CHEMISTRY

38th and 39th Class, 02-11-2021

Dr. K. Ananthanarayanan

Associate Professor (Research)

Department of Chemistry

Room No 319, 3rd Floor, Raman Research Park

Email : ananthak@srmist.edu.in

Phone : 9840154665

Dr K Ananthanarayanan   Page 1

Virtual lab.

To estimate the amount of ferrous ion in the given sample by potentiometric titration

Expt. No.:6

Calculate the concentration of an unknown analyte by performing a redox titration

Redox titration

SRM
INSTITUTE OF SCIENCE & TECHNOLOGY

❑ **Oxidation-reduction reaction** between the titrand and the tirant. Here the end point is detected using a potentiometer

❑ Potentiometric titrations involves the **measurement of the potential of a suitable indicator electrode with respect to a reference electrode** as a function of titrant volume.

❑ **SCE is used as the reference electrode**. Platinum metal foil, dipped in Fe^{2+} solution is used as **the indicator electrode**.

3

Potentiometric titration

SRM
INSTITUTE OF SCIENCE & TECHNOLOGY

❑ **Volumetric method** for the measurement of **changes in the e.m.f between two electrodes on the addition of titrant** of **known concentration to a solution of unknown concentration**.

❑ In this potentiometric titration setup an **indicator electrode (Pt electrode) and reference electrode (calomel) is coupled to form electrochemical cell.**

❑ The overall cell potential is calculated as :

$$E_{cell} = E_{ind} - E_{ref} + E_{sol}$$

❑ E_{sol} is the **potential drop over the test solution** between the two electrodes which is recorded at intervals as the titrant is added.

11/3/2021   4

Potentiometric titration

Reference or Counter electrode : It has the *constant potential/EMF*

Ag/AgCl electrode, Calomel electrode

Indicator or Working electrode - It responds to the *change in the concentration of the analyte solution.*

Electrolyte - contains the *analyte solution*

Combination electrode – Both *reference* and *indicator electrode*

11/3/2021   5
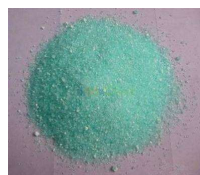
Apparatus required

❑ Digital Potentiometer (ORP sensor)

❑ **S**aturated **C**alomel **E**lectrode, **SCE** (Reference Electrode)

❑ Platinum electrode (Working/Indicator Electrode)

❑ Burette (25 mL)

❑ Pipette (10 mL)

❑ Beakers (250 mL)

