QUESTIONS AND PROBLEMS

Titration Concepts

1. Define briefly each of the following terms: (a) titrant, (b) standard solution, (c) end point, (d) equivalence point.
2. What is a primary standard? List the requirements of a satisfactory primary standard.
3. What requirements must a chemical reaction fulfill to be used for a titration? List the four types of reactions that can be used as titration reactions.
4. The hardness of water (Ca^{2+} + Mg^{2+}) can be determined by a complex-formation titration with EDTA. Outline a technique by which the hardness of water used in an industrial plant can be measured continuously.
5. Explain how a flowing sample can be titrated continuously.
6. For each of the following, calculate the equivalent weight of both reactants in terms of formula weight. (For example, eq wt = form wt/2.)

(a) $2NaOH + H_2C_2O_4 \rightarrow Na_2C_2O_4 + 2H_2O$
(b) $2HCl + Ba(OH)_2 \rightarrow BaCl_2 + 2H_2O$
(c) $I_2 + H_2S \rightarrow S + 2HI$
(d) $2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$
(e) $Pb(NO_3)_2 + H_2SO_4 \rightarrow PbSO_4(s) + 2HNO_3$
(f) $AgNO_3 + 2NaCN \rightarrow Ag(CN)_2^- + {}^2Na^+ + NO_3^-$

Sample Molarity Problems

7. Calculate the molarity of each of the following solutions.

(a) $AgNO_3$, 117.4 g/L
(b) KSCN, 0.972 g/100 mL
(c) $BaCl_2 \cdot 2H_2O$, 200 mg/L
(d) Na_2SO_4, 72.0 mg/72 mL

8. Calculate the total amount of compound (in milligrams) in each of the following solutions.

(a) 100 mL of 0.500*M* NaOH
(b) 10.0 mL of 0.100*M* Br_2
(c) 24.7 mL of 0.100*M* KSCN
(d) 5.00 mL of 0.010*M* $KMnO_4$

9. Calculate the volume of 12.0*M* hydrochloric acid needed to prepare 1.0 L of approximately 0.25*M* hydrochloric acid.
10. Calculate the volume of 50% (16*M*) sodium hydroxide needed to prepare 2.0 L of approximately 0.1*M* sodium hydroxide.
11. Calculate the molarity of concentrated phosphoric acid (85% by weight), specific gravity 1.69.
12. Calculate the molarity of concentrated hydrobromic acid (48% by weight), specific gravity 1.486.

Standardization

13. A solution of hydrochloric acid is standardized and found to be 1.183*M*. Calculate the volume of this solution that, diluted to 1.000 L in a volumetric flask, produces a 0.1000*M* solution of hydrochloric acid.
14. Exactly 46.32 mL of sodium hydroxide is used to titrate a 1,200.0-mg sample of primary standard potassium acid phthalate, or KHP (form wt = 204.2). Calculate the molarity of the sodium hydroxide to four significant figures.

15. Exactly 24.69 mL of hydrochloric acid is required to titrate a 278.0-mg sample of the primary standard *tris*(hydroxymethyl)aminomethane according to the following reaction:

$$HCl + (CH_2OH)_3CNH_2 \rightarrow (CH_2OH)_3CNH_3^+Cl^-$$

Calculate the molarity of the HCl.

16. A 8.5332-g portion of primary standard silver nitrate (form wt = 169.9) is weighed into a 500-mL volumetric flask and diluted to volume. Calculate its molarity. In deciding on significant figures, recall that the tolerance for a 500-mL volumetric flask is of the order of 0.1 mL.
17. A 10.00-mL sample of sodium chloride solution is diluted to 50.00 mL. A 20.00-mL aliquot is then withdrawn and titrated with 3.923 mL of 0.0110*M* silver nitrate. Calculate the molarity of the 10.00 mL of NaCl.
18. A 25.00-mL sample of calcium chloride solution is diluted to 50.00 mL. A 20.00-mL aliquot is then withdrawn and titrated with 3.923 mL of 0.0110*M* silver nitrate. Calculate the molarity of the 25.00 mL of $CaCl_2$.
19. A 395.6-mg sample of primary standard arsenic(III) oxide is dissolved in 25.00 mL of acid, forming two molecules of H_3AsO_3 for each molecule of As_2O_3 (form wt = 197.84).

