

Chem 201 Lecture 3b

Volumetric Analysis

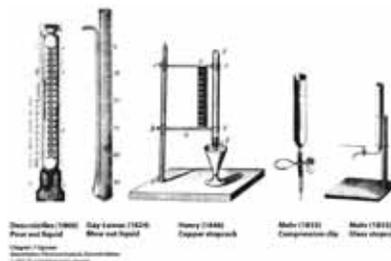
Last time

Review Equilibria and Thermodynamics
Types of equilibria: K_{sp} and K_f

Today

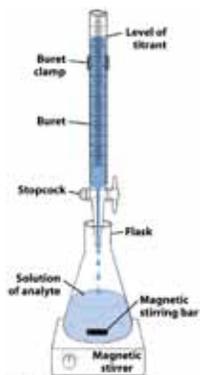
Volumetric analysis
Kjeldahl Titration

Chapt 7 - volumetric analysis



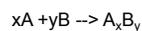
Terms

Terms we'll encounter:
-analyte
titrant
equivalence point
indicator
titration error
blank titration
primary standard
standardization
standard solution
direct titration
back titration
endpoint detection
Kjeldahl nitrogen - protein assay
Mohr Titration
Volhard Titration
Fajans Titration



Titration: setting up algebraic equation at equivalence point

Consider titration of A and B. General titration equation:



At equivalence point, " V_e ":

equivalents A = # equivalents of B

$(\# \text{mol A})(y) = (\# \text{mol B})(x)$ (not obvious?)

mole equiv's for acids/bases

Mole-equivalent or just "equivalent" or just "eq".

eq = #mol x # H⁺'s transferred

Consider

a) HCl: # mole-eq H⁺, so # eq HCl=#mol HCl

b) H₂SO₄: # eq H₂SO₄= # mol H₂SO₄ x 2

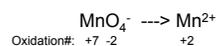
c) Base, Al(OH)₃ # eq Al(OH)₃ = # mol Al(OH)₃ x 3

equiv's for redox reagents

eq = # mol reagent x #electrons transferred

Consider

Reduction of permanganate, MnO₄⁻



Oxidation#: +7 -2 +2

so: # eq.MnO₄⁻ = # mol MnO₄⁻x___

Note: It is assumed you know how to determine the oxidation numbers...

Remember that MV = # mol

Very useful relationship:

MV = mol/L x L = moles

Or, MV = mol/L x mL = mmoles

Example:

Given: 25.0 mLs of 0.200 M H₂SO₄ ,

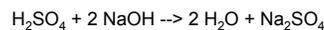
mol H₂SO₄ = (25.0 x 10⁻³ L)(0.200M) = 5.00 x 10⁻³ mol

Or,

mmol H₂SO₄ = (25.0mL)(0.200M) = 5.00 mmol

Titration: setting up algebraic equation at equivalence point for acid-base titration

Consider a titration of H₂SO₄ and NaOH :



@ e.p. : # equiv H₂SO₄ = # equiv NaOH

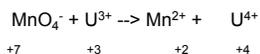
$$(\# \text{mol H}_2\text{SO}_4)(2) = (\# \text{mol NaOH})(1)$$

But: #mol H₂SO₄ = M_{H₂SO₄} V_{H₂SO₄} and #mol NaOH=M₂V₂

Then 2 M₁V₁ = M₂V₂ where "1"=H₂SO₄ and "2" = NaOH

Titration: setting up algebraic equation at equivalence point for redox titration

Consider a titration U³⁺ (analyte) with MnO₄⁻ (titrant):



+7 +3 +2 +4

(U³⁺ loses 1 e⁻, Mn gains 5 e⁻.)

@ e.p. : # equiv MnO₄⁻ = # equiv U³⁺

$$(\# \text{mol MnO}_4^-)(5) = (\# \text{mol U}^{3+})(1)$$

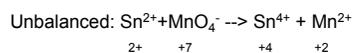
#mol MnO₄⁻ = M₁V_e and #mol U³⁺ = M₂V₂

Then 5 M₁V_e = M₂V₂ where "1"=MnO₄⁻ and "2" = U³⁺

5

Another example: redox titration

Titrate 20.0 mL of 0.100M Sn²⁺ with 0.100M MnO₄⁻ to get Sn⁴⁺ +Mn²⁺: Predict V_e .



