Chapter 3: End-of-Chapter Solutions
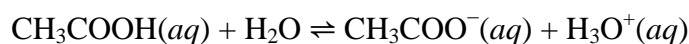
1. The equilibrium constant expressions are:

$$K_1 = \frac{[A][B]}{[C]} \qquad K_2 = \frac{[A]^2[B]^2}{[C]^2}$$

$$K_2 = \frac{[A]^2[B]^2}{[C]^2} = \frac{[A][B]}{[C]} \frac{[A][B]}{[C]} = (K_1)(K_1) = K_1^2$$
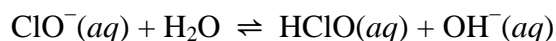
2. Some possibilities are:

- Vinegar is 8 % acetic acid, CH_3COOH. The equilibrium on reacting with water is:

$$CH_3COOH(aq) + H_2O \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

$$K_a' = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

- Clorox and many cleaners contain sodium hypochlorite; the sodium salt of hypochlorous acid, HClO:

$$ClO^-(aq) + H_2O \rightleftharpoons HClO(aq) + OH^-(aq)$$

$$K_b' = \frac{[HClO][OH^-]}{[ClO^-]}$$

- Disodium EDTA, the disodium salt of ethylenediamminetetraacetic acid, is very common in soaps and shampoos. It complexes the Ca^{2+} and Mg^{2+} found in hard water, which would otherwise form a precipitate (soap scum) with surfactants.

$$EDTA^{4-}(aq) + Ca^{2+}(aq) \rightleftharpoons Ca(edta)^{2-}(aq)$$
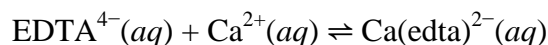
$$K_f' = \frac{[Ca(edta)^{2-}]}{[EDTA^{4-}][Ca^{2+}]}$$

- Soluble lead acetate, $Pb(CH_3COO)_2$, is contained in hair darkening products. The Pb^{2+} ions react with sulfur in hair protein to form lead sulfide (PbS) precipitates that adhere to hair. The subsequent equilibrium is:
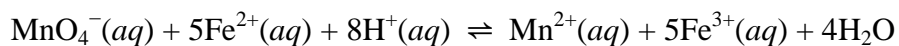
$$PbS(s) \rightleftharpoons Pb^{2+}(aq) + S^{2-}(aq)$$
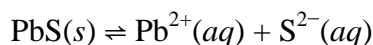
$$K_{sp}' = [Pb^{2+}][S^{2-}]$$

3.
(a) 0.05 M $KMnO_4$ + 0.05 M $FeCl_2$

MnO_4^- can Fe^{2+} can undergo a redox reaction, K^+ and Cl^- are spectator ions:

$$MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightleftharpoons Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O$$

$$K' = \frac{[Mn^{2+}][Fe^{3+}]^5}{[MnO_4^-][Fe^{2+}]^5[H^+]^8}$$
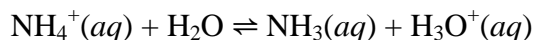
(b) 0.05 M HCl + 0.05 M NaOH

These species are a strong acid and a strong base, respectively. Cl^- and Na^+ are spectator ions, the H^+ and OH^- undergo a neutralization reaction, and the resulting equilibrium is:
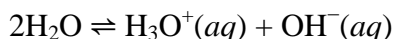
$$2H_2O \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$
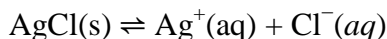$$K_w' = [H_3O^+][OH^-]$$

(c) 0.05 M HCl + 0.05 M NH_3

Another neutralization reaction, but in this case involving a weak base. The reaction product is NH_4^+, a weak acid, and the equilibrium is:

$$NH_4^+(aq) + H_2O \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

$$K_a' = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

d) 0.05 M HCl + 0.05 M $AgNO_3$

a precipitation reaction:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
$$K_{sp}' = [Ag^+][Cl^-]$$

e) 0.05 M $CaCl_2$ + 0.05 M $(NH_4)_2C_2O_4$

a precipitation reaction:
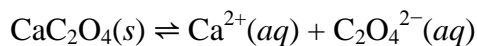
$$CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$
$$K_{sp}' = [Ca^{2+}][C_2O_4^{2-}]$$

