Ion-electron half equations

The following half equations need to be recalled.

Acidified manganate(VII) ions

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$

colour change - purple to colourless

Acidified dichromate ions

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$

colour change - orange to green

Iodine to iodide ions

$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$

colour change - brown to colourless

Thiosulfate ions

$2S_2O_3^{2-}(aq) \rightleftharpoons S_4O_6^{2-}(aq) + 2e^-$

Aqueous thiosulfate ions and aqueous iodine

Aqueous $S_2O_3^{2-}$ ions are oxidised by aqueous I_2. The $S_2O_3^{2-}$ solution is placed in the burette; the I_2 is pipetted into the conical flask. The $S_2O_3^{2-}$ solution is run into the flask until the colour, due to I_2, fades to a pale-yellow colour. At this point starch solution is added as an indicator, turning the mixture dark blue. The end point is when the blue colour is decolourised.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

Aqueous iodide ions and aqueous copper(II) ions

$$2Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI(s) + I_2(aq)$$

The blue solution loses its colour. A white precipitate of CuI forms along with a brown solution of I_2.

The I_2 can then be titrated with $S_2O_3^{2-}$.

Aqueous dichromate ions and iron(II) ions

Aqueous $Cr_2O_7^{2-}$ is placed in the burette and added to a conical flask where it oxidises aqueous Fe^{2+}.

An indicator is required.

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Fe^{2+}(aq) \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l) + 6Fe^{3+}(aq)$$

The interconversion of dichromate ions, $Cr_2O_7^{2-}$ and chromate(VI) ions, CrO_4^{2-} is **NOT** redox as the chromium does not change its oxidation number. The colour change is orange to yellow and vice versa.

$$Cr_2O_7^{2-}(aq) + OH^-(aq) \rightleftharpoons 2CrO_4^{2-}(aq) + H^+(aq)$$

Aqueous manganate(VII) ions and iron(II) ions

The potassium manganate(VII) solution must always be standardised by titration with a standard solution of a reducing agent such as iron(II) ammonium sulfate. The aqueous MnO_4^- is placed in the burette and the Fe^{2+} solution pipetted into the conical flask with an excess of aqueous sulfuric acid. These titrations require no indicator. As soon as all the Fe^{2+} has been oxidised, the next drop of MnO_4^- gives a pink colour to the contents of the flask.

Half equations are combined to give an overall ionic equation:

$Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + e^-$

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$

$$\mathbf{MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{2+}(aq)}$$

25.00 g of $FeSO_4.7H_2O$ was dissolved in water and made up to 1.00 dm^3 using excess dilute sulfuric acid. 25.0 cm^3 of this solution was titrated with aqueous $KMnO_4$. 25.55 cm^3 of the $KMnO_4$ solution was required for complete oxidation.

Calculate the concentration of the $KMnO_4$ solution in mol dm^{-3}.

M_r $FeSO_4.7H_2O$ = 278.0

moles $FeSO_4.7H_2O$ = 25.00/278.0 = 0.08933

moles Fe^{2+} = 0.08933

$[Fe^{2+}]$ = 0.08993 mol dm^{-3}

$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{2+}(aq)$$

moles Fe^{2+} in 25.0 cm^3 = 0.08993 × (25.0 / 1000) = 2.248×10^{-3}

moles MnO_4^- in 25.55 cm^3 = 2.248×10^{-3} / 5 = 4.496×10^{-4}

$[KMnO_4]$ = 4.496×10^{-4} / (25.55 / 1000) = 0.0176 mol dm^{-3}