2. Tartaric acid, 15% (w/v). Dissolve 225 g of tartaric acid in sufficient water to give 1500 mL of solution. Filter before use if the solution is not clear. (This solution is sufficient for about 50 precipitations.)

**PROCEDURE**

Clean and mark three medium-porosity sintered-glass crucibles (Note 1); bring them to constant mass by drying at 110°C for at least 1 hr.

Weigh (to the nearest 0.1 mg) samples containing 30 to 35 mg of nickel into individual 400-mL beakers (Note 2). In the hood, dissolve each sample in about 50 mL of 6 M HCl with gentle warming. Carefully add approximately 15 mL of 6 M HNO₃, and boil gently to expel any oxides of nitrogen that may have been produced. Dilute to about 200 mL and heat to boiling. Introduce about 30 mL of 15% tartaric acid and sufficient concentrated NH₃(aq) to produce a faint odor of NH₃ in the vapors over the solutions (Note 3); then add another 1 to 2 mL of NH₃(aq). If the solutions are not clear at this stage, proceed as directed in Note 4. Make the solutions acidic with HCl (no odor of NH₃), heat to 60° to 80°C, and add about 20 mL of the 1% dimethylglyoxime solution. With good stirring, add 6 M NH₃ until a slight excess exists (faint odor of NH₃) plus an additional 1 to 2 mL. Digest the precipitates for 30 to 60 min, cool for at least 1 hr, and filter.

Wash the solids with water until the washings are free of Cl⁻/H⁺ (Note 5). Bring the crucibles and their contents to constant mass at 110°C. Report the percentage of nickel in the sample. The dried precipitate has the composition Ni(C₄H₇O₂N₂)₂ (288.92 g/mol).

**Notes**

1. Medium-porosity porcelain filtering crucibles or Gooch crucibles with glass pads can be substituted for sintered-glass crucibles in this determination.
2. Use a separate stirring rod for each sample and leave it in the beaker throughout.
3. The presence or absence of excess NH₃ is readily established by odor; use a waving motion with your hand to waft the vapors toward your nose.
4. If Fe₂O₃·xH₂O forms on addition of NH₃, acidify the solution with HCl, introduce additional tartaric acid, and neutralize again. Alternatively, remove the solid by filtration. Thorough washing with a hot NH₃/NH₄Cl solution is required; the washings are combined with the solution containing the bulk of the sample.
5. Test the washings for Cl⁻ by collecting a small portion in a test tube, acidifying with HNO₃, and adding a drop or two of 0.1 M AgNO₃. Washing is judged complete when little or no turbidity develops.

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**37C NEUTRALIZATION TITRATIONS**

**Discussion**

Neutralization titrations are performed with standard solutions of strong acids or bases. While a single solution (of either acid or base) is sufficient for the titration of a given type of analyte, it is convenient to have standard solutions of both acid and base available in case back-titration is needed to locate the end point more exactly. The concentration of one solution is established by titration against a primary standard; the concentration of the other is then determined from the acid/base ratio (that is, the volume of acid needed to neutralize 1.000 mL of the base).
37C-1 The Effect of Atmospheric Carbon Dioxide on Neutralization Titrations

Water in equilibrium with the atmosphere is about $1 \times 10^{-5}$ M in carbonic acid as a consequence of the equilibrium

$$\text{CO}_2(g) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3(aq)$$

At this concentration level, the amount of 0.1 M base consumed by the carbonic acid in a typical titration is negligible. With more dilute reagents ($<0.05$ M), however, the water used as a solvent for the analyte and in the preparation of reagents must be freed of carbonic acid by boiling for a brief period.

Water that has been purified by distillation rather than by deionization is often supersaturated with carbon dioxide and may thus contain sufficient acid to affect the results of an analysis.\(^4\) The instructions that follow are based on the assumption that the amount of carbon dioxide in the water supply can be neglected without causing serious error. For further discussion of the effects of carbon dioxide in neutralization titrations, see Section 16A-3.

37C-2 Preparation of Indicator Solutions for Neutralization Titrations

Discussion

The theory of acid/base indicators is discussed in Section 14A-2. An indicator exists for virtually any pH range between 1 and 13.\(^5\) Directions follow for the preparation of indicator solutions suitable for most neutralization titrations.

PROCEDURE

Stock solutions ordinarily contain 0.5 to 1.0 g of indicator per liter. (One liter of indicator is sufficient for hundreds of titrations.)

1. **Bromocresol green.** Dissolve the sodium salt directly in distilled water.
2. **Phenolphthalein, thymolphthalein.** Dissolve the solid indicator in a solution consisting of 800 mL of ethanol and 200 mL of distilled or deionized water.