(a) Calculate the molarity of H_3AsO_3.
(b) Calculate the normality of the H_3AsO_3 (for oxidation to H_3AsO_4).

20. A 25.00-mL sample of 0.0300*N* (0.0150*M*) H_3AsO_3 is oxidized to H_3AsO_4 by 24.10 mL of iodine (I_2) titrant.

(a) Calculate the molarity of the I_2.
(b) Calculate the normality of the I_2.

21. A 93.0-mg sample of primary standard As_2O_3 is dissolved to give two molecules of H_3AsO_2 per one molecule of As_2O_3. The resulting H_3AsO_3 is oxidized to H_3AsO_4 in a reaction in which two ions of Ce^{4+} react with one molecule of H_3AsO_3. If 18.40 mL of Ce^{4+} is used and the formula weight of As_2O_3 is 197.84, calculate:

(a) The molarity of the Ce^{4+}
(b) The normality of the Ce^{4+}

Calculation of Percentage or Concentration

22. A 0.500-g sample containing sodium dihydrogen phosphate is titrated with sodium hydroxide:

$$OH^- + H_2PO_4^- \rightarrow HPO_4^{2-} + H_2O$$

If 23.06 mL of 0.0985*M* sodium hydroxide is required for the titration, what is the percentage of NaH_2PO_4 in the sample?

23. Tin(II) is titrated with dichromate according to the following balanced equation:

$$Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \rightarrow 3Sn^{4+} + 2Cr^{3+} + 7H_2O$$

Calculate the weight of tin(II) in a sample that requires 20.00 mL of 0.1000*M* $Cr_2O_7^{2-}$ for titration. (The atomic weight of tin is 118.7.)

24. Fluoride in a uranium salt is determined by reacting a 1.037-g sample with water vapor at 1000°C, distilling the fluoride as HF, and titrating the fluoride in the distillate with 3.14 mL of 0.1000*M* thorium nitrate:

$$Th^{4+} + 4F^- \rightarrow ThF_4(s)$$

Calculate the percentage of fluoride in the sample.

25. A 300.0-mg sample of acid contains either impure H_3PO_4 or impure NaH_2PO_4. It is titrated with 21.00 mL of 0.1000*M* sodium hydroxide to the phenolphthalein end point to give the HPO_4^{2-} ion. Calculate the %H_3PO_4 (form wt = 98.00) and the %NaH_2PO_4 (form wt = 119.98) and decide whether the results are reasonable for either or both.
26. Calculate the percentage purity of a 500.0-mg sample of impure sodium carbonate that requires 22.00 mL of 0.1800*M* HCl for complete neutralization.
27. A 300.0-mg sample of impure $MgCl_2$ is titrated with 45.00 mL of 0.1000*M* $AgNO_3$ to $2AgCl + Mg(NO_3)_2$.

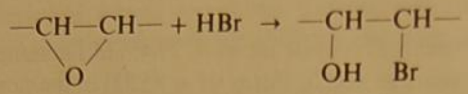
    (a) Calculate the percentage chloride (at wt = 35.45) in the sample.
    (b) Calculate the percentage $MgCl_2$ (form wt = 95.23) in the sample.

