

## CHEMISTRY ONLINE

- TUITION -

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## CHEMISTRY PHYSICAL CHEMISTRY

Level \& Board

TOPIC:

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## Equilibria - 2

1) 

(a) $2 \mathrm{CH}_{3} \mathrm{OH}+3 \mathrm{O}_{2} \rightarrow 2 \mathrm{CO}_{2}+4 \mathrm{H}_{2} \mathrm{O}$
(b) Sulphur dioxide and Nitrogen dioxide
(c) 1. Low temperature

As the forward reaction is exothermic at low temperature, the reaction will go forward to produce high yield of methanol.

## 2. High pressure

As the forward reaction goes to fewer gas to fewer gas molecules, the reaction will go forward at high pressure.
(d) (i) It helps to remove carbon dioxide from air which is responsible for green - house
effect and global warming.
(ii)

|  | $\mathrm{CO}_{2}$ | $+\mathrm{H}_{2}$ | $\rightleftharpoons \mathrm{CO}$ | $+\mathrm{H}_{2} \mathrm{O}$ |
| :---: | :---: | :---: | :---: | :---: |
| Initial moles | 0.50 | 0.50 | 0.20 | 0.20 |
| Equilibrium <br> moles | $(0.5-\mathrm{x})$ | $(0.50-\mathrm{x})$ | $(0.20+\mathrm{x})$ | $(0.20+\mathrm{x})$ |
| Equilibrium <br> concentration <br> mole dm <br> -3 | $\frac{0.5-\mathrm{x}}{1}$ | $\frac{0.50-x}{1}$ | $\frac{0.20+\mathrm{x}}{1}$ | $\frac{0.20+\mathrm{x}}{1}$ |

$K_{C}=\frac{[\mathrm{CO}]\left[\mathrm{H}_{2} \mathrm{O}\right]}{\left[\mathrm{CO}_{2}\right]\left[\mathrm{H}_{2}\right]} \quad \Rightarrow 1.44=\frac{(0.20+x)^{2}}{(0.50-x)^{2}} \quad \Rightarrow x=0.18$
at equilibrium moles of $\left(\mathrm{CO}_{2}\right)=$ moles of $\left(\mathrm{H}_{2}\right)=0.50-0.18=0.32$
moles of $(\mathrm{CO})=$ moles of $\left(\mathrm{H}_{2} \mathrm{O}\right)=0.20+0.18=0.38$
2)
(a) Acids are species that donate protons (hydrogen ions) when dissolve in water. Bases are species that accept protons when dissolve in water.
(b) (i) When chlorine is substituted in ethanoic acid, $K_{\mathrm{a}}$ value increase and acid becomes stronger. It is due to electron withdrawing effect of chlorine making $\mathrm{O}-\mathrm{H}$ bond weaker causing moles $\mathrm{H}+$ ions to be free.
(i) $\left[H^{+}\right]=\sqrt{K_{a}[\text { Acid }]}$

$$
=\sqrt{\left(1.3 \times 10^{-3}\right) \times 0.1}=0.0114 \mathrm{~mol} \mathrm{dm}^{-3}
$$

$-\log \left[H^{+}\right]=-\log 0.0114$

$$
\text { pH = } 1.94
$$

(iii)

