CALCULATIONS IN ANALYTICAL CHEMISTRY

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Preface

Titrimetric methods occupy an important position among the classical methods of analysis and are based mainly on acid–base, complexation, precipitation, and redox reactions in aqueous media. The principles underlying these chemical reactions are dealt with in most introductory courses, including undergraduate quantitative analysis courses. Competence in this area of quantitative analysis is enhanced by solving problems. This book presents a collection of worked-out examples and problems in titrimetric analysis. It is intended as a workbook—not as a textbook—that can be used to supplement any textbook in analytical chemistry.

The examples and problems in this workbook are based on the corresponding graphical illustrations, which have been accurately drawn with the aid of a digital computer and an x–y plotter. The graphical representations constitute the foundation of the book. Each problem provides sufficient information to identify one of the coordinates of a point on any of the curves; the solution involves calculating the value of the remaining coordinate from a knowledge of the appropriate equilibria. If the calculation is carried out correctly, the answer will agree with the value of the coordinate that can be obtained from the graph. For example, in a simple acid–base titration, the volume and molarity of the base and the volume and molarity of the acid added will give a value for the fraction titrated, that is, the x-coordinate in the acid–base titration curve. From a knowledge of the acid–base chemistry, it should be possible to calculate the pH of the resulting solution, that is, the value of the y-coordinate that corresponds to the fraction titrated.

In other words, all the answers to the problems, and consequently the validity of all the calculations, can be verified by reference to the appropriate graph. All the information given in the problems is summarized in the graphs, and the answers to the problems are built into them as well. Every point on a curve constitutes a problem as well as the answer to a problem. This approach to problem solving at the undergraduate level is unique.

In all calculations involving equilibrium constants, it is important to use values of the constants that correspond to the solution condition specified in the problems. It will be assumed that in all the examples and problems, aqueous solutions at 25°C are employed. If meaningful answers to the problems are required, all equilibrium constants must be corrected for ionic strength effects.

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Introduction

Fundamental Concepts

Stoichiometric Principles

In quantitative chemical analysis, the calculations involved are based on stoichiometric relationships that can be deduced from balanced chemical reactions. For example, when $CaCO_3$ is reacted with HCl, according to the balanced chemical equation, $CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$, 1 mol of $CaCO_3$ requires 2 mol of HCl for complete reaction. The *algebraic* relationship between the number of moles of $CaCO_3$ that reacted, n_{CaCO_3}, and the number of moles of HCl that reacted, n_{HCl}, is expressed as

$$n_{HCl} = 2 \times n_{CaCO_3}$$

The number of moles of $CaCO_3$ that reacted, n_{CaCO_3}, is multiplied by the factor 2—*not* the number of moles of HCl that reacted, n_{HCl}—although here 2 mol of HCl is required to balance the chemical equation. The reason for this is evident from the following example.

Example 1

A solution containing 8.00 mmol of HCl is added to 9.00 g of solid $CaCO_3$. How many moles of $CaCO_3$ are left unreacted? [molecular weight (MW) of $CaCO_3$ is 100.09]

A 9.00-g sample of $CaCO_3$ contains $\frac{9.00}{100.09} \times 1000 = 89.92$ mmol of $CaCO_3$.

Hence, the problem can be restated as follows: How many moles of $CaCO_3$ are left unreacted when 8.00 mmol of HCl is added to 89.92 mmol of $CaCO_3$?

It may be deduced from the balanced chemical equation,

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

that 2 mmol of HCl reacts with 1 mmol of $CaCO_3$. Therefore, 8.00 mmol of HCl must react with $\left(\frac{1}{2} \times 8.00\right)$ or 4.00 mmol of $CaCO_3$, and the number of moles of $CaCO_3$ left unreacted is

$$\frac{89.92 - 4.00}{1000} = .0859$$

The identical result may be deduced from the algebraic relationship between the number of moles of HCl that reacted and the number of moles of $CaCO_3$ that reacted:

$$\text{Number of moles of HCl} = n_{HCl} = \frac{8.00}{1000}$$

$$\text{Number of moles of } CaCO_3 = n_{CaCO_3}$$

From the balanced chemical equation

$$n_{HCl} = 2 \times n_{CaCO_3}$$

$$n_{CaCO_3} = \frac{n_{HCl}}{2} = \frac{8.00}{1000 \times 2} = \frac{4.00}{1000}$$

Therefore, the number of moles of $CaCO_3$ left unreacted is

$$\frac{9.00}{100.09} - \frac{4.00}{1000} = .0859$$

This example also shows the manner in which grams, moles, and millimoles of the compound $CaCO_3$, with a molecular weight of 100.09, are interrelated.

