

CHAPTER 7

INTRODUCTION TO CHEMISTRY FOR THE PETROLEUM LABORATORY

Section I. Matter

GENERAL

Chemistry is a science that deals with the composition and properties of substances or matter, of which everything is composed. In the petroleum laboratory, the laboratory specialist will be responsible to identify chemical substances (perform qualitative analysis) and estimate quantities present (perform quantitative analysis) in their examination of fuel samples. This chapter addresses some of the basic terms, formulas, tests, and equipment they will use.

DEFINITION

Matter is anything that has mass and occupies space. The smallest unit or component of matter is an atom. There are over 100 different kinds of atoms in the world and all matter is made of one or more of these atoms. Since matter can be broken down into its component(s), in addition to classifying it by its current state (solid, liquid, or gas), it can also be classified according to its composition or components.

State. Matter classified by state may exist as a solid, having a definite shape and volume. It may exist as a liquid, having a definite volume but no definite shape. It may also exist as a gas, having no definite shape or volume. The state in which matter exists depends on the prevailing temperature and pressure conditions.

Composition. Matter classified according to its composition will fall into the following categories.

- Element. An element is matter that contains only one type of atom. Therefore, each kind of atom is called an element. Gold is an element since it is made only of gold atoms. The names of each of these known elements has been abbreviated with an approved symbol. All of the known elements are listed by their symbol in Figure 7-1, page 7-2.

- Compound. A compound is matter that is made up of two or more elements, that are chemically combined in a very definite proportion. Compounds can be broken apart. The abbreviation for a compound is called a formula. The formula shows the proportion in which the elements are combined in the compound. Rust is a compound. It is made from the elements iron and oxygen. Examples of other compounds and their formulas are shown in Table 7-1, page 7-2.

- Mixture. A mixture is matter that consists of either two or more elements or compounds (or both) blended together in any proportion. Unlike a compound, it usually absorbs all the properties of the ingredients that went into it. The constituents of a mixture can be separated and recovered by physical or mechanical methods. This is in contrast to compounds, whose constituents must be separated by a chemical process. The following are some types of mixtures:

- Homogeneous mixture. In a homogeneous mixture the composition and properties are the same.
- Heterogeneous mixture. In a heterogeneous mixture the various components are ~~like~~ **unlike**.
- Emulsion. An emulsion is a mixture of very small droplets of a liquid in another liquid.

- Suspension. A suspension contains very small, solid particles dispersed within a liquid which does not dissolve them. The solid particles tend to settle upon standing.
- Solution. In a solution, the dispersed particles are single atoms, molecules, or ions and are too small to be seen even with high magnification.

QUANTITY OF MATTER

Laboratory personnel use the metric system to measure matter. See Appendix C for conversion charts for area, length, temperature, flow, weights, volume and force. Table 7-2, page 7-3 lists frequently used measurement units and prefixes used in the laboratory. Also, there are unique terms that chemists and laboratory personnel use to describe matter discussed in the following paragraphs.