❑ Standard volumetric flask

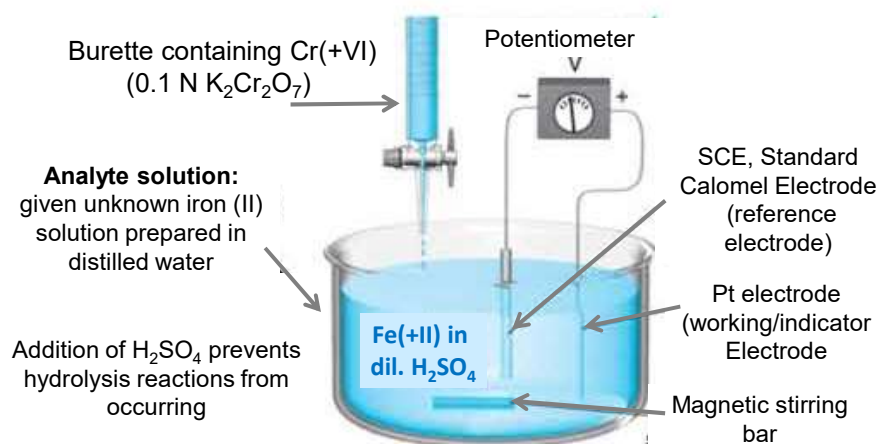# Reagents

- ❑ **Ferrous Ammonium Sulphate (FAS)** solution

- ❑ Std. $K_2Cr_2O_7$ (0.1N) solution

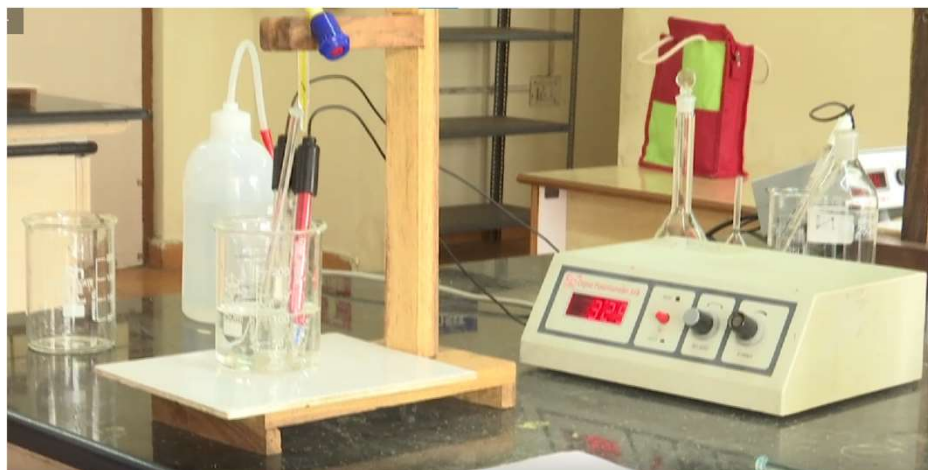- ❑ dil. H_2SO_4 solution

---

Potentiometric titration

Burette containing Cr(+VI)
(0.1 N $K_2Cr_2O_7$)

Potentiometer

Analyte solution:
given unknown iron (II)
solution prepared in
distilled water

SCE, Standard
Calomel Electrode
(reference
electrode)

Pt electrode
(working/indicator
Electrode

Fe(+II) in
dil. H_2SO_4

Addition of H_2SO_4 prevents
hydrolysis reactions from
occurring

Magnetic stirring
bar

Experimental set up - picture

Principle

❑ The cell set up : $Hg|HgCl_2(s),KCl\ (1N)\ ||\ Fe^{2+}\ |\ Fe^{3+},\ Pt$

❑ The chemical reaction taking place :

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \quad (E^O = 1.33\ V)$$
(Cr in +6 state)   (Cr in +3 state)

$$[Fe^{2+} \rightarrow Fe^{3+} + e^-]6 \quad (E^O = 0.77\ V)$$

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$
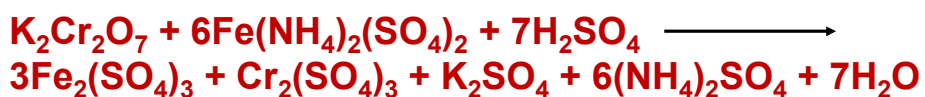---
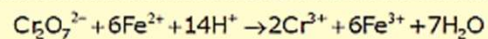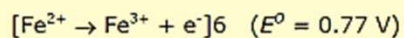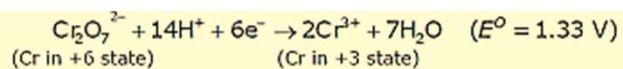
❑ Fe^{2+} is oxidised to Fe^{3+} as $K_2Cr_2O_7$ is progressively added.

❑ Pt electrode kept in contact with Fe^{2+} /Fe^{3+} mixture acts as redox electrode

Therefore, 1 mole of $Cr_2O_7^{2-}$ (the oxidizing agent) reacts with 6 moles of Fe^{2+} (the reducing agent) to form 6 moles of Fe^{3+} and 2 moles of Cr^{3+}.

$K_2Cr_2O_7 + 6Fe(NH_4)_2(SO_4)_2 + 7H_2SO_4 \longrightarrow$
$3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 6(NH_4)_2SO_4 + 7H_2O$

❑ The **1:6 mole ratio** with respect to the amounts of $Cr_2O_7^{2-}$ and Fe^{2+} consumed will provide the stoichiometric basis for all of the calculations in this experiment.

11/3/2021   11

Principle

$$E = E^0 - \frac{2.303\ RT}{nF} \log Q$$

standard potential — number of electrons — Faraday constant — reaction quotient

$$E = E^o_{Oxd/Red} + \frac{0.0591}{n} \log_{10} \frac{[Oxd]}{[Red]}$$

E, E^o, [Oxd], [Red] and 'n' are the experimental electrode potential at room temperature, standard reduction potential, concentration of oxidised form, concentration of reduced form and number of electrons involved in the redox process of the system respectively.
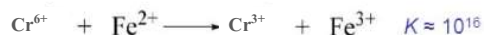
11/3/2021   12
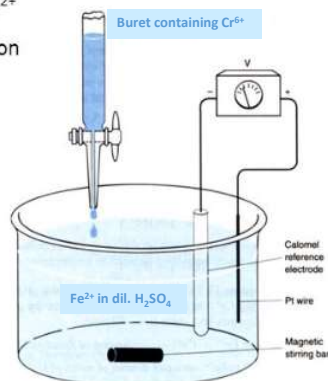
6

Principle contd..