37C-3 Preparation of Dilute Hydrochloric Acid Solutions

Discussion

The preparation and standardization of acids are considered in Sections 16A-1 and 16A-2.

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\(^4\)Water that is to be used for neutralization titrations can be tested by adding 5 drops of phenolphthalein to a 500-mL portion. Less than 0.2 to 0.3 mL of 0.1 M OH\(^-\) should suffice to produce the first faint pink color of the indicator. If a larger volume is needed, the water should be boiled and cooled before it is used to prepare standard solutions or to dissolve samples.

PROCEDURE

For a 0.1 M solution, add about 8 mL of concentrated HCl to about 1 L of distilled water (Note). Mix thoroughly, and store in a glass-stoppered bottle.

Note
It is advisable to eliminate CO₂ from the water by means of preliminary boiling if very dilute solutions (<0.05 M) are being prepared.

37C-4 Preparation of Carbonate-Free Sodium Hydroxide

Discussion
See Sections 16A-3 and 16A-4 for information concerning the preparation and standardization of bases.

Standard solutions of base are reasonably stable as long as they are protected from contact with the atmosphere. Figure 37-4 shows an arrangement for preventing the uptake of atmospheric carbon dioxide during storage and when the reagent is dispensed. Air entering the vessel is passed over a solid absorbent for CO₂, such as soda lime or Ascarite II.⁶ The contamination that occurs as the solution is transferred from this storage bottle to the buret is ordinarily negligible.

As an alternative to the storage system shown in Figure 37-4, a tightly capped low-density polyethylene bottle can usually provide sufficient short-term protection against the uptake of atmospheric carbon dioxide. Before capping, the flexible bottle is squeezed to minimize the interior air space. Care should also be taken to keep the bottle closed except during the brief periods when the contents are being transferred to a buret. Sodium hydroxide solutions will ultimately cause a polyethylene bottle to become brittle.

Figure 37-4  Arrangement for storage of standard base solutions.

⁶Thomas Scientific, Swedesboro, NJ. Ascarite II consists of sodium hydroxide deposited on a nonfibrous silicate structure.
The concentration of solutions of sodium hydroxide decreases slowly (0.1 to 0.3% per week) when the base is stored in glass bottles. The loss in strength is caused by the reaction of the base with the glass to form sodium silicates. For this reason, standard solutions of base should not be stored for extended periods (longer than 1 or 2 weeks) in glass containers. In addition, bases should never be kept in glass-stoppered containers because the reaction between the base and the stopper may cause the stopper to “freeze” after a brief period. Finally, to avoid the same type of freezing, burets with glass stopcocks should be promptly drained and thoroughly rinsed with water after use with standard base solutions. This problem is avoided with burets equipped with Teflon stopcocks.

**PROCEDURE**

If so directed by the instructor, prepare a bottle for protected storage (see Figure 37-4). Transfer 1 L of distilled water to the storage bottle (see the Note in Section 37C-3). Decant 4 to 5 mL of 50% NaOH into a small container (Note 2), add it to the water, and mix thoroughly. Use extreme care in handling 50% NaOH, which is highly corrosive. If the reagent comes into contact with skin, immediately flush the area with copious amounts of water.

Protect the solution from unnecessary contact with the atmosphere.

**Notes**

1. A solution of base that will be used up within 2 weeks can be stored in a tightly capped polyethylene bottle. After each removal of base, squeeze the bottle while tightening the cap to minimize the air space above the reagent. The bottle will become embrittled after extensive use as a container for bases.

2. Be certain that any solid Na₂CO₃ in the 50% NaOH has settled to the bottom of the container and that the decanted liquid is absolutely clear. If necessary, filter the base through a glass mat in a Gooch crucible; collect the clear filtrate in a test tube inserted into the filter flask.

**37C-5 The Determination of the Acid/Base Ratio**

**Discussion**

If both acid and base solutions have been prepared, it is useful to determine their volumetric combining ratio. Knowledge of this ratio and the concentration of one solution permits calculation of the molarity of the other.

**PROCEDURE**

Instructions for placing a buret into service are given in Sections 2G-4 and 2G-6; consult these instructions if necessary. Place a test tube or a small beaker over the top of the buret that holds the NaOH solution to minimize contact between the solution and the atmosphere.