The stoichiometric relationships that can be deduced from the balanced chemical reaction

$$aA + bB \longrightarrow cC$$

are $b \cdot n_A = a \cdot n_B$ where n_A and n_B are the number of moles of A and B, respectively, that react;

$c \cdot n_A = a \cdot n_C$ where n_C is the number of moles of product that is formed from n_A mol of reactant A;

$b \cdot n_C = c \cdot n_B$ where n_C is the number of moles of product that is formed from n_B mol of reactant B.

Example 2

A sample of iron ore (.5356 g) is dissolved in H_2SO_4. All the iron(III) is reduced quantitatively to iron(II), and the solution is titrated with a standard potassium dichromate solution made by dissolving .4836 g of $K_2Cr_2O_7$ in 1 liter of water. If 28.46 ml of the $K_2Cr_2O_7$ is required to reach the endpoint in the titration, calculate the percentage of iron (% Fe) in the sample of iron ore. (Fe 55.847; MW $K_2Cr_2O_7$ 294.18.)

The balanced chemical equation for this determination is

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

The algebraic expression that gives the relationship between the number of moles of $K_2Cr_2O_7$ that reacted and the number of moles of Fe^{2+} that reacted is

$$6 \times n_{K_2Cr_2O_7} = n_{Fe^{2+}}$$

But $n_{K_2Cr_2O_7} = V_l \times M$ where V_l is the volume of $K_2Cr_2O_7$ in liters and M is the molarity of $K_2Cr_2O_7$. The volume of the titrant required, in liters, multiplied by the concentration of the titrant, in moles per liter, gives the number of moles of the titrant that reacted. If the volume of the titrant, in milliliters, is multiplied by the concentration of the titrant in moles per liter, the number of millimoles of titrant that reacted is obtained. Hence

$$n_{K_2Cr_2O_7} = \frac{28.46}{1000} \times \frac{.4836}{294.18} = 4.679 \times 10^{-5} \text{ mol}$$

and

$$n_{Fe} = 4.679 \times 10^{-5} \times 6 \text{ mol}$$

Therefore, in the ore sample

$$\% \text{ Fe} = \frac{4.679 \times 10^{-5} \times 6 \times 55.847 \times 100}{.5356} = 2.927$$

Concentrations of Solutions

A standard solution is defined as a solution that has a known concentration. The concentration of a solution can be expressed in a number of different ways: molarity (M), molality (m), weight percent (%w/w), parts per million (ppm), and parts per billion (ppb). A solution that is made by dissolving .5844 g NaCl in water and made up to the mark in a 1-liter volumetric flask is a solution that contains .0100 mol NaCl per liter and is defined as a .0100 M solution. In such a solution the exact amount of the solvent (water) that is present is not known because the dissolved NaCl (solute) occupies an unknown fraction of the total volume of the solution. If the density of the solution is known, the exact amounts of solute and solvent that are present in this solution can be calculated. On the other hand, if .5844 g of NaCl is dissolved in 1 kg of water, the resulting solution is a 1 *m* solution of NaCl. In this solution, the exact amounts of solute and of solvent present are known. The following examples illustrate the uses of various methods of expressing concentrations of solutions and also show the relationship between molarity, molality, and weight percent.

Example 3

How many milliliters of concentrated (conc.) HCl (MW 36.461), 37.2% w/w and density (1.19 g/ml), are required to make 5 liters of a 6.00 *M* solution? How many milliliters of this 6.00 *M* solution are required to react quantitatively with 12.00 g of Na_2CO_3 (MW 105.99)?

One hundred grams of the conc. HCl solution contains 37.2 g or $\frac{37.2}{36.461}$ mol HCl. One liter of the conc. HCl solution contains

$$\frac{37.2}{36.461} \times \frac{1.19}{100} \times 1000 = 12.14 \text{ mol HCl}$$

The conc. HCl solution is therefore 12.14 *M*.