SRM
INSTITUTE OF SCIENCE & TECHNOLOGY

Voltage Change as a Function of Added Titrant

➤ Consider the Titration Reaction (essentially goes to completion):

$$Cr^{6+} + Fe^{2+} \longrightarrow Cr^{3+} + Fe^{3+} \quad K \approx 10^{16}$$

➤ Cr^{6+} is added with a buret to a solution of Fe^{2+}

➤ Pt electrode responds to relative concentration of Fe^{3+}/Fe^{2+} & Cr^{6+}/Cr^{3+}

➤ Calomel electrode used as reference

Indicator half-reactions at Pt electrode:

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \quad E^0 = 0.767 \text{ V}$$

$$Cr^{6+} + 3e^- \longrightarrow Cr^{3+} \quad E^0 = 1.33 \text{ V}$$

Buret containing Cr^{6+}

Fe^{2+} in dil. H_2SO_4

Calomel reference electrode

Pt wire

Magnetic stirring bar

Principle contd..

SRM
INSTITUTE OF SCIENCE & TECHNOLOGY

❑ Considering the present titration, the two systems of relevance, viz., **Fe(III)/Fe(II) and Cr(VI)/Cr(III) have E⁰ values of 0.76 V, 1.36 V** respectively, with a large potential difference of **0.6 V and hence, quantitative oxidation of Fe(II) to Fe (III) by Cr (VI)** should be possible.

$$E_{Fe(III)/Fe(II)} = E^o_{Fe(III)/Fe(II)} + \frac{0.0591}{1} \log_{10} \frac{[Fe(III)]}{[Fe(II)]} \ , \quad E^o_{Fe(III)/Fe(II)} = 0.76 \text{ V}$$

$$E_{Cr(VI)/Cr(III)} = E^o_{Cr(VI)/Cr(III)} + \frac{0.0591}{3} \log_{10} \frac{[Cr(VI)]}{[Cr(III)]} \ , \quad E^o_{Cr(VI)/Cr(III)} = 1.36 \text{ V}$$
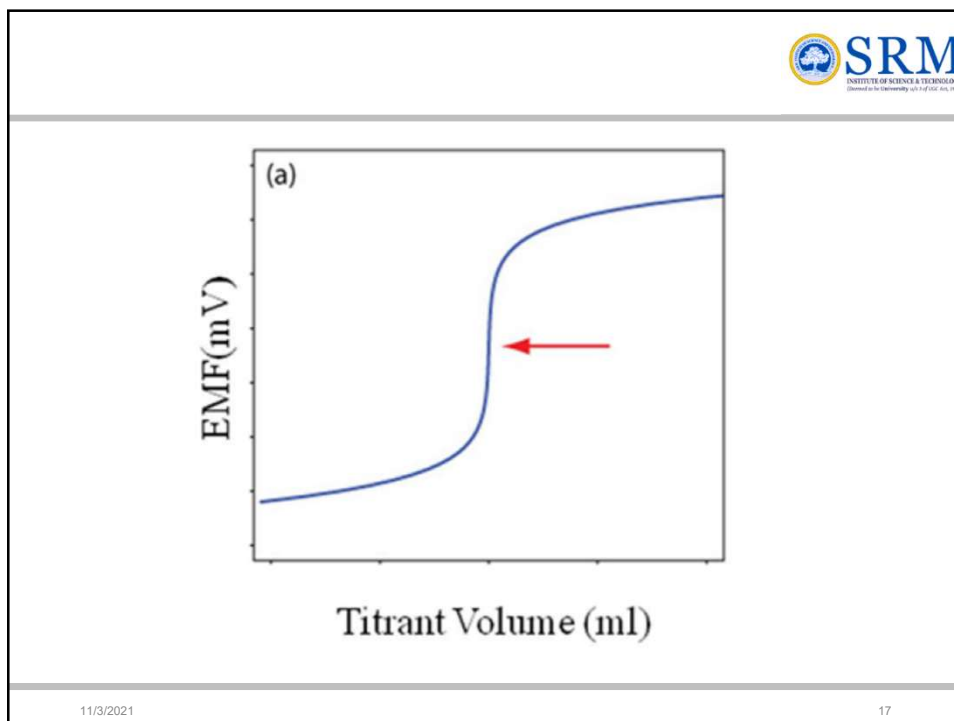
Titration curve
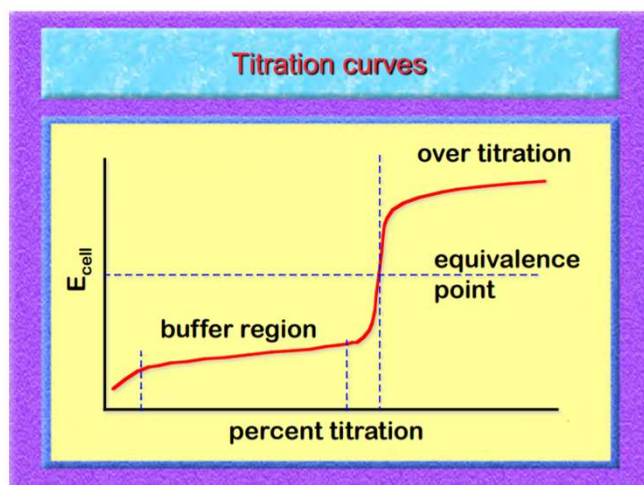
Principle contd..

