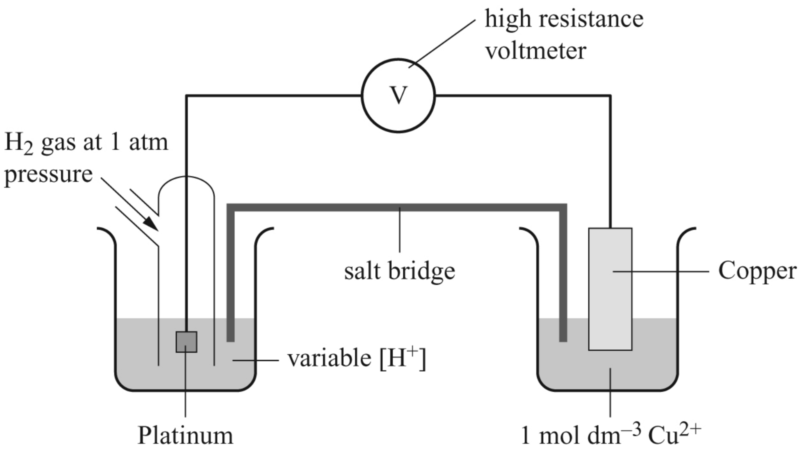
Chapter 21: Further aspects of equilibria

Homework marking scheme

1 This question is a difficult one and should be used to stretch and challenge.



The apparatus used is:

salt bridge	[1]
voltmeter	[1]
hydrogen gas at 1 atm pressure	[1]
1 mol dm^{-3} HCl	[1]
copper half-cell	[1]
salt bridge and voltmeter	[1]
‘high resistance’ (as type of voltmeter)	[1]

Use of the Nernst equation

$$E_{cell} = E^{\theta} + \frac{0.059}{z} \log_{10} [\text{ion}]$$ [1]

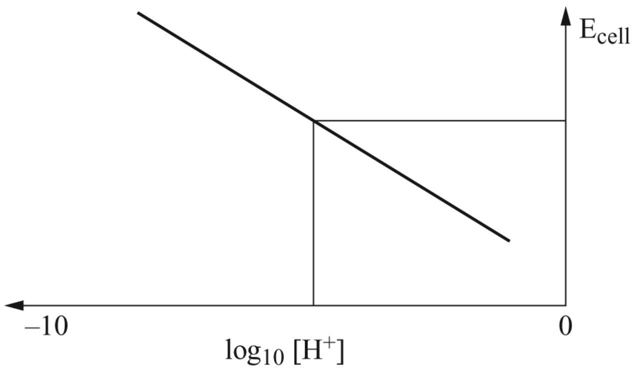
E^{θ} = 0.00 V for the hydrogen electrode [1]

If a graph is plotted for $\log_{10}[H^+]$ (horizontal axis) against E_{cell} (vertical axis) then it should be a straight line with slope $\frac{0.059}{z}$ (where z = number of electrons involved in the half-cell equation). [1]

The concentration of the H^+ ion is varied by using the various solutions of buffers, HCl and NaOH [1]
and the voltage measured. [1]

The equilibrium $H_2(g) \rightleftharpoons 2H^+(aq) + 2e^-$ moves to the right-hand side if the $[H^+]$ is decreased
the electrode potential therefore becomes more negative
the overall cell potential increases. [1]

Therefore, the graph will look like the one shown below:



two axes [1]
straight line in correct direction [1]
the value of $\log_{10}[H^+]$ can be found from $\log_{10}[H^+] = -pH$ [1]
the buffers of pH 4, 7 and 9 therefore have values for $\log_{10}[H^+]$ equal to −4, −7 and −9 [1]
The $\log_{10}[H^+]$ for 0.1 mol dm^{-3} is −1. [1]

The $[H^+]$ in the 0.1 mol dm^{-3} NaOH $= \dfrac{1\times10^{-14}}{OH^-} = 10^{-13}$.

therefore, pH = 13. [1]
If a solution of unknown pH is used then the voltage is measured and the value of $\log_{10}[H^+]$ read off from the graph. [1]

2 **a** The oxidation state of the bromine is zero in Br_2
it rises to +1 in HOBr and therefore is oxidised [1]
it decreases to −1 in HBr and is therefore reduced. [1]
Simultaneous oxidation and reduction is disproportionation. [1]

b **i** A strong acid is fully dissociated in aqueous solution. [1]
A weak acid is only partially dissociated in aqueous solution. [1]

ii in HBr, $[H^+] = 10^{-pH} = 10^{-1} = 0.1$ mol dm^{-3}. [1]
All the HBr has dissociated into H^+ ions and it is therefore a strong acid. [1]

