c=0.5 \times 10^{3} \mathrm{~mol} \mathrm{~m} \mathrm{~m}^{-3}$ and $i=1$ (as glucose dissolves without ionizing, each mole of glucose produces one mole of dissolved particles). Hence, $\Pi=1 \times 500 \times R T=500 R T$

For $0.5 \mathrm{M} \mathrm{CaCl}_{2}, c=0.5 \times 10^{3} \mathrm{~mol} \mathrm{~m} ~$ and $i=3\left(\right.$ as $\mathrm{CaCl}_{2} \rightarrow \mathrm{Ca}^{2+}+2 \mathrm{Cl}^{-}$, each mole of $\mathbf{C a C l}_{2}$ produces three moles of particles). Hence, $\Pi=3 \times 500 \times R T=$ 1500 RT.

For $0.5 \mathrm{M} \mathrm{NaCl}, c=0.5 \times 10^{3} \mathrm{~mol} \mathrm{~m} ~$ and $i=2\left(\right.$ as $\mathrm{NaCl} \rightarrow \mathrm{Na}^{+}+\mathrm{Cl}^{-}$, each mole of NaCl produces two moles of particles). Hence, $\Pi=2 \times 500 \times R T=1000 R T$.

Therefore, in order of increasing osmotic pressure:

$$
0.5 \mathrm{M} \text { glucose }<0.5 \mathrm{M} \mathrm{NaCl}^{2}<0.5 \mathrm{M} \mathrm{CaCl}_{2}<1 \mathrm{M} \mathrm{HCl}<1 \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}
$$

3. Using osmotic pressure, $\Pi=c R T$,

$$
\begin{aligned}
c= & \frac{\Pi}{R T}=\frac{(95 \mathrm{~Pa})}{\left(8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right) \times((25+273) \mathrm{K})} \\
& =3.8 \times 10^{-2} \mathrm{~mol} \mathrm{~m}^{-3}=3.8 \times 10^{-5} \mathrm{M}
\end{aligned}
$$

As concentration $=\frac{\text { number of moles }}{\text { volume }}$, the number of moles present in 1.00 mL is:

$$
\begin{aligned}
\text { number of moles }=n & =c \times V=\left(3.8 \times 10^{-5} \mathrm{~mol} \mathrm{~L}^{-1}\right) \times\left(1.00 \times 10^{-3} \mathrm{~L}\right) \\
& =3.8 \times 10^{-8} \mathrm{~mol}
\end{aligned}
$$

As the amount corresponds to $\mathbf{1 . 0 0} \mathbf{~ m g}$, the molar mass of the protein is given by:

$$
\text { molar mass }=\frac{\text { mass }}{\text { number of moles }}=\frac{m}{n}=\frac{\left(1.00 \times 10^{-3} \mathrm{~g}\right)}{\left(3.8 \times 10^{-8} \mathrm{~mol}\right)}=26000 \mathrm{~g} \mathrm{~mol}^{-1}
$$

4. The molar mass of salt $(\mathbf{N a C l})$ is $(\mathbf{2 2 . 9 9}(\mathbf{N a})+35.45(\mathrm{Cl})) \mathrm{g} \mathrm{mol}^{1}=58.44 \mathrm{~g} \mathrm{~mol}^{-1}$. 59 g of salt therefore corresponds to:

$$
\text { number of moles }=n=\frac{\text { mass }}{\text { molar mass }}=\frac{59 \mathrm{~g}}{58.44 \mathrm{~g} \mathrm{~mol}^{-1}}=1.0 \mathrm{~mol}
$$

As this amount is dissolved in 1000 g of water, the molality of solute is:

$$
\text { molality }=\frac{\text { number of moles of solute }(\mathrm{mol})}{\text { mass of solvent }(\mathrm{kg})}=\frac{1.0 \mathrm{~mol}}{\left(1000 \times 10^{-3} \mathrm{~kg}\right)}=1.0 \mathrm{~mol} \mathrm{~kg}^{-1}
$$