2+ +7 +4 +2

(therefore: Sn loses 2e⁻, Mn gains 5 e⁻.)

So at e.p. #eq MnO₄⁻ = #eq Sn²⁺

$$\# \text{mol MnO}_4^- \times 5 = \# \text{mol Sn}^{2+} \times 2$$

5M₁V_e = 2 M₂V₂ (where 1 = MnO₄⁻ and 2 = Sn²⁺)

So V_e=(2/5)(M₂V₂/M₁) =(2/5)(.100)(20.0)/(.100)=8.00mL

Kjeldahl titration

Be able to do problems like the example on page 125

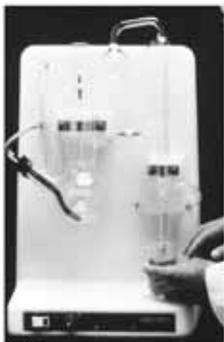


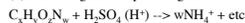
Figure 7.8
Kjeldahl's Chemical Analysis, Second Edition
© 2004 W. H. Freeman and Company

Kjeldahl Titration

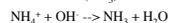
For nitrogen analysis of foods, for example

Steps:

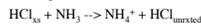
(1) solid weighed sample is digested in boiling sulfuric acid at 300°C.



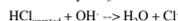
(2) NH_4^+ is made basic (NH_3) with excess OH^- .



(3) NH_3 is distilled into a receiver containing known moles of excess HCl.



(4) Unreacted HCl is back titrated with standard NaOH to determine mol HCl consumed by NH_3 :



$$\text{mol } H^+ \text{ total} - \text{mol } H^+ \text{ reacted} = \text{mol } NH_3 = \text{mol N in } C_xH_yO_zN_w$$

Kjeldahl Analysis example (study example in textbook)

Example: If 0.500g meat is dissolved and the NH_3 evolved is distilled into 50.0 mL of 0.110M HCl. The resulting solution (HCl_{xs}) titrated with 0.100M requires 25.0 mLs to reach equivalence pt. What's the % N in the meat?

$$\text{Solution: mol } HCl_{total} = MV = (0.110M)(50.0mL) = 5.50mmol$$

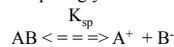
$$mmol \ HCl_{xs} = M_{OH}V_{OH} = (0.100M)(25.0mL) = 2.50 \text{ mmol}$$

$$mmol \ HCl_{reacted} = 5.50mmol - 2.50mmol = 3.00mmol = mmol \ NH_3$$

$$\text{So } \% \ N = (3.00 \times 10^{-3} \text{ mol})(14.0g/mol)(100\%)/(0.500g) = 8.40\%$$

Precipitation titrations

Consider a sparingly soluble compound, AB. The K_{sp} equil is:



If $K_{sp} \ll 1$, then can titrate A^+ with B^- ; or B^- with A^+

Titration equation would be: $A^+ + B^- \rightarrow AB(s)$

Of course, pptn won't occur until the product of $[A^+][B^-] > K_{sp}$.

Example: $Ag^+ + I^- \rightarrow AgI$

20.0 mLs of 0.100M $Ag(NO_3)$ is titrated with 0.0800M potassium iodide, KI. (note K_{sp} of $AgI = 8.3 \times 10^{-17}$).

Answer the following questions:

1) What is the equivalence point?

2) What is $[Ag^+]$ and pAg^+ at:

a) $V_i = 0.00mL$

b) After addg 10.0 mLs (i.e. $V_i < V_{ep}$)

c) At exactly $V_i = V_{ep}$.

d) At $V_i > V_{ep}$, say, $V_i = 35.0 \text{ mLs}$,

Solution to previous example

1) What is the e.p.?