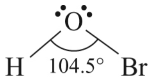
iii in HOBr, $[H^+] = 10^{-pH} = 10^{-4.83} = 1.48 \times 10^{-5}$ mol dm^{-3}. [1]
Only a small fraction of the HOBr dissociates into H^+ ions and it is therefore a weak acid. [1]

iv $K_a = \dfrac{[H^+]_{eq}[OBr^-]_{eq}}{[HOBr]_{eq}} = \dfrac{[H^+]^2}{[HOBr]_{start}}$ [1]

therefore, $K_a = \dfrac{(1.48\times10^{-5})^2}{0.1} = 2.19 \times 10^{-9}$ mol dm^{-3} [1]

c **i** [1]

ii



correct drawing [1]
correct bond angle. [1]

d **i** $2H^+(aq) + 2I^-(aq) + OBr^-(aq) \rightarrow H_2O(l) + I_2(aq) + Br^-(aq)$

correct reactants and products [1]

balancing. [1]

ii The orange/brown colour in the aqueous layer would fade [1]

and the cyclohexane layer would go purple. [1]

iii The I_2 molecule is nonpolar [1]

therefore, it is more soluble in the nonpolar solvent. [1]

3 **a** $K_a = 10^{-pK_a} = 10^{-7.2}$ [1]

$= 6.31 \times 10^{-8}$ mol dm^{-3} [2]

(take 1 mark off if units are incorrect)

$[H^+] = \sqrt{K_a \times [H_2PO_4^-]} = 7.94 \times 10^{-5}$ mol dm^{-3}

(this is because $K_a = \dfrac{[H^+]^2}{[H_2PO_4^-]}$) [1]

$pH = -\log_{10}[H^+] = 4.10$ [1]

b **i** A buffer is a mixture of a weak acid and its conjugate base. [1]

It resists changes in pH. [1]

ii The equilibrium present in the buffer is $H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$. [1]

If unwanted H^+ ions are added they combine with the HPO_4^{2-} [1]

to form the largely undissociated weak acid $H_2PO_4^-$ and are therefore removed, leaving the pH near constant. [1]

If unwanted OH^- ions are added they are neutralised by the H^+ ions thus disturbing the equilibrium. [1]

More $H_2PO_4^-$ dissociates until the K_a returns to its proper value and pH remains near constant. [1]

iii $K_a = \dfrac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}$ [1]

rearranging the formula gives $[H^+] = K_a \times \dfrac{[H_2PO_4^-]}{[HPO_4^{2-}]}$ [1]

$[H^+] = 6.31 \times 10^{-8} \times \dfrac{0.01}{0.06} = 1.05 \times 10^{-8}$ mol dm^{-3} [1]

$pH = -\log_{10}[H^+] = 7.98$ [1]

iv The equilibrium $H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$ would be displaced to the left [1]

in order to remove the added $H_2PO_4^-$ ions (Le Chatelier's principle). [1]

Therefore, $[H^+]$ increases and pH decreases. [1]

c **i** Ca^{2+} and PO_4^{3-} [2]

ii $Ca_3(PO_4^{3-})_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$ [1]

iii $K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$ [1]

iv solubility $= 2.48 \times 10^{-6}$ mol dm^{-3} [1]

$[Ca^{2+}] = 3 \times 2.48 \times 10^{-6} = 7.44 \times 10^{-6}$ mol dm^{-3} [1]

and $[PO_4^{3-}] = 2 \times 2.48 \times 10^{-6} = 4.96 \times 10^{-6}$ mol dm^{-3} [1]

$K_{sp} = (7.44 \times 10^{-6})^3 \times (4.96 \times 10^{-6})^2 = 1.01 \times 10^{-26}$ mol^5 dm^{-15} [2]

(take one mark off for incorrect units).

v There is a strong attraction between the +2 calcium ions and the −3 phosphate ions. [1]

Therefore, when the gaseous ions form the ionic lattice a lot of energy is produced as strong ionic bonds are formed. [1]

vi The enthalpies of hydration of the Ca^{2+} ions and the PO_4^{3-} ions are not sufficiently negative (enough) [1]

to overcome the large amount of energy needed to produce the gaseous ions from the ionic lattice (−L.E.). [1]