

Unit-3 Principles involved in Volumetric & Gravimetric estimations.

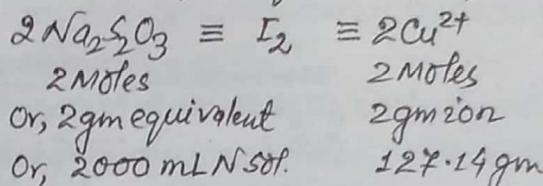
⇒ Volumetric estimation of Cu^{2+} :

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Principle: When potassium iodide (KI) solution is added in excess to a Cu^{2+} solution, KI is quantitatively oxidised to liberate I_2 . The amount of liberated I_2 is equivalent to the Cu^{2+} present in the solution. The liberated I_2 can be titrated with a standard ($N/10$) sodium thiosulphate ($Na_2S_2O_3$) solution using $\frac{1}{2}$ % starch solution as an indicator.



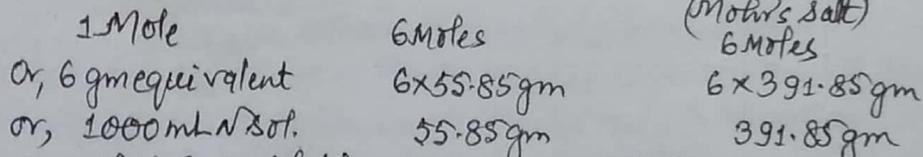
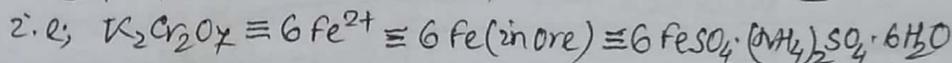
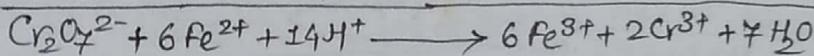
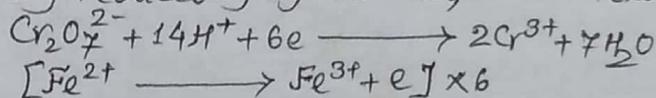
Equivalence relation from equation (1) & (2):



∴ 1 mL N $Na_2S_2O_3$ solution \equiv 0.06357 gm Cu^{2+} or Cu.

⇒ Volumetric estimation of Iron (Fe):

Principle: Iron (Fe^{2+}) is estimated in given sample of Mohr's salt/iron ores by an oxidising agent $KMnO_4$ or $K_2Cr_2O_7$ in presence of dilute (2N) H_2SO_4 . The ore is usually dissolved in HCl, the Fe^{3+} reduced to Fe^{2+} . The solution is titrated with standard $KMnO_4$ / $K_2Cr_2O_7$ solution in acidic medium using 1% N-phenylanthranilic acid solution in 0.005 M NaOH as an external indicator in case of $K_2Cr_2O_7$ titration. Determination/estimation of Fe^{2+} with $K_2Cr_2O_7$ solution preferred over $KMnO_4$ solution due to (i) an excellent primary standard (ii) its aqueous solution stable indefinitely (iii) it is used only in acidic medium, and is reduced rapidly at RT to a green Cr^{3+} salt. (iv) less easily reduced by organic matter, and stable towards light.



∴ 1 mL N $K_2Cr_2O_7$ solution \equiv 0.056 gm Fe/ Fe^{2+} ion \equiv 0.392 gm Mohr's salt.

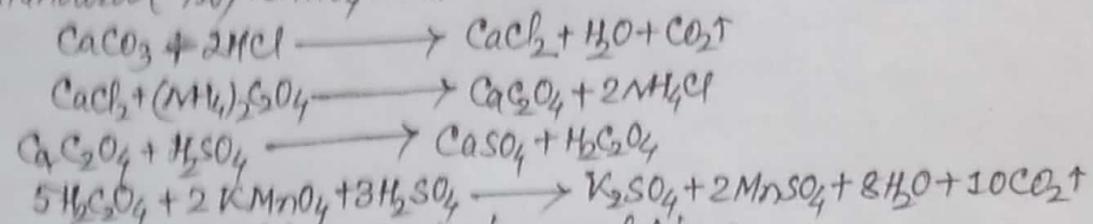
The green colour due to formation of Cr^{3+} ions by reduction of $K_2Cr_2O_7$ makes it impossible to ascertain the end point, so a redox indicator (1% N-phenylanthranilic acid in 0.005 M NaOH) used.