- ❑ The reduction potential of single electrode depends initially on the ratio of Fe^{2+} / Fe^{3+}
- ❑ During the titration of **Fe^{2+} in H_2SO_4 medium, with $K_2Cr_2O_7$,this ratio varies to a little extent at the beginning**
- ❑ Suddenly near the end point there occurs a sudden change in the **ratio of Fe^{3+} /Fe^{2+} as the equivalence point is reached.**
- ❑ This results **in the sudden increase in e.m.f of the cell at equivalence point**

$$E = E^oFe^{2+} + E^oCr_2O_7^{2-}$$

before equivalence

$$E = E^o + \frac{0.0591}{n} \log \frac{[\ Fe^{3+}\ ]}{[\ Fe^{2+}\ ]}$$

At equivalence

after equivalence

$$E = E^o + \frac{0.0591}{n} \log \frac{[Cr_2O_7^{2-}]}{[\ Cr^{3+}\ ]}$$

$$E = \left[E^o - \frac{RT}{nF} \, ln \, \frac{a_{red}}{a_{oxid}} \right] - E^o_{ref}$$

$$E = \left[E^o - \frac{RT}{nF} \, ln \, \frac{[Fe^{2+}]}{[Fe^{3+}]} \right] - 0.2422$$

$$E^o_{SCE} = 0.2422V$$

$$E^o_{Fe^{3+}|Fe^{2+}} = 0.77V$$

Procedure

❏ The given ferrous iron solution is **made up to a known volume (say 100mL) in a standard measuring flask.**

❏ Exactly **10 mL of the made up Fe^{2+} solution** is pipetted out into a clean **250mL beaker**. About **10mL of dil.H_2SO_4 and 100mL of distilled water** are added to it.

❏ A **platinum electrode is dipped into this solution and coupled with the standard calomel electrode**. The resultant cell is then incorporated into the potentiometric circuit.

❏ Standard **$K_2Cr_2O_7$ solution, taken in a burette**, is added in instalments of **1mL into the beaker and the cell e.m.f is measured** after each addition with **proper mixing.**

❏ The process is continued **till and also well beyond the equivalence point as indicated by an abrupt change in e.m.f**

11/3/2021   19

Procedure contd..

❏ Note the **volume of $K_2Cr_2O_7$ solution required for complete oxidation of Fe^{2+} solution from the plot of e.m.f Vs volume of standard $K_2Cr_2O_7$ solution** added.

❏ Calculate the normality of given **Fe^{2+} solution using the formula $N_1V_1 = N_2V_2$**

❏ One more similar titration is performed by **adding 0.2 mL portions of $K_2Cr_2O_7$ solution close to the end point (1mL on either side of the range)** and tabulating the measured e.m.f corresponding to each addition.

❏ Graph is plotted *(i) e.m.f Vs volume of $K_2Cr_2O_7$ solution*
               (ii) ΔE / ΔV Vs volume of $K_2Cr_2O_7$ solution

❏ The **exact end point can be determined from the plot of ΔE / ΔV Vs volume of $K_2Cr_2O_7$ solution**

11/3/2021   20

Principle contd..

First Derivative Curve

$\frac{\Delta E}{\Delta V}$

Volume of $K_2Cr_2O_7$ (cm³)

EMF(mV)