28. A 500.0-mg sample of chloride requires 15.50 mL of 0.1100*M* $AgNO_3$ for tiration by an accurate end point. Calculate the percentage chloride (at wt = 35.45).
29. A 1.000-g portion of the same sample in the previous problem requires 31.50 mL of 0.1050*M* $AgNO_3$ with a questionable end point. Calculate the percentage Cl^- and compare results.
30. An impure 1.0000-g sample of arsenious acid (H_3AsO_3) is oxidized to H_3AsO_4 by titrating with 45.00 mL of 0.0800*N* (0.0400*M*) iodine (I_2). Calculate the percentage H_3AsO_3 (form wt = 125.9) and percentage As (at wt = 74.92).
31. A 377.0-mg sample of As_2O_3 is dissolved to give two molecules of H_3AsO_3 per one molecule of As_2O_3 and is oxidized to H_3AsO_4 with 31.48 mL of 0.0502*M* (0.1040*N*) iodine (I_2). Calculate the percentage of As_2O_3 (form wt = 197.84) in the sample.

Back-Titration Problems

32. Iron(III) is best determined by addition of excess EDTA, followed by back-titration with a metal ion that reacts rapidly with EDTA. A 700.0-mg sample is dissolved, 20.00 mL of 0.0500*M* EDTA is added, and the excess EDTA is titrated with 5.08 mL of 0.0420*M* copper(II). Calculate the percentage of Fe_2O_3 in the sample.
33. The rate of diffusion of a volatile organic acid from container A into container B, which contains 2.00 mL of 0.8040*M* potassium hydroxide, is being measured. After 2 hours, the acid in A requires 1.53 mL of 0.0100*M* sodium hydroxide for titration; the excess potassium hydroxide in B requires 1.90 mL of of 0.2000*M* hydrochloric acid for titration. Calculate (a) the amount of organic acid in each container and (b) the percentage of organic acid that has diffused into B.
34. Aluminum(III) and zinc(II) both react with EDTA to form a 1:1 soluble complex. A 550.0-mg sample is analyzed for aluminum(III) by adding 50.00 mL of 0.0510*M* EDTA and back-titrating the excess EDTA with 14.40 mL of 0.0480*M* zinc(II). Calculate the percentage of aluminum in the sample.
35. A 50.00-mL aliquot of 0.1000*M* calcium nitrate is added to a 1.0000-g sample containing sodium fluoride. After the calcium fluoride precipitate has been filtered and collected, the excess calcium(II) is titrated with EDTA. This titration requires 24.20 mL of 0.0500*M* EDTA. Calculate the percentage of NaF in the sample.
36. Calculate the percentage iodide (at wt = 126.9) in a 1.0000-g sample to which is added an excess of 50.00 mL of 0.1000*M* $AgNO_3$. The unreacted $AgNO_3$ is then back-titrated with 16.00 mL of 0.0800*M* KSCN, producing AgSCN(s).
37. Calculate the percentage of sodium carbonate (form wt = 106.0) in a 510.0-mg impure sample that requires 50.00 mL of 0.1111*M* excess $AgNO_3$ for the precipitation of Ag_2CO_3. The unreacted $AgNO_3$ is back-titrated with 11.00 mL of 0.1050*M* KSCN, producing AgSCN(s).

38. Calculate the percentage of potassium arsenate (form wt = 256.2) in a 620.0-mg impure sample that requires 50.00 mL of 0.1111*M* excess $AgNO_3$ for the precipitation of Ag_3AsO_4. The unreacted $AgNO_3$ is back-titrated with 12.00 mL of 0.1010*M* KSCN, producing AgSCN(s).
39. The epoxy group, which is found in organic chemicals used to make resins and other polymers, may be determined analytically by reacting it with HBr to form a nonacidic bromohydrin:



A 0.4000-g sample of a pure epoxy compound is allowed to react with 20.00 mL of 0.1000*M* HBr. The excess HBr then requires 6.15 mL of 0.1080*M* sodium hydroxide for titration. Calculate the formula weight of the organic compound, assuming that only one epoxy group is present in the molecule.

