

**Marks**  
**8**

- An Ag electrode immersed in a saturated aqueous solution of AgBr has a reduction potential of 0.437 V at 25 °C with respect to the standard hydrogen electrode. Calculate the solubility product of AgBr at 25 °C.

The standard potential for the reduction  $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$ ,  $E^\circ = +0.80 \text{ V}$ .

The aqueous solution of AgBr will have  $[\text{Ag}^+(\text{aq})]$  equal to the solubility of AgBr. This solution has a non-standard concentration of  $\text{Ag}^+(\text{aq})$  and its potential is given by the Nernst equation with  $n = 1$  for this reduction:

$$E = E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{RT}{F} \ln \left( \frac{1}{[\text{Ag}^+(\text{aq})]} \right)$$

$$E = (+0.80 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(1 \times 96485 \text{ C mol}^{-1})} \ln \left( \frac{1}{[\text{Ag}^+(\text{aq})]} \right) = +0.437 \text{ V}$$

This gives  $[\text{Ag}^+(\text{aq})] = 7.25 \times 10^{-7}$ .

As dissolution of AgBr(s) leads to equal amounts of  $\text{Ag}^+(\text{aq})$  and  $\text{Br}^-(\text{aq})$ , this is also equal to  $[\text{Br}^-(\text{aq})]$ . Thus:

$$K_{\text{sp}} = [\text{Ag}^+(\text{aq})][\text{Br}^-(\text{aq})] = (7.25 \times 10^{-7})^2 = 5.3 \times 10^{-13}$$

Answer:  $K_{\text{sp}} = 5.3 \times 10^{-13}$

A Pd electrode immersed in an aqueous solution containing 0.01 Pd(NO<sub>3</sub>)<sub>2</sub> M and 1.00 M NaCl has a reduction potential of -0.860 V at 25 °C with respect to the Ag electrode above. Calculate the stability constant of the complex ion,  $[\text{PdCl}_4]^{2-}$ , at 25 °C.

The standard potential for the reduction  $\text{Pd}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pd}(\text{s})$ ,  $E^\circ = +0.92 \text{ V}$ .

The reduction potential of the Pd cell is -0.860 V with respect to the Ag electrode, which has a potential of +0.437 V. Thus,

$$E = (-0.860 + 0.437 \text{ V}) = -0.423 \text{ V}.$$

The aqueous solution will have a non-standard concentration of  $\text{Pd}^{2+}(\text{aq})$  and its potential is given by the Nernst equation with  $n = 2$  for this reduction:

$$E = E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{RT}{2F} \ln \left( \frac{1}{[\text{Pd}^{2+}(\text{aq})]} \right)$$

$$E = (+0.92 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(2 \times 96485 \text{ C mol}^{-1})} \ln \left( \frac{1}{[\text{Pd}^{2+}(\text{aq})]} \right) = -0.423 \text{ V}$$

This gives  $[\text{Pd}^{2+}(\text{aq})] = 3.7 \times 10^{-46}$ .

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For the formation of  $[\text{PdCl}_4]^{2-}(\text{aq})$ , the reaction table is:

	$\text{Pd}^{2+}(\text{aq})$	$4\text{Cl}^{-}(\text{aq})$	$\rightleftharpoons$	$[\text{PdCl}_4]^{2-}$
<b>Initial</b>	<b>0.01</b>	<b>1.00</b>		<b>0</b>
<b>Equilibrium</b>	$3.7 \times 10^{-46}$	<b>0.96</b>		<b>0.01</b>

As  $[\text{Pd}^{2+}(\text{aq})]_{\text{eq}}$  is so small, *essentially* all of the initially present  $\text{Pd}^{2+}$  reacts with  $4\text{Cl}^{-}$  to make  $[\text{PdCl}_4]^{2-}$  so  $[\text{Cl}^{-}]_{\text{eq}} = 1.00 - 4 \times 0.01 \text{ M} = 0.96 \text{ M}$  and  $[\text{PdCl}_4]^{2-} = 0.01 \text{ M}$ .

Hence:

$$K_{\text{stab}} = \frac{[\text{PdCl}_4^{2-}]}{[\text{Pd}^{2+}][\text{Cl}^{-}]^4} = \frac{0.01}{(3.7 \times 10^{-46})(0.96)^4} = 3 \times 10^{43}$$

Answer:  $3 \times 10^{43}$