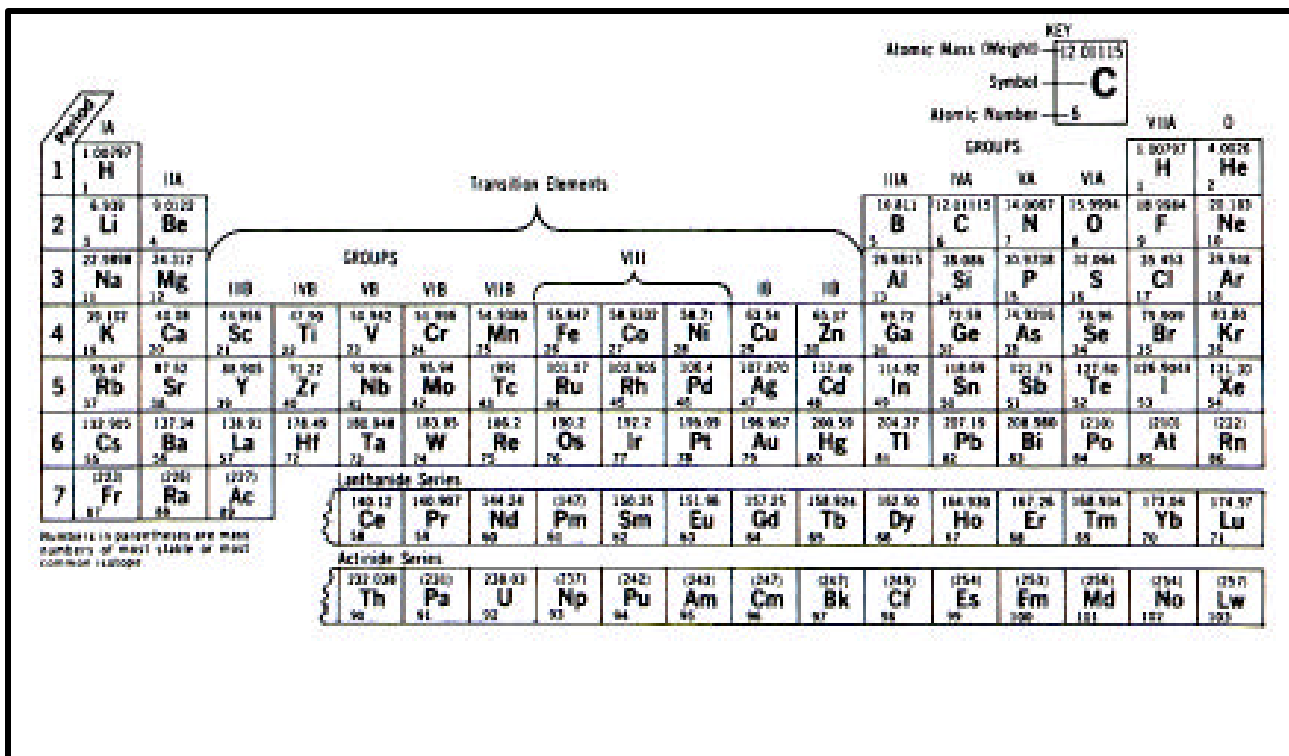


Figure 7-1. Periodic table of the elements

Table 7-1. Examples of components and formulas

Compound	Formula
Sodium chloride	NaCl
Methane	CH ₄
Sodium Oxide	Na ₂ O
Ethane	C ₂ H ₆

Mole. The mole is a term used to describe a quantity of matter which is equal to 6.023×10^{23} particles (atoms, molecules, or ions) of that matter. It also works out to be the molecular weight of a substance, expressed in grams. The symbol for mole is mol.

Atomic Mass. The atomic mass (weight) of an element is provided in the periodic chart. This number represents two things: (1) the mass of an atom in atomic mass units and (2) more importantly, for the petroleum laboratory specialist, the weight, in grams, of one mole of atoms of an element.

Equivalent Weight. The equivalent weight is the weight of a substance, in grams, that would react with or displace one gram of hydrogen ions in a compound. The equivalent weight of a substance is found by dividing its molecular or formula weight by the total number of electrons its metallic component has lost in forming the compound (its total positive valence). For example, the equivalent weight of $MgCl_2$ is found by dividing its formula weight, 95 grams, by 2, since the magnesium atoms have each lost two electrons in forming the ionic bonds with chlorine. The equivalent weight of $MgCl_2$ is 47.5 grams.

Molecular or Formula Weight. The molecular or formula weight of a compound is the weight, in grams, of one mole of molecules of the compound.

It is found by adding the atomic weights of all the constituent elements. For example, to determine the formula weight of magnesium chloride, ($MgCl_2$), do the following:

- Step 1. Refer to the periodic chart, for the atomic weight of magnesium. It is 24. There is one mole of these ions in one mole of $MgCl$
- Step 2. Refer to the periodic chart for the atomic weight of chlorine. It is 35.5. $MgCl_2$ contains two moles of chlorine ions, so the atomic weight must be doubled.
- Step 3. To the weight on one mole of magnesium ions (24 grams), add the weight of two moles of chloride ions (71 grams) to arrive at the weight of one mole of $MgCl_2$ (95 grams).

MEW. The MEW is the equivalent weight divided by 1,000.