The number of moles HCl in 5 liters of a 6.00 *M* solution is (5 × 6.00). Hence

$$5 \times 6.00 = V_l\ 12.14$$

where V_l = volume in liters of the 12.14 *M* solution that is required to make 5 liters of the 6.00 *M* solution of HCl:

$$V_l = \frac{5 \times 6.00}{12.14} = 2.47 \text{ liters}$$

Therefore, the number of milliliters required is 2.47 × 1000 = 2470.

The balanced chemical equation for the reaction of Na_2CO_3 with HCl is

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

The algebraic relationship between the number of moles of Na_2CO_3 and the number of moles of HCl required for complete reaction is

$$n_{HCl} = 2 \times n_{Na_2CO_3}$$

But

$$n_{Na_2CO_3} = \frac{12.00}{105.99}$$

$$n_{HCl} = 2 \times \frac{12.00}{105.99} = V_l \times 6.00$$

$$V_l = \frac{2 \times 12.00}{105.99 \times 6} = .03774 \text{ liters}$$

The number of milliliters of 6.00 M HCl required to react quantitatively with 12.00 g Na_2CO_3 is 37.74.

Example 4

Concentrated nitric acid (HNO_3 MW 63.01) is 15.9 M and has a density of 1.42 g/ml. Calculate the weight percent of HNO_3 in the concentrated acid and the molality of the solution.

One liter of concentrated acid contains 15.9 mol HNO_3 or (15.9 × 63.01) g HNO_3. One hundred grams of concentrated acid contains

$$\frac{15.9 \times 63.01 \times 100}{1000 \times 1.42} = 70.6 \text{ g } HNO_3$$

The conc. HNO_3 is therefore 70.6% w/w.

One liter of concentrated acid or 1420 g of concentrated acid contains (15.9 × 63.01) g HNO_3 and (1420 − 15.9 × 63.01) g water, that is, (1420 − 15.9 × 63.01) g water contains 15.9 mol HNO_3.

Therefore, 1000 g water contains $\frac{15.9 \times 1000}{1420 - 15.9 \times 63.01}$ mol HNO_3.

The molality of the conc. HNO_3 is 38.0.

Example 5

Derive an algebraic relationship between the molarity M of an aqueous solution and its molality m if the density of the aqueous solution is d g/ml and the molecular weight of the solute is G.

One thousand milliliters of an M molar solution contains ($M \times G$) g of solute and ($1000 \times d - M \times G$) g of the solvent water. One thousand grams of water contains

$$\frac{M \times G \times 1000}{1000 \times d - M \times G} \text{ g solute}$$

or

$$\frac{M \times 1000}{1000 \times d - M \times G} \text{ mol solute}$$

Therefore, the molality of the solution is given by

$$m = \frac{M \times 1000}{1000 \times d - M \times G}$$

In very dilute solutions $d \rightarrow 1$ and ($M \times G$) is negligible in comparison with $1000 \times d$. Under these conditions, $m \approx M$.

Example 6

The concentration of SO_2 in ambient air is found to be .055 ppm. How many milligrams of SO_2 are present in 1 m^3 of ambient air? The density of air = .001185 g/ml (at 25°C and 760 torr).

10^6 g of air contains .055 g SO_2

$\frac{10^6}{1.185 \times 10^{-3}}$ ml of air contains .055 g SO_2

One cubic meter (10^6 ml) contains

$$.055 \times \frac{1.185 \times 10^{-3}}{10^6} \times 10^6 \times 10^3 = .065 \text{ mg } SO_2$$

Calculations in Gravimetric Analysis

Chemical reactions that are assumed to proceed to completion and that form insoluble products are employed in gravimetric analysis. A reagent is added to a solution containing the species that is to be determined and the precipitate that is formed is separated and weighed. It is necessary that the precipitated compound have a definite stoichiometry and be free of impurities. In certain instances the precipitate must be converted, usually by heating or ignition, into an appropriate form that has a definite stoichiometry and can be weighed conveniently. The following examples illustrate the application of stoichiometric calculations in gravimetric analysis.