(c) (i) $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}+\mathrm{OH}^{-} \rightarrow \mathrm{CH}_{3} \mathrm{CO}_{2}^{-}+\mathrm{H}_{2} \mathrm{O}$
$\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}+\mathrm{H}^{+} \rightarrow \mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{HH}$
(ii) $\mathrm{pK}_{\mathrm{a}}=-\log _{10} \mathrm{~K}_{\mathrm{a}}=-\log _{10} 1.7 \times 10^{-5}=4.77$
$p H=p K_{a}+\log \frac{[\text { salt }]}{[\text { Acid }]}$
$=4.77+\log \frac{0.2}{0.1}=4.77+0.30=5.07$
3)
(i) $\mathrm{K}_{\mathrm{sp}}=\left[\mathrm{Ca}^{2+}\right]\left[\mathrm{OH}^{-}\right]^{2}, \quad$ units $=\mathrm{mol}^{3} \mathrm{dm}^{-9}$
(ii) Moles of acid $\left(\mathrm{H}^{+}\right)=0.05 \times \frac{21}{1000}=1.05 \times 10^{-3}$
same moles of $\mathrm{OH}^{-}$are present in $21 \mathrm{~cm}^{3}$ moles $\mathrm{I} 25 \mathrm{~cm}^{3}$ of $\mathrm{Ca}(\mathrm{OH})_{2}$.
$\left[\mathrm{OH}^{-}(\mathrm{aq})\right]=\left(1.05 \times 10^{-3}\right) \times \frac{1000}{25}=4.2 \times 10^{-2}\left(\mathrm{~mol} \mathrm{dm}^{-3}\right)$
$\left[\mathrm{Ca}^{2+}(\mathrm{aq})\right]=\frac{1}{2} \times 4.2 \times 10^{-2}=2.1 \times 10^{-2}\left(\mathrm{~mol} \mathrm{dm}^{-3}\right)$
(iii) $\mathrm{Ca}(\mathrm{OH})_{2}$ will be less soluble in $0.1 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{NaOH}$ because of common ion effect.
4)
(c) (i) $K_{\text {sp }}=\left[\mathrm{Pb}^{2+}\right]\left[\mathrm{Cl}^{-}\right]^{2} \quad$ units $=\mathrm{mol}^{3} \mathrm{dm}^{-9}$
(ii) Suppose $\left[\mathrm{Pb}^{2+}\right]=\mathrm{x}$
$\Rightarrow\left[\mathrm{Pb}^{2+}\right] \times\left[\mathrm{Cl}^{-}\right]^{2}=(x)(2 x)^{2}$
$\Rightarrow K_{\text {sp }}=4 x^{3}$
$\Rightarrow x=\sqrt[3]{\frac{K_{s p}}{4}}=\sqrt[3]{\frac{2.0 \times 10^{-5}}{4}}=1.71 \times 10^{-2}$
(iii) $\left[\mathrm{Pb}^{2+}\right]=\frac{2 \times 10^{-5}}{(0.5)^{2}}=8.0 \times 10^{-5} \quad \mathrm{~mol} \mathrm{dm}^{-3}$
(iv) Solubility of $\mathrm{PbCl}_{2}$ is decreased because of common ion effect.
5)
(a) (i) order with respect to $\left[\mathrm{CH}_{3} \mathrm{CHO}\right]=1$
order with respect to $\left[\mathrm{CH}_{3} \mathrm{OH}\right]=1$
order with respect to $\left[\mathrm{H}^{+}\right]=1$
(ii) Rate of reaction $=\mathrm{k}\left[\mathrm{CH}_{3} \mathrm{CHO}\right]\left[\mathrm{CH}_{3} \mathrm{OH}\right]\left[\mathrm{H}^{+}\right]$
(iii) Units $\mathrm{mol}^{-2} \mathrm{dm}^{6} \mathrm{~s}^{-1}$
(iv) Rate of reaction $=\frac{0.20}{0.20} \times \frac{0.20}{0.1} \times \frac{0.20}{0.05}$
$=2 \times 4=8$ times as fast as reaction 1.

Hence relative rate of reaction $=8$.
(b) (i) \& (ii)

|  | $\left[\mathrm{CH}_{3} \mathrm{CHO}\right]$ <br> $/ \mathrm{mol} \mathrm{dm}^{-3}$ | $\left[\mathrm{CH}_{3} \mathrm{OH}\right]$ <br> $/ \mathrm{mol} \mathrm{dm}^{-3}$ | $\left[\mathrm{H}^{+}\right]$ <br> $/ \mathrm{mol} \mathrm{dm}^{-3}$ | $[$ acetal A] <br> $/ \mathrm{mol} \mathrm{dm}^{-3}$ | $\left[\mathrm{H}_{2} \mathrm{O}\right]$ <br> $/ \mathrm{mol} \mathrm{dm}^{-3}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| At start | 0.20 | 0.10 | 0.05 | 0.00 | 0.00 |
| At equilibrium | $(0.20-\mathrm{x})$ | $(0.10-2 \mathrm{x})$ | 0,05 | x | x |
| At equilibrium | 0.175 | 0.05 | 0.05 | 0.025 | 0.025 |