Molar Volume. Molar volume is a term associated with the measurement of gases. Gas volume varies with temperature and pressure. The molar volume of a gas is the volume occupied by one mole of its molecules under certain stated pressure and temperature conditions. For example, one mole of ideal gas will occupy a volume of 22.4 liters in a closed container at a temperature of $0^\circ C$ ($273^\circ K$) and a pressure of one atmosphere (760 millimeters of mercury).

Table 7-2. Metric system of measure

Property Of Matter Measured	Metric Unit Used	Metric Prefix	Stands For-
weight (mass)	gram		
volume	liter	milli-	$\frac{1}{1000}$
distance	meter	centi-	$\frac{1}{100}$
temperature	Celsius degree	kilo-	1000

Section II. Reagents and Solutions

GENERAL

The use of solutions is important in the daily analytical work performed in the petroleum laboratory. The laboratory technician must be able to prepare solutions of very accurately known concentrations. Some definitions and procedures associated with the preparation of these solutions are discussed below.

EQUATIONS

A chemical equation is used to represent the changes that occur when chemicals react or combine to form new compounds. An equation gives the qualitative nature of a reaction (what compounds or elements combine and what compounds are produced) and also describes the quantitative nature of a reaction (how much of each reactant is needed and how much of the products will be formed). An equation shows the formulas of the starting materials and products, the proportions in which the starting materials combine, and the proportions in which the products are formed. An equation is shorthand for a reaction. Although it does not tell everything, it is extremely useful for the solution of many chemical problems.

REAGENTS

A reagent is a chemical substance that is used for analyses because of its known reaction with other chemical substances. Such analyses are performed through observations of the effects of reagents on unknown substances. A qualitative analysis can identify an unknown when certain results are produced by a certain reagent. A quantitative analysis can then determine the amount of the substance present gravimetrically (by weighing) or volumetrically (by measuring volume).

SOLUTIONS

A solution is a homogenous mixture of two or more substances in which the mixed substances' particles are molecular in size and are uniformly distributed. The dissolved particles cannot be seen, do not settle out upon standing, and are easily removed by filtration. In the petroleum laboratory, the primary concern is in creating solutions in three ways. These three types of solutions involve dissolving gas in a liquid; dissolving solid in a liquid; and dissolving liquid in a liquid. Common terms used in the preparation of solutions are defined below.

- A solvent is the substance that does the dissolving.
- A solute is the substance that is dissolved or dispersed among the solvent particles.
- Solubility is a description of the degree to which a substance will dissolve in a particular solvent.

FACTORS AFFECTING SOLUBILITY

Petroleum laboratory technicians must create solutions for many of the chemical tests they do. It is important that they understand the factors that effect solubility, so they perform their job efficiently. The solubility of a solute and solvent depends on the following factors:

- The nature of the substances mixed is very significant. In general, the rule "like dissolves like" is true. This means that if the molecular structure of the solute and solvent particles is similar, they will probably exhibit an appreciable degree of solubility. For example, an aromatic compound is generally more soluble in benzene (another aromatic compound) than in water or ethanol.
- Temperature is another important consideration. The solubility of a solid solute in a liquid

solvent generally increases when the temperature of the solvent is increased. However, the solubility of a gas in a liquid decreases with increased temperature.

- Pressure is significant only in a gas-liquid type of solution. The solubility of a gas increases when the pressure increases.
- The speed with which a solid solute may be dissolved in a liquid solvent is increased by granulating or powdering the solid and by agitating or stirring the mixture.

CONCENTRATIONS OF SOLUTIONS

The concentration of a solution is a quantitative expression of the amount of solute that is dissolved in a certain amount of solvent. Technicians choose the particular expression for concentration depending on their intended use for the solution. Concentrations are expressed in any one of the following ways.