The freezing point depression, $\Delta T_{\mathrm{f}}$, is given by:

$$
\Delta T_{\mathrm{f}}=i K_{\mathrm{f}} m
$$

where $i$ is the amount ( mol ) of particles in solution, $K_{\mathrm{f}}$ is the molar freezing point depression or cryoscopic constant of the solvent and $m$ is the molality of the solute. As $\mathbf{N a C l}$ dissolves to give two ions, $\mathbf{i}=2$. Hence,

$$
\Delta T_{\mathrm{f}}=2 \times\left(1.86 \mathrm{~K} \mathrm{~kg} \mathrm{~mol}^{-1}\right) \times\left(1.0 \mathrm{~mol} \mathrm{~kg}^{-1}\right)=3.8 \mathrm{~K}
$$

As pure water freezes at 273.15 K at atmospheric pressure, the solution will freeze at $\mathbf{( 2 7 3 . 1 5}-\mathbf{3 . 8}) \mathrm{K}=269.4 \mathrm{~K}$.
5. The reaction table in terms of concentrations is:

|  | $\mathrm{C}_{3} \mathrm{H}_{6} \mathrm{O}_{3}(\mathrm{aq})$ | $\rightleftharpoons$ | $\mathbf{H}^{+}(\mathrm{aq})$ | $\mathrm{C}_{3} \mathrm{H}_{5} \mathrm{O}_{3}{ }^{-}(\mathrm{aq})$ |
| :--- | :--- | :--- | :--- | :--- |
| initial | 0.100 |  | 0 | 0 |
| change | $-x$ |  | $+x$ | $+x$ |
| equilibrium | $0.100-x$ |  | $x$ | $x$ |

As the $\left[\mathrm{C}_{3} \mathrm{H}_{6} \mathrm{O}_{3}\right]_{\text {dissociated }}=\left[\mathrm{H}^{+}(\mathrm{aq})\right]$, the percentage of $\mathrm{C}_{3} \mathrm{H}_{6} \mathrm{O}_{3}$ which dissociate is given by:

$$
\text { percentage dissociation }=\frac{\left[\mathrm{C}_{3} \mathrm{H}_{6} \mathrm{O}_{3}(\mathrm{aq})\right]_{\text {dissociated }}}{\left[\mathrm{C}_{3} \mathrm{H}_{6} \mathrm{O}_{3}(\mathrm{aq})\right]_{\text {initial }}} \times 100=\frac{x}{0.100} \times 100=3.7 \%
$$

Therefore,

$$
x=3.7 \times 10^{-3} \mathrm{M}
$$

Hence, at equilibrium, $\left[\mathrm{C}_{3} \mathrm{H}_{6} \mathrm{O}_{3}(\mathrm{aq})\right]=0.100-x=(0.100)-\left(3.7 \times 10^{-3}\right)=0.096 \mathrm{M}$ and $\left[\mathrm{H}^{+}(\mathrm{aq})\right]=\left[\mathrm{C}_{3} \mathrm{H}_{5} \mathrm{O}_{3}^{-}(\mathrm{aq})\right]=x=3.7 \times 10^{-3} \mathrm{M}$. The values of pH and $\mathrm{K}_{\mathrm{a}}$ are therefore:

$$
\begin{aligned}
& \mathrm{pH}=-\log _{10}\left(\left[\mathrm{H}^{+}(\mathrm{aq})\right]\right)=-\log _{10}\left(3.7 \times 10^{-3}\right)=2,4 \\
& K_{\mathrm{a}}=\frac{\left[\mathrm{H}^{+}(\mathrm{aq})\right]\left[\mathrm{C}_{3} \mathrm{H}_{5} \mathrm{O}_{3}^{-}(\mathrm{aq})\right]}{\left[\mathrm{C}_{3} \mathrm{H}_{6} \mathrm{O}_{3}(\mathrm{aq})\right]}=\frac{\left(3.7 \times 10^{-3}\right) \times\left(3.7 \times 10^{-3}\right)}{(0.096)}=1.4 \times 10^{-4}
\end{aligned}
$$

