particles to come close thus inhibits the formation of larger aggregates

H_2A^{-1} HA^{-2} A^{-3}

K_{a1} K_{a2} K_{a3}

$$\text{pH of } H_2A^{-1} = -\frac{1}{2}\log\left\{\frac{K_W K_{a1} + K_{a1}K_{a2}[H_2A^{-1}]}{K_{a1} + [H_2A^{-1}]}\right\} \approx -\frac{1}{2}\log\left[K_{a1}K_{a2}\right]$$

$$\text{pH of } HA^{-2} = -\frac{1}{2}\log\left\{\frac{K_W K_{a2} + K_{a2}K_{a3}[HA^{-2}]}{K_{a2} + [HA^{-2}]}\right\} \approx -\frac{1}{2}\log\left[K_{a2}K_{a3}\right]$$

titration is one with pK_a close to the equivalence point pH endpoint with the volume recorded as $V_{0\text{-}Ph}$. On the same solution, methylred is then added and an additional volume is required to reach the end point recorded as $V_{Ph\text{-}MR}$

- Step 1: Assign oxidation numbers to each of the species in the reaction

$$\underset{+3\,-2}{NO_2^{-1}} + \underset{+7\,-2}{MnO_4^{-1}} \leftrightarrows \underset{+5\,-2}{NO_3^{-1}} + \underset{+4}{MnO_2}$$

- Step 2: Identify oxidation and reduction reactions and indicate the number of electrons lost or gained, respectively

Oxidation: $\underset{+3}{NO_2^{-1}} \leftrightarrows \underset{+5}{NO_3^{-1}} + 2e^-$

Reduction: $\underset{+7}{MnO_4^{-1}} + 3e^- \leftrightarrows \underset{+4}{MnO_2}$

- Step 3: Balance the reaction by multiplying a factor on both sides of the reaction so that the numbers of electrons on both reactions are the same

Oxidation ×**3**: $3\,\underset{+3}{NO_2^{-1}} \leftrightarrows 3\,\underset{+5}{NO_3^{-1}} + 6e^-$

Reduction ×**2**: $2\,\underset{+7}{MnO_4^{-1}} + 6e^- \leftrightarrows 2\,\underset{+4}{MnO_2}$

$$3\,NO_2^{-1} + 2\,MnO_4^{-1} \leftrightarrows 3\,NO_3^{-1} + 2\,MnO_2$$

- Step 4: Balance the charges (by adding H^+ or HO^-) and number of hydrogen and/or oxygen atoms (by adding H_2O) on both sides of the equation
- In acidic medium, add H_2O to the oxygen-deficient side and supply H^+ to balance the hydrogen

$$3\,NO_2^{-1} + 2\,MnO_4^{-1} + \mathbf{2\,H^+} \leftrightarrows 3\,NO_3^{-1} + 2\,MnO_2 + \mathbf{H_2O}$$

- In basic medium, balance assuming reaction was in acidic medium. Neutralize H^+ by adding HO^{-1} on both sides of the reaction and simplify

$$3\,NO_2^{-1} + 2\,MnO_4^{-1} + 2\,H^+ + \mathbf{2\,HO^{-1}} \leftrightarrows 3\,NO_3^{-1} + 2\,MnO_2 + H_2O + \mathbf{2\,HO^{-1}}$$

$$3\,NO_2^{-1} + 2\,MnO_4^{-1} + \mathbf{2\,H_2O} \leftrightarrows 3\,NO_3^{-1} + 2\,MnO_2 + \mathbf{H_2O} + 2\,HO^{-1}$$

$$3\,NO_2^{-1} + 2\,MnO_4^{-1} + \mathbf{H_2O} \leftrightarrows 3\,NO_3^{-1} + 2\,MnO_2 + \mathbf{2\,HO^{-1}}$$

3. Standard electrode potential

- The potential of a half-cell reaction with the standard hydrogen electrode (SHE) used as anode when the activities of all reactants and products are taken as unity, that is, 1M concentration and 1 atm partial pressure
- Usually listed as standard reduction potential ($\varepsilon_{red}°$) where a positive value implies that the electrode was used as a cathode and the SHE as anode
- High value of reduction potential indicates that the electrode is a good oxidizing agent

Nernst equation

- Formulated by Walther Hermann Nernst (1864-1941)
- Accounts for the effect of concentration on electrode potentials

For a half-cell reduction reaction…Ox ⇆ Red + **n**e⁻

$$\varepsilon_{Red} = \varepsilon°_{Red} - \frac{RT}{nF}\ln\frac{a_{Red}}{a_{Ox}}$$

where ε_{Red} = actual cell potential [V], $\varepsilon°_{Red}$ = standard reduction potential [V], R = 8.314 J-mol^{-1}-K^{-1}, T = temperature [K], n = number of electrons that appear in the half-cell reaction [mol], a = activity [ ] and F, Faraday's constant = 96485.3399 coul-(mol e$^-$)$^{-1}$

At 25°C and for a given cell…

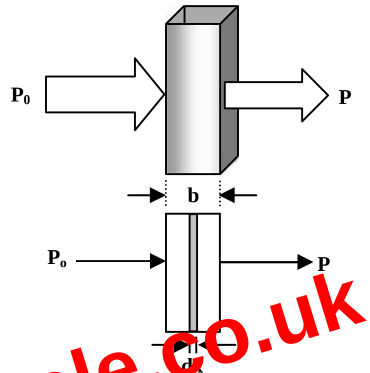
$$\varepsilon_{cell} = \varepsilon°_{cell} - \frac{0.05916}{n}\log Q$$

$$COD = \frac{\left(V_{Fe^{+2}}^{mL,blank} - V_{Fe^{+2}}^{mL,sample}\right)\left(M_{Fe^{+2}}\right) \times \frac{1\ mmol\ K_2Cr_2O_7}{6\ mmol\ Fe^{+2}} \times \frac{6\ mmol\ O_2}{4\ mmol\ K_2Cr_2O_7} \times \frac{32\ mg\ O_2}{1\ mmol\ O_2}}{volume\ sample\ (L)}$$