- Normality. Normality neutralizers acids and bases. A 1N solution contains one gram-equivalent weight of the solute per liter (1,000 ml) of solution.

$$\text{Normality} = \frac{\text{number of equivalent weights of solute}}{\text{liters of solution}}$$

- Molarity. Molarity determines volumes. A 1M solution contains one gram-molecular weight of solute per liter of solution.

$$\text{Molarity} = \frac{\text{molecular weights of solute}}{\text{liters of solution}}$$

- Molality. Molality is concerned with weights during the test. A 1M solution contains one gram-molecular weight of solute per 1,000 grams of solvent.

$$\text{Molality} = \frac{\text{molecular weights of solute}}{1,000 \text{ grams of solvent}}$$

- Percent by Weight. This method describes grams of solute per 100 grams of solution.

$$\text{Percent by weight} = \frac{\text{weight of solute}}{\text{weight of solution}} \times 100\%$$

- Percent by Volume. This method describes the volume of solute per 100 volume units of solution.

$$\text{Percent by volume} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\%$$

PREPARING SOLUTIONS

Calculations dealing with neutralization of acids and bases generally use normality. Acid/base neutralization chemical reactions are important in petroleum laboratory work, and are described later. For now, it is important to know that using the concept of normality makes it easy to determine the progress of these reactions, and to determine how much acid and base is needed to complete the reaction. Solutions of the same normality contain the same number of equivalent weights per unit volume. Equal volumes of solutions of equal normality are equivalent. Therefore, 10 milliliters of 1N KOH (a base) would neutralize 10 milliliters of any 1N acid solution, whether the acid be HCl or H₂SO₄. Mathematically, the above statements are summarized by the following:

$$(m_1)(N_1) = (m_2)(N_2)$$

$$N_1 V_1 = N_2 V_2$$

PRIMARY STANDARDS

A primary standard is a known substance, with properties that make it useful, as a reference in standardization. The properties of a primary standard should include a high equivalent weight, usually greater than 50. It should be chemically stable and should not absorb atmospheric moisture readily. It also should react completely when neutralized. Primary standards are also rather weak acids and bases, which makes them safer to handle than secondary standards. Common primary standards are discussed below.

- KHP. This primary standard is used to standardize bases because it is acidic. It has an equivalent weight equal to its molecular weight

(203.22 grams). Titration of KHP requires the use of phenolphthalein indicator. Other primary standards that can be used to standardize bases are: $H_2C_2O_4$ (oxalic acid), $H_2C_2O_4 \cdot 2H_2O$, C_6H_5COOH , and NH_2SO_3H .

- Na_2CO_3 . Anhydrous sodium carbonate is used to standardize acids because it is basic. Its equivalent weight (53.00 grams) is equal to one-half its molecular weight (106.0 grams). Titration of Na_2CO_3 requires the use of methyl orange indicator, since the use of phenolphthalein would yield a false end point.

- Other primary standards that can be used to standardize acids are $KHCO_3$, Tl_2CO_3 , $Na_2B_4O_7 \cdot 10H_2O$, and $Na_2C_2O_4$.

- $H_2C_2O_4$ (oxalic acid), $H_2C_2O_4 \cdot 2H_2O$ (oxalic acid dihydrate), C_6H_5COOH (benzoic acid), and NH_2SO_3H (sulfamic acid) may be used to standardize bases.

SECONDARY STANDARDS

Although secondary standards (substances commonly found in laboratories) can function just as well as a primary standard, they are called secondary standards because of certain characteristics that make them less desirable than primary standards. Foremost among these is the fact that substances typically used as secondary standards are strong acids and bases, making them extremely hazardous to handle. They also have low equivalent weights which means relatively high concentrations must be used to neutralize substances. The secondary standard should be of about the same normality as the solution to be standardized. Some examples are discussed below.

- Most strong acids, such as HCl and H_2SO_4 , can be used satisfactorily as secondary standards.

- The strong bases usually used as secondary standards are KOH and $NaOH$.

STANDARDIZATION

Standardization is the process of obtaining a standard solution. A standard solution is one whose concentration is known to the fourth decimal place. In general, standard solutions are either acidic or basic. An acidic solution is standardized with a base and a basic solution is standardized with an acid. When a solution is standardized, comparison is made of volumes of solution of known and unknown concentration which undergo a neutralization.