At e.p., $\#eq \ Ag^+ = \#eq \ I^-$

$\#moles \ Ag^+ = \#mol \ AgNO_3 = \#mol \ I^- = \#mol \ KI$

$$M_{Ag}V_{Ag} = M_{KI}V_{KI}$$

$$(0.100M)(20.0mL) = (0.0800M)(V_{ep})$$

$$V_{ep} = (20.0mL)(0.100/0.0800) = 25.0 \text{ mLs}$$

Solution...

2) What is $[Ag^+]$ and pAg^+ at:

a) $V_1 = 0.00mL$

Before adding anything: $[Ag^+] = 0.100 M$ since

$AgNO_3 \rightarrow Ag^+ + NO_3^-$

And $pAg^+ = -\log[Ag^+] = -\log(0.100) = 1.000$

Solution...

b) After adding 10.0 mLs (i.e. $V_1 < V_{ep}$), $[Ag^+] = ?$

(all I^- reacts with Ag^+ to form AgI).

so $[Ag^+] = (\text{moles } Ag^+_{\text{remaining}}) / (\text{total vol}) =$

$(\text{moles } Ag^+_{\text{initially}} - \text{moles } Ag^+_{\text{reacted}}) / V_{\text{tot}}$

$= (M_{Ag} V_{Ag} - M_I V_I) / (V_{Ag} + V_I)$

$= \frac{\{(1.100)(20.0) - (0.0800)(10.0)\}}{\{20.0 + 10.0\}}$

$M_{Ag} = (2.00 - 0.800) / 30.0 = 0.0400 M$

$pAg^+ = -\log(0.0400) = 1.398$

Solution...

c) At exactly $V_1 = V_{ep}$, what is $[Ag^+]?$ Use K_{sp} equil.

Equilibrium case: $AgI \rightleftharpoons Ag^+ + I^-$

$K_{sp} = [Ag^+][I^-] = 8.3 \times 10^{-17}$

$[Ag^+]^2 = 8.3 \times 10^{-17}$ or $[Ag^+] = 9.1 \times 10^{-9} M$.

$pAg^+ = -\log(9.1 \times 10^{-9}) = 8.041$

Study this approach carefully.

Solution...

d) At $V_1 > V_{ep}$, say, $V_1 = 35.0 mL$ s, what is $[Ag^+]?$

Use K_{sp} equilibrium:

$AgI(s) \rightleftharpoons Ag^+ + I^-$

first determine $[I^-]_{xs}$: assume all Ag^+ reacts.

$mmol I^-_{\text{added}} = 0.0800M(35.0mL) = 2.80 mmol$

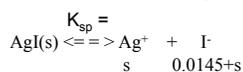
$mmol I^-_{\text{reacted}} = mmol Ag^+ = (0.100M)(20.0mL) = 2.00 mmol$

So, $[I^-] = (mmol_{\text{added}} - mmol_{\text{Ag}}) / (20+35)mL$

$= (2.80 - 2.00) / 55 = 1.45 \times 10^{-2} M$

Solution:

Hence, we can write for the K_{sp} equilibrium:



at equilibrium:

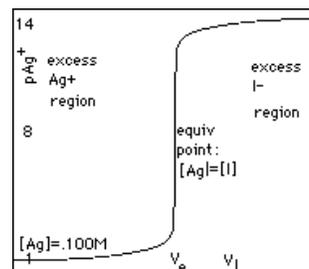
$[Ag^+] = s$, $[I^-] = 1.45 \times 10^{-2} + s$: $(s)(1.45 \times 10^{-2} + s)$

$\approx 1.45 \times 10^{-2}$ (5% rule) $\Rightarrow s \approx 8.3 \times 10^{-17} / 1.45 \times 10^{-2}$

$\Rightarrow s = 5.72 \times 10^{-15}$, or, we can write:

$\Rightarrow pAg^+ = -\log(5.72 \times 10^{-15}) = 14.2$

pAg^+ vs mL I^- graph is *sigmoidal*



Short cuts...for $V_1 < V_{ep}$

Revisit question 2) b): After addg 10.0 mLs (i.e. $V_1 < V_{ep}$), $[Ag^+] = ?$

$[Ag^+] = [Ag^+]_0(\text{fraction free})(\text{dilution factor})$

$$= (.100M) \left\{ \frac{25.0 - 10.0}{25} \right\} \left\{ \frac{20.0}{20.0 + 10.0} \right\}$$

$$= (0.100M) \left(\frac{15.0}{25.0} \right) \left(\frac{20.0}{30.0} \right) = 0.0400M$$

$$pK_{Ag^+} = -\log(.0400) = 1.398 \quad (\text{compare to } 1.398 \text{ as before})$$

Try this using the shortcut:

Say: $V_1 = 19$ mLs for the previous problem.

