

4. *Precipitation from Mixed Solvents.* An example is illustrated in Figure 4-3. A metal-organic complex such as copper 8-hydroxyquinolate is formed in water containing enough of a volatile organic solvent (acetone) to keep the complex dissolved. As the acetone evaporates, the solution becomes predominately aqueous, and the copper-organic complex precipitates as well-formed crystals.
5. *Valency Change.* This is less common. One example is the slow oxidation of cerium(III) iodate, which is soluble, to cerium(IV) iodate, which is insoluble.

### QUESTIONS AND PROBLEMS

#### Principles and Methods

1. An aqueous solution contains dissolved lead nitrate and sodium nitrate. The lead(II) is precipitated by the dropwise addition of sodium chromate,  $\text{Na}_2\text{CrO}_4$ . When an excess of sodium chromate has been added, what will be (a) the primary adsorbed ion and (b) the counter ion?
2. Which is easier to wash away or replace by an ion from the wash solution: the primary adsorbed ion or the counter ion? Explain briefly.
3. Define (a) supersaturation and (b) relative supersaturation in terms of  $Q$  and  $S$ . What precipitation conditions will minimize  $Q$ ? What precipitation conditions can be used to decrease the supersaturation by increasing  $S$ ?
4. What is digestion? In what ways can digestion improve the quality of an analytical precipitate?
5. Explain how precipitation from homogeneous solution results in a precipitate with better purity and particle size than can be obtained by conventional precipitation.
6. Suggest two different methods of precipitating calcium oxalate from homogeneous solution for the gravimetric determination of calcium.
7. Briefly define the following terms, giving one example of each: (a) occlusion, (b) isomorphous replacement, (c) postprecipitation.
8. A radiochemist has a solution containing only  $1 \mu\text{mole}$  ( $10^{-6}$  mole) of a radioactive metal ion per liter. How can he quickly isolate about  $1 \mu\text{mole}$  of this metal as a solid compound for purposes of counting the radioactivity?
9. What is peptization and how is it caused? With which types of precipitate is peptization likely to occur?
10. Although many procedures state that a temperature of approximately  $900^\circ\text{C}$  is needed to ignite a magnesium ammonium phosphate precipitate to form magnesium pyrophosphate, one authority claims that a dull red heat (about  $500^\circ\text{C}$ ) is sufficient. Suggest an experimental way of determining who is right.
11. Explain how sunlight can cause the results of gravimetric chloride determination to be either too high or too low, depending on the circumstances.
12. If barium sulfate is precipitated so that  $\text{Ba}^{2+}$  is the primary adsorbed ion, which of the following anions would you expect to be the predominating counter ion: bromide, chlorate, or chloride? (Consult a chemical handbook for solubility data to help answer this question.)
13. In the gravimetric sulfate determination, how does the coprecipitation of potassium sulfate affect the results? In the same determination, how does the coprecipitation of barium nitrate affect the results?

14. Explain why a silica precipitate must be dehydrated and how dehydration is accomplished.
15. What is the purpose of performing a *corrected* silica determination? Outline the scheme for this determination.
16. Suggest a gravimetric method for the separate determination of both constituents in each of the following mixtures (note that the order in which the constituents are precipitated is frequently important): (a)  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ; (b)  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ; (c)  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ; (d)  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ .
17. Limestone is primarily  $\text{MgCa}(\text{CO}_3)_2$  but also contains some silicates and small amounts of iron and aluminum. Outline a sequential procedure for determining calcium, magnesium, aluminum plus iron, and silica in limestone.
18. Consult Tables 4-2 and 4-3 and outline in the proper order a separation scheme for isolating each element in a brass containing Cu, Fe ( $\sim 1\%$ ), Pb, Sn, and Zn.
19. Hydrous tin(IV) oxide is precipitated by addition of nitric acid in a manner somewhat analogous to the precipitation of silica by acid. Consult a handbook for a volatile tin(IV) compound with which the weight of the tin oxide could be corrected for coprecipitated impurities.