TITRATION

Titration is the process of determining the volume of reagent solution required to react with a solution of another substance. Titration measures the volumes of the unknown and standard solutions. Since the concentration of the standard is known, the concentration of the unknown may be calculated by applying these fundamental relationships

$$\text{Normality} = \frac{\text{number of milliequivalent weights}}{\text{number of milliliters of solution}}$$

$$\text{Number of milliequivalents (Reactant 1)} = \text{number of milliequivalents (Reactant 2)}$$

$$\text{Number of milliequivalents} = \text{normality} \times \text{milliliters}$$

Substituting the above expression into relationship 2 leads to the relationship:

$$\text{Normality} \times \text{milliliters (Reactant 1)} = \text{Normality} \times \text{milliliters (Reactant 2)}$$

Or:

$$n_1 \times m_1 = n_2 \times m_2$$

These relationships enable further calculations to be made, dealing with the determination of the weight of substances reacting with the standard solution.

STANDARDIZATION BY TITRATION

Assume that a 0.1N solution of an acid is to be prepared and standardized. A quantity of one liter is required. The following steps describe the procedure.

- Step 1. Select a basic primary standard for an acidic solution, usually sodium carbonate. Note from the container the milliequivalent weight and assay values.
- Step 2. Calculate the weight of primary standard required to neutralize about 40 milliliters of 0.1N acid with the use of the equation. DFP represents decimal fractional purity.

$$\text{weight needed (MG)} = \frac{(N)(40\text{ml})(\text{MEW})}{\text{DFP}}$$

- Step 3. Weigh a clean and dry Erlenmeyer flask on the analytical balance.
- Step 4. Add the grams of primary standard calculated in Step 2 above, and record the weight to the fourth decimal place.
- Step 5. Dissolve the primary standard in an unmeasured quantity of water.
- Step 6. Add two or three drops of methyl orange.
- Step 7. Using burets, titrate the solution in the flask with the acid solution to be standardized.
- Step 8. Repeat the titration procedures at least two more times.
- Step 9. For each titration, calculate the normality (to four decimal places) of the acid solution by using the following equation:

$$N = \frac{(\text{DFP})(\text{weight of primary standard})}{(\text{ml of acid})(\text{MEW primary standard})}$$

- Step 10. Obtain the average value of the acid's normality and label the standardized solution for identification. If any solution differs from the mean by ± 0.0005 N, rerun the titration process.

pH SCALE

The pH scale determines the acidic or basic range of a substance (see Figure 7-2, page 7-8).

The scale has a range from one to fourteen, with seven being neutral. Acids have a pH of 1-6.999;

bases have a pH of 7.001-14; and neutral is 7.000. When acids and bases are mixed together, the pH is altered. When an acid and base is mixed in equal proportions based on their normality, they will combine to become a salt based liquid or neutral substance. Characteristics of acids and bases are stated below.

- Acid characteristics include: turn blue litmus paper red, and have a pH less than 7.00.
- Base characteristics include: turn red litmus paper blue, and have a pH greater than 7.00.

INDICATORS

Indicators are dyes that change color or shade of color when the pH (degree of acidity or alkalinity) of a solution changes. Therefore, they can be used to indicate the concentration of hydrogen ions in solutions of acids and bases. They are also used in volumetric analysis to mark the end point of titration. Indicators used in the petroleum laboratory are as follows:

- Methyl Orange. This indicator has a pH range of 3.1 (red) to 4.4 (yellow-orange). It is also used in the presence of carbonate radicals (anything containing the CO_3 atom group such as $\text{TL}_2 \text{CO}_3$). The solution is made by dissolving 0.1 grams in 100 milliliters of distilled water. The end point is an orange-brown.
- Methyl purple. This indicator has a pH range of 4.8 (purple) to 5.4 (green). The change from purple to green is fast and is preceded by a change from purple to light gray. This indicator is also used in the lamp sulfur test and is prepared according to the test method.
- Paranitrophenol. This indicator has a pH range of 5.0 (colorless) to 7.0 (yellow-green). It is also used only when called for in ASTM test procedures. The solution is made by dissolving 0.5 grams of p-nitrophenol in 100 milliliters of distilled

water and filtering if necessary. The end point is pale yellow.