Titrant Volume (ml)
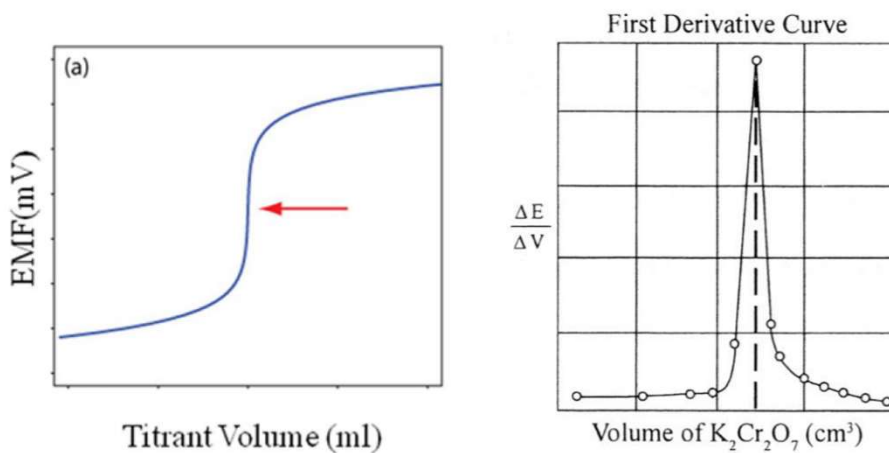
11/3/2021   21

Tabular column

Table-1 : FAS Vs $K_2Cr_2O_7$ (pilot titration)

S.No.	Volume of $K_2Cr_2O_7$ (mL)	emf (volts)
1		
13		

11/3/2021   22

Tabular column

Table- 2 : FAS Vs $K_2Cr_2O_7$ (fair titration)

S.No.	Volume of $K_2Cr_2O_7$ (mL)	emf (volts)	Δ E (Volts)	Δ V (mL)	Δ E / Δ V (volts/mL)
1					
24					

11/3/2021   23

Tabular column

Point	V_i (mL)	mV_i	ΔV^* (mL)	ΔmV	$\Delta mV/\Delta V$ (mL)$^{-1}$
1	V_1	mV_1	---	---	---
2	V_2	mV_2	$V_2 - V_1$	$mV_2 - mV_1$	$(mV_2 - mV_1)/(V_2 - V_1)$
3	V_3	mV_3	$V_3 - V_2$	$mV_3 - mV_2$	$(mV_3 - mV_2)/(V_3 - V_2)$
4	V_4	mV_4	$V_4 - V_3$	$mV_4 - mV_3$	$(mV_4 - mV_3)/(V_4 - V_3)$
...					

11/3/2021   24

12

Calculation

FAS Vs $K_2Cr_2O_7$
$N_1V_1 = N_2V_2$
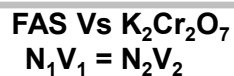
Volume of pipette solution (FAS) = V_1 mL (10 mL)

Volume of $K_2Cr_2O_7$ = V_2 mL (from graph of fair titration)

Normality of $K_2Cr_2O_7$ = N_2 (0.1 N)

Normality of FAS (N_1) = ?

Strength of FAS = N_1 $= \frac{V_2 N_2}{V_1}$

Amount of Fe^{2+} (g/L) = Eq. wt. of Fe x Normality of Fe^{2+}

Amount of Fe^{2+} in 100 mL $= \dfrac{55.85 \text{ x Normality of } Fe^{2+}}{10}$

Result

❑ **The amount of ferrous ion present in the given solution =**

Precautions to be taken

❑ Dichromate is toxic to the environment. After the experiment, excess dichromate and the analyte are to be discarded in the designated waste bottles located on the reagent bench.
❑ Dichromate solution should be freshly prepared.
❑ Burette and pipette should be rinsed with the solution to be taken in it.
❑ There should not be any leakage in the burette.
❑ Sulfuric acid waste must be placed in the plastic, labeled acid waste container under the acid fume hood. (Alternatively, it may be neutralized with sodium bicarbonate safety solution)

11/3/2021   27

Table -1 Ferrous Ammonium Sulphate Solution vs Potassium dichromate solution

Sl.No.	Volume of $K_2Cr_2O_7$ solution (mL)	EMF (mV)	
1	0	362	
2	1	368	
3	2	417	
4	3	433	
5	4	450	
6	5	471	
7	6	495	Sudden increase in EMF
8	7	691	
9	8	721	
10	9	729	
11	10	752	
12	11	757	
13	12	764	
14	13	770	
15	14	776	

Table -2

Ferrous Ammonium Sulphate Solution Vs Potassium dichromate solution

Sl.No.	Volume of K$_2$Cr$_2$O$_7$ solution (mL)	EMF (mV)	ΔE (mV)	ΔV (mL)	ΔE/ΔV
1	4.8	448	----	------	-----
2	5	456			
3	5.2	460			
4	5.4	464			
5	5.6	469			
6	5.8	472			
7	6.0	477			
8	6.2	480			
9	6.4	488			
10	6.6	493			
11	6.8	501			
12	7.0	514			

13	7.2	525			
14	7.4	564			
15	7.6	668			
16	7.8	689			
17	8	699			
18	8.2	708			
19	8.4	715			
20	8.6	721			
21	8.8	724			
22	9.0	728			
23	9.2	734			
24	9.4	740			