6. (a) Hydrochloric acid is a strong acid so the reaction,

$$
\mathrm{HCl}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq})
$$

goes to completion, generating one mole of $\mathrm{H}_{3} \mathrm{O}^{+}$for every mole of $\mathbf{H C l}$.
0.14 M HCl therefore gives:

$$
\begin{aligned}
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=0.14 \mathrm{M}} \\
& \mathbf{p H}=-\log _{10}\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=-\log _{10}[0.14]=0.85
\end{aligned}
$$

(b) Nitric acid is a strong acid so the reaction,

$$
\mathrm{HNO}_{3}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{NO}_{3}{ }^{-}(\mathrm{aq})
$$

goes to completion, generating one mole of $\mathrm{H}_{3} \mathrm{O}^{+}$for every mole of $\mathrm{HNO}_{3}$.
$0.0025 \mathrm{M} \mathrm{HNO}_{3}$ therefore gives:

$$
\begin{aligned}
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=0.0025 \mathrm{M}} \\
& \mathbf{p H}=-\log _{10}\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=-\log _{10}[0.0025]=\mathbf{2 . 6 0}
\end{aligned}
$$

(c) Sodium hydroxide is a strong base so the reaction,

$$
\mathrm{NaOH}(\mathrm{aq}) \rightarrow \mathrm{Na}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})
$$

goes to completion, generating one mole of $\mathrm{OH}^{-}$for every mole of $\mathbf{N a O H}$.
0.048 M NaOH therefore gives:

$$
\left[\mathrm{OH}^{-}\right]=0.048 \mathrm{M}
$$

As $K_{w}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=10^{-14}$, this gives

$$
\begin{aligned}
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{10^{-14}}{0.048}=2.1 \times 10^{-13} \mathrm{M}} \\
& \mathrm{pH}=-\log _{10}\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=-\log _{10}\left[2.1 \times 10^{-13}\right]=12.7
\end{aligned}
$$

(d) Barium hydroxide is a strong base so the reaction,

$$
\mathrm{Ba}(\mathrm{OH})_{2}(\mathrm{aq}) \rightarrow \mathrm{Ba}^{2+}(\mathrm{aq})+2 \mathrm{OH}^{-}(\mathrm{aq})
$$

goes to completion, generating two moles of $\mathrm{OH}^{-}$for every mole of $\mathrm{Ba}(\mathrm{OH})_{2}$.
$3.7 \times 10^{-3} \mathrm{M} \mathrm{Ba}(\mathrm{OH})_{2}$ therefore gives:

$$
\left[\mathrm{OH}^{-}\right]=2 \times\left(3.7 \times 10^{-3}\right)=0.0074 \mathrm{M}
$$

As $\mathrm{K}_{\mathrm{w}}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=\mathbf{1 0}^{-14}$, this gives

$$
\begin{aligned}
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{10^{-14}}{0.0074}=1.4 \times 10^{-12} \mathrm{M}} \\
& \mathrm{pH}=-\log _{10}\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=-\log _{10}\left[1.4 \times 10^{-12}\right]=12
\end{aligned}
$$

7. The titration is a $\mathbf{1 : 1}$ reaction between a strong acid and a strong base.
(a) (i) Before any base is added, $\left[\mathrm{H}^{+}(\mathrm{aq})\right]=\mathbf{0 . 1 0 0} \mathrm{M}$ and so $\mathrm{pH}=-\log _{10}(0.100)=\mathbf{1 . 0 0}$.
(ii) $\quad \mathrm{As} \mathrm{OH}^{-}(\mathrm{aq})$ is added, the $\left[\mathrm{H}^{+}(\mathrm{aq})\right]$ decreases.