What is $[Ag^+]$ and pAg^+ ?

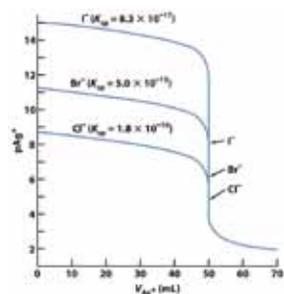
$$[Ag^+] = (0.100M) \left(\frac{25.0 - 19.0}{25.0} \right) \left(\frac{20.0}{20.0 + 19.0} \right)$$

$$= (0.100M) \left(\frac{6.0}{25.0} \right) \left(\frac{20.0}{39.0} \right) = .0123M$$

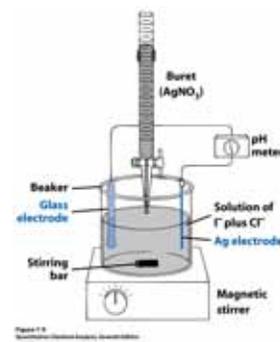
$$pAg^+ = -\log[Ag^+] = 1.910$$

If Ag^+ is titrant, I^- is analyte:

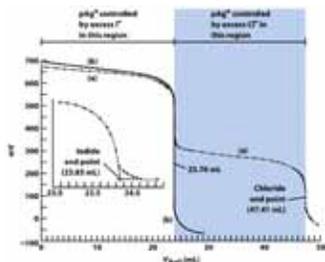
Textbook uses Ag^+ is titrant. The graph is still sigmoidal.



If two analytes: Cl^- and I^-



The pAg^+ vs V_{Ag^+} has 2 ep's



3 types of argentometric titrations (i.e. involving Ag^+)

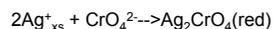
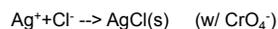
There are 3 types of titrations commonly employed:

1. Mohr
2. Volhard
3. Fajans

Know the equations involved in these titrations.

Mohr Titrations

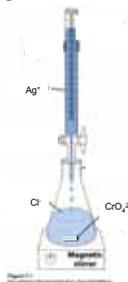
Useful for determination of Cl^- for example in sea water by precipitating it with Ag^+ to form AgCl ppt.



problems: need Ag^+_{xs} to see e.p.

Correction? *Blank titration*

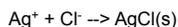
Standardize with NaCl of similar conc.



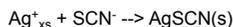
Volhard titration

Useful for halide titration using Ag^+ and a back titration

A known excess Ag^+ solution is added:



$\text{AgCl}(s)$ is filtered and the Ag^+_{xs} is *back titrated* with KSCN in presence of Fe^{3+} :



Excess SCN^- then reacts with Fe^{3+}



Volhard titration

The $[\text{Cl}^-]$ is determined as follows:

Moles Cl^- = total mol Ag^+ added - mol Ag^+ excess

$$\text{So } [\text{Cl}^-] = (M_{\text{Ag}^+}V_{\text{ag}^+} - M_{\text{SCN}^-}V_e) / V_{\text{Cl}^-}$$

Problems?

AgCl has to be filtered off because otherwise the red color would fade since AgSCN is less soluble than AgCl . So AgCl would slowly redissolve and AgSCN would form thus removing FeSCN^{2+} . This is not a problem when determining Br^- or I^- .

Fajans titration

Fajans Titration uses an adsorption indicator.

Before e.p., Cl^- is excess and the AgCl crystals have more Cl^- ions, therefore (-) charged. After e.p. slight Ag^+ excess, and so AgCl precipitate becomes slightly + charged.

The adsorption dye is usually anionic. So it adsorbs to the + precipitate changing the color of the dye.

