## CHEM1109 Answers to Problem Sheet 5

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

$$
\Pi=M R T
$$

where $M$ is the molarity of the solution. Hence,

$$
\left.M=\frac{\Pi}{\mathrm{RT}}=\frac{\left(8.3 \times 10^{-5} \mathrm{~atm}\right)}{(0.08206 \mathrm{Latm} \mathrm{~K}} \mathrm{mol}^{-1}\right) \times((25+273) \mathrm{K}) \quad=3.4 \times 10^{-6} \mathrm{M}
$$

As the pressure is given in units of atm, $R=0.08206 \mathrm{Latm} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$ has been used, leading to molarity in units of $\mathrm{mol}^{\mathbf{- 1}}$ or M .
2. The osmotic pressure for strong electrolyte solutions is given by:

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

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

For $1 \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}, M=1$ and $i=2\left(\right.$ as $\mathrm{H}_{2} \mathrm{SO}_{4} \rightarrow \mathrm{H}^{+}+\mathrm{HSO}_{4}{ }^{2-}$, each mole of $\mathrm{H}_{2} \mathrm{SO}_{4}$ produces two moles of particles). Note that there is very little dissociation of $\mathrm{HSO}_{4}{ }^{-}$into $\mathrm{H}^{+}$and $\mathrm{SO}_{4}{ }^{2-}$ at this pH . Hence, $\Pi=2 \times 1 \times \mathrm{RT}=2 R T$.

For $1 \mathrm{MHCl}, M=1$ and $i=2\left(\right.$ as $\mathrm{HCl} \rightarrow \mathrm{H}^{+}+\mathrm{Cl}^{-}$, each mole of $\mathbf{H C l}$ produces two moles of particles). Hence, $\Pi=2 \times 1 \times R T=2 R T$

For 0.5 M glucose, $M=0.5$ and $i=1$ (as glucose dissolves without ionizing, each mole of glucose produces one mole of dissolved particles). Hence, $\Pi=0.5 \times 1 \times R T=0.5 R T$

For $0.5 \mathrm{M} \mathrm{CaCl}_{2}, M=0.5$ and $i=3$ (as $\mathbf{C a C l}_{2} \rightarrow \mathrm{Ca}^{2+}+2 \mathrm{Cl}^{-}$, each mole of $\mathrm{CaCl}_{2}$ produces three moles of particles). Hence, $\Pi=3 \times 0.5 \times R T=1.5 R T$.

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

Therefore, in order of increasing osmotic pressure:

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

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

$$
M=\frac{\Pi}{R T}=\frac{\left(95 \times 10^{-3} \mathrm{kPa}\right)}{\left(8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right) \times((25+273) \mathrm{K})}=3.8 \times 10^{-5} \mathrm{M}
$$

As the pressure is given in Pa, $R=8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}=\mathrm{kPa} \mathrm{L} \mathrm{mol}^{-1} \mathrm{~K}^{-1}$ is used requiring the conversion of 95 Pa to $95 \times 10^{=3} \mathrm{kPa}$. This leads to the molarity in mol L ${ }^{-1}$.

Alternatively, the pressure can first be converted to atmospheres, using 1 atm $=$ $1.01325 \times \mathbf{1 0}^{5}$ Pa.,

$$
\Pi=95 \mathrm{~Pa}=\frac{95}{1.01325 \times 10^{5}} \mathrm{~atm}=9.4 \times 10^{-4} \mathrm{~atm}
$$

Using $R=0.08206 \mathrm{~L} \mathrm{~atm} \mathrm{~K}^{-1} \mathrm{~mol}^{-1} \mathrm{M}$,

$$
M=\frac{\Pi}{R T}=\frac{\left(9.4 \times 10^{-4} \mathrm{~atm}\right)}{\left(0.08206 \mathrm{Latm} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right) \times((25+273) \mathrm{K})}=3.8 \times 10^{-5} \mathrm{M}
$$

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 $(\mathbf{2 2 . 9 9}(\mathbf{N a})+\mathbf{3 5 . 4 5}(\mathbf{C l})) \mathrm{g} \mathrm{mol}^{1}=\mathbf{5 8 . 4 4} \mathrm{g} \mathrm{mol}^{-1}$.

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 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, $\Delta T_{f}$, is given by:

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

where $i$ is the amount ( mol ) of particles in solution, $\boldsymbol{K}_{\mathrm{f}}$ 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 (273.15-3.8) $\mathrm{K}=\mathbf{2 6 9 . 4} \mathrm{K}$.
5. The reaction table in terms of concentrations is:

|  | $\mathrm{C}_{3} \mathrm{H}_{6} \mathrm{O}_{3}(\mathrm{aq})$ | $\rightleftharpoons$ | $\mathrm{H}^{+}(\mathrm{aq})$ | $\mathrm{C}_{3} \mathrm{H}_{5} \mathrm{O}_{3}{ }^{-}(\mathrm{aq})$ |
| :--- | :--- | :--- | :--- | :--- |
| 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:

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=0.0025 \mathrm{M}
$$

$$
\mathrm{pH}=-\log _{10}\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=-\log _{10}[0.0025]=2.60
$$

(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 $\mathrm{Ba}(\mathrm{OH})_{2}$.
$3.7 \times 10^{-3} \mathrm{M} \mathrm{Ba}(\mathbf{O H})_{2}$ therefore gives:

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

As $\mathrm{K}_{\mathrm{w}}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=10^{-14}$, 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 $1: 1$ 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 $\mathbf{p H}=-\log _{10}(0.100)=\mathbf{1 . 0 0}$.
(ii) $\quad$ As $\mathbf{O H}^{-}(\mathrm{aq})$ 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, $\mathbf{p H}=-\log _{10}(\mathbf{0 . 0 0 5 3})=\mathbf{2 , 2 8}$
(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 0.100 M NaOH 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, $\mathrm{pOH}=-\log _{10}(\mathbf{0 . 0 0 4 7 6})=\mathbf{2 , 3 2}$ and $\mathrm{pH}=14.00-2.32=11.7$
(v) When 75.0 mL 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.