Record the initial volumes of acid and base in the burets to the nearest 0.01 mL. Do not attempt to adjust the initial reading to zero. Deliver 35 to 40 mL of the acid into a 250-mL conical flask. Touch the tip of the buret to the inside wall of the flask, and rinse down with a little distilled water. Add two drops of phenolphthalein
(Note 1) and then sufficient base to render the solution a definite pink. Introduce acid dropwise to discharge the color, and again rinse down the walls of the flask. Carefully add base until the solution again acquires a faint pink hue that persists for at least 30 s (Notes 2 and 3). Record the final buret volumes (again, to the nearest 0.01 mL). Repeat the titration. Calculate the acid/base volume ratio. The ratios for duplicate titrations should agree to within 1 to 2 ppt. Perform additional titrations, if necessary, to achieve this order of precision.

Notes
1. The volume ratio can also be determined with an indicator that has an acidic transition range, such as bromocresol green. If the NaOH is contaminated with carbonate, the ratio obtained with this indicator will differ significantly from the value obtained with phenolphthalein. In general, the acid/base ratio should be evaluated with the indicator that is to be used in subsequent titrations.
2. Fractional drops can be formed on the buret tip, touched to the wall of the flask, and then rinsed down with a small amount of water from a squeeze bottle.
3. The phenolphthalein end point fades as CO₂ is absorbed from the atmosphere.

37C-6 Standardization of Hydrochloric Acid against Sodium Carbonate

Discussion
See Section 16A-2.

PROCEDURE

Dry a quantity of primary-standard Na₂CO₃ for about 2 hr at 110°C (see Figure 2-9), and cool in a desiccator. Weigh individual 0.20-g to 0.25-g samples (to the nearest 0.1 mg) into 250-mL conical flasks, and dissolve each in about 50 mL of distilled water. Introduce 3 drops of bromocresol green, and titrate with HCl until the solution just begins to change from blue to green. Boil the solution for 2 to 3 min, cool to room temperature (Note 1), and complete the titration (Note 2). Determine an indicator correction by titrating approximately 100 mL of 0.05 M NaCl and 3 drops of indicator. Boil briefly, cool, and complete the titration. Subtract any volume needed for the blank from the titration volumes. Calculate the concentration of the HCl solution.

Notes
1. The indicator should change from green to blue as CO₂ is removed during heating. If no color change occurs, an excess of acid was added originally. This excess can be back-titrated with base, provided that the acid/base combining ratio is known; otherwise, the sample must be discarded.
2. It is permissible to back-titrate with base to establish the end point with greater certainty.

37C-7 Standardization of Sodium Hydroxide against Potassium Hydrogen Phthalate

Discussion
See Section 16A-4.
PROCEDURE

Dry a quantity of primary-standard potassium hydrogen phthalate (KHP) for about 2 hr at 110°C (see Figure 2-9), and cool in a desiccator. Weigh individual 0.7-g to 0.8-g samples (to the nearest 0.1 mg) into 250-mL conical flasks, and dissolve each in 50 to 75 mL of distilled water. Add 2 drops of phenolphthalein; titrate with base until the pink color of the indicator persists for 30 s (Note). Calculate the concentration of the NaOH solution.

Note
It is permissible to back-titrate with acid to establish the end point more precisely. Record the volume used in the back-titration. Use the acid/base ratio to calculate the net volume of base used in the standardization.

37C-8 The Determination of Potassium Hydrogen Phthalate in an Impure Sample

Discussion
The unknown is a mixture of KHP and a neutral salt. This analysis is conveniently performed concurrently with the standardization of the base.

PROCEDURE
Consult with the instructor concerning an appropriate sample size. Then follow the directions in Section 37C-7.

37C-9 Determining the Acid Content of Vinegars and Wines

Discussion
The total acid content of a vinegar or a wine is readily determined by titration with a standard base. It is customary to report the acid content of vinegar in terms of acetic acid, the principal acidic constituent, even though other acids are present. Similarly, the acid content of a wine is expressed as percent tartaric acid, even though there are other acids in the sample. Most vinegars contain about 5% acid (w/v) expressed as acetic acid; wines ordinarily contain somewhat less than 1% acid (w/v) expressed as tartaric acid.

PROCEDURE
1. If the unknown is a vinegar (Note 1), pipet 25.00 mL into a 250-mL volumetric flask and dilute to the mark with distilled water. Mix thoroughly, and pipet 50.00-mL aliquots into 250-mL conical flasks. Add about 50 mL of water and 2 drops of phenolphthalein (Note 2) to each, and titrate with standard 0.1 M NaOH to the first permanent (≈30 s) pink color.
   Report the acidity of the vinegar as percent (w/v) CH₃COOH (60.053 g/mol).
If the unknown is a wine, pipet 50.00-mL aliquots into 250-mL conical flasks, add about 50 mL of distilled water and 2 drops of phenolphthalein to each (Note 2), and titrate to the first permanent (≈30 s) pink color. Express the acidity of the sample as percent (w/v) tartaric acid, C_2H_4O_2(COOH)_2 (150.09 g/mol) (Note 3).