Miscellaneous Calculations

40. A newly synthesized organic reagent is found to form a complex with calcium(II). To learn more about the nature of the complex, a 50.0-mg sample of the reagent (form wt = 181.2) is titrated with calcium(II) using a calcium-ion electrode to detect the titration end point. This titration requires 11.46 mL of 0.0120*M* calcium chloride. What is the combining ratio of reagent to calcium in the complex?
41. A complex containing bismuth and iodide is decomposed, after which the iodide ion is titrated with silver(I) and the bismuth(III) with EDTA. A 550-mg sample requires 14.50 mL of 0.0500*M* EDTA for titration of the bismuth, and a 440-mg sample requires 23.25 mL of 0.1000*M* silver(I) for titration of the iodide. Calculate the ratio of iodide to bismuth in the original complex.
42. A 10.00-mL aliquot of sulfuric acid solution requires 28.16 mL of 0.1000*M* sodium hydroxide for titration. What volume of 0.1000*M* $BaCl_2$ will be required to titrate a second 10.00-mL aliquot of the H_2SO_4 solution if $BaSO_4$ is precipitated?
43. A 345.0-mg sample of a pure unknown monoprotic acid is dissolved and titrated with 27.40 mL of 0.1000*M* NaOH. Calculate the formula weight of the monoprotic acid.

6. (a) fwNaOH, $fwH_2C_2O_4/2$
(b) fwHCl, $fwBa(OH)_2/2$
(c) $fwI_2/2$, $fwH_2S/2$
(d) $fwFeCl_3$, $fwSnCl_2/2$
(e) $fwPb(NO_3)_2/2$, $fwH_2SO_4/2$
(f) $fwAgNO_3$, 2 x fwNaCN

7. (a) 117.4/169.9 = 0.691 M
(b) 9.72g/L/97.18 = 0.100 M
(c) 0.200 x 5/244.3 = .0004 M
(d) 72.0/72 x 142.0 = 0.007 M

8. (a) 100 x 0.500 x 40.00 = 2.00×10^3 mg
(b) 10.0 x 0.100 x 79.91 x 2 = 160 mg
(c) 24.7 x 0.100 x 97.18 = 240 mg
(d) 5.00 x 0.010 x 158.0 = 7.9

9. mlHCl x 12.0 = 1000 x 0.25 mlHCl = 20.8

10. mlNaOH x 16 = 2000 x 0.1 mlNaOH = 12.5

11. $\frac{1690 \text{ mg/ml} \times 0.85}{98.00} = 14.7$ M

12. $\frac{1486 \times 0.48}{80.92} = 8.8$ M

13. mlHCl x 1.183 = 1000 x 0.1000; mlHCl = 84.5

14. (46.32)(M) 204.2 = 1200; M = 0.1269

15. (24.69)(M)(121.14) = 278.0; M = 0.0929_5

16. $\frac{8.5332 \times 2}{169.9} = 0.10045$ M (5 signif. figs.)

17. 10.00 → 50.00 (3.923)(0.0110) = (20.00)(M)
M = 0.00216 original soln = 5 x 0.00216 = 0.01079 M

18. (3.923)(0.0110) = (25.00)(M) M = 0.00173
orig. soln. = 2 x 0.00173 = 0.00345 M

19. $As_2O_3 \rightarrow 2H_3AsO_4$
(a) $\frac{395.6 \text{ mg}}{197.84} = \frac{2.000 \text{ mmoles}}{25.00 \text{ mL}} = 0.0800$ M
H_3AsO_4 = 2 x 0.0800 = 0.1600 M
(b) 2e' change/mole, so 0.1600 x 2 = 0.3200 N

20. (a) (24.10)(M) = (25.00)(0.0150) M = 0.01556 I_2
(b) I_2 = 2 x 0.01556 = 0.03112 N.