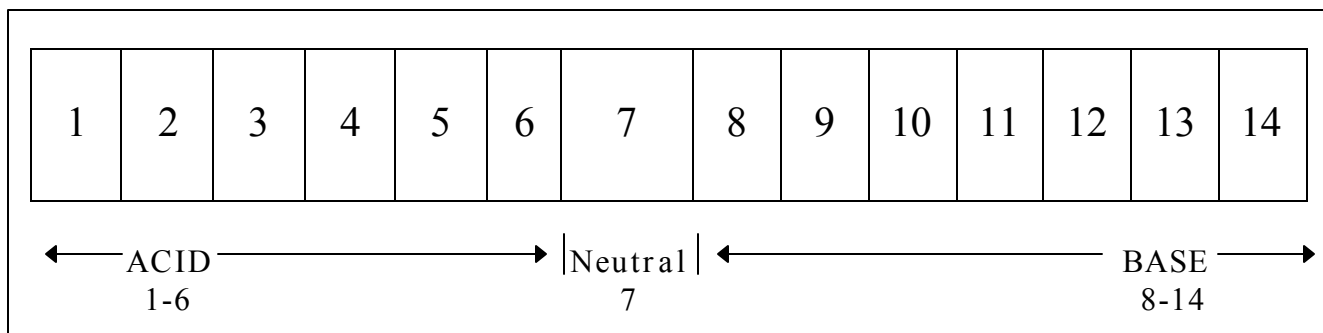


Figure 7-2. pH Scale

- Phenolphthalein. This indicator has a pH range of 8.0 (colorless) to 9.8 (red). It is also used in the absence of carbonate radicals. The solution is made by dissolving 1.0 grams in milliliters of 90 percent ethyl alcohol. The end point is faint black.
- P-Naphtholbenzein. This indicator has a pH range of 8.2 (amber) to 10.5 (blue). It will go from amber to olive green to clear green to bluish green to blue. This indicator is also used in the neutralization number test and is prepared according to the test method.

Section III. Balances and Weighing

GENERAL

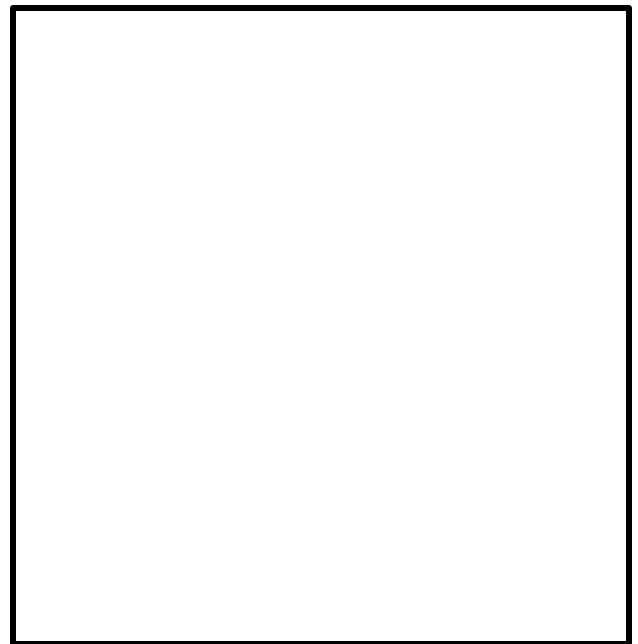
Weighing is a necessary part of preparing solutions and is used in many tests in the laboratory. The petroleum laboratory has several types of balances for specific purposes.

ANALYTICAL BALANCE

The analytical balance is used for precision weighing (0.0001 gram) of small quantities. Figure 7-3 is a single-pan analytical balance with advanced features. Those features include: easy-to-read display, separate sealed keys and automatic calibration. General procedures for using this balance are listed on the following page. Again, the manufacturer's handbook should be available when using the balance



Figure 7-3. Analytical balance



Weighing Press the TARE to zero the display. Place the object(s) to be weighed on the pan. Read the displayed weight after the display is stable (i.e. when the no-motion symbol indicates stability by switching off or on).

Weighing-In Place a container on the pan. Press the TARE key or use a remote switch to zero the display. Fill the container until the target weight is reached. When mixing ingredients in a container press TARE after each addition.

Weighing-Out. Place a full container on the pan. Press TARE to zero the display. When anything is subsequently removed from the container the amount removed will be displayed as weight loss.

Weighing a Deviation. Place a reference or standard sample weight on the pan. Press TARE and then remove the weight, weight loss will be displayed. Now any sample weight placed on the pan will indicate its deviation from reference in terms of a positive or negative display. This function is useful in check-weighing operations.