Example 7

A .1500-g sample of zinc metal that contains an inert impurity is dissolved in acid and the zinc precipitated as zinc ammonium phosphate ($ZnNH_4PO_4$). The precipitate is separated and ignited to zinc pyrophosphate ($Zn_2P_2O_7$). If the weight of the zinc pyrophosphate is .3333 g, calculate the percentage of zinc (% Zn) in the original sample. (Zn 65.38; P 30.974)

The balanced chemical equation can be written as

$$2Zn^{2+} \longrightarrow 2ZnNH_4PO_4 \longrightarrow Zn_2P_2O_7$$

The algebraic relationship between the number of moles of zinc in the sample (n_{Zn}) and the number of moles of zinc pyrophosphate ($n_{Zn_2P_2O_7}$) formed is

$$n_{Zn} = 2 \times n_{Zn_2P_2O_7}$$

$$n_{Zn} = 2 \times \frac{.3333}{304.71}$$

In a .1500-g sample

$$2 \times \frac{.3333}{304.71} \times 65.38 \text{ g Zn}$$

In a 100-g sample

$$\frac{2 \times .3333 \times 65.38 \times 100}{304.71 \times .1500} \text{ g Zn}$$

In the sample

$$\% \text{ Zn} = 95.35$$

Example 8

A mixture contains only NaCl and KCl. When .1500 g of this mixture is dissolved and precipitated with $PtCl_4$, a precipitate of K_2PtCl_6 that weighs .2222 g is formed. (The NaCl does not react with $PtCl_4$ to form an insoluble precipitate.) Calculate the percentage of Na in the mixture. (Na 22.99; K 39.10; Cl 35.45; Pt 195.1)

The balanced chemical reaction for the formation of the insoluble compound K_2PtCl_6 is

$$2KCl + PtCl_4 \longrightarrow K_2PtCl_6$$

The algebraic expression that relates the number of moles of K_2PtCl_6 formed to the number of moles of KCl in the mixture is

$$\begin{aligned} n_{KCl} &= 2 \times n_{K_2PtCl_6} \\ &= \frac{2 \times .2222}{486.0} \\ &= 9.144 \times 10^{-4} \text{ mol KCl} \\ &= 9.144 \times 10^{-4}\ 74.55 \text{ g KCl} \\ &= .06817 \text{ g KCl} \end{aligned}$$

The number of grams of NaCl in the mixture is

$$.1500 - .06817 = .08183$$

In the mixture

$$\begin{aligned} \% \text{ Na} &= .08183 \times \frac{22.99}{58.44} \times \frac{100}{.1500} \\ &= 21.46 \end{aligned}$$

Example 9

A mixture contains CaO and $CaCO_3$ only. When this mixture is ignited and cooled in a desiccator, there is a 5% loss in weight. Calculate the percentage of $CaCO_3$ in the mixture. (Ca 40.08)

The chemical reaction that occurs upon ignition and results in the weight loss is

$$CaCO_3 \longrightarrow CaO + CO_2$$

If 100 g of the mixture is ignited, 5 g is lost as CO_2. Let the number of moles of CO_2 lost be n_{CO_2}:

$$n_{CO_2} = n_{CaCO_3}$$

$$\frac{5}{44.00} = n_{CaCO_3}$$

The number of grams of $CaCO_3$ in 100 g of the mixture is

$$\frac{5}{44.00} \times 100.08 = 11.37$$

In the mixture

$$\%\ CaCO_3 = 11.37$$

Example 10

The sulfate in .2345 g of a mixture containing only K_2SO_4 and Na_2SO_4 is precipitated by the addition of an excess of $BaCl_2$. The weight of the $BaSO_4$ precipitate formed is .3456 g. Calculate the percentage of K_2SO_4 in the mixture. (Na 22.99; K 39.10; S 32.06; Ba 137.33)

The balanced chemical equations for the formation of the $BaSO_4$ precipitate are

$$Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4$$

$$K_2SO_4 + BaCl_2 \longrightarrow BaSO_4$$

The algebraic expression that gives the relationship between the number of moles of $BaSO_4$ formed, n_{BaSO_4}, the number of moles of Na_2SO_4, $n_{Na_2SO_4}$, and the number of moles of K_2SO_4, $n_{K_2SO_4}$, is

$$n_{Na_2SO_4} + n_{K_2SO_4} = n_{BaSO_4}$$

Let x g of K_2SO_4 be present in the mixture. Then $(.2345 - x)$ g of Na_2SO_4 is present in the mixture:

$$\frac{.2345 - x}{142.04} + \frac{x}{174.26} = \frac{.3456}{233.39}$$

$$1.647 = 7.040x + 5.739x = 1.480$$

$$x = \frac{.1670}{1.301}$$

$$= .1284 \text{ g}$$