#### Gravimetric Factor and Percentage Problems

20. For each of the following, indicate (but do not calculate) the gravimetric factor.

	Weighed	Sought	Factor
(a)	AgBr	Br	
(b)	AgBr	$\text{C}_6\text{H}_5\text{Br}$	
(c)	$\text{BaSO}_4$	S	
(d)	$\text{BaSO}_4$	$\text{K}_2\text{SO}_4$	
(e)	$\text{BaSO}_4$	$\text{FeS}_2$	
(f)	$\text{Mg}_2\text{P}_2\text{O}_7$	MgO	
(g)	$\text{Mg}_2\text{P}_2\text{O}_7$	P	
(h)	$\text{CO}_2$	$\text{CaMg}(\text{CO}_3)_2$	
(i)	$\text{CeF}_3$	F	

21. Calculate the weight of CaO that should be obtained from 100 mg of pure tooth enamel,  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ , after dissolving the enamel sample, removing the phosphate, precipitating calcium as  $\text{CaC}_2\text{O}_4$ , and igniting the precipitate to CaO for weighing.
22. Calculate the percentage of uranium in  $\text{U}_3\text{O}_8$ .
23. Calculate the weight of silver chloride that will be produced by precipitating the chloride from 1 g of pure potassium chloride.
24. Compute the volume of solution containing 40 mg/mL of silver nitrate needed to completely precipitate the chloride from 1 g of pure potassium chloride.
25. Calculate the volume of solution containing 60 mg/mL of barium chloride dihydrate needed to completely precipitate the sulfate from 1 g of pure potassium sulfate.
26. What volume of a solution containing 18.0 g/L of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) is needed to precipitate the lanthanum as lanthanum oxalate,  $\text{La}_2(\text{C}_2\text{O}_4)_3$ , from 1.000 g sample containing 20% lanthanum?
27. Calculate the weight of silica ( $\text{SiO}_2$ ) precipitate that would be obtained from a 1 g sample of pure  $\text{NaAl}(\text{SiO}_3)_2$ .
28. A 1.05-g steel sample was fused in an oxygen atmosphere. The carbon in the steel was converted to carbon dioxide and swept by a stream of oxygen into a weighed absorption tube. The carbon dioxide absorbed caused a gain of 0.040 g in the weight of the absorption tube. Calculate the percentage of carbon in the steel.

29. Phosphate can be determined gravimetrically by precipitation as ammonium phosphomolybdate and weighing as  $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ . If 10.0 mg of precipitate is the smallest that can be collected and weighed to within  $\pm 1.0\%$ , calculate the smallest weight of phosphate ( $\text{PO}_4$ ) that can be determined by this procedure.
30. Suppose that hydrous ferric oxide coprecipitates 1% of its ignited weight of calcium. If a limestone sample is 30% calcium, what is the maximum percentage of  $\text{Fe}_2\text{O}_3$  that can be present in the sample and cause no more than 1/1000 of the calcium in solution to be coprecipitated?

**Environmental and Health Analysis Problems**

31. The FDA tolerance for mercury in foods is 0.5 ppm (0.5 mg/kg). A 113.0-g sample of fish taken from Lake Erie is found by indirect analysis to contain 0.11 mg of mercury. (a) Calculate the percentage of mercury in the fish. (b) Show by calculation whether the mercury content exceeds FDA standards.
32. The range of the toxic metal cadmium in a typical 1.12-g cigarette has been found to be 1.14–1.90 micrograms. (Up to 50% of the cadmium is exhausted in smoke not inhaled.) (a) Calculate the *percentage* range of cadmium in a typical cigarette. (b) A particular cigarette weighs 1.08 g and contains 0.00015% Cd; assuming that only three-fourths of the cigarette is smoked, calculate the minimum amount of cadmium that enters the lungs from it.
33. Mercury ingested by fish exists in lakes primarily as soluble  $\text{CH}_3\text{Hg}^+$  or insoluble  $(\text{CH}_3)_2\text{Hg}$ . A certain sample of pike contained 3.5 ppm of mercury. Use the appropriate gravimetric factor to calculate the ppm of (a)  $\text{CH}_3\text{Hg}^+$  in the sample and (b)  $(\text{CH}_3)_2\text{Hg}$  in the sample.
34. The phosphate in a 1.000-g fertilizer sample was precipitated as magnesium ammonium phosphate,  $\text{MgNH}_4\text{PO}_4$ . Ignition at  $900^\circ\text{C}$  converted the precipitate to magnesium pyrophosphate,  $\text{Mg}_2\text{P}_2\text{O}_7$ , which weighed 0.2550 g. Calculate the percentage of phosphorus in the fertilizer.
35. An organic insecticide was decomposed by an oxygen combustion procedure to convert the chlorine in the molecule to water-soluble chloride. The chloride was then precipitated as silver chloride. A 0.7715-g precipitate of silver chloride was obtained from a 0.500-g sample of the insecticide. Calculate the percentage of chlorine in the insecticide.