4.
First convert the number of grams of product to number of moles:

$$\frac{2.947 \text{ g } MgNH_4PO_4 \cdot 6H_2O}{245.4 \text{ g/mol}} = 0.01201 \text{ mol } MgNH_4PO_4 \cdot 6H_2O$$

Convert to mol of P:

$$0.01201 \text{ mol } MgNH_4PO_4 \cdot 6H_2O \quad \frac{1 \text{ mol P}}{1 \text{ mol } MgNH_4PO_4 \cdot 6H_2O} \quad 0.01201 \text{ mol P}$$

Convert mol of P to grams of P:
(0.01201 mol P) (30.974 g/mol) = 0.3719 g P

Find weight percent:

$$\text{wt-\%} = \frac{0.3719 \text{ g P}}{3.459 \text{ g test portion}} \times 100 \text{ \%} = 10.75 \text{ \%}$$

5. Sample calculation for the first measurement:

$$\frac{0.1225 \text{ g Fe}_2\text{O}_3}{159.69 \text{ g/mol}} = 0.7671 \text{ mmol Fe}_2\text{O}_3$$

$$0.7671 \text{ mmol Fe}_2\text{O}_3 \quad \frac{2 \text{ mol Fe}}{1 \text{ mol Fe}_2\text{O}_3} \quad \frac{55.845 \text{ g Fe}}{\text{mol Fe}} = 0.08568 \text{ g Fe}$$

$$\text{wt-\%} = \frac{0.08568 \text{ g Fe}}{0.4793 \text{ g test portion}} \times 100 \text{ \%} = 17.88 \text{ \%}$$

Repeating for the other samples and finding the average gives: 17.77 ± 0.10 % or 17.8 ± 0.1 %

6.
(1.9482 g)/(143.32 g/mol) = 0.013593 mol
and
(0.013593 mol)(58.443 g/mol NaCl) = 0.79441 g NaCl

a)

$$\text{wt-\%} = \frac{0.79441 \text{ g NaCl}}{98.75 \text{ g test portion}} \times 100 \text{ \%} = 0.8045 \text{ \%}$$

b) parts per thousand = 0.8045 % × 10 = 8.045 ‰

c)

$$[\text{NaCl}] = \frac{0.013593 \text{ mol NaCl}}{(98.75 \text{ g})/(1.01 \text{ g/mL})} \quad \frac{1000 \text{ mL}}{1.0 \text{ L}} = 0.1390 \text{ M}$$

7.
(413.6 s)(0.04825 C/s) = 19.96 C

$$\frac{19.96 \text{ C}}{96,485 \text{ C/mol}} \quad 0.0002068 \text{ mol e}^-$$

$$(0.0002068 \text{ mol e}^-)(1 \text{ mol I2/2 mol e}^-) \quad \frac{1 \text{ mol vitamin C}}{1 \text{ mol I}_2} = 0.0001034 \text{ mol vitamin}$$
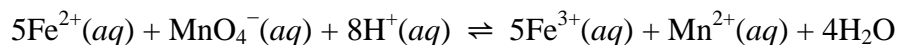
(0.0001034 mol vitamin C)(176.06 g=mol) = 0.01821 g vitamin C

$$\text{wt-\%} = \frac{0.01821 \text{ g vitamin C}}{0.0200 \text{ g sample}} \ 100 \text{ \%} = 91.0 \text{ \%}$$

8.
(a)
The analyte is Fe^{2+} and the titrant is MnO_4^-:

$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightleftharpoons 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O$$

(b)
$$(0.03491 \text{ L})(0.002045 \text{ M MnO}_4^-) \ \frac{5 \text{ mol Fe}^{2+}}{1 \text{ mol MnO}_4^-} = 3.5695\times10^{-4} \text{ mol Fe}$$

(c)
$$(3.5695\times10^{-4} \text{ mol Fe})(55.845 \text{ g/mol}) = 0.01993 \text{ g Fe}$$

d)
The precipitate contained $(3.5695\times10^{-4}$ mol $FePO_4)(150.816$ g/mol$) = 0.05383$ g $FePO_4$.
The amount of $AlPO_4$ is then
$$\frac{(0.0663 \text{ g} - 0.05383 \text{ g})}{121.953 \text{ g/mol}} = 1.022\times10^4 \text{ mol}$$
which equals 6.119×10^{-4} g Al.