21. $As_2O_3 + 4\ Ce^{4+} \rightarrow$ Products
(a) (18.40)(M)(1/4)(197.84) = 93.0 mg; M = 0.1022
(b) Normality is also 0.1022

22. $\frac{(23.06)(0.0985)(120.0)(100)}{(500)} = 54.5\%$ NaH_2PO_4

23. (20.00)(0.1000)(118.7)(3) = 712.2 mgSn

24. $\frac{(3.14)(0.1000)(4)(19.00)(100)}{1037} = 2.30\%$

25. $\frac{(21.00)(0.1000)\frac{(98.00)}{2}100}{300.0} = 34.30\%$ H_3PO_4

$\frac{(21.00)(0.1000)(119.98)100}{300.0} = 83.99\%$ NaH_2PO_4

Either is reasonable if we assume the H_3PO_4 sample to be dilute

26. $\frac{(22.00)(0.1800)\frac{105.99}{2}100}{500.0} = 41.97\%$ Na_2CO_3

27. (a) $\frac{(45.00)(0.1000)(35.45)100}{300.0} = 53.18\%\ Cl$

(b) $53.18 \times \frac{95.23}{(2)(35.45)} = 71.42\%\ MgCl_2$

28. $\frac{(15.50)(0.1100)(35.45)100}{500.0} = 12.09\%\ Cl$

29. $\frac{(31.50)(0.1050)(35.45)100}{1000.0} = 11.73\%\ Cl$ The difference is more than 3%

30. $\frac{(45.00)(0.0400)(125.9)100}{1000.0} = 22.66\%\ H_3AsO_3$

31. $\frac{(31.48)(0.0502)\ \frac{197.84}{2}\ 100}{377.0}$ 41.46% As_2O_3

32. $\frac{[(20.00)(0.0500)] - [(5.08)(0.0420)]}{700} = (\frac{1}{2})(159.7) = 8.97\%\ Fe_2O_3$

33. A: $1.53 \times 0.0100 = 0.0153$ mmole

B: $[(2.00)(0.8040)] - [(1.90)(0.2000)] = 1.228$ mmole

$\frac{1.228}{1.228 + 0.0153}\ 100 = 98.77\%$ diffused

34. $\frac{[(50.00)(0.0570)(14.40)(0.0480](26.98)100}{550.0} = 9.12\%\ Al$

35. $(50.00)(0.1000) - (24.20)(0.0500) = 3.790$ mmole Ca

$\frac{(3.790)(2)(41.99)100}{1000.0} = 31.83\%\ NaF$

36. $\frac{[(50.00)(0.1000) - (16.00)(0.0800)](126.9)100}{1000.0} = 47.21\%\ I$

37. $(50.00)(0.1111) - (11.00)(0.1050) = 4.395$ mmole Ag^+

$\frac{(4.395)(\frac{1}{2})(106.0)100}{510.0} = 45.67\%\ Na_2CO_3$

38. $(50.00)(0.1111) - (12.00)(0.1010) = 4.343$ mmole Ag

$\frac{(4.343)(1/3)(256.2)(100)}{620.0} = 59.82\%\ K_3AsO_4$

39. $(20.00)(0.1000) - (6.15)(0.1080) = 1.336$ mmole HBr

(1.336)(f.wt.) = 400.0 f.wt. = 299.4

40. $(11.46)(0.0120) = 0.1375$ mmole Ca

$\frac{50.0}{181.2} = 0.2759$ mmole reagent

Ratio Ca:Reag = 0.498; complex is $CaReag._2$

41. $\frac{(23.25)(0.1000)}{440} = 0.00528$ mmole I/mg

$\frac{(14.50)(0.0500)}{550} = 0.00132$ mmole Bi/mg

Ratio I:Bi = 400_5; complex is BiI_4^-

42. $\frac{(28.16)(0.1000)}{2} = 1.408$ mmole H_2SO_4

(V)(0.1000) = 1.408 V = 14.08 mL $BaCl_2$

43. (27.40)(0.1000)(f.wt.) = 345.0 (f.wt.) = 125.9