**Moon Rock and Earth Rock Analyses**

36. The calcium from a 0.6000-g limestone sample was precipitated as calcium oxalate and ignited to calcium carbonate for weighing. The ignited precipitate weighed 0.2820 g. Calculate the percentage of calcium in the limestone.
37. In the determination of silica (weighed as  $\text{SiO}_2$  after precipitation and dehydration), metal ion impurities are often coprecipitated. In a “corrected” silica determination, the impure precipitate is weighed, the silica is volatilized by reaction with HF to form volatile  $\text{SiF}_4$  or  $\text{H}_2\text{SiF}_6$ , and the impurities remaining are weighed. From the following data, calculate the correct percentage of silica in a rock sample.

$$\text{Wt sample} = 1.000 \text{ g}$$

$$\text{Silica} + \text{Impurities} = 0.1262 \text{ g}$$

$$\text{Pcpt. after HF treatment} = 0.0012 \text{ g}$$

38. Samples of anorthositic rock from the moon contain about 46%  $\text{SiO}_2$  and 29%  $\text{Al}_2\text{O}_3$ . (a) Calculate the percentages of Si and Al in this category of lunar rock. (b) A specific

mineral with the formula  $\text{CaAl}_2\text{Si}_2\text{O}_8$  has been found to occur in the anorthositic rock. If this mineral were the major constituent in the rock, could its composition account for the high aluminum and silicon content of the anorthosite?

39. An unknown mineral containing calcium, iron, and the metasilicate ion,  $\text{SiO}_3^{2-}$ , was discovered in the Apollo 11 lunar samples. It contained 16.2% Ca, 22.5% Fe, 22.6% Si, and 38.7% O. Calculate the empirical formula of this mineral.
40. Lunar samples have contained from 6% to 11% titanium, much more than most terrestrial rocks. The mineral ilmenite,  $\text{FeTiO}_3$ , has been found in some lunar samples. If it were the only titanium mineral present, what percentage of it would have to be present to account for the 11% titanium?

**Calculation of Empirical Formulas and Molecular Formulas**

41. A 0.3999-g sample of reagent grade  $\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$  was dissolved and analyzed for aluminum by the aluminum oxinate method in Experiment 4. If the precipitate of aluminum oxinate,  $\text{Al}(\text{C}_9\text{H}_6\text{NO})_3$ , weighed 0.4185 g, calculate the value of  $x$ , the number of water molecules in the reagent.
42. An organic compound has the formula  $\text{C}_6\text{H}_6-x\text{OCl}_x$ . A sample of the pure compound weighing 0.1500 g was decomposed and the chloride precipitated and weighed as silver chloride. The precipitate weighed 0.4040 g. Calculate the value of  $x$  and give the correct formula for the compound.
43. A sample of the pure compound  $(\text{CH}_3)_4\text{NBr}_x$  weighing 0.0962 g was dissolved and treated with a reducing agent to ensure that all bromine was present as  $\text{Br}^-$ . A precipitate of silver bromide weighing 0.1730 g was obtained. Calculate the value of  $x$  in the formula of the compound.
44. An organic compound containing only carbon and oxygen is found by analysis to contain 50.0% C and 50.0% O. Its molecular weight is  $289 \pm 2$ . Calculate its empirical formula.
45. Anhydrous potassium hydrogen sulfate,  $\text{KHSO}_4$ , loses water when heated. If a 0.1359-g sample of  $\text{KHSO}_4$  loses 9.0008 g of water, calculate the formula of the chemical compound remaining.