e) weight percent for each element is:

$$\text{wt-\%} = \frac{0.01993 \text{ g Fe}}{50.02 \text{ g sample}} \times100 \text{ \%} = 0.03984 \text{ \% Fe}$$

$$\text{wt-\%} = \frac{6.119\times10^{-4} \text{ g Al}}{50.02 \text{ g sample}} \times100 \text{ \%} = 0.00122 \text{ \% Al}$$

9.
(a)
$$(0.1000 \text{ M})(0.03500 \text{ L}) = 3.50 \text{ mmol H}^+ = 3.50 \text{ mmol OH}^-$$

$$[OH^-] = \frac{3.50 \text{ mmol OH}^-}{0.05000 \text{ L}} = 0.0700 \text{ M}$$

(b)
phenol red. Neutralization of a strong base with a strong acid produces a titration end point pH near 7.

Brian M. Tissue, *Basics of Analytical Chemistry and Chemical Equilibria*, (J. Wiley, New York, 2013).

(c) At 30.0 mL of titrant, the endpoint has not been reached.
OH^-, Ca^{2+}, Cl^- (H^+ is present at $< 10^{-7}$ M)

(d) At 40.0 mL of titrant, the endpoint has been passed.
H+, Ca^{2+}, Cl^- (OH^- is present at $< 10^{-7}$ M)

(e)
Add a known amount of strong acid and back titrate the excess acid with a standard base.

10.
Back titration result:

$(0.01104 \text{ L})(0.1177 \text{ M SCN}^-) \dfrac{1 \text{ mol Ag}^+}{1 \text{ mol SCN}^-} = 1.2994 \times 10^{-3} \text{ mol Ag}^+$

Total Ag^+ added to test portion:

$(0.03555 \text{ L})(0.1015 \text{ M Ag}^+) = 3.6083 \times 10^{-3} \text{ mol Ag}^+$

Amount of Ag^+ reacted with Cl^-:
$3.6083 \times 10^{-3} \text{ mol Ag}^+ - 1.2994 \times 10^{-3} \text{ mol Ag}^+ = 2.3089 \times 10^{-3} \text{ mol Ag}^+$

Amount of Cl^- in test portion:

$2.3089 \times 10^{-3} \text{ mol Ag}^+ \dfrac{1 \text{ mol Cl}^-}{1 \text{ mol Ag}^+} = 2.3089 \times 10^{-3} \text{ mol Cl}^-$

Concentration of Cl^- in test portion:
$\dfrac{2.3089 \times 10^{-3} \text{ mol Cl}^-}{0.05000 \text{ L}} = 0.04618 \text{ M Cl}^-$

11.
Back titration result:

$(0.01805 \text{ L})(0.0955 \text{ M Mg}^{2+}) \dfrac{1 \text{ mol EDTA}}{1 \text{ mol Mg}^{2+}} = 1.7238 \times 10^{-3} \text{ mol EDTA}$

Total EDTA added to test portion:

$(0.02500 \text{ L})(0.1347 \text{ M EDTA}) = 3.3675 \times 10^{-3} \text{ mol EDTA}$

Amount of EDTA reacted with Ca^{2+}:
$3.3675 \times 10^{-3} \text{ mol EDTA} - 1.7238 \times 10^{-3} \text{ mol EDTA} = 1.6437 \times 10^{-3} \text{ mol EDTA}$

Amount of Ca^{2+} in test portion:

$1.6437 \times 10^{-3} \text{ mol EDTA} \dfrac{1 \text{ mol Ca}^{2+}}{1 \text{ mol EDTA}} = 1.6437 \times 10^{-3} \text{ mol Ca}^{2+}$

$$1.6437 \times 10^{-3} \text{ mol Ca}^{2+} \; \frac{1 \text{ mol CaCO}_3}{1 \text{ mol Ca}^{2+}} \; \frac{100.087 \text{ g CaCO}_3}{\text{mol CaCO}_3} = 0.16452 \text{ g CaCO}_3$$

$$\text{wt-\%} = \frac{0.16452 \text{ g CaCO}_3}{1.000 \text{ g solid}} \times 100 \text{ \%} = 16.45 \text{ \% CaCO}_3$$

12.