Notes
1. The acidity of bottled vinegar tends to decrease on exposure to air. It is recommended that unknowns be stored in individual vials with snug covers.
2. The amount of indicator used should be increased as necessary to make the color change visible in colored samples.
3. Tartaric acid has two acidic hydrogens, both of which are titrated at a phenolphthalein end point.

37C-10 The Determination of Sodium Carbonate in an Impure Sample

Discussion
The titration of sodium carbonate is discussed in Section 16A-2 in connection with its use as a primary standard; the same considerations apply for the determination of carbonate in an unknown that has no interfering contaminants.

PROCEDURE
Dry the unknown at 110°C for 2 hr, and then cool in a desiccator. Consult with the instructor on an appropriate sample size. Then follow the instructions in Section 37C-6.
Report the percentage of Na_2CO_3 in the sample.

37C-11 The Determination of Amine Nitrogen by the Kjeldahl Method

Discussion
These directions are suitable for the Kjeldahl determination of protein in materials such as blood meal, wheat flour, pasta products, dry cereals, and pet foods. A simple modification permits the analysis of unknowns that contain more highly oxidized forms of nitrogen.7

In the Kjeldahl method (see Section 16B-1), the organic sample is digested in hot concentrated sulfuric acid, which converts amine nitrogen in the sample to ammonium sulfate. After cooling, the sulfuric acid is neutralized by the addition of an excess of concentrated sodium hydroxide. The ammonia liberated by this treatment is then distilled into a measured excess of a standard solution of acid; the excess is determined by back-titration with standard base.

Figure 37-5 illustrates typical equipment for a Kjeldahl distillation. The long-necked container, which is used for both digestion and distillation, is called a Kjeldahl flask. In the apparatus in Figure 37-5a, the base is added slowly by partially

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opening the stopcock from the NaOH storage vessel; the liberated ammonia is then carried to the receiving flask by steam distillation.

In an alternative method (Figure 37-5b), a dense, concentrated sodium hydroxide solution is carefully poured down the side of the Kjeldahl flask to form a second, lower layer. The flask is then quickly connected to a spray trap and an ordinary condenser before loss of ammonia can occur. Only then are the two layers mixed by gentle swirling of the flask.

Quantitative collection of ammonia requires the tip of the condenser to extend into the liquid in the receiving flask throughout the distillation step. The tip must be removed before heating is discontinued, however. Otherwise, the liquid will be drawn back into the apparatus.

Two methods are commonly used to collect and determine the ammonia liberated from the sample. In one, the ammonia is distilled into a measured volume of standard acid. After the distillation is complete, the excess acid is back-titrated with standard base. An indicator with an acidic transition range is required because of the acidity of the ammonium ions present at equivalence. A convenient alternative, which requires only one standard solution, involves the collection of the ammonia in an unmeasured excess of boric acid, which retains the ammonia by the reaction

\[ H_3BO_3 + NH_3 \rightarrow NH_4^+ + H_2BO_3^- \]

The dihydrogen borate ion produced is a reasonably strong base that can be titrated with a standard solution of hydrochloric acid.

\[ H_2BO_3^- + H_3O^+ \rightarrow H_3BO_3 + H_2O \]

At the equivalence point, the solution contains boric acid and ammonium ions; an indicator with an acidic transition interval (such as bromocresol green) is again required.
PROCEDURE

Preparing Samples
Consult with the instructor on sample size. If the unknown is powdered (such as blood meal), weigh samples onto individual 9-cm filter papers (Note 1). Fold the paper around the sample and drop each into a Kjeldahl flask. (The paper keeps the samples from clinging to the neck of the flask.) If the unknown is not powdered (such as breakfast cereals or pasta), the samples can be weighed by difference directly into the Kjeldahl flasks.

Add 25 mL of concentrated H₂SO₄, 10 g of powdered K₂SO₄, and the catalyst (Note 2) to each flask.

Digestion
Clamp the flasks in a slanted position in a hood or vented digestion rack. Heat carefully to boiling. Discontinue heating briefly if foaming becomes excessive; never allow the foam to reach the neck of the flask. Once foaming ceases and the acid is boiling vigorously, the samples can be left unattended; prepare the distillation apparatus during this time. Continue digestion until the solution becomes colorless or faint yellow; 2 to 3 hr may be needed for some materials. If necessary, cautiously replace the acid lost by evaporation.