**Special Problems**

46. Write equations for the formation of the curd of the digested silver halide from:
  - (a) Adding excess  $\text{AgNO}_3$  to  $\text{NaBr}$
  - (b) Adding excess  $\text{AgClO}_4$  to  $\text{NaCl}$
47. Write equations for the formation of the curd of the digested silver bromide from:
  - (a) Adding excess  $\text{NaBr}$  to  $\text{AgNO}_3$
  - (b) Adding excess  $\text{KBr}$  to  $\text{AgClO}_4$
48. State whether each solution can be used to wash insoluble silver chloride after precipitation of chloride with excess silver nitrate and also after precipitation of silver ion with excess potassium chloride.
  - (a) Dilute  $\text{HNO}_3$
  - (b) Dilute  $\text{NH}_4\text{NO}_3$
  - (c) Dilute  $\text{HCl}$
  - (d) Dilute  $\text{H}_2\text{SO}_4$
49. Which of the following solutions would not be a good wash solution for washing silver chloride precipitated with excess silver nitrate?
  - (a) Dilute  $\text{HNO}_3$
  - (b) Dilute acetic acid
  - (c) Dilute  $\text{HBr}$
  - (d) Dilute  $\text{H}_2\text{SO}_4$

1.-19. See text

20. All answers are ratios of the formula weights indicated.

(a) Br/AgBr (b)  $C_6H_5Br/AgBr$  (c)  $S/BaSO_4$  (d)  $K_2SO_4/BaSO_4$ (e)  $FeS_2/2BaSO_4$  (f)  $2MgO/Mg_2P_2O_7$  (g)  $2P/Mg_2P_2O_7$ (h)  $CaMg(CO_3)_2/2CO_2$  (i)  $3F/CeF_3$ 

$$21. 100 \times \frac{5 \times fwCaO}{Ca_5(PO_4)_3OH} = \frac{100 \times 280.4}{502.3} = 55.8 \text{ mg}$$

$$22. U = \frac{238.03 \times 3}{842.09} = 100 = 84.80\% \text{ mg}$$

$$23. 1.000 \times \frac{fwAgCl}{fwKCl} = 1.922 \text{ g. AgCl}$$

$$24. 1000 \times \frac{fwAgNO_3}{fwKCl} = \frac{2282 \text{ mg}}{40 \text{ mg/ml}} = 57.0 \text{ ml}$$

$$25. 1000 \times \frac{fwBaCl_2 \cdot 2H_2O}{fwK_2SO_4} = \frac{1405 \text{ mg}}{60 \text{ mg/ml}} = 23.4$$

$$26. 200 \times \frac{3 fwH_2C_2O_4}{2 fwLa_2(C_2O_4)_3} = \frac{194 \text{ mg}}{18 \text{ mg/ml}} = 10.78 \text{ ml}$$

$$27. 1.000 \times \frac{2 fwSiO_2}{fwNaAl(SiO_3)_2} = 0.594 \text{ g}$$

$$28. \frac{0.040 \times \frac{f \cdot w \cdot C}{fwCO_2} \times 100}{1.05} = 1.04\% \text{ C}$$

$$29. \frac{10 \times fwPO_4}{fw(NH_4)_3PMo_{12}O_{40}} = \frac{10 \times 94.97}{1876.35} = 0.506 \text{ mg}$$

$$30. 1/1000 \text{ of Ca} = 0.03\%$$

$$Fe_2O_3 \times 0.01 = 0.03; Fe_2O_3 = 3.0\%$$

$$31. (a) \frac{0.00011}{113.0} \times 100 = 9.7 \times 10^{-5}\% \text{ Hg}$$

$$\frac{0.11}{113.0} \times 1000 = 0.97 \text{ ppm}$$

$$32. (a) \frac{1.14 \times 10^{-6}}{1.12} \times 100 = 1.0 \times 10^{-4}\% \text{ Cd}$$

$$\frac{1.90}{1.12} \times 10^{-6} \times 100 = 1.7 \times 10^{-4}\% \text{ Cd}$$

$$(b) 1.08 \times 10^6 \mu\text{g} \times 1.5 \times 10^{-6} \times 0.75 = 1.22 \mu\text{g}$$

