Fundamentals of Analytical Chemistry

Chapter 16

Applications of Neutralization Titrations

Homework

- 19-31, 32, 33, 35, 39, 40, 48

Standard Acid Solutions

- No strong, primary standard acids
  - Constant boiling HCl solution (780 torr ≥ P ≥ 670 torr)
  - $\frac{mass\ const.\ boiling\ HCl\ (g)}{mol\ H_3O^+} = 164.673 + 0.02039P$
  - More commonly, standardization vs. a primary standard base
    - Sodium carbonate (Na_2CO_3)
      - $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2CO_3$
      - $H_2CO_3 \rightarrow H_2O + CO_2$; CO_2 can be removed by boiling
  - TRIS (or THAM)
    - *Tris*-(hydroxymethyl)aminomethane
    - $(HOCH_2)_3CNH_2 + HCl \rightarrow (HOCH_2)_3CNH_3^+ + Cl^-$

Standard Base Solutions

- Most common is NaOH
  - Must protect from atmospheric CO_2
    - $CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O$
    - Only affect endpoint when that endpoint is basic
    - Carbonate error
  - Solid hydroxides always have carbonete
    - High concentration of hydroxide will precipitate the carbonate
  - Standardization with primary standard potassium hydrogen phthalate

Elemental Analysis

- Sulfur
  - Burned in air, then bubbled through hydrogen peroxide
    1) $S + O_2 \rightarrow SO_2$
    2) $SO_2 + H_2O_2 \rightarrow H_2SO_4$

Titrate with standard NaOH

$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

Kjeldahl Analysis

- Determination of Nitrogen
  - Nitrogen containing compound is digested, nitrogen is converted to ammonia which is then distilled and titrated with a standard acid or back-titrated with a standard acid and base.
  - If nitrogen content is known (or approximated) can determine amount of another analyte

Kjeldahl Analysis

$C_aH_bO_cN_d$ + excess H_2SO_4 → a CO_2 + ½ b H_2O + d NH_4HSO_4

The solution is then cooled and NaOH added

d NH_4HSO_4 + excess NaOH → d NH_3 + other stuff

The solution is then heated, driving off the NH_3, which is bubbled into a solution. For the back-titration method, the solution contains standard HCl in excess; for the direct titration the solution contains boric acid (The boric acid is converted to borate which is then directly titrated with HCl.)

d NH_3 + (d+e) HCl → d NH_4Cl

e HCl + e NaOH → e NaCl + e H_2O

Kjeldahl Analysis

- Can calculate moles of nitrogen originally present
  - moles N = moles of acid consumed
- Relate to mass of analyte
  - If formula of compound is known, compare moles of nitrogen to moles of compound
  - If %N is known, use %N to calculate mass of analyte
    - If 'gravimetric factor' is known, multiply by the gravimetric factor to get mass of analyte

Problem 16-38

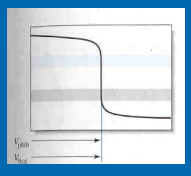
- A 0.9092 g sample of wheat flour was analyzed by the Kjeldahl procedure. The ammonia formed was distilled into 50.00 mL of 0.05063 M HCl; a 7.46 mL back titration with 0.04917 M NaOH was required. Calculate the percent protein in the flour. (Gravimetric Factor for this protein wrt wheat is 5.70)

Problem 16-38

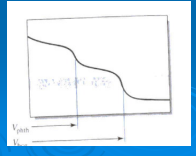
- Moles of acid consumed
  - Moles originally present – moles excess
    - Originally present = 50.00 x 0.05063 = 2.531_5 mmol
    - Excess
      - NaOH + HCl → H_2O + NaCl
      - mmol NaOH = 7.46 x 0.04917 = 0.366_8
      - mmol HCl = mol NaOH = 0.366_8
    - $2.531_5 - 0.366_8 = 2.164_7$ mmol consumed
    - 2.164_7 mmol acid = 2.164_7 mmol N
    - 2.164_7 mmol N x 14.0067 = 30.32 mg N
- Mass of protein
  - 30.32 mg N x 5.70 = $172._8$ mg protein
  - ($172._8$ mg p / 909.2 mg s) x 100% = 19.0% protein

Carbonate/Hydroxide Mixtures

- Pure NaOH
  - Vol BG = Vol P

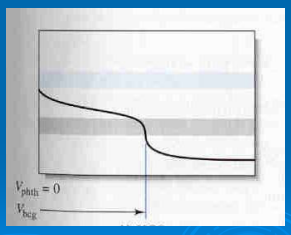


- Pure Na_2CO_3
  - Vol BG = 2 x Vol P



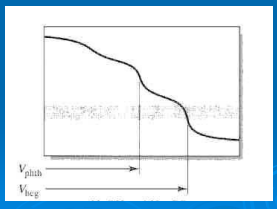
Carbonate/Hydroxide Mixtures

- Pure $NaHCO_3$
  - Vol P = 0



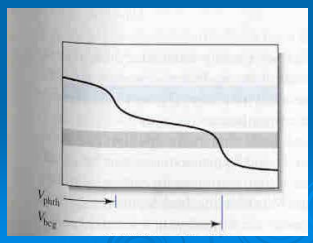
Carbonate/Hydroxide Mixtures

- Mixture NaOH and Na_2CO_3
  - Vol P < Vol BG < Vol 2P



Carbonate/Hydroxide Mixtures

- Mixture Na_2CO_3 + $NaHCO_3$
  - Vol BG > 2 x Vol P



Carbonate/Hydroxide Mixtures

- Quantitative Determinations
  - Determine what type of mixture (if any!)
  - Find the part of the curve due to the carbonate that is unaffected by the presence of the impurity
    - Calculate moles of carbonate
  - Find total moles from the part of the curve with the impurity
    - Total moles = moles carbonate + moles of impurity
      - We know moles of carbonate from previous!