(iii) $K_{c}=\frac{\left[\mathrm{CH}_{3} \mathrm{CH}\left(\mathrm{OCH}_{3}\right)_{2}\right]\left[\mathrm{H}_{2} \mathrm{O}\right]}{\left[\mathrm{CH}_{3} \mathrm{CHO}\right]\left[\mathrm{CH}_{3} \mathrm{OH}\right]^{2}}$
units $=\mathrm{mol}^{-1} \mathrm{dm}^{3}$
(iv) $K_{c}=\frac{\left[\mathrm{CH}_{3} \mathrm{CH}\left(\mathrm{OCH}_{3}\right)_{2}\right]\left[\mathrm{H}_{2} \mathrm{O}\right]}{\left[\mathrm{CH}_{3} \mathrm{CHO}\right]\left[\mathrm{CH}_{3} \mathrm{OH}\right]^{2}}$
$=\frac{0.025 \times 0.025}{0.175 \times(0.05)^{2}}=1.4286 \mathrm{~mol}^{-1} \mathrm{dm}^{3}$
6)
(a) (i) The thermal stability decreases from HCl to Hi .
(ii) $2 \mathrm{HX} \rightarrow \mathrm{H}_{2}+\mathrm{X}_{2}$

The thermal decomposition of HX depends on the strength of the $\mathrm{H}-\mathrm{X}$ bond.
Down the Group, the atomic size of $X$ increase and its orbital, used for bonding, becomes more diffuse. Hence, orbital overlap between $H$ and $X$

Therefore thermal stability of these hydrides decreases down the Group.
(b) $K_{c}=\frac{[\mathrm{HI}]^{2}}{\left[\mathrm{H}_{2}\right] \times\left(\mathrm{I}_{2}\right)}, \quad$ No units.
(c) (i) As the number of moles on the right hand side and left hand side of the equation are same, increasing the pressure will have no effect on the equilibrium position.
(ii) Decreasing the temperature would favour that side of the reaction which produces more heat. As the forward reaction is exothermic, the equilibrium will move to the right hand side of the reaction
(d)

$$
\mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g}) \quad \rightleftharpoons 2 \mathrm{HI}(\mathrm{~g})
$$

| initial moles | 0.02 | 0.02 | 0 |
| :--- | :--- | :--- | :--- |
| moles at equilibrium | $0.02-\mathrm{x}$ | $0.02-\mathrm{x}$ | 2 x |
| concentration (in mol $/ \mathrm{dm}^{3}$ ) |  |  |  |
| at equilibrium | $\frac{0.02-x}{1}$ | $\frac{0.02-x}{1}$ | $\frac{2 x}{1}$ |

$=\frac{[H I]^{2}}{\left[H_{2}\right] \times\left(I_{2}\right)}$
$59=\frac{(2 x)^{2}}{(0.02-x)(0.02-x)}$
$59=\frac{(2 x)^{2}}{(0.02-x)^{2}}$
$\sqrt{59}=\frac{2 x}{0.02-x}$
$0.02 \sqrt{59}-\sqrt{59} x=2 x$
$2 \mathrm{x}+\sqrt{59} \mathrm{x}=0.02 \sqrt{59} \Rightarrow x=\frac{0.02 \sqrt{59}}{2+\sqrt{59}}=0.01587 \approx 0.016$
$\therefore$ at equilibrium, moles of $\mathrm{HI}=2 \times 0.01587$
$=0.03174 \approx 0.032 \mathrm{~mol}$
moles of $\mathrm{H}_{2}=$ moles of $\mathrm{I}_{2}=0.02-0.01587$
$=0.00413=0.004 \mathrm{~mol}$
(a) (i) $\mathrm{NH}_{3}+\quad \mathrm{HZ} \rightarrow \mathrm{NH}_{4}^{+}+\mathrm{Z}^{-}$
$\mathrm{CH}_{3} \mathrm{OH}+\mathrm{HZ} \quad \rightarrow \quad \mathrm{CH}_{3} \mathrm{OH}_{2}^{+}+\mathrm{Z}^{-}$
(ii) $\mathrm{NH}_{3}+$
$\mathrm{B}^{-} \quad \rightarrow \quad \mathrm{NH}_{2}^{-}+\mathrm{BH}$
$\mathrm{CH} 3 \mathrm{OH}+\mathrm{B}^{-} \rightarrow \mathrm{CH}_{3} \mathrm{O}^{-} \mathrm{BH}$
(a) (i) A reaction that can go in either direction.
(ii) A dynamic equilibrium occurs when the rate of the forward reaction is equal to the rate of the backward reaction.
(b) In a buffer solution at equilibrium.

$$
\mathrm{HZ}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{Z}^{-}+\mathrm{H}_{3} \mathrm{O}^{+} .
$$