$$33. (a) 3.5 \times \frac{fwCH_3Hg}{fwHg} = 3.8 \text{ ppm}$$

$$(b) 3.5 \times \frac{fw(CH_3)_2Hg}{fwHG} = 4.0 \text{ ppm}$$

$$34. \frac{0.2550 \times \frac{2 fwP}{fwMg_2P_2O_7} \times 100}{1.000} = 7.10\% \text{ P}$$

$$35. \frac{0.7715 \times \frac{fwCl}{fwAgCl} \times 100}{0.500} = 38.17\% \text{ Cl}$$

$$36. \frac{0.2820 \times \frac{f \cdot w \cdot Ca}{f \cdot w \cdot CaCO_3} \times 100}{0.6000} = 18.82\% \text{ Ca}$$

$$37. \frac{0.1262 - 0.0012}{1.000} \times 100 = 12.5\% \text{ SiO}_2$$

38. (a) 22% Si, 15.6% Al

(b) Yes for Al (19.4% in  $CaAl_2Si_2O_8$ ); Almost for Si (20% in  $CaAl_2Si_2O_8$ ).

$$39. \text{Ca} = \frac{16.2}{40} = 0.405, \quad \text{Fe} = \frac{22.5}{55.85} = 0.403,$$

$$\text{Si} = \frac{22.6}{28} = 0.807, \quad \text{O} = \frac{38.7}{16} = 2.419.$$

Divide each by the smallest ratio (0.403), giving a relative ratio of Ca:Fe:Si:O of 1:1:2:6.

Formula is  $\text{CaFe}(\text{Si})_2$ .

40. 100 g. of sample is to contain 11 g. of Ti

$$11 \times \frac{\text{fw} \cdot \text{FeTiO}_3}{\text{fw} \cdot \text{Ti}} = 34.8\% \text{ FeTiO}_3$$

$$41. 0.3999 \times \frac{2\text{fwAl}(\text{C}_9\text{H}_6\text{NO})_3}{\text{fwAl}_2(\text{SO}_4)_3 \cdot x \text{H}_2\text{O}} = 0.4185$$

$$\text{f} \cdot \text{w} \cdot \text{Al}_2(\text{SO}_4)_3 \cdot x \text{H}_2\text{O} = 877.2 \quad x = 29.7 (\sim 30)$$

$$42. 0.4040 \times \frac{72 + 6 - x + 16 + 35.5x}{143.5x} = 0.1500 \quad x = 5.00 (\text{C}_6\text{HOC}_5)$$

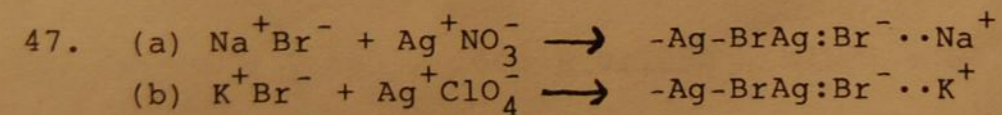
$$43. 0.1730 \times \frac{60 + 14 + 79.9x}{187.8x} = 0.0962 \quad x = 3.02, (\text{CH}_3)_4\text{NBr}_3$$

$$44. \text{C} = \frac{50}{12} = 4.167, \quad \text{O} = \frac{50}{16} = 3.125, \quad \text{Ratio C:D} = \frac{4.167}{3.125} = 1.33$$

$$(a) \text{C}_4\text{O}_3 \quad (b) \frac{289}{\text{f} \cdot \text{w} \cdot \text{C}_4\text{O}_3} = 3, \quad \text{C}_{12}\text{O}_9$$

45.  $135.9/135.9 = 1.0$  mmole  $\text{KHSO}_4$ ;  $0.5$  mmole  $\text{H}_2\text{O}$ ; Formula is  $\text{K}_2\text{S}_2\text{O}_7$

46. See text.



48. (a) Ok (b) Ok (c) Not ok with excess  $\text{AgNO}_3$ , ok with excess  $\text{K}^+\text{Cl}^-$  (d) Not sufficiently volatile.

49. (b), (c) and (d) would not be good