THE HARVARD TRIP BALANCE

The Harvard trip balance, shown in Figure 7-4, page 7-10 is a precision balance used for weighing substances in the petroleum laboratory. It should be used on a reasonably flat and level surface. In this setting a very near balance should be attained with the beam and tare poises all the way to the left. Some of its operational features are discussed below.

Zeroing the Balance. If the scale does not balance at zero when set upon its working surface, adjust the knurled zero adjust knob at the right end of the beam. (It is also advisable to check the zero balance periodically since foreign material may accumulate on the plate or beams and cause a slight change in the balancing position)

Weighting. After a zero balance has been obtained, the specimen to be weighed is placed on the left platform of the balance. The poises are then moved to a position which will restore the scale to balance. The lower poise is moved to the right until the first notch is reached which causes the right platform of the scale to drop. The lower poise is then moved back one notch which will cause the right platform to again rise. The upper poise is then moved to the right until the scale is brought into balance. The resultant weight is then read directly from the beams by adding the amount indicated on the lower and upper beams.

Use of the Tare Poise. To use the tare poise, first slide the poise to an approximate balance position, and then rotate the poise to obtain final balance. An internal screw thread allows the tare poise to be precisely positioned in either direction by simply rotating it. (When the tare poise is not in use, it should be slid firmly to the left until it makes contact with a stop.)

Specific Gravity Determination. For the purpose of suspending specimens for immersion weightings, bent pins are provided near the bottom of the scale plate loops which are accessible from the underside of the scale base. The balance can be mounted on a Clamp and Rod Support. There is a half-inch clearance hole provided underneath the base that slips on over the end of the rod. The procedure for weighing a suspended specimen is the same as that for weighing a specimen on the scale platform.

Care and Maintenance. When the balance is not in use, be sure to remove the load from the weighing pan and to replace the rubber washers to lift the pivots off the bearings. Avoid storing the balance in a place where vibrations will be transmitted to it. Keep the balance clean at all times, being particularly careful not to let dirt accumulate in the vicinity of the bearings. Never lubricate the scale bearings. The bearings in these balances are high grade polished agate V-blocks and the knife



Figure 7-4. Harvard trip balance

edges are hardened, precision-ground steel. This type of bearing works best when clean and dry. Should the bearings become dirty, attempt to clean by blowing out with air blast. If this is unsuccessful, the bearing covers will have to be removed. In replacing the bearing covers, it is necessary that the hardened blue steel friction plate is replaced in the recess provided.

Cleaning Magnet Faces. From time to time, it is necessary to clean accumulated debris from the magnet faces. This is best done by inserting a piece of adhesive tape into the magnet slot and pressing it against the magnet face. This will pick

up attracted material and prevent it from interfering with movement of the damper vane.

TRIPLE BEAM BALANCE

The triple beam balance is used when precise weighing is not required. For instance, it would be used when determining the approximate weight of tubes to be centrifuged. General instructions for using the triple beam balance, are provided in the following paragraphs. Figure 7-5, page is a photograph of the triple beam balance.