Molecular Absorption Spectrometry

A. Absorption Process and Beer-Lambert Law

- If a beam of light passes through a glass container filled with liquid, the emergent radiation is always less powerful than that entering
- Consider a block of absorbing matter where a beam of monochromatic radiation of radiant power, $\mathbf{P_0}$ strikes the surface perpendicularly and passes through the length of the material, **b**
- The emergent or transmitted radiation will always have less radiant power, **P** than the entering or incident radiation
- The fraction of incident radiation transmitted by the solution, $\mathbf{P/P_0}$ is called transmittance and related to absorbance according to the equation:



$$A = -\log T = -\log \frac{P}{P_0}$$

where A = absorbance, T = transmittance, P_0 = incident radiant power [W], and P = transmitted radiant power [W]

- **Beer-Lambert's law** states that the absorbance is directly proportional to the concentration of the absorbing species and to the path length

$$A = -\log T = -\log \frac{P}{P_0} = \varepsilon bc$$

where ε = molar absorptivity [L-mol^{-1}-cm^{-1}], b = path length [cm] and c = concentration [mol-L^{-1}]

B. Quantitative Analysis

1. *Standard addition method*

- Involves addition of several increments of a standard solution to aliquots ofsamples of the same size and the resulting solution upon adding the color development reagent is then diluted to a fixed volume (V_T) and measured for its absorbance
- Assume several identical aliquots of the unknown solution of volume $\mathbf{V_x}$ were treated with several increments of standard solution of volume $\mathbf{V_s}$ of known concentration $\mathbf{C_s}$ and diluted to a fixed final volume $\mathbf{V_T}$.
- If each of these solutions were assumed to obey Beer's law, the absorbance ($\mathbf{A_S}$)of each solution is described by:

$$A_s = \frac{\varepsilon b V_S C_S}{V_T} + \frac{\varepsilon b V_X C_X}{V_T} = kV_S C_S + kV_X C_X = mC_S + b$$

where $k = \varepsilon b/V_T$, $m = kV_S$ and $b = kC_XV_X$

70. The 300 mg sample of impure Na_2SO_4 (142.04) was dissolved in sufficient water and the sulfate was precipitated by the addition of 35.00 mL of 0.1022 M $BaCl_2$. The precipitate was removed by filtration and the remaining $BaCl_2$ consumed 6.79 mL of 0.2467 M EDTA for titration to the Calmagite endpoint. Calculate the purity of the sample.
    a. 80% b. 85% c. 90% d. 95%

71. A 0.8521 gram sample of an alloy was found to contain Cu (63.55) and Zn (65.41) with small amounts of Pb (207.2) and Hg (200.59). The sample was dissolved in nitric acid and diluted to 500 mL. A 10 mL aliquot was treated with KI to mask the Hg and the resulting solution required 7.06 mL of 0.0348 M EDTA solution. A second 25 mL aliquot was treated with ascorbic acid and the pH was adjusted to 2.00to reduce Hg^{+2} and the metallic Hg was removed from the solution. To this solution, thiourea was then added to mask the Cu and the resulting solution required 8.58 mL for titration. The lead ion was titrated in a 250 mL in the presence of NaCN to mask Cu, Zn and Hg and required 3.11 mL for titration. Calculate the percentage of Cuand Hg in the sample of alloy.
    a. 47% Cu and 3% Hg c. 53% Cu and 7% Hg
    b. 44% Cu and 5% Hg d. 56% Cu and 5% Hg

72. Commonly, the analyte in a sample is present in two different oxidation states. Pre-reduction is then necessary before titration. One of the metallic reductors is zinc soaked in a dilute solution of mercuric chloride. This reductor is known as __________.
    a. Walden reductor c. Lindlars catalyst
    b. Devarda Alloy d. Jones reductor

73. At pH = 7 and a pressure of 1 bar, the potential for the half reaction, $2H^+_{(aq)} + 2e^- \rightarrow H_{2\,(g)}$ is__________.
    a. 0 V b. –0.414 V c. –0.828 V d. –1.255 V

74. Which of the following is <u>false</u> about iodine as an oxidizing agent in titration?
    a. Standard iodine solutions have low smaller electrode potential
    b. Sensitive and reversible indicators are readily available
    c. Iodine is very soluble in water and losses are minimal
    d. The solution lacks stability and requires regular standardization

75. What is the molarity of a $KMnO_4$ solution standardized against 1.356 gram $Na_2C_2O_4$ (134 $^{g}/_{mol}$) requiring 25.1 mL of the solution in acidic medium?
    a. 0.161 M b. 0.403 M c. 1.008 M d. 0.856 M

76. All of the following is used as oxidant in redox titrations <u>**except**</u>
    a. $KMnO_4$ b. Cerium (IV) c. $K_2Cr_2O_7$ d. Iodide

77. A sample of iron ore weighing 385.6 mg was dissolved in acid and passed through a Jones reductor. The resulting solution 52.36 mL of 0.01436 M $K_2Cr_2O_7$ for titration to the diphenylamine sulfonic acid endpoint. Calculate % Fe_3O_4 (231.55 $^{g}/_{mol}$) in the ore sample.
    a. 15.05% b. 45.15% c. 90.30% d. 67.98%

78. A sample of pyrolusite weighing 0.2400 gram was treated with excess KI. The iodine liberated required 46.24 mL of 0.1105 M $Na_2S_2O_3$ solution. Calculate % MnO_2 (86.94)