When an acid is added, the reaction moves to the left as follows:

$$
\mathrm{H}^{+}+\mathrm{Z}^{-} \rightarrow \mathrm{HZ}
$$

Hence, the Buffer solution is able to maintain it's pH by shifting the equilibrium
To the left or right.
(c) (i) $K_{c}=\frac{\left[\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COO}^{-}\right]\left[\mathrm{H}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}\right]}$
as $\left[\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COO}^{-}\right]\left[\mathrm{H}^{+}\right]$

$$
\begin{aligned}
\Rightarrow\left[H^{+}\right] & =\sqrt{K_{a}\left[\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}\right]} \\
& =\sqrt{0.5 \times 1.34 \times 10^{-5}}=2.588 \times 10^{-3} \mathrm{~mol} / \mathrm{dm}^{3}
\end{aligned}
$$

$$
\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]
$$

$$
=2.587 \approx 2.59
$$

(ii) $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{H}+\mathrm{NaOH} \longrightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{Na}+\mathrm{H}_{2} \mathrm{O}$.
(iii) Total Moles of propanoic acid $=0.5 \times \frac{100}{1000}=0.05$.

Hence, the acid is in excess.

1 mole sodium hydroxide produces 1 mole of sodium propanoate.
$\therefore$ concentration of propanoate $=0.03 \div \frac{100}{1000}=0.2 \mathrm{~mol} / \mathrm{dm}^{3}$
(iv) $\mathrm{pH}=-\log 10 \mathrm{~K}_{\mathrm{a}}+\log _{10}\left(\frac{[\text { Salt }]}{[\text { Acid }]}\right)$

$$
\begin{aligned}
& =-\log _{10}\left(1.34 \times 10^{-5}\right)+\log _{10}\left(\frac{0.3}{0.2}\right) \\
& =5.049 \approx 5.05
\end{aligned}
$$

(d) $\mathrm{G}=\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COCl}$

H is $\mathrm{SOCl}_{2}$
J is NaCl
8)
(c) (i)

- $\mathrm{K}_{\mathrm{a}}$ is larger than that of ethanol because the $\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}$ion stabilized by charge delocalization.
- $K_{a}$ is smaller than that of chloroethanoic acid because the electronegative chlorine atom in $\mathrm{ClCH}_{2} \mathrm{CO}_{2} \mathrm{H}$ makes the $\mathrm{ClCH}_{2} \mathrm{CO}_{2}^{-}$ion more stable.
(ii) $\left[\mathrm{H}^{+}\right]=\sqrt{\mathrm{K}_{a} \times\left[\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}\right]}$

$$
\begin{aligned}
& =\sqrt{1.75 \times 10^{-5} \times 0.1}=0.0013229 \\
p H & =-\log _{10}\left[\mathrm{H}^{+}\right] \\
& =-\log _{10}[0.0013229]=2.8785 \approx 2.88 .
\end{aligned}
$$

(d) (i) $\mathrm{NaOH}+\mathrm{CH}_{3} \mathrm{COOH} \rightarrow \mathrm{CH}_{3} \mathrm{COONa}+\mathrm{H}_{2} \mathrm{O}$

$$
\Longrightarrow 1 \text { mol of } \mathrm{NaOH} \text { requires } 1 \text { moles of } \mathrm{CH}_{3} \mathrm{COOH} \text {. }
$$

moles of $\mathrm{CH}_{3} \mathrm{COOH}=0.100 \times \frac{\text { www.chemistryonlinetuition.com }}{1000}=0.001$ moles
moles on $\mathrm{NaOH}=0.100 \times \frac{20}{1000}=0.002$ moles
$\therefore$ remaining moles of NaOH at the end of addition $=0.002-0.001=0.001$ moles
(ii) Total volume of solution $=30 \mathrm{~cm}^{3}=0.03 \mathrm{dm}^{3}$

Concentration of NaOH at the end $=\frac{0.001}{0.03}=0.03333 \mathrm{~mol} / \mathrm{dm}^{3}$
$\mathrm{NaOH} \rightarrow \mathrm{Na}^{+}+\mathrm{OH}^{-}$

$$
\begin{aligned}
& \therefore[\mathrm{OH}-]=0.0333 \mathrm{~mol} / \mathrm{dm}^{3} . \\
& \text { (iii) } \mathrm{K}_{\mathrm{w}}=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right] \Rightarrow\left[\mathrm{H}^{+}\right]=\frac{K_{w}}{\left[\mathrm{OH}^{-}\right]} \\
& =\frac{1 \times 10^{-14}}{0.0333}=3.0 \times 10^{-13} \mathrm{~mol} / \mathrm{dm}^{3}
\end{aligned}
$$