When digestion is complete, discontinue heating, and allow the flasks to cool to room temperature; swirl the flasks if the contents show signs of solidifying. Cautiously add 250 mL of water to each flask and again allow the solution to cool to room temperature.

Distillation of Ammonia
Arrange a distillation apparatus similar to that shown in Figure 37-5. Pipet 50.00 mL of standard 0.1 M HCl into the receiver flask (Note 3). Clamp the flask so that the tip of the adapter extends below the surface of the standard acid. Circulate water through the condenser jacket.

Hold the Kjeldahl flask at an angle and gently introduce about 60 mL of 50% (w/v) NaOH solution, taking care to minimize mixing with the solution in the flask. The concentrated caustic solution is highly corrosive and should be handled with great care (Note 4). Add several pieces of granulated zinc (Note 5) and a small piece of litmus paper. Immediately connect the Kjeldahl flask to the spray trap. Cautiously mix the contents by gentle swirling. The litmus paper should be blue after mixing is complete, indicating that the solution is basic.

Bring the solution to a boil, and distill at a steady rate until one half to one third of the original volume remains. Control the rate of heating to prevent the liquid in the receiver flask from being drawn back into the Kjeldahl flask. After distillation is judged complete, lower the receiver flask to bring the adapter well clear of the liquid. Discontinue heating, disconnect the apparatus, and rinse the inside of the condenser with small portions of distilled water, collecting the washings in the receiver flask. Add 2 drops of bromocresol green to the receiver flask, and titrate the residual HCl with standard 0.1 M NaOH to the color change of the indicator.

Report the percentage of nitrogen and the percentage of protein (Note 6) in the unknown.

Notes
1. If filter paper is used to hold the sample, carry a similar piece through the analysis as a blank. Acid-washed filter paper is frequently contaminated with measurable amounts of ammonium ion and should be avoided if possible.
2. Any of the following catalyze the digestion: a crystal of CuSO₄, 0.1 g of selenium, 0.2 g of CuSeO₃. The catalyst can be omitted, if desired.

3. A modification of this procedure uses about 50 mL of 4% boric acid solution instead of the standard HCl in the receiver flask. After distillation is complete, the ammonium borate produced is titrated with standard 0.1 M HCl, with 2 to 3 drops of bromocresol green as indicator.

4. If any sodium hydroxide solution comes into contact with your skin, wash the affected area immediately with copious amounts of water.

5. Granulated zinc (10 to 20 mesh) is added to minimize bumping during the distillation; it reacts slowly with the base to produce small bubbles of hydrogen that prevent superheating of the liquid.

6. The percentage of protein in the unknown is calculated by multiplying the % N by an appropriate factor: 5.70 for cereals, 6.25 for meats, and 6.38 for dairy products.

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### 37D PRECIPITATION TITRATIONS

As noted in Section 13F, most precipitation titrations make use of a standard silver nitrate solution as titrant. Directions follow for the volumetric titration of chloride ion using an adsorption indicator.

#### 37D-1 Preparing a Standard Silver Nitrate Solution

**PROCEDURE**

Use a top-loading balance to transfer the approximate mass of AgNO₃ to a weighing bottle (Note 1). Dry at 110°C for about 1 hr but not much longer (Note 2), and then cool to room temperature in a desiccator. Weigh the bottle and contents (to the nearest 0.1 mg). Transfer the bulk of the AgNO₃ to a volumetric flask using a powder funnel. Cap the weighing bottle, and reweigh it and any solid that remains. Rinse the powder funnel thoroughly. Dissolve the AgNO₃, dilute to the mark with water, and mix well (Note 3). Calculate the molar concentration of this solution.

**Notes**

1. Consult with the instructor concerning the volume and concentration of AgNO₃ to be prepared. The mass of AgNO₃ to be taken is as follows:

<table>
<thead>
<tr>
<th>Silver Ion Concentration, M</th>
<th>1000 mL</th>
<th>500 mL</th>
<th>250 mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>16.9</td>
<td>8.5</td>
<td>4.2</td>
</tr>
<tr>
<td>0.05</td>
<td>8.5</td>
<td>4.2</td>
<td>2.1</td>
</tr>
<tr>
<td>0.02</td>
<td>3.4</td>
<td>1.8</td>
<td>1.0</td>
</tr>
</tbody>
</table>

2. Prolonged heating causes partial decomposition of AgNO₃. Some discoloration may occur, even after only 1 hr at 110°C; the effect of this decomposition on the purity of the reagent is ordinarily imperceptible.

3. Silver nitrate solutions should be stored in a dark place when not in use.