⇒ Volumetric estimation of Calcium (Ca^{2+}):

Calcium (Ca^{2+}) is estimated in given sample of limestone/Ca-ore/ Ca^{2+} salt sol. by permanganometry (using standard $KMnO_4$ sol.). The Ca-ore/limestone ($CaCO_3$) is first treated with dilute HCl to give $CaCl_2$ solution. When $CaCl_2$ / Ca^{2+} solution is treated

(2)

Calcium
With hot ammonium oxalate solution, oxalate (CaC_2O_4) is formed. The calcium oxalate is decomposed by dilute H_2SO_4 to free oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), which is then titrated with standard (N/10) KMnO_4 solution.



From above equations, equivalence relation:

$$2\text{KMnO}_4 \equiv 5\text{H}_2\text{C}_2\text{O}_4 \equiv 5\text{CaCl}_2 \equiv 5\text{CaCO}_3 \equiv 5\text{Ca or Ca}^{2+}$$

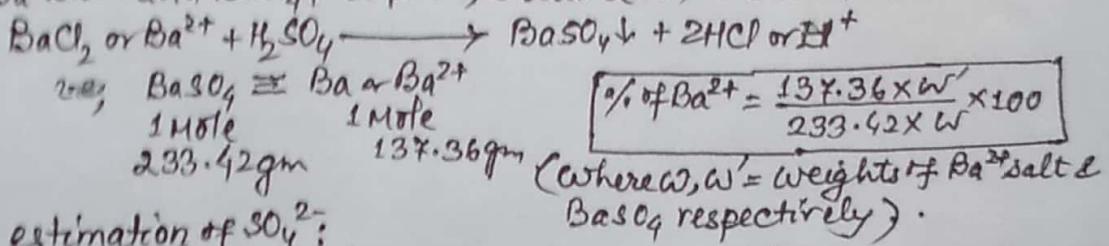
2 Moles or, 10 gmequ.
or, 1 gmequivalent
or, 1000 mL N solution

5 Moles
or, 0.5 mole
or, 20.04 gm

$\therefore 1 \text{ mL N KMnO}_4 \text{ solution} = 0.0204 \text{ gm Ca or Ca}^{2+}$.

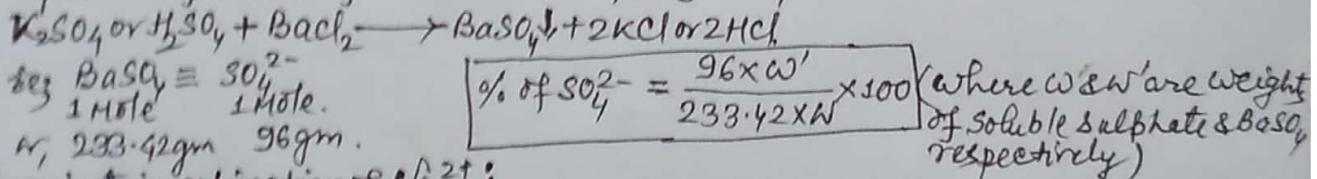
Gravimetric estimation of Ba^{2+}

When an excess of dilute H_2SO_4 is slowly added to a solution of Ba^{2+} salt (e.g. BaCl_2), barium is quantitatively precipitated as BaSO_4 (Barium sulphate). Knowing the weight of Ba^{2+} salt and BaSO_4 precipitate, barium (Ba^{2+}) is estimated in barium salt.



Gravimetric estimation of SO_4^{2-}

When an excess of a dilute solution of BaCl_2 is slowly added to a hot solution of a soluble sulphate (e.g. K_2SO_4 or Fe_2SO_4) solution containing a little conc. HCl or H_2SO_4 , the sulphate (SO_4^{2-}) present in solution quantitatively precipitated as BaSO_4 . Knowing the weights of BaSO_4 & soluble sulphate salt, SO_4^{2-} in soluble sulphate can be estimated. The precipitation is done at boiling temp. and weakly acidic medium in order to prevent the possible formation of Ba^{2+} salts as CrO_4^{2-} , CO_3^{2-} & PO_4^{3-} .



Gravimetric estimation of Ni^{2+}

When an alcoholic solution of dimethylglyoxime (H_2DMG) is added to neutral or faintly acidic hot solution of Ni^{2+} salt, nickel is quantitatively precipitated as inner complex, nickel dimethylglyoximate (scarlet red). A slight excess of aqueous ammonia (NH_4OH) free from CO_3^{2-} added during precipitation of Ni^{2+} , since precipitate is insoluble in its amm. salts. Only a slight of the reagent should be used, since H_2DMG is not very soluble in water or in very dilute ethanol and may precipitate, if a very large excess is added, some of the precipitate may dissolve. Knowing weights (w, w') of Ni^{2+} salt & nickel dimethylglyoximate ppt, Ni^{2+} is estimated.