The average of the three titrations is 0.05620 L.

trial	titrant vol (L)
1	0.0555
2	0.0571
3	0.056
average	0.05620
stdev	0.00082
RSD	0.015

Titration result:

$$(0.05620 \text{ L})(0.0200 \text{ M Pb}^{2+}) \; \frac{1 \text{ mol EDTA}}{1 \text{ mol Pb}^{2+}} = 1.124 \times 10^{-3} \text{ mol EDTA}$$

$$1.124 \times 10^{-3} \text{ mol EDTA} \; \frac{1 \text{ mol Cu}^{2+}}{1 \text{ mol EDTA}} = 1.124 \times 10^{-3} \text{ mol Cu}^{2+}$$

Since 25.0 mL of solution was determined from the 250.0 mL that the brass was dissolved in, there is a 10-fold factor to multiply:

$$(1.124 \times 10^{-3} \text{ mol Cu}^{2+})(10) \; \frac{63.546 \text{ g Cu}}{\text{mol}} = 0.71426 \text{ g Cu}$$

$$\text{wt-\%} = \frac{0.71426 \text{ g Cu}}{1.062 \text{ g brass}} \times 100 \text{ \%} = 67.26 \text{ \%}$$
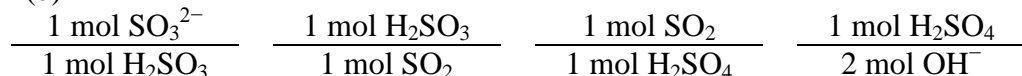
Propagating the RSD from the three titrations, (67.26 %)(0.015) = 1.0 %, gives a final result of: 67.3 ± 1.0 % Cu

13.
(a)
- The initial reaction is a neutralization to convert the analyte to a new form.
- Conversion of SO_2 to H_2SO_4 is a redox reaction.
- Titration of the H_2SO_4 with OH^- is another neutralization reaction.

(b)
$$\frac{1 \text{ mol SO}_3^{2-}}{1 \text{ mol H}_2\text{SO}_3} \qquad \frac{1 \text{ mol H}_2\text{SO}_3}{1 \text{ mol SO}_2} \qquad \frac{1 \text{ mol SO}_2}{1 \text{ mol H}_2\text{SO}_4} \qquad \frac{1 \text{ mol H}_2\text{SO}_4}{2 \text{ mol OH}^-}$$

Overall: $\dfrac{1\ \text{mol SO}_3{}^{2-}}{2\ \text{mol OH}^-}$

(c)
Since the titration is a strong acid and a strong base, phenol red is the best choice. In practice, phenolphthalein, which goes from colorless to pink at pH 8 is also suitable.

(d)
Ba^{2+} and $SO_4{}^{2-}$ form a $BaSO_4$ precipitate. Adding the soluble $BaCl_2$ should show a precipitate to confirm the presence of $SO_4{}^{2-}$. The acid-base titration is not specific for sulfuric acid, so the presence of sulfate should be confirmed.

14.

advantages	disadvantages
Coulometry is an absolute measure and does not depend on other standards for calibration.	Like other classical methods, it is not sensitive enough for trace analysis.
Since it is an electrochemical method, it can be automated for rapid and unattended analysis.	Not all analytes can be determined by electrochemical methods.

15.

titration	gravimetry
Requires standard solutions and volumetric glassware.	Requires only a balance for measurement.
Requires a reaction that goes to completion and a means of detecting the end point.	Requires a reaction that converts the analyte to a pure, weighable form.
Can be automated.	

16.
Even with the best glassware, balance, and technique, the purity of a primary standard will always be a limit in a chemical analysis.

17.

titration	gravimetry
The endpoint is often difficult to observe.	Some analyte is left in solution.
If the analyst overshoots the endpoint, the result will be erroneously high.	The result will be erroneously low due to the lost analyte.

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