$\therefore \mathrm{pH}=-\log _{10}\left[\mathrm{H}^{+}\right]$

$$
=-\log _{10}\left(3.0 \times 10^{-13}\right)=12.52
$$


(v)

| Indicator | pH at which <br> colour changes | Place one tick only <br> in this column |
| :---: | :---: | :---: |
| malachite green | $0-1$ |  |
| thymol blue | $1-2$ |  |
| bromophenol | $3-4$ |  |
| thymolphthalein | $9-10$ |  |

9) 

(a) (i) $4 \mathrm{FeS}_{2}+11 \mathrm{O}_{2} \rightarrow 2 \mathrm{FeO}_{3}+8 \mathrm{SO}_{2}$
(b) (i) The reaction of sulfur trioxide with water is very exothermic and produces harmful acid mist.
(ii) $\mathrm{SO}_{3}+\mathrm{H}_{2} \mathrm{SO}_{4} \rightarrow 2 \mathrm{H}_{2} \mathrm{SO}_{4}$
(c) (i)

(d) (i) Advantage: Reaction rate is high.

Explanation: More molecules have energy greater then activation energy and therefore there will be more fruitful collisions between particles.

Disadvantage: As the forward reaction is exothermic, increasing the temperature will favour that side of the reaction which absorbs heat i.e. the left hand side of the reaction.
(ii) $K_{p}=\frac{P_{S O_{3}^{2}}}{P_{S O_{3}^{2}} \times P O_{2}}$
(iii)

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

Initial number of moles: 2020
$(-1.80) \quad(-0.9)$
$\begin{array}{llll}\text { moles of equilibrium: } & 0.2 & 1.1 & 0\end{array}$
sum of moles at equilibrium $=0.2+1.1+1.80=3.1$
mole fraction of $\mathrm{SO}_{3}=\frac{1.8}{3.1}=0.581$
mole fraction of $\mathrm{SO}_{2}=\frac{0.2}{3.1}=0.065$
mole fraction of $\mathrm{O}_{2}=\frac{1.1}{3.1}=0.355$
$\therefore K_{p}=\frac{\left(0.581 \times\left(2 \times 10^{5}\right)\right)^{2}}{\left(0.065 \times\left(2 \times 10^{5}\right)\right)^{2 \times\left(0.355 \times\left(2 \times 10^{5}\right)\right)}}$
units $=\mathrm{Pa}^{-1}$
10)
(d) (i) $\mathrm{K}_{\mathrm{sp}}=\left[\mathrm{Ca}^{2+}\right]^{3}\left[\mathrm{PO}_{4}{ }^{3-}\right]^{2}$
(ii) $\mathrm{Ca}_{3}\left(\mathrm{PO}_{4}\right)_{2} \longrightarrow 3 \mathrm{Ca}^{2+}+2 \mathrm{PO}_{4}{ }^{3-}$

$$
\begin{aligned}
& {\left[\mathrm{Ca}^{2+}\right]=3 \times\left(2.50 \times 10^{-6}\right)=7.6 \times 10^{-6} \mathrm{~mol} / \mathrm{dm}^{3}} \\
& {\left[\mathrm{PO}_{4}^{3-}\right]=2 \times\left(2.50 \times 10^{-6}\right) 5 \times 10^{-6} \mathrm{~mol} / \mathrm{dm}^{3}} \\
& \mathrm{~K}_{\mathrm{sp}}=\left[\mathrm{Ca}^{2+}\right]^{3}\left[\mathrm{PO}_{4}^{3-}\right]^{2} \\
& \quad=\left[7.5 \times 10^{-6}\right]^{3}\left[5 \times 10^{-6}\right]^{2}=1.05 \times 10^{-26} \mathrm{~mol}^{5} \mathrm{dm}^{-15}
\end{aligned}
$$

(e) (i) The enthalpy change when 1 mole of an ionic compound is formed from it's gaseous ions.
(ii) $\mathrm{Mg}^{2+}$ has a smaller ionic radius than $\mathrm{Ca}^{2+}$


- Founder \& CEO of Chemistry Online Tuition Ltd.
- Completed Medicine (M.B.B.S) in 2007
- Tutoring students in UK and worldwide since 2008
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