This is due to the acid-base reaction and due to the increase in volume.
Up until the equivalence point:

$$
\left[\mathrm{H}^{+}(\mathrm{aq})\right]=\frac{n_{\mathrm{H}^{+}}}{V}=\frac{n_{\mathrm{H}^{+}}(\text {initial })-n_{\mathrm{OH}-}(\text { added })}{V_{\text {total }}}
$$

or

$$
\left[\mathrm{H}^{+}(\mathrm{aq})\right]=\frac{\left(c_{\mathrm{H}^{+}}(\text {initial }) \times V(\text { initial })\right)-\left(c_{\mathrm{OH}^{-}}(\text {added }) \times V(\text { added })\right.}{(V(\text { initial })+V(\text { added }))}
$$

Thus, when 25.0 mL of 0.100 M NaOH has been added:

$$
\left[\mathrm{H}^{+}(\mathrm{aq})\right]=\frac{(0.100 \mathrm{M} \times 0 . .050 \mathrm{~L})-(0.100 \mathrm{M} \times 0.025 \mathrm{~L})}{((0.050+0.0250) \mathrm{L})}=0.033 \mathrm{M}
$$

Hence, $\mathbf{p H}=-\log _{10}(\mathbf{0 . 0 3 3})=1.48$
(iii) When 45.0 mL of $\mathbf{0 . 1 0 0} \mathrm{M} \mathrm{NaOH}$ has been added:

$$
\left[\mathrm{H}^{+}(\mathrm{aq})\right]=\frac{(0.100 \mathrm{M} \times 0.050 \mathrm{~L})-(0.100 \mathrm{M} \times 0.045 \mathrm{~L})}{((0.050+0.0450) \mathrm{L})}=0.0053 \mathrm{M}
$$

Hence, $\mathbf{p H}=-\log _{10}(0.0053)=2,28$
(iv) Addition of 50.0 mL of 0.100 NaOH will exactly neutralize the acid.

Hence, $\mathbf{p H}=7.00$
(v) Beyond the equivalence point, the added base is simply being diluted as there is no acid left to react with:

$$
\left[\mathrm{OH}^{-}(\mathrm{aq})\right]=\frac{n_{\mathrm{OH}^{-}}}{V}=\frac{n_{\mathrm{OH}^{-}}(\text {total })-n_{\mathrm{H}^{+}}(\text {initial })}{V_{\text {total }}}
$$

As 50.0 mL of $\mathbf{0 . 1 0 0} \mathrm{M} \mathrm{HCl}$ was present initially, $\boldsymbol{n}_{\mathrm{H}^{+}}+($initial $)=5.00 \times 10^{-\mathbf{3}}$ mol.
55.0 mL of $\mathbf{0 . 1 0 0} \mathbf{M ~ N a O H}$ corresponds to $5.50 \times 10^{-3} \mathbf{~ m o l}$ and when this has been added, the total volume is $(0.050+0.055) \mathrm{L}=0.105 \mathrm{~L}$. Hence

$$
\left[\mathrm{OH}^{-}(\mathrm{aq})\right]=\frac{(0.00550 \mathrm{~mol})-(0.00500 \mathrm{~mol})}{(0.105 \mathrm{~L})}=0.00476 \mathrm{M}
$$

Hence, $\mathrm{pOH}=-\log _{10}(\mathbf{0 . 0 0 4 7 6})=2,32$ and $\mathrm{pH}=14.00-2.32=11.7$
(v) When $75.0 \mathbf{m L}$ of $\mathbf{0 . 1 0 0} \mathrm{M} \mathrm{NaOH}$ has been added, $\boldsymbol{n}_{\mathrm{OH}}-($ total $)=7.50 \times \mathbf{1 0}^{-3}$ mol and the total volume is $(0.050+0.075) \mathrm{L}=0.125 \mathrm{~L}$. Hence

$$
\left[\mathrm{OH}^{-}(\mathrm{aq})\right]=\frac{(0.00750 \mathrm{~mol})-(0.00500 \mathrm{~mol})}{(0.125 \mathrm{~L})}=0.0200 \mathrm{M}
$$

Hence, $\mathrm{pOH}=-\log _{10}(\mathbf{0 . 0 2 0 0})=1.70$ and $\mathrm{pH}=14.00-1.70=12.3$
(b) Using these values, the $\mathbf{p H}$ curve for the titration can be constructed and is shown below.