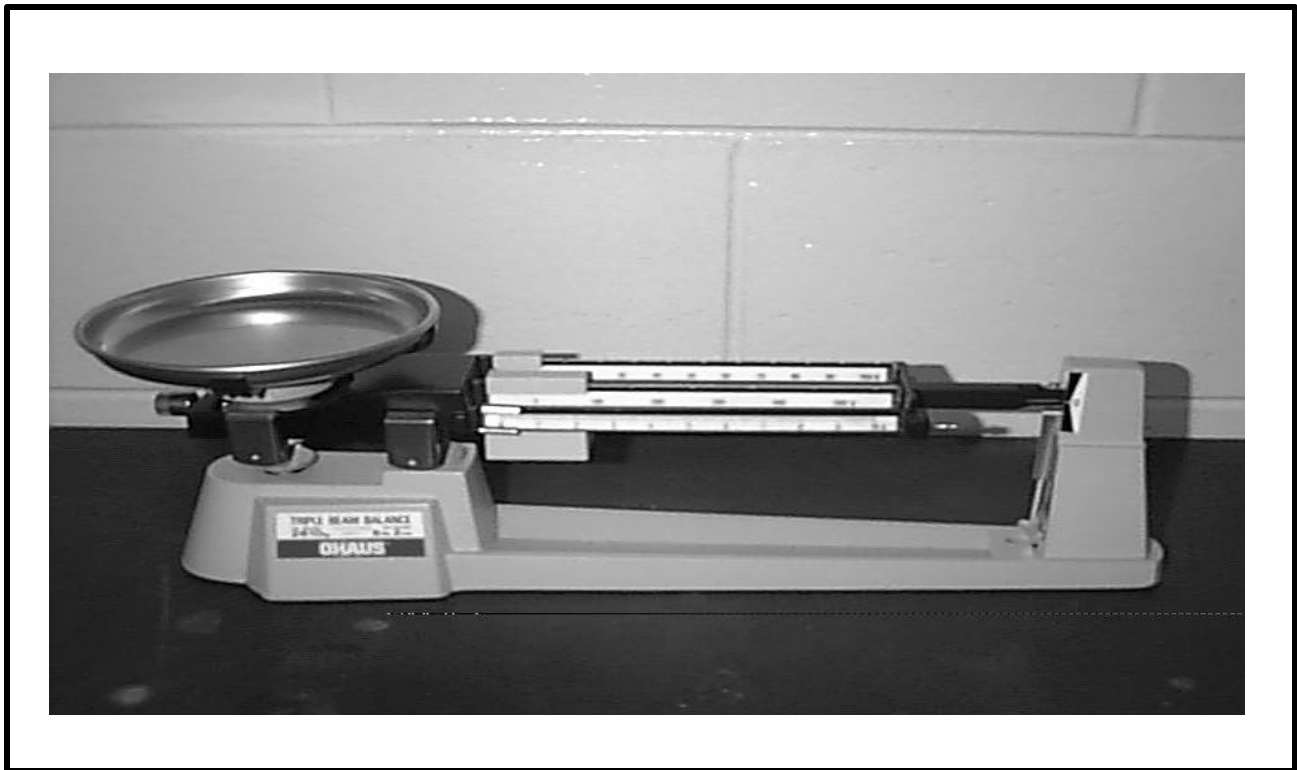


Figure 7-5. Triple beam balance

Leveling and Zero Balance. Select a reasonably flat and level surface on which to use the balance. The beam should be near a zero balance with all poises at zero, and the tare poise against its stop to the extreme left (tare models only). A final zero balance is attained by means of the knurled zero. Adjust the knob at the left end of the beam. Check the zero balance periodically since foreign material may accumulate on the plate or beams and cause a slight change in the balance position. Whenever the balance is moved, the zero balance must be rechecked, since it will be affected by a change in the inclination of the working surface.

Weighing. After obtaining a zero balance, place the substance to be weighed on the load receiving platform. Move the center poise to the first notch where it causes the beam pointer to drop, then move back one notch and the pointer

will rise. On metric models, proceed by manipulating the rear poise in the same manner. Then slide the front poise to the position that brings the beam into balance. On avoirdupois models, proceed by sliding either the front or rear poise to the position that brings the beam into balance. The weight of the substance is then directly read by adding the values indicated by the poises. While not in use, the attachment weights store conveniently along the trough in the base of the balance.

Use of the Tare Poise. Slide the poise to an approximate balance position, and rotate the poise to obtain final balance. An internal screw thread allows the tare poise to be precisely positioned in either direction by simply rotating it. When the tare poise is not in use, it should be slid firmly to the left until it makes contact with a stop.

Care and Maintenance. Keep the balance clean at all times; do not let dirt accumulate in the vicinity of the bearings. Do not apply oil or any lubricant to the knives or bearings. Blowing the bearings out with a dry air blast is a very effective way of cleaning them and it is recommended that this be done periodically to maintain the utmost of sensitivity in the balance. From time to time, it is necessary to clean accumulated

debris from the magnet face. This is best done by inserting a piece of adhesive tape into the magnet slot and pressing it against the magnet face. This will pick up attracted material and prevent it from interfering with movement of the damper vane. When transporting the balance, take care that it does not receive any sharp blows and is not subjected to unnecessary rough treatment. When the balance is not in use, be sure to remove the